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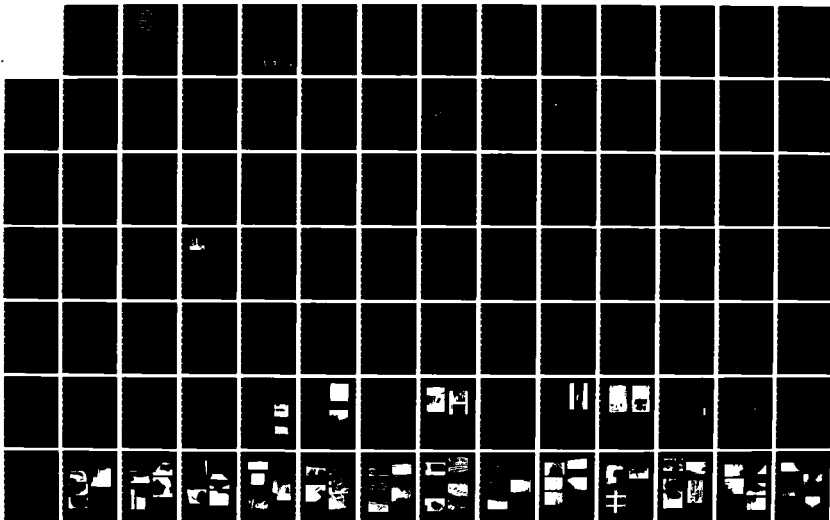
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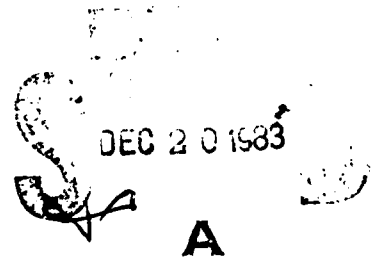
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Proceedings of 1980 Symposium “Wood Adhesives— Research, Application, and Needs”

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- AD#: P002 414 TITLE: The Role of Adhesion and Adhesives in the Wood Products Industry.
- P002 415 Status and Forecast for Supply, Demand, and Cost of Wood Adhesives and Binders.
 - P002 416 Molecular Properties of Phenolic Adhesives.
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 - P002 418 Effect of Resin Types and Formulation on Internal Bond Strength Bond Strength and Dimensional Stability of Hardwood Flakeboard.
 - P002 419 Carbohydrate Transformation Bonding of Lignocellulosic Materials.
 - P002 420 Exterior Adhesive from Sulfite Mill Effluent.
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 - P002 424 Adhesive Trouble Shooting in the Wood Industry.
 - P002 425 Formaldehyde from UF-Bonded Panels--Its Measurement and Its Relation to Air Contamination.
 - P002 426 Reduction of Formaldehyde Levels in Mobile Homes.
 - P002 427 Formaldehyde Testing in Mobile Homes: Source Materials, Test Methods and Conditions.
 - P002 428 Polymeric Isocyanate as Wood Product Binders.
 - P002 429 Isocyanate Adhesives as Binders for Composition Board.
 - P002 430 EPI (Emulsion Polymer/Isocyanate) - A New Structural Adhesive.
 - P002 431 Properties of Elastomer-Based Construction Adhesive at Service Temperatures in Wood Buildings.
 - P002 432 Structural Bonding of CFA (Chromated Copper Arsenate)-Treated Wood Foundations.
 - P002 433 Determination of Working Stresses for Structural Adhesives.
 - P002 434 Adhesives for Mobile Homes--Response from the Private Sector.
 - P002 435 Methodology for Determining the Durability of Sealants.
 - P002 436 Evaluating Durability of Adhesive-Bonded Wood Joints.

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P002 439	Bonding by Surface Reaction.
P002 440	Adhesives for Wood Composites.
P002 441	Recent Advances in Plywood Technology.
P002 442	Curing Urea-Formaldehyde Adhesives in Thick Particleboard Mats.
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PREFACE

The 1980 symposium on "Wood Adhesives--Research, Application, and Needs" was cosponsored by the Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, and the Wood Technology Section of Washington State University, Pullman. It was held September 23-25, 1980, at the Wisconsin Center Building on the campus of the University of Wisconsin.

The purpose of this symposium was to exchange information and ideas, and to stimulate new research and development among researchers, producers, and consumers of adhesives for use in the wood industry. Adhesives are some of the most important raw materials used in the wood industry today. With the ever increasing need to produce large pieces of wood from small pieces, to use materials now considered residues, and to use our timber resources more efficiently, the important role of adhesives in wood processing continues to expand.

This symposium followed only 5 years after the 1975 symposium on "Adhesives for Products from Wood" which had been the first meeting of this kind since 1960. This increasing frequency reflects a growing need to exchange information about new technology as it develops at an ever increasing rate in efforts to keep pace with industry and consumer needs.

The 1980 symposium stressed the use of renewable materials in adhesives but also reviewed current bonding practices, research needs, unsolved problems, and provided a forum for discussing approaches to problem solution. Important topics included the status and forecast for the future of wood adhesives, the use of renewable resources, specialty adhesives, formaldehyde emissions from bonded wood products, isocyanate adhesives, structural applications, and durability.

These proceedings of the 1980 symposium contain all the papers presented and, consequently, they should provide a good overview of recent developments and current status of adhesives for wood. They should also provide background for future conferences and help fulfill the need for improved communication and information exchange between all parties concerned with the development and use of adhesive technology.

W. E. Johns, Washington State University
Robert H. Gillespie, U.S. Forest Products Laboratory

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THE ROLE OF ADHESION AND ADHESIVES

IN THE WOOD PRODUCTS INDUSTRY^{1/}

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Forest Products Laboratory, Forest Service
U.S. Department of Agriculture
Madison, Wis.

ABSTRACT

The phenomenon of adhesion plays an important role in over 70 percent of all wood and wood-based products, including paper products. The future of the wood industry will require an even higher dependence on operations involving adhesion, a trend fostered/partially by the (changing character of the forest resource) partially by the need to extract greater quantities of wood from the same forest base, and partially from the newly recognized potential for producing new wood materials with superior properties to serve a variety of engineering needs.

The growth of knowledge on the subject of adhesives and adhesion has produced some exciting scientific and technical discoveries. More discoveries of equal importance are possible and can be anticipated, with much of the driving force coming from the need to find substitutes for the threatened shortage of petrochemicals.

This symposium and others to follow will help greatly in accelerating the achievement of this objective.

INTRODUCTION

The subject of adhesives and adhesion is one of the most important knowledge areas for the future of the forest products industry. The phenomenon of adhesion as a physical and chemical action is invoked in perhaps 70 percent or more of all wood materials in use today, and the percentage could be higher in the future. This includes laminated beams, plywood, laminated veneer products, various fiberboards, particleboards, overlays, all paper products, and all paints and finishes applied for protective or decorative effects. Furthermore, some special impregnating treatments require

¹Paper presented as the keynote address at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

²Formerly Assistant Dean, College of Engineering, Washington State University, Pullman, Wash.

consideration of a chemical action to bond the material to the wood substance internally.

Engineers working on new concepts for more efficient design of wood structures, have found that bonding components together in lieu of nailing, or in addition to nailing, provides increased load-carrying capacity and increased stiffness in the final structure. The effect is particularly apparent when sheathing, for example, is bonded to studs or subfloor to

joists (6).³ Conversely, and perhaps more importantly, the same load-carrying capacity and stiffness can be achieved with less wood, thus contributing to lower cost and conservation of the timber resource. This trend is now well-established and is expected to continue to grow in the future, adding greatly to the future impact of adhesives and adhesion on wood use.

³Numbers in parenthesis refer to references listed at the end of this paper.

While adhesion most often connotes the use of an adhesive to achieve a bond, this is not always the case. For example, the bond formed between fibers in a paper sheet does not require an adhesive; rather, the production process promotes the formation of hydrogen bonds between cellulose molecules on the surface of fibers in close proximity. Another example of a different type of bonding lies in a special class of high-density fiberboard produced by a wet process in which the natural lignin present on the fiber is caused to flow under heat and pressure. The thermoplastic action of the lignin then bonds adjacent fibers together somewhat as in the original wood.

This type of bonding without adhesives, though quite old as a technology, has inspired an exciting new wave of research activity which seeks to promote the action by means of catalysts. In the field of wood bonding it is difficult to conceive of a more elegant solution to the problem of shortages of adhesive materials.

Economists and foresters who study the supply and demand for timber and who can predict the character of future forests, provide clear evidence that bonding of wood will be the dominant operation in wood processing plants throughout foreseeable decades. The pattern of small logs and the need to recover higher percentages of usable material from the forest, will foster greater use of bonding techniques such as laminating, end and edge joining, veneer products in the form of panels and lumber, flake products also in the form of panels and lumber, and combinations of veneer and flakes or other types of particles.

Although the character of the wood raw material may be the more obvious driving force toward the greater use of bonding as a wood processing operation, other factors contribute to the trend. Perhaps the most important of these is the fact that highly desirable technical gains emerge from the process. For example, the mere act of bonding two or more pieces together to serve as one piece, results in greater uniformity of the material from a statistical standpoint. Furthermore, the control of processing variables can insure uniformity of product from day to day and year to year, and some processes also permit varying the properties at will. Hence, a level of reliability--a matter of great concern to engineers and designers--can be achieved far exceeding that of random solid wood products. However, this reliability is almost entirely dependent upon the quality of the bonds.

A second factor arises from consideration of long-term impacts of depletable resources in contrast to the renewable character of the

forest resource. It is now considered inevitable by recognized futurists that certain resources will be exhausted within a matter of centuries. In this context, wood will play an increasingly important role in substituting for those materials facing extinction thus conserving them for future generations while maintaining the standard of living for more people at a comfortable level. It is fortunate indeed that the science and technology of wood has developed to the point that wood materials with superior properties can now be assured for the larger role envisioned for the forest resource. It is hoped that national policymakers for materials will give this fact more serious consideration in the future when formulating guidelines for best use of the world's critical resources.

It stands everlastingly to the credit of workers in the field of adhesives that bonding operations have kept pace with other technical developments and will continue to do so. This symposium and others to follow attest to the importance of this subject.

HISTORICAL PERSPECTIVE OF WOOD BONDING

While the term "adhesive" refers to a material, and the term "adhesion" to a physical-chemical phenomenon, the term "bond" includes both of these, together with a substrate, or adherend. Thus, two pieces of like or unlike material are considered bonded together if they can transmit stress and act as a single unit. Although this definition is not totally consistent in actual practice, it is useful in discussing the technical aspects of the operation even when no adhesive is used to form the bond.

Historically, early consideration of the bonding action involved only the substrate and the adhesive film spread over its surface (Fig. 1A). This primitive two-component system required only that the adhesive penetrate the open structure on the surface of the wood and then harden. It was an adequate concept of wood bonding throughout the ages, until about 1919. At that time, more reliable bonding of wood aircraft parts spurred research on the basic phenomenon. The idea of the bond having to be only as strong as the wood won early acceptance among scientists. It is curious, however, that the idea that the "glue" could be made to appear stronger simply by using stronger wood for the substrate took a number of years to be discovered. It is also curious that in those days an adhesive material became a "glue" when used to bond wood.

The early history of research on adhesives and adhesion forms a most fascinating chapter in the development of ideas on this subject. Of particular interest is the work

of several groups of scientists trying to elucidate the bonding action in terms of mechanical versus specific adhesion. One group whose illustrious members included McBain, Lee, and Hopkins, working in England, sought to justify the theory that adhesion on wood surfaces was primarily a mechanical action (10,11). A second group working in the United States believed that for good adhesion, a chemical action had to occur between wood and adhesive which they called specific adhesion. This group included Truax, Browne, and Brouse at the Forest Products Laboratory in Madison, Wis. (1,2,18). Although both groups practiced the best available experimental techniques and both exercised due restraint and diplomacy, it is obvious that an exciting game of science was in progress over a period of several years. In the end, both teams appear to have retreated to an intermediate position, accepting the possibility that both mechanical and specific adhesion were involved, but still squabbling as to the definition of porosity with respect to the wood surface. The published works of these two groups remain as a classic example of theories proposed, disputed, purposefully researched and re-researched to provide enlightenment for all.

Continuing the historical perspective of wood bonding, it is useful to review the concept of linkages as proposed by A. A. Marra (8). In this concept, the bonding action is seen as a series of links analogous to a chain, the failure of any one of which would lead to the failure of the chain. As implied in figure 1A, early consideration of this subject failed to perceive the variability of wood as a factor in a union. When bonding involves two pieces of wood--as it most often does--adhesion must occur on two different surfaces before a true bond is formed. Variability between pieces of wood to be joined is itself composed of many factors such as species, moisture content, grain angles, sapwood and heartwood, proportion of earlywood and latewood, density, strength, pH, temperature, and many others. All of these can affect adhesion differentially with respect to the two pieces of wood. When recognition of this fact finally occurred, the bonding action was conceived as having three links, i.e., the adhesive layer and the two pieces of wood on either side as shown in figure 1B. It is immediately evident that on a purely statistical basis, the chance of a factor being present unfavorable to the bonding action becomes at least double, and the technical demand on the function of the adhesive can be seen as much more formidable. Although seemingly a minor discovery in retrospect, this three-linkage concept provided wood technologists and adhesive specialists with an

important tool for progress in bonding operations and in the performance of the bonds in service.

Useful as the three-linkage concept was in its time, it proved to be merely a stepping stone to even greater understanding of the bonding action. Research now began to concentrate on the interface between wood and adhesive where the fundamental adhesive action takes place. This is depicted in figure 1C where links 2 and 3 are shown as new additions to the links in the chain, either of which may be responsible for inadequate bond performance.

This is now a five-link chain.⁴ Here, in links 2 and 3, the physics and chemistry of the adhesive meet the physics and chemistry of the wood on a macro, micro, and molecular scale. Surface roughness and surface porosity interact with adhesive viscosity and adhesive fillers, and reactive components of the adhesive meet receptive sites on cellulose and lignin molecules.

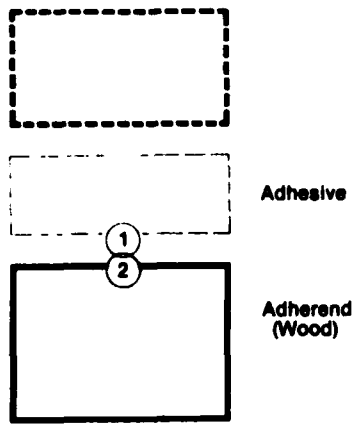
The enormous flexibility and adaptability required of the adhesive can be seen in the characterization of the wood surface shown in figure 2. Excised cell walls (end view) present opportunities for primary and secondary bonds to develop between cellulose and adhesive. Unexcised cell walls require bonds to form between lignin and adhesive. Often, cell walls are collapsed or shattered, requiring the adhesive to penetrate and interact with protoplasmic residues on the interior cell lumens. These residues are also a part of the interface in the excised cells. Furthermore, sloping grain results in openings to cell lumens on the surface, which then become channels for the adhesives to escape from the action point. The two wood interfaces may also vary as to earlywood or latewood, or heartwood and summerwood, each with varying potential for promoting or denying adhesion.

Other surface phenomena also come into play. These include contamination, oxidation, and any extractives that may exude to the surface. A more recent consideration is the so-called surface inactivation that may occur during drying, particularly high-temperature drying. This was a major consideration in the development of preheat bonding techniques in which heat sufficient to cure the adhesive is stored in the surface layers of the wood before the adhesive is applied (9).

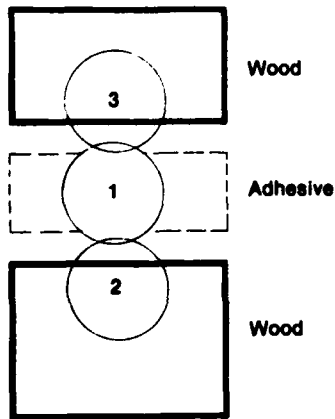
Similar considerations apply to the adhesive film as the other part of the interface.

⁴Note that the chain-link concept constitutes a symmetry around the center link (1) and that while each link has an exact counterpart on the opposite side, each link carries its own power to destroy the chain.

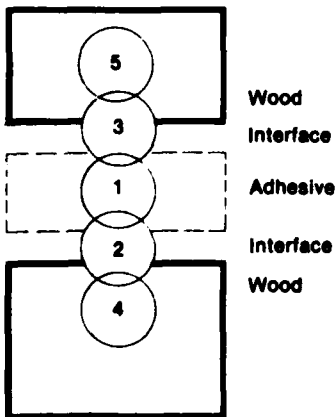
A. Earliest concept of wood bonding.



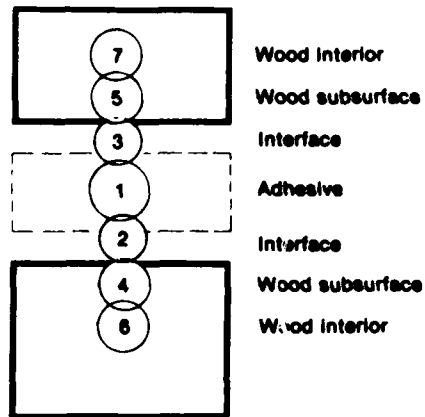
B. Recognition of effect of wood variability in wood bonding.



C. Recognition of effect of interface characteristics on wood bonding.



D. Recognition of subsurface damage due to surface preparation as a factor in wood bonding.



E. Recognition of differential migration of adhesive components within the film adjacent to wood surface.

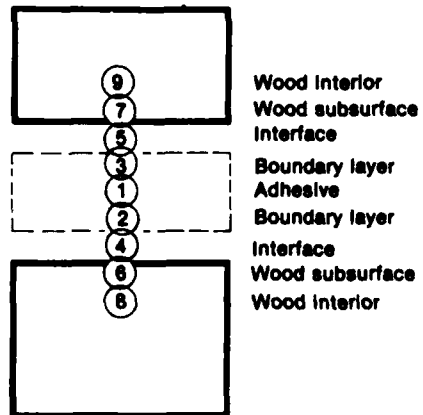


Figure 1.--Historical perspective of wood bonding: A concept of linkages.

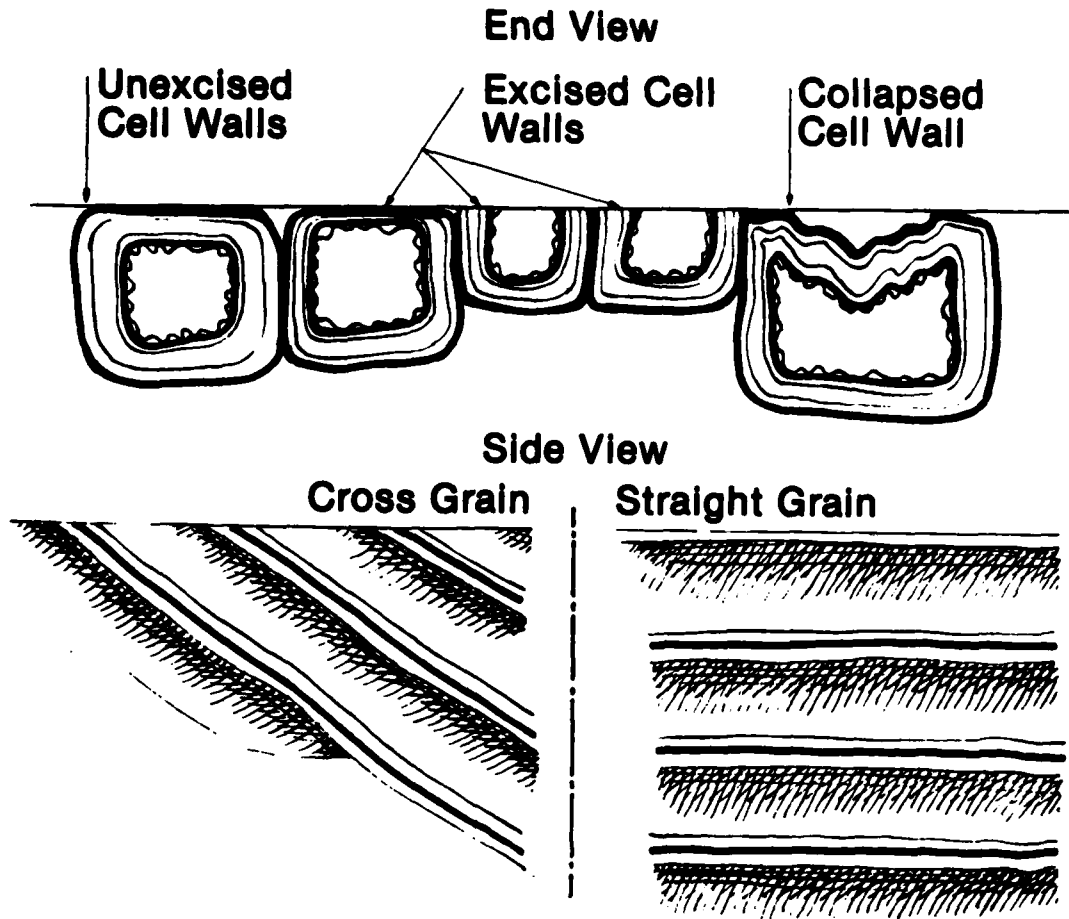


Figure 2.--Sketch of microscopic character of wood surface.

The viscosity of the adhesive is a prime factor, but this varies with time, and indeed, from one surface of the film to the other as assembly time progresses. In some cases, the method of applying heat and the direction of heat flow also affect the adhesive interface, and the effect may vary from one side of the adhesive film to the other, as in preheat bonding. Finally, the reactivity of the adhesive eventually manifests itself at the interface to create that component of the bond known as specific adhesion. Considerable insight regarding the interface has been obtained by measurement of the contact angle between adhesive and adherend, and by measurement and study of surface roughness.

The five-link chain concept described previously provided a good base for studying adhesion phenomena, and again better adhesive performance most certainly resulted from the new knowledge gained. However, despite the gain in experimental precision, investigators often found that excessive variability plagued

their research results and that occasionally experiments produced conflicting data. Low shear strength combined with high wood failure under otherwise good gluing conditions finally led to suspicion that some important factor was still at large and running wild. Careful research finally traced the culprit to the subsurface area of the wood substrate. It was found that this area can be damaged during the preparation of the surface either by the cutting action of the tool, or by a combination of roll pressure and the characteristics of the wood at that point. In some cases, damage can occur as a consequence of excessive pressure applied to bring the surfaces together. Because early failure at this point constitutes technical failure of the bond, this subsurface zone was identified as another critical link in the chain. Figure 1D illustrates this new factor as links 4 and 5.

The final links in the chain were fashioned after considerable in-depth study of the action of various components of the adhesive in the

film. These last two are shown in Figure 1E as links 2 and 3. Since the adhesive is a mixture of various molecular sizes of the adhesive chemical from monomers and dimers to fairly large molecules, and various solvents and fillers, it was considered reasonable to expect some movement or stratification of the components as the polymerization reaction proceeds. For example, as adhesive and wood come together, the solvent nearest the surface is absorbed into the wood, creating a gradient in the film. Similarly, the smaller molecular pieces of adhesive material are more mobile and can diffuse more readily toward the surface of the film and thus be more available to penetrate the smaller interstices of the wood. Again, this action produces a gradient in the film. These actions can be both beneficial and destructive in the formation of bonds for long-term performance. For example, penetration of the smaller molecules into the minute structure of the cell walls promotes specific adhesion, and repairs damaged cells below the surface. On the other hand, excessive movements of the adhesive molecules toward the wood causes the remaining film to become only an inert layer of filler, incapable of developing its own cohesive strength. The result would be an ignominious failure of link 1.

These last two links bring to nine the number of links in the chain comprising the bond between two pieces of wood. Although it seems unlikely that additional links will be necessary to describe the bonding action, these nine links are the result of decades of research, and since research on adhesion is an activity of continuing importance, it is entirely possible that new links will be discovered in the future.

It is evident from this brief recitation of factors affecting adhesion that bonding is a complex operation. It seems safe to say that it is the most complex operation in the processing of any wood product. As a process on which the future of the wood industry depends, it is worthy of substantial emphasis in every wood research laboratory.

STEERING COMMITTEE FOR ACCELERATED TESTING OF ADHESIVES (SCATA)

Because of the complexity of the bonding operation, the uncertain relationships between the various factors and the expected performance in service, and the difficulty of eliminating this uncertainty, wood bonding eventually reached a plateau following World War II beyond which no further progress of significance was anticipated. Early in the 1960's, three west coast lumber associations recognized the importance of adhesive technology for the future needs of their members in extracting higher

values from the available logs. A meeting was called by the associations to which industry, government, and university scientists were invited to express their views of the current and future prospects for glued lumber products. The outcome of that meeting was a dismal assessment, the crux of which was the inability to predict the long-term performance of any new glued wood product, and particularly of any new adhesive developed for the product.

At the conclusion of the meeting, interested scientists were invited to remain for a discussion of action needed to overcome the large gap in knowledge. Although it was recognized that the gap existed because of the fact that the research task was nearly impossible to accomplish, and that no one had yet developed the courage and resources to do it, a small group of scientists vowed to tackle it in an unprecedented effort. The group was dubbed the Steering Committee for Accelerated Testing of Adhesives (SCATA) and it included one scientist from each university in the Northwest, a scientist from an adhesive manufacturer, a scientist from the wood industry, one from government, and one from an association. This group of nine met regularly for all-day sessions and painstakingly worked out the dimensions of the problem and started to dissect it into parts for separate but coordinated attack.

The charge was certainly ambitious: To develop accelerated test methods for predicting the service life of any glued wood product under any condition of service, with any adhesive, including "Adhesive X" still in the test tube, particularly the latter. The SCATA group considered all types of glued wood products likely to be produced in the future, the types of environmental exposures they would have to endure, the stresses (both external and internal), the biological degradation influences, the manufacturing processes, and the range of variability in each category. Specimen design representative of the variety of products became a major concern. Methods of accelerating the aging process were discussed at length in a search for a reasonable sequence that would produce incremental degradation capable of meaningful extrapolation to some predetermined minimum. Finally, the selected accelerated test methods would have to be confirmed by actual exposure of matched specimens at a number of locations in the United States and Canada for a period of at least 20 years.

A number of studies were carried out under the auspices of SCATA and an early review was published by Worth (20). Northcott at the Western Canadian Forest Products Laboratory worked on bond-degrading systems in an effort to develop a standard degradation pattern for a number of currently available time-tested adhesives (12). This was intended to provide

a background against which to compare the performance of any "Adhesive X" that might come along. Kreibich and Freeman at the Weyerhaeuser Company developed a continuous machine for accelerated testing of new adhesive formulations (7). Strickler at Washington State University worked on the design of test specimens including a novel idea for a standardized particle-type substrate to reduce variability (14). Courier at Oregon State University, together with Northcott and Kreibich, analyzed numerous and complex degradative influences and determined which should be considered in accelerated testing schedules (13).

This coordinated SCATA work continued for about 9 years, with the effort culminating in a grand plan to correlate accelerated testing with long-range exposure tests. The first plan called for over 2 million specimens to be made and tested, while subsequent plans sought to reduce the number. However, despite the best efforts, the cost of such a project appeared to be out of reach. The inexorable killer in these plans was the fact that the large number of specimens needed to deal with normal wood variability itself created an even larger source of variability due to the necessarily expanded manufacturing operation to produce the specimens. The additional specimens needed to cover this source of variability proved fatal to the project.

About this time, Troughton at the Western Canadian Forest Products Laboratory (15-17) and Gillespie at the U.S. Forest Products Laboratory (4,5) revealed a possible new approach to prediction of adhesive performance. This involved consideration of bond energies, hydrolysis potentials, and Arrhenius reaction rates as degradation models, and appeared to offer a direct route to characterization of "Adhesive X". It was also obviously low cost compared to the proposed SCATA approach. For these two reasons--the high cost of the SCATA plan and the promise of the Troughton-Gillespie approach--SCATA activities abated.

CONCLUSION

While work has continued on the "chemical" approach to the prediction of adhesive performance, the problem originally addressed by SCATA nearly 20 years ago still remains. Perhaps it should be classed as a "mission impossible," and cannot be solved. Nevertheless, ways must now be found to make progress in adhesive development in the absence of completely evaluated test methods for predicting long-range adhesive performance. Meantime, from a research standpoint, it appears that rate functions under controlled degradative conditions offers one of the best approaches to this problem. In addition, fundamental

studies of fracture mechanics such as those by Ebevele, River, and Koutsky (3), and those by White and Green (19) are extremely important in understanding the interface area and the contribution of the substrate to bond quality. Furthermore, a higher order of complexity can be anticipated when the newer families of composite wood materials are subjected to the same searching understanding of bond quality and durability as were solid wood and plywood.

Because of the importance of adhesives and adhesion to the future of the wood industry, and in view of the lack of feasibility of SCATA's grand plan, it is indeed heartening to participate in another sustained effort to promote progress in this field. This symposium should do much to encourage greater emphasis on adhesive studies in many laboratories, and I wish it great success to this end.

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AD P 002415

STATUS AND FORECAST FOR SUPPLY, DEMAND,
AND COST OF WOOD ADHESIVES AND BINDERS^{1/}

By

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ABSTRACT

The past and future growth of wood adhesives and binders is summarized in consumption, cost, and availability. The origin of raw materials for wood adhesives and binders is presented with reflections upon U.S.A. and world-wide demand for natural gas and petroleum oil. A forecast is presented for the future supply, demand, and cost of wood adhesives and binders based on up-to-date industry forecasts.

INTRODUCTION

Before discussing the forecast for wood binders and adhesives for the near future, it would be extremely helpful to review the previous growth of wood adhesives and binders in the U.S.A.

Because the U.S.A. is no longer 100% sufficient in petroleum oil and natural gas, and because political incidents have occurred affecting the flow of these raw materials into and within the U.S.A., many wood products consumers have become concerned of the availability of wood binders derived from these raw materials. In addition, because the price of petroleum oil has increased almost 1000% in the last decade and natural gas has risen sharply since 1973, the combination of dubious availability and rising costs has inspired considerable new research into alternate wood adhesives and binders from sources of raw materials other than petrochemicals and natural gas.

In Table 1 we obtain insight into consumer wood product types, utilizing wood adhesives and binders produced from petrochemical and natural gas derived raw materials. There are approximately twenty-two consumer wood product types listed in this

^{1/} Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

table of which at least fifteen can be classified as requiring wood adhesives and binders. These fifteen consumer wood product types consume over 40% of all the synthetic thermosetting resins produced in the U.S.A. Since urea-formaldehyde and phenol-formaldehyde synthetic resins comprise a majority of the 40% thermosetting resins consumed by the Forest Products Industries, we will be referring to them almost specifically in our comments.

A review of the past growth of urea-formaldehyde adhesives and binders for the period 1962 - 1978, with projections into 1983, is presented in Table 2. One of the largest growth rates ever for a thermosetting resin was recorded over the period 1962 - 1973 for urea-formaldehyde resins at an annual rate of approximately 13%. During this period of time, the cost of urea-formaldehyde resin barely increased, while consumption tripled. Consumption slowed, however, after 1973 and only exceeded the consumption rate of 1973 in 1978.

Melamine-formaldehyde resin parallels the trend of urea-formaldehyde resin in cost and growth rate. Concurrently, it required five years from the peak of the 1973 consumptions to return urea-formaldehyde and melamine-formaldehyde binder consumption to their previous consumption highs. During this period of time, urea-formaldehyde resin almost doubled in cost, and melamine-formaldehyde

Table 1.--Wood products requiring synthetic resins derived from petrochemicals or natural gas

Wood Product Type	Synthetic Resin or Petrochemical
Softwood Plywood	Phenol-formaldehyde Adhesives
Hardwood Plywood	Phenol-formaldehyde, Urea-formaldehyde, Melamine-formaldehyde Adhesives
Laminated Beams	Phenol-formaldehyde, Resorcinol-formaldehyde Adhesives
Flooring & Decking	Phenol-formaldehyde, Melamine-formaldehyde, Resorcinol-formaldehyde Adhesives
Treated Lumber & Poles	Perchlorophenol, Cresols, Diesel Oil
Underlayment Particleboard	Urea-formaldehyde Binders, Wax Emulsions
Industrial Particleboard	Urea-formaldehyde Binders, Wax Emulsions, Polyester Fillers, Phenol-formaldehyde Binders, Urethane/isocyanate Binders
Medium Density Fiberboard	Urea-formaldehyde, Melamine-formaldehyde Binders, Wax Emulsions
Wet-formed Hardboard	Phenol-formaldehyde Binders, Wax Emulsions
Dry-formed Hardboard	Phenol-formaldehyde Binders, Wax Emulsions
Wet-formed Insulation Board	Urea-formaldehyde, Phenol-formaldehyde Binders, Wax Emulsions
Structural Panelboard	Phenol-formaldehyde Binders & Adhesives, Wax Emulsions
Paper Overlays	Polyester, Phenol-formaldehyde, Melamine-formaldehyde & Urea-formaldehyde Saturants
Low Pressure Decorative Laminates	Melamine-formaldehyde Saturants
High Pressure Decorative Laminates	Phenol-formaldehyde, Melamine-formaldehyde Saturants
Paperboard Products	Cationic Urea-formaldehyde & Polyamide Wet Strength Agents, Styrene/Acrylic Emulsion Sizing Agents
Paper Towing	Cationic Melamine-formaldehyde Agents
Paper Coatings	Melamine-formaldehyde, Urea-formaldehyde, Styrene/Acrylic Emulsion Binders, Hydrocarbon Resins, Phenolics, Vinyl Acetate Emulsions
Furniture Finishes	Alkyd/Urea-formaldehyde & Melamine-formaldehyde Base Coats; Water Based Acrylics Base Coats; Alkyd/Amine, Alkyd/Acrylic Topcoats; Alkyd/Urea-formaldehyde Topcoats
Oil & Air Filter Paper Products	Melamine-formaldehyde and Phenol-formaldehyde Saturants
Paper Tubing Products	Phenol-formaldehyde Saturants
Molded Wood Products	Phenol-formaldehyde, Urea-formaldehyde, and Melamine-formaldehyde Binders

Table 2.--Consumption & cost of urea-formaldehyde & melamine-formaldehyde resins in the U.S.A.

Year	Consumption of Urea-formaldehyde Resin, (Millions of Lbs., Dry Basis)	Urea-formaldehyde Average Selling Price (Dry Basis)	Consumption of Melamine-formaldehyde Resins (Millions of Lbs., Dry Basis)	Melamine-formaldehyde Average Selling Price (Dry Basis)
1962	340.9	9	149	43
1972	729.3	9	199.5	35
1973	1,236.8	9	205.0	34
1974	1,031.5	15	204.3	46
1975	909.2	18	147.9	53
1976	1,041.4	18	188.4	54
1977	1,162.9	16	198.1	58
1978	1,365	17	214	59
1979	1,355	17	192	58
1983	1,575	-	255	-

Table 3.--Anticipated growth of urea-formaldehyde & melamine-formaldehyde resins (1978 - 1983) in wood products

Consumption of Melamine-formaldehyde Resins in Wood Products (Millions of Lbs., Dry Basis)

Year	Laminates	Paper Treating & Coating	Other Wood Products	Totals	Annual % Growth	% of Total M-F Market
1978	42	27	10	79	-	37%
1983	50	30	12	92	3.2%	36%

Consumption of Urea-formaldehyde Resins in Wood Products (Millions of Lbs., Dry Basis)

Year	Particleboard	Medium Density Fiberboard	Plywood	Totals	Annual % Growth	% of Total U-F Market
1978	910	135	95	1,140	-	83.5%
1983	1,030	190	100	1,340	3.5	85.1%

resins increased by 75% in cost. Both of these synthetic resins reflect the cost of natural gas, which was approximately \$0.40/Mcf in 1973, and which was approximately \$2.75/Mcf in 1978. Particleboard production, which utilizes almost 85% of the urea-formaldehyde resin consumed in the U.S.A., is expected to grow at a rate of only 2-3% annually between 1980 and 1983.

Despite intensifying concern over formaldehyde emissions, it appears unlikely that suitable alternate binders will replace urea-formaldehyde resins in wood applications during the next five years. Moreover, technological improvements in both resin manufacture and application should continue to reduce the problem of free formaldehyde. It appears that the largest market--particleboard--is reaching a point of maturity and the growth rate of urea-formaldehyde resins is slowing down. Moreover, amino-aldehyde resins in general are established products that have less potential for developing new uses and will probably grow at an overall rate of only 3-4% annually between 1980 and 1983, only slightly higher than the particleboard production rate, as seen in Table 3.

The second of the two most popular wood adhesives and binders in the U.S.A. is phenol-formaldehyde resins. Phenolic resins grew at a nominal rate of 4-5% per year in the decade from 1953 - 1963. However, in the next decade, beginning in 1963 and ending in 1973, phenol-formaldehyde resins grew at a rapid rate--7-8% annually. One of the reasons phenolic resins showed an excellent growth rate during this period was due to the sizeable increase in production of fiberglass insulation, building and home construction products, and especially plywood panels, as can be seen in Table 4. However, for the period 1980 - 1983, phenol-formaldehyde resins are expected to grow 3.5-4.5% annually, reflecting a somewhat slower growth rate and reflecting a maturing of the home and building construction markets consuming this type of wood adhesive and binder.

In conclusion, after a decade of very rapid growth--averaging between 8-13% annually, urea-formaldehyde and phenol-formaldehyde resins consumption appears to be slowing down with both product types expected to grow at a nominal rate of 3-4.5% for the next three years.

ORIGIN OF RAW MATERIALS

Now that we have reviewed the past, current, and future growth demands for wood

chemicals and binders--primarily urea-formaldehyde and phenol-formaldehyde binders and adhesives, the origin of the raw material base for these chemicals should be reviewed. Figure 1 shows the origin of urea-formaldehyde binders to be natural gas which is used to produce methanol and ammonia, which are the building blocks for this product. Methanol is the starting point raw material for manufacturing formaldehyde, which is the building block for many wood product adhesives and binders. Ammonia is the starting point raw material for urea and many other plastics. Figure 2 shows that 50% of the methanol produced in the U.S.A. is required for formaldehyde production. Phenol-formaldehyde and urea-formaldehyde resin production together consume 55% of the formaldehyde produced in the United States. There has been a real concern that the U.S.A. will deplete its holdings of natural gas, and this could lead to a shortage of urea-formaldehyde resins. However, the deregulation of natural gas has led to discovery of considerable new natural gas deposits which has allowed the U.S.A. to remain competitive in chemical formaldehyde pricing despite possible importation of methanol based on cheap international natural gas. However, the long-term world-wide supply for methanol is expected to be tight due to the increasing demand for methanol in the product lines other than formaldehyde. Agricultural urea consumes the major part of U.S.A. chemical urea and really establishes the pricing of urea going into urea-formaldehyde resins. Only 10% of the chemical urea produced in the U.S.A. is required by amino-aldehyde resins, as noted in Figure 3.

Phenol-formaldehyde resins are affected by both natural gas and petroleum oil raw material demands. The statements already made for amino-aldehyde resins concerning the natural gas/formaldehyde portion of the raw material can be reiterated for phenol-formaldehyde adhesives. Chemical phenol is derived from benzene, a building block derived from petroleum, as seen in Figure 4. Several other useful chemicals and plastics also require benzene as a building block, most noticeably--polyester resins and polyurethanes--both of which are very valuable high growth plastics. About 20% of the petrochemical benzene produced in the U.S.A. is used to produce phenol; therefore, phenolic resins must compete with the other product lines shown in Figure 5 for raw material. Since consumption of benzene is fairly well dispersed, no one particular market outlet would appear to create any demand problems. If there is a potential problem, it is the fact that benzene is pro-

Table 4.--Consumption of phenol-formaldehyde adhesive in softwood plywood production for the U.S.A.

Year	Softwood Plywood Production (Billions, P. ² , 3/8")	Composite Plywood (Billions, P. ² , 3/8")	Pounds Consumed Phenol-formaldehyde Adhesive (Billions) (1)
1960	7.8	-	0.457
1965	12.4	-	-
1970	14.3	-	0.875
1973	-	-	-
1975	15.3	-	-
1976	17.5	-	-
1977	19.4	-	1.219
1978	19.9	0.20	1.288
1980	20.95	-	1.299
1983	21.95	1.25	1.536
1986	22.85	-	1.606

(1) 40% N. V. Maximal Basis

(2) Starter A - C, 3/8" 1000 P.²

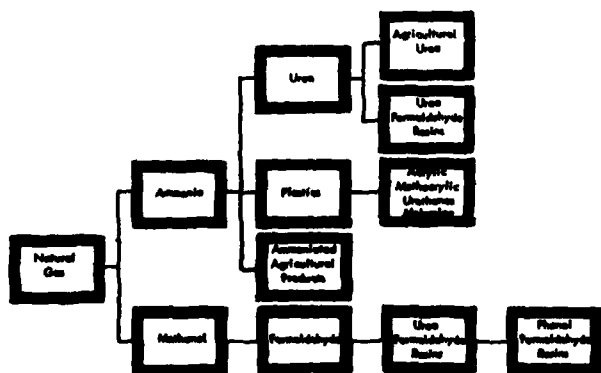


Figure 1.

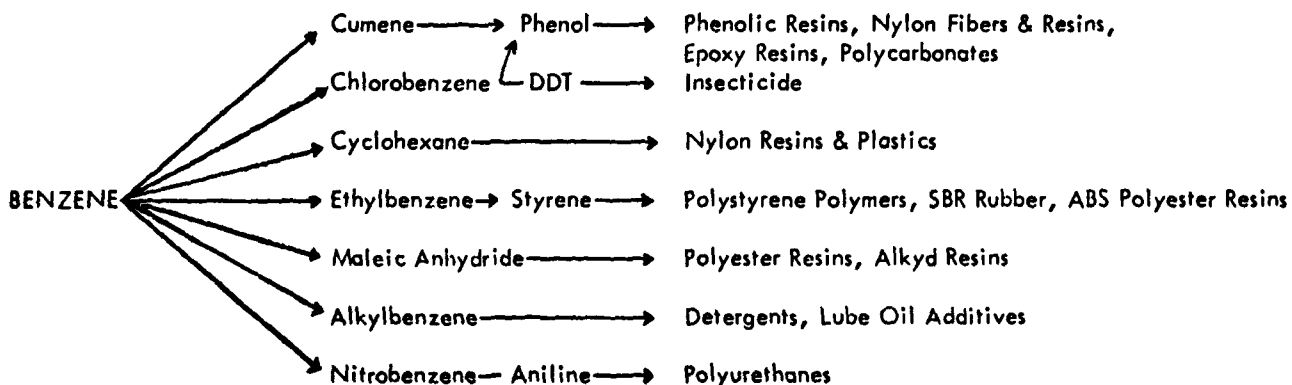


Figure 4.--Major benzene derivatives

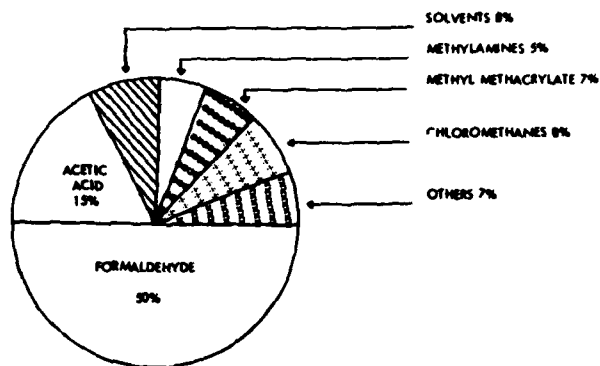


Figure 2.--Methanol end-uses

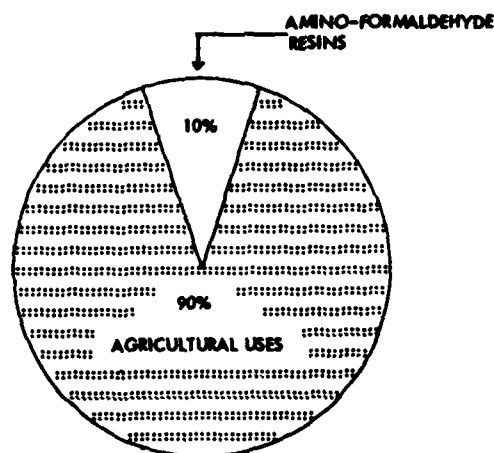


Figure 3.--Distribution of chemical urea in the U.S.A.

duced from toluene, as seen in Figure 6. The markets mentioned previously for benzene require almost 65% of all the toluene produced by the petrochemical industry. There is some real competition for toluene, as can be seen in Figure 7, since almost 90% of the toluene produced in the U.S.A. is currently consumed as an octane booster for the unleaded gasoline pool. Another way of categorizing this is that the gasoline industry uses nine times more aromatics than does the petrochemical industry. If one considers that the U.S.A. is expected to use approximately 75% unleaded gasoline in the total gasoline pool by 1985, there could be a potential problem since only 45% of the total U.S.A. gasoline pool had converted to unleaded gasoline as of June 1980, as seen in Figure 8. Unleaded gasoline requires 20-30% aromatics in the form of mostly toluene and xylene to maintain the octane number. Fortunately, other non-aromatic octane boosters have been approved and are being injected into the unleaded gasoline pool to free up aromatics for both the petrochemical and consequently the Forest Products Industries. For whatever reason, if benzene should tighten up, competition would be rigorous from the other plastics consumers mentioned previously.

Table 5 shows the distribution of crude oil into consumer products in the United States. This table shows that a very low percentage market volume of chemical raw materials (approximately 4%) is available to the petrochemical industry with the aromatics available being only 1.1% by volume. These aromatics go into thermoplastic resins such as polyethylene and thermosetting resins such as phenolics, polyesters, and polyurethanes. Table 6 shows that there are five basic thermosetting resins and approximately 12-14 thermoplastic resins being produced from the 1.0% aromatics derived from petroleum oil. The thermosets, which include phenolics, comprise only about 14% of the total synthetic resins produced in the U.S.A. The Forest Products Industries rely heavily upon thermosetting resins in that almost 40% of all thermoset resins manufactured are used in wood products of some type. Growth figures show the consumption of thermoplastic resins has increased much more rapidly over the last ten years than that of the thermosetting resins. In the event of either a petroleum oil, aromatics, or benzene shortage, the wood industries can expect thermoplastics consuming industries to vigorously compete for their sizeable share of the available raw materials. Many forecasters are predicting the growth of thermoplastics to continue at a healthy rate of 7-8% annually compared to a growth rate for thermosets of only 3-4% annually.

Table 7 shows that despite wide-sweeping price increases for all thermosetting and thermoplastic resins during the first seven months of 1980, urea-formaldehyde resins, particularly, are still a bargain based on comparison of thermosetting resins as of July 1980. Isocyanate binders are also petroleum derived and have an average cost of \$1.03/lb. for wood application and \$1.10/lb. for non-wood application. There has been recent interest in these as wood binders. Cost of thermosetting resin varies from a low of \$0.165/solid lb. to \$1.03/solid lb. In almost each instance, the cost of wood binder adhesive compares favorably with the average cost of non-wood type thermosetting resins going into other industries; thus, the 40% of thermosetting resins being sold into the wood industries are apparently being marketed at a fair price.

FORECAST OF PETROLEUM AND NATURAL GAS DERIVED WOOD ADHESIVES AND BINDERS

Table 8 shows some basic relationships among natural gas, chemical urea and methanol in relationship to urea-formaldehyde resin pricing. This relationship indicates the approximate increase in cost of urea-formaldehyde resin for various costs of natural gas. Basically, for each (increase of) \$0.50/Mcf of natural gas, U-F resins will increase by \$0.011/solid lb. In the same table we see the relationship of petroleum oil, benzene, phenol, and phenol-formaldehyde adhesive given a fixed cost of formaldehyde. Basically, this table shows that once the cost of petroleum oil reaches \$30/barrel, thereafter each \$0.04/lb. phenol increases the cost of phenolic adhesive by approximately \$0.025/solid lb. Table 9 shows that despite benzene being the main source of refined petroleum products, which have increased by 299.5% from 1971 - 1979, the corresponding rise in synthetic resin prices has been only 128.3%.

CONCLUSIONS

Gasoline demand in the United States peaked in 1979 and began to decline in 1980. This has relieved considerably the pressure on aromatics and wood binder materials. The approval by the EPA of non-aromatic octane boosters to unleaded gasoline, such as methyl tertiary butyl ether, tertiary butyl alcohol, and a substance known as MMT have freed up to approximately 17% additional aromatics for use in plastics and other industries such as the wood industries. The rapid growth of gasohol plants in the U.S.A. is beginning to

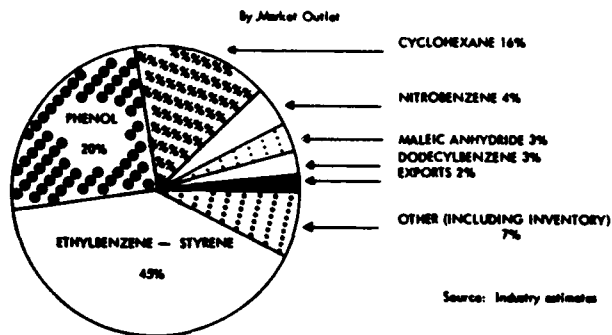


Figure 5.--Petrochemical benzene end-uses:

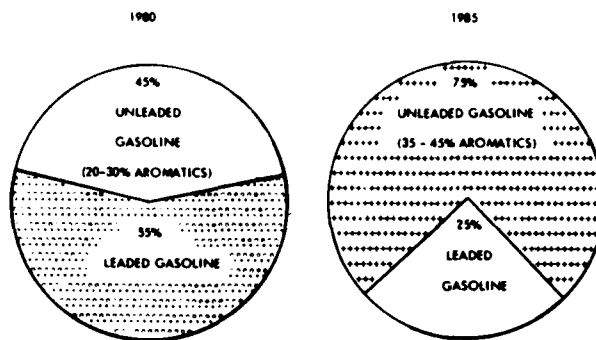


Figure 8.--Effect of change in unleaded gasoline consumption on aromatics in the U.S.A.

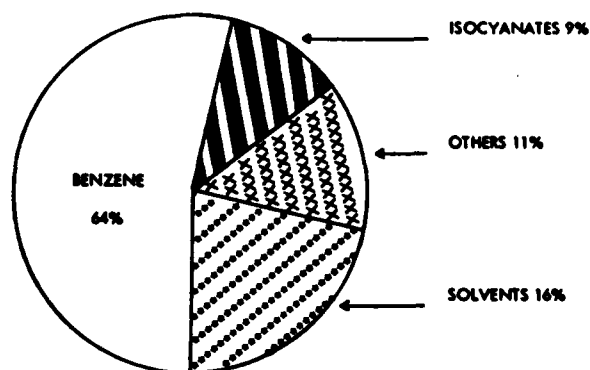


Figure 6.--U.S.A. toluene consumption into petrochemical industry.

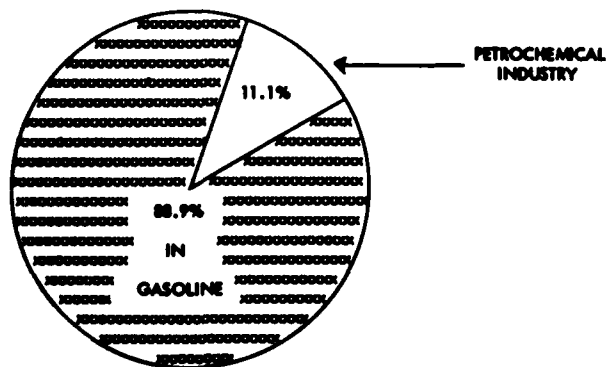


Figure 7.--Total toluene consumption in the U.S.A.

Table 5.--Distribution of crude oil into consumer products in the U.S.A.

Market Outlet	% By Volume
Gasoline	44.2
Diesel Fuel	21.4
Heating Fuel	11.5
Asphalt, Lubricants, Waxes & Misc.	12.2
Aircraft Fuel	6.6
Petrochemical Industry	
Aromatics	1.1
Olefins & Hydrocarbon Solvents	3.0
Total Petrochemicals	4.1
GRAND TOTAL	100.0

Table 6.--Comparison of wood products adhesives & binders with other synthetic resins

	Billions of Lbs., Consumed 1979 (Dry Lbs.)	Billions of Lbs., Consumed, Wood Products 1979 (Dry Lbs.)	% Used in Wood Products
THERMOSETS			
Epoxy	0.361	-	
Polyester	1.147	0.130	
Urea-formaldehyde	1.367	1.150	
Melamine-formaldehyde	0.200	0.080	
Phenol-formaldehyde	1.781	0.461	
Total Thermosets	4.833	1.821	37.3
THERMOPLASTICS			
Low Density Polyethylene	7.793		
High Density Polyethylene	5.010		
Polypropylene	3.840		
Acrylonitrile/Butadiene/Styrene	1.191		
Styrene Acrylonitrile	0.124		
Polystyrene	4.005		
Styrene Butadiene Latexes	0.607		
Other Styrene Latexes	0.030		
Styrene Polymers	0.179		
Nylon	0.327		
Polyvinyl Chloride	4.119		
Vinyl Acetate Monomer	0.739		
Polyvinyl Alcohol	0.148		
Other Vinyls	0.220		
Total Thermoplastics	30.433		
Grand Totals, Thermosets & Thermoplastics	35.310		5.2

Table 8.--Effect of natural gas on cost of urea-formaldehyde resins

Natural Gas Cost/Mcf	Chemical Urea Cost/Ton	Methanol Cost/Gal.	Urea-formaldehyde Resin Cost/Solid Lb.
\$2.00	\$170	\$0.60	\$0.1540
\$2.50	\$180	\$0.70	\$0.1630
\$3.00	\$190	\$0.80	\$0.1760
\$3.50	\$200	\$0.90	\$0.1870

EFFECT OF PETROLEUM OIL, BENZENE, AND PHENOL ON COST OF PHENOLIC RESINS

Petroleum Oil, Avg. Cost/Barrel	Benzene Cost/Gal.	Phenol Cost/Lb.	Phenol-formaldehyde Adhesive Cost/Solid Lb.
\$17.00	\$0.65	\$0.17	\$0.206
\$24.00	\$1.00	\$0.27	\$0.273
\$30.00	\$1.50	\$0.35	\$0.325
\$34.50	\$1.75	\$0.395	\$0.353
\$39.00	\$2.00	\$0.43	\$0.378

Table 7.--Cost of thermosetting resins in the U.S.A.

THERMOSETTING RESINS	SOLID COST/LB., 1 AUGUST 1980	
	AV. OF ALL TYPES	AV. OF WOOD PRODUCT CONSUMPTION TYPES
EPOXY	\$1.07/LB.	-
POLYESTER	\$0.56/LB.	\$0.56/LB.
MELAMINE-FORMALDEHYDE	\$0.70/LB.	\$0.58/LB.
UREA-FORMALDEHYDE	\$0.23/LB.	\$0.165 - \$0.175/LB.
PHENOL-FORMALDEHYDE	\$0.48/LB.	\$0.32 - \$0.34/LB.
ISOCYANATE	\$1.10/LB.	\$1.03/LB.

Table 9.--Producer price indexes for major rival materials in the U.S.A.*

Product	Price Increase (1971-1979)
Refined Petroleum Products	299.5%
Synthetic Resins	128.3%
Primary Aluminum	137.2%
Plywood	149.3%
Glass Containers	165.5%
Carbon Steel	165
Metal Container	169.4
Leather	329.4
Natural Rubber	204

*U. S. Bureau of Labor Statistics

have an effect on both fuel quantity and petroleum oil pricing.

After a decade of phenomenal growth, most wood products markets using synthetic resins have matured sufficiently in their consumption of binders and adhesives so that the future growth will be nominal, and this could lead to greater pricing stability and a secure raw material availability. The slower anticipated growth of synthetic resins for the next 3-5 years should allow a reasonable supply position of product for the Forest Products Industries.

The cost of most wood binders and adhesives compares favorably with the cost of similar products used in non-wood applications. The overall cost of synthetic resins from 1971 - 1979 was less than the increase of rival materials.

Most major wood adhesives and binder suppliers are conducting research to utilize raw materials which are not dependent upon natural gas and petroleum to supplement the current adhesives and binders being marketed today. Naturally occurring products, reactive residues, extenders, and other possibilities exist to supplement the supply of current wood binders and chemicals being utilized by the Forest Industries. All of these factors added together give confidence that the future cost and availability of wood binders and adhesives is more secure than any time in recent years.



AD P 002416

MOLECULAR PROPERTIES OF PHENOLIC ADHESIVES¹

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ABSTRACT

A study in our laboratory is attempting to relate the molecular properties of phenolics to their performance as wood adhesives. As part of that study, gel permeation chromatography was coupled with laser light scattering to measure molecular weight distribution of selected laboratory and commercial resins. This experimental approach is explained briefly with emphasis on application rather than theory.

INTRODUCTION

Phenol-formaldehyde (PF) resins dominate the American marketplace as exterior plywood adhesives because, when cured, the glue line is waterproof, infusible, and very durable. Phenol prices have increased significantly in the last 3 years and likely will continue to climb because phenol is derived from petroleum. One response of the resin industry to high phenol prices has been to try substituting naturally occurring phenolics such as lignin from pulping operations and bark tannins for the petroleum-derived phenol. But few of these adhesives have resulted in satisfactorily glued products under normal use (Hemingway 1979). The reasons for failures in both PF and substituted resins often are unknown because of the lack of a sound scientific understanding of the relationships between polymer properties and glue line performance.

Molecular parameters of resin polymers, such as molecular weight distribution, average molecular weight, residual reactivity, and degree of branching are believed to be primary variables that influence resin bulk properties such as liquid viscosity and rheology, gel time, and ability to flow and penetrate in a glue line.

¹Paper presented at the Symposium on Wood Adhesives, Madison, Wisconsin, September 23-25, 1980. Portions of the research reported here were conducted while J. D. Wellons was on sabbatical with Monsanto Chemical Company, St. Louis, Missouri. Dr. A. S. Kenyon and Mr. Phil Gillhan are gratefully acknowledged for that support.

These molecular parameters should influence both gluing process variables as well as quality of the resulting bond.

The technology is currently available to quantify these molecular parameters of resins and provide a sound scientific basis for resin synthesis. Some of the instrumentation, particularly high-performance gel permeation chromatography (GPC) in series with low-angle laser light scattering, only recently became accessible to the resin chemist for determining molecular weight distribution. This presentation focuses on successes at applying the GPC-light scattering system to molecular characterization of phenolic resins.

GPC-LIGHT SCATTERING SYSTEM

GPC has been used extensively to separate phenolic polymers by size. A sample solution of phenolic polymers is injected into a solvent stream and pumped through columns packed with porous particles. In theory, the porous particles separate the molecules by size because the smaller molecules penetrate more pores, requiring more time than large molecules to traverse the columns. As the phenolic polymers exit the columns (largest molecules first), the amounts of separated fractions are determined by ultraviolet (UV) spectroscopy or differential refractometry and recorded as a chromatogram.

A GPC separation, based on the hydrodynamic volume of the molecule, may or may not represent the true molecular weight distribution of that sample. In a good solvent, a molecule will be highly extended, have a large hydrodynamic

volume, and elute rapidly; in a poor solvent, the molecule will be less extended and elute slowly. But if the solvent is so poor that molecules aggregate, they will have an artificially large hydrodynamic volume and elute rapidly; conversely, if molecules are attracted to the porous packing material, they will elute slowly, as if smaller than they really are. However, except for aggregation, these difficulties may be overcome by inserting a light-scattering detector into the GPC system in series with a UV detector or differential refractometer. The response of these detectors as polymer elutes from the GPC columns may be used to calculate the actual molecular weight of those polymer fractions (fig. 1). No external standards are needed. The calculated molecular weights are not dependent on elution time and so are unaffected by branching, differences in hydrodynamic volume, or temporary adsorption to the packing material.

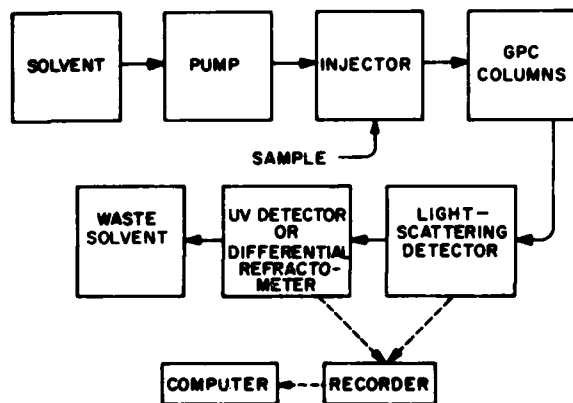


Figure 1.—Flow diagram for GPC-light scattering system.

The light scattered by a polymer solution depends primarily on the concentration of the molecules and their weight-average molecular weight. If a laser is used as the light source so that the scattered light may be measured at small angles ($2-7^\circ$) from dilute polymer solutions ($\sim 10^{-4}$ g/ml), then weight-average molecular weights may be calculated from

$$\frac{KC}{\bar{R}_\theta} = \frac{1}{\bar{M}_w} + 2A_2C \quad (1)$$

where: K = polymer optical constant
 C = concentration
 \bar{R}_θ = excess Rayleigh scattering at angle θ
 \bar{M}_w = weight-average molecular weight
 A_2 = second virial coefficient.

The concentration, C , is determined from the UV detector or differential refractometer and the excess Rayleigh scattering, \bar{R}_θ , from the light-scattering detector. The other constants in Eq. 1 are obtained empirically. The polymer optical constant, K , is calculated from measured optical properties of the polymer solution by

$$K = \frac{2}{N} \frac{\pi^2 n^2}{\lambda^4} \frac{dn}{dc}^2 (1 + \cos^2\theta) \quad (2)$$

where: n = refractive index of solvent

$\frac{dn}{dc}$ = change in refractive index of solvent by dissolved polymer

N = Avogadro's number

λ = wavelength of incident light.

The second virial coefficient, A_2 , is determined by measuring \bar{R}_θ for a series of solutions of known concentration and calculating the shape for a graph of KC/\bar{R}_θ versus C . Details of this analysis may be found in Ouano 1976 and Wellons and Gollob 1980.

To calculate a molecular weight distribution such as that shown in figure 2 from GPC-light scattering data requires that the GPC system separate the polymer into fractions of reasonably similar molecular weights. Under ideal conditions, the polymer fraction in the light-scattering detector at any instant will be narrow in molecular weight distribution (fig. 2 inset). Under those conditions, the weight-average molecular weight (\bar{M}_w) can be used to estimate the number-average molecular weight (\bar{M}_n) for each successive fraction, allowing calculation of the true molecular weight distribution for the whole sample.

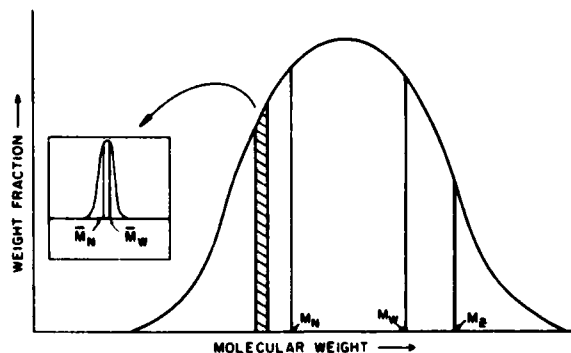


Figure 2.—Molecular weight distribution of polymer sample and ideal distribution (inset) of a separated fraction. \bar{M}_n = number-average molecular weight; \bar{M}_w = weight-average molecular weight; M_z = Z-average molecular weight.

GPC-LIGHT SCATTERING OF PHENOLICS IN TETRAHYDROFURAN

Most previous studies of the GPC of phenolic resins used either mixtures of dimethylformamide (DMF) and water (Armonas 1970) or tetrahydrofuran (THF) as the chromatographic solvent. Mixed solvents are usable for light-scattering measurements only if all solvents have the same refractive index; thus, the DMF-water system is not usable.

Phenolic resins are not soluble in THF unless neutralized. When we neutralized phenolic resins in water and allowed them to precipitate, a significant portion of the resin solids did not redissolve in THF (Wellons and Gollob 1980). When we neutralized the resins in THF-water mixtures, no precipitate appeared, but the chromatographic columns were gradually plugged by microgel particles of undissolved resin. When PF resin samples were collected during resin manufacture (as reaction time increased), neutralized in THF and water, and injected into the liquid chromatograph, the portion of the sample ultimately reaching the UV detector decreased to about 1/6 of the injected sample after the resin had been cooked only 60 minutes (fig. 3). Presumably, the higher molecular weight fractions were lost. In addition, the light-scattering response was very low because the change in refractive index of

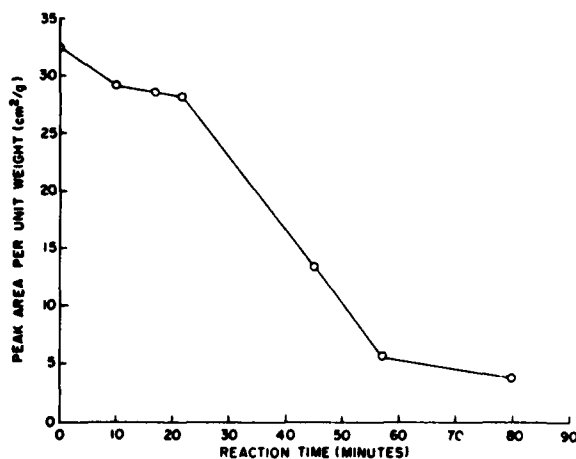


Figure 3.—Area of UV peak per gram of resin injected into chromatograph. Phenolic resin was acetic acid neutralized and pumped in 100-percent THF at a rate of 1 ml/min through μ styragel² columns (10^3 -500-500 Å) to a UV(280 nm) detector.

² μ styragel is a registered trademark of the Waters Company, Milford, Massachusetts.

the solvent (dn/dc) is very low for the THF-phenolic system. These studies convinced us that THF is not an adequate solvent for either GPC or light scattering of phenolic resins.

To improve the solubility of the phenolic resins in THF, we prepared acetate derivatives (Wellons and Gollob 1980). Unfortunately, the total sample did not acetylate sufficiently to be THF soluble with any procedures available. Furthermore, when different procedures were used to acetylate the same PF resins, each sample produced a very different light-scattering response when injected in the GPC-light scattering system. The light-scattering response was significantly reduced when acetic acid, HAC (Fig. 4a), was used in place of hydrochloric acid, HCl (Fig. 4b), to neutralize the sample before acetylation. Because these acetylation procedures may not have been free of artifacts, we felt this approach may be of questionable value.

Many other solvents, including dimethyl formamide with and without LiBr, alcohols, ethers, and ketones, were evaluated, but only one—hexafluoroisopropanol (HFIP)—was found that dissolved phenolics readily.

GPC-LIGHT SCATTERING OF PHENOLICS IN HFIP

A number of experiments³ with HFIP have convinced us that this solvent is very effective for GPC-light scattering measurement with phenolic resins. All resins studied, even highly advanced plywood resins, are soluble in HFIP, provided the resin sample is neutralized in a water-dioxane solution so that no precipitate forms, and then freeze-dried before being dissolved in HFIP.⁴ Variations of the neutralization procedure all result in the same molecular weights, which are consistent with expected values. HFIP is especially valuable for light-scattering experiments because its low refractive index (1.2649) changes substantially when phenolic polymer is dissolved in it, thus increasing the responsiveness of the light-scattering photometer.

To use the GPC-light scattering system for phenolic resin solids, we needed values of the refractive index increment, dn/dc , and the second virial coefficient, A_2 . Because the freeze-dried solids contained not only phenolic resin solids but also sodium acetate and

³Unpublished results from our laboratory.

⁴One part (by weight) of liquid resin is diluted with 1 part water and 1 part dioxane. After thorough mixing, the resulting solution is neutralized to a pH of 7 by dioxane containing 4-percent acetic acid and freeze-dried.

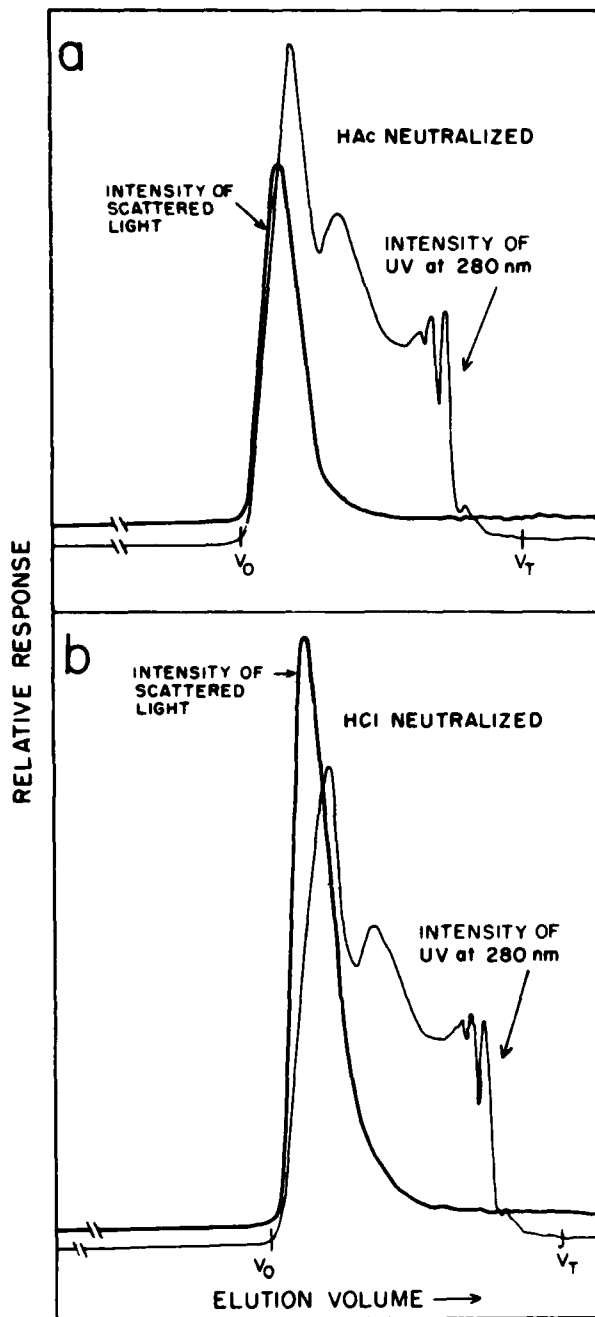


Figure 4.—GPC and light scattered from (a) acetic acid (HAc) neutralized and (b) hydrochloric acid (HCl) neutralized PF resin acetates. Neutralized phenolic resin was freeze-dried, acetylated, and pumped in 100-percent THF at a rate of 1.5 ml/min through μ styragel columns (10^5 - 10^4 - 10^3 -500-500-100 Å).

residual amounts of acetic acid, dioxane, and water, we could not measure the dn/dc of phenolic resin solids by comparing the refractive index of pure HFIP with a solution of the freeze-dried solids. Instead, for selected samples, we had to determine the exact amount of those other ingredients in the freeze-dried solids and prepare matched solutions of HFIP plus freeze-dried solids and HFIP plus equal amounts of all ingredients in the freeze-dried solids except the phenolic resin solids. The difference in refractive index between these pairs of solutions per gram of phenolic resin solids is the dn/dc of those phenolics in HFIP. The consistency of the results at various levels of solids (table 1) attests to the reliability of this method. The second virial coefficient, A_2 , was determined empirically (by the method previously described) to be $\sim 1 \times 10^{-4}$; such a low value indicates further that HFIP is almost a θ solvent for phenolic solids and is ideal for light-scattering measurements.

To evaluate HFIP as a GPC-light scattering solvent, we analyzed both laboratory-synthesized resins at various cook times and commercially available resins. Experience with polyesters and with nylon had indicated that polymer association in HFIP could be avoided by dissolving 0.08 percent by weight of sodium trifluoroacetic acid (NATFAT) in HFIP.⁵ The results reported here were obtained in HFIP containing 0.08-percent NATFAT,⁶ although subsequent research suggests that this much additive may not be necessary. GPC (fig. 5a) and light-scattering (fig. 5b) curves for a resin at various stages of cooking illustrate that the chromatographic system separates the sample into fractions to which the light-scattering detector responds strongly.

The gradual shift of the peaks from near the total permeation volume (V_T) of the columns toward the exclusion volume (V_0) is expected. As molecular weight increases during the resin cook, larger molecules should elute earlier,

⁵Personal communication with Dr. A. S. Kenyon, Monsanto Chemical Company, St. Louis, Missouri, 1980.

⁶The GPC-light scattering experiments consisted of injecting 10 to 20 μ l of a 1- to 2-percent solution of phenolic resin solids into a solvent stream of HFIP + 0.08-percent NATFAT (Waters liquid chromatograph model ALC/GPC-201). That solution was pumped through a series of μ styragel GPC columns (10^6 - 10^5 - 10^4 - 10^3 Å) at a rate of 1 ml/min, then through a Chromatix KMX-6 laser light-scattering detector ($\theta = 6-7^\circ$, $\lambda = 632.8$ nm) and a Waters R-401 differential refractometer.

Table 1.--Refractive index increment (dn/dc) of phenolic resin solids in HFIP

Sample	Total solids	Phenolic solids	dn/dc
1	6.06	3.46	0.287
2	8.72	4.97	0.285
3	12.16	6.93	0.284
4	14.83	8.46	0.285
5	17.48	9.96	0.286

i.e., nearer to V_0 . The molecular weight distributions calculated from the data in figure 5 are shown in figure 6 and the average molecular weights reported in table 2. The smoothness of these distributions and their steady shift to higher molecular weights as cook time increases are consistent with theory and suggest no artifacts. These results were quite reproducible. Similar measurements on commercial resins (table 3) resulted in number-average molecular weights that agreed reasonably with results obtained when the manufacturers used osmotic pressure.

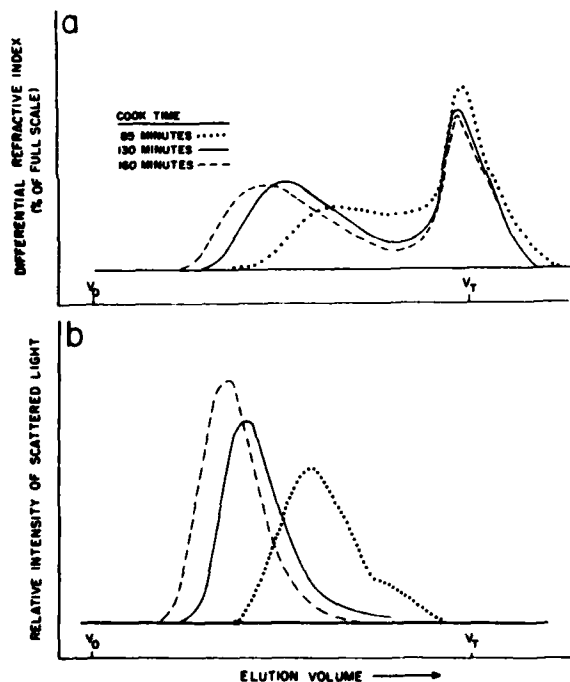


Figure 5.--(a) GPC and (b) relative intensity of the light scattered from phenolic resin solutions as a function of cook time. Phenolic resin was acetic acid neutralized in water-dioxane, freeze-dried, and pumped in HFIP + 0.08-percent NATPAT at a rate of 1 ml/min through μ styragel columns (10^0 - 10^5 - 10^4 - 10^3).

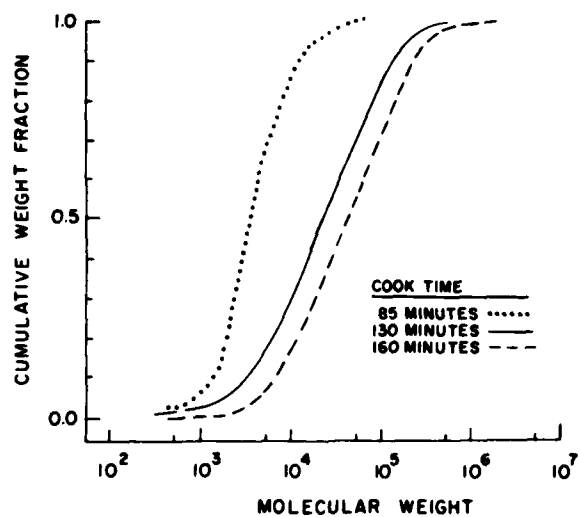


Figure 6.--Cumulative molecular weight distributions of phenolic resin solids after various cook times.

Table 2.--Molecular weights¹ of phenolic resin after various cook times

Cook time	\bar{M}_N	\bar{M}_W	\bar{M}_Z
min			
45	--2	--	--
85	2,400	5,600	14,200
130	6,600	42,400	138,000
160	11,900	99,200	335,000

¹ \bar{M}_N = number-average molecular weight;

\bar{M}_W = weight-average molecular weight; \bar{M}_Z = Z-average molecular weight.

²Too low to measure.

Table 3.--Molecular weights of commercial phenolic resins

Resin type	\bar{M}_N	\bar{M}_W	\bar{M}_Z
Particleboard	2,300	4,600	7,400
Hardboard			
Dry process	1,200	3,100	6,800
Wet process	2,300	9,400	35,000
Plywood	9,800	84,500	436,000

The GPC-light scattering analysis of phenolic resins in HFIP has two major shortcomings. First, HFIP is expensive (~ \$300/liter) and very volatile. However, it is readily recycled so that only 5 to 10 ml are consumed per sample. Second and more importantly, HFIP cannot be used on μ styragel columns of pore size less than 10^3 Å; thus, molecules smaller than 500 Daltons are not effectively resolved from each other. Furthermore, the light-scattering detector is not able to detect such small molecules even if they are chromatographed effectively. Notice in figure 5a that although the GPC signal is large near V_T , the scattered light (fig. 5b) is negligible in this same region. The large GPC peak at V_T is primarily due to sodium acetate from the resin neutralization and to residual dioxane from the freeze drying—not just to phenolic resin solids. Subsequent studies using a UV detector verified that only 10 to 15 percent of the total resin solids are included in that large peak at V_T . Thus, these analyses do exclude as much as 15 percent of the resin sample from the calculated molecular weight distributions. That exclusion could significantly affect \bar{M}_N but would have little effect on \bar{M}_W or \bar{M}_Z .

We are now developing techniques to assign molecular weights to those low molecular weight fractions with elution volume rather than scattered light. These refined calculation methods should provide better molecular weights. In any event, results such as these already give the resin chemist a rapid means for determining how resin synthesis variables influence the molecular properties of particular resins.

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AD P 002417

ACID-CATALYZED PHENOLIC BONDING OF WOOD¹

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ABSTRACT

Strong acids could be used as catalysts for several wood adhesives, including some from renewable resources. In the past, however, strong acids were found to migrate from the cured glue-line and attack the wood nearby, thus destroying the joint. Because of the potential usefulness of acid-catalyzed adhesives, two concepts for potentially reducing the acid attack were tested: Chemical entrapment of phenolic-like acids in the growing adhesive molecules, and physical entrapment of bulky acid molecules--including polymeric acids--within the cured resin matrix. The kinetics of these acid catalysts were determined and compared to resins containing standard catalysts. Other tests assessed the amount of acid that could be extracted and the durability of actual panels bonded with acid-cured glue-lines. Present results indicate that acid migration has not been decreased by either of the two methods.

INTRODUCTION

For more than 20 years exterior-durable and waterproof adhesives for wood products have been either alkaline-catalyzed phenolic resins, resorcinol resins, or phenol-resorcinol resins. The alkaline-catalyzed phenolic adhesives have been used in hot pressing operations, mainly for such wood panel products as plywood and particleboard, where heat transfer is quick enough to promote fast cure of the resin. The significantly higher-priced resorcinol and phenol-resorcinol resins are used mostly for thicker laminations where their greater reactivity compensates for the cool or only moderately warm bonding conditions.

Chemicals are added to these resins to make them cure in the desired temperature region for the manufacturer's convenience. Phenolic resins for wood are predominantly catalyzed by alkali. Alkaline phenolics are usually formulated to have pH values of 7 to 11, which is not high enough to damage wood

structure (8).² However, the rate of reaction only increases with more alkali up to additions of one mole of caustic per mole of phenol (5). Additional caustic only helps improve resin solubility and storage stability. Resins having resorcinol as the active portion are generally reacted at pH values of 6 to 9, and are therefore harmless to wood substance.

Acid-catalyzed phenolics were used for wood products commercially in the 1940's and 1950's, until durability problems appeared (2,7). The problems of glue-line failures were associated with wood's susceptibility to degradation by acids, i.e., hydrolysis. The usual acid range for reasonable room-temperature cure times of phenolic resins is from a pH of 1.0 and down (4,9). Little and Pepper (9) found pH 1.0 to be a barrier pH, so-called because the setting or curing time rises sharply as the pH values of resins increase from below 0 to near 1.0. Unfortunately, acids at pH values of 2.0 and below attack wood (8). After reviewing the literature on this problem, Chugg and Gray (3)

¹Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

²Numbers in parentheses refer to literature cited at the end of this report.

recommended working at pH values between 2.5 and 11.0. Thus at the pH region of real usefulness for cold-setting applications, the wood degradation problems are very serious. Because of the long-term degradation problems, most uses of acid-curable resins for structural components ceased in the 1950's, although some workers in the U.S.S.R. were doing active research on this problem in the mid 1970's.

With the 1973 oil embargo and subsequent dramatic rise in oil prices, wood products manufacturers and scientists began to look for cheaper ways of producing products which depended on petrochemicals, such as phenolic and resorcinolic resins. In a wood-composite product such as particleboard, glue began to make up a substantial portion of the manufacturing cost. There are two approaches to reducing costs that can be attained by changes in the adhesives: (1) Cheaper processing, (2) cheaper glues; or a combination of these. The process could be made cheaper by raising the production rate (by speeding up resin cure) or by lowering energy consumption (lowering the temperature threshold for reaction). Alternatively, the more expensive resorcinolic glues could be replaced by less expensive, durable, low-temperature curing glue; or new glues could be produced from cheaper raw materials, such as certain renewable resources attainable in the United States. To maintain lower overall costs, the new glues would need to be used in processes nearly unchanged from traditional phenolic glues.

All of the above benefits might be obtained by using acid-catalyzed adhesives.

Acid catalysis can cure phenolic resins much quicker at high catalyst concentrations than can alkaline catalysts, because on the acidic side reactivity is proportional to the hydrogen ion concentration (5,6,10), even at high concentrations.

As noted above, at pH values of 1.0 or below, acid phenolics will cure in hours at room temperature, and so might replace the much more expensive resorcinol and phenol-resorcinol adhesives.

Two types of resins that could be produced from renewable resources and are possible durable adhesive candidates are the furans (derived from hemicellulose) and lignin polymers (obtained from pulping wastes). Both of these systems are catalyzed by acid.

Still missing is a way to stop hydrolysis of the wood. Two general techniques are available for use with presently available acid-curing phenolic resins: (1) Decrease the migration (diffusion) of large amounts of the acid catalyst to the wood; and (2) neutralize the acid, after the resin is cured and before much damage is done. This work reports on experiments using the first of these two techniques.

There seemed to be two ways of decreasing the migration of acid: (1) Tie the acid chemically into the resin structure, e.g., by using organic acids which possess phenol-like structure and reactive sites; and (2) trap the acid physically within the cured resin structure, by using bulky acid molecules.

Certain requirements need to be met by any acid used as a nonleachable catalyst for phenolic resin. The addition of aqueous solutions of acids such as sulfuric, hydrochloric, or acetic, causes the resin to precipitate (12). Consequently, the more compatible sulfonic acid derivatives of aromatic hydrocarbons, such as toluene sulfonic acid, are used. Such a strong acid is used because less of it must be added, in comparison to a carboxylic acid, to achieve a given acidity for catalysis.

To compete against present resins, the acid-catalyzed resins must be able to be cured faster than the hot-press alkaline phenolics or to cure nearly as fast as the room-temperature-curing resorcinol resins.

Because pH is a logarithmic function of acid concentration, a nominal ten-fold decrease of acid concentration is required to change the resin pH from 1.0, which is common for a just-catalyzed room-temperature curing liquid resin, to values greater than 2.0, near which value wood becomes resistant to attack by acids. To accomplish this ten-fold decrease in effective acid concentration requires that less than one-tenth of the acid be extractable from the cured resin.

The final requirement is that the acid performs its function in service, providing strong, durable bonds for wood in use.

MATERIALS

The resin for trials was a commercial acid-catalyzed phenolic resin containing 70 percent solids, with a pH near 7.8. The viscosity of an as-received batch of resin measured 440 cp. An alkaline-catalyzed phenolic resin (pH 11.4), used at the Forest

Products Laboratory to bond structural flake-board, was used in a comparison of cure speeds.

The selection of acids was guided by the two techniques for trapping acids. For potential chemical entrapment, simple, phenolic-like acids were chosen: phenol sulfonic acid (PSA) and hydroquinone sulfonic acid (HSA). For physical entrapment there were two categories: polymeric and bulky monomeric acids. β -naphthalene sulfonic acid (NSA) was chosen as a bulky monomeric acid. The first choice for a polymeric acid was an experimental lignosulfonate. This had been dialyzed to obtain the more acidifiable low molecular weight fraction, nominally below 3,500 daltons. Even after acidification and concentration of this material, when 22 pph of it was added to the resin the mixture pH was 3.50, not nearly low enough for an acid cure. The next choice was a commercial polystyrene sulfonate available in the acid state and in several molecular weight grades. The two grades used in this work had nominal weight-average molecular weights of 70,000 (PSS-70) and 120,000 (PSS-120) daltons, and were obtained as 2.06N and 2.09N aqueous solutions, respectively. These grades contain about 2 percent residual sulfuric acid as contaminant.

The chemical structures of the catalysts used are shown in Figure 1. Paratoluene sulfonic acid (TSA), which has been used extensively in the past for catalyzing acid phenolics, was used as a control.

SULFONIC ACIDS USED AS CATALYSTS

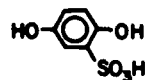
TOLUENE S.A. (TSA)



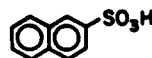
PHENOL S.A. (PSA)



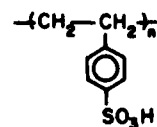
HYDROQUINONE S.A. (HSA)



NAPHTHALENE S.A. (NSA)



POLYSTYRENE S.A. (PSS)



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Figure 1.--Chemical structures of the acid catalysts used.

The monomeric acids were generally made up to 2.00N solutions, usually in methanol. The PSA was obtained as a 65 percent solution, and it was diluted to 2.00N with methanol. Solutions at the desired concentration were also made from crystals of NSA and of the hydrate of TSA. The potassium salt of HSA was acidified in an ion-exchange column and then brought to 2.00N in water solution.

METHODS

Differential Scanning Calorimetry

The altered rates of the cure reaction were determined by differential scanning calorimetry. With the wide differences in reaction rates obtained, the simplest measurement was the temperature corresponding to the peak of the curing exotherm (T_{pk}) obtained during a constant-rate temperature scan from 27° to 200° C. The scan rate was 10° C/min. A drop-let, 10 to 20 mg, was sealed in a capsule consisting of two stainless steel pans and an O-ring. This arrangement prevented any significant evaporation of volatiles from this resin up to vapor pressures around 300 psi, e.g., of water below 200° C. In the initial experiments a sample of resin was stepwise acidified with a chosen acid, stirred, and its pH measured. At chosen pH values a drop-let was transferred to a capsule for a DSC scan. Meanwhile, the resin sample was being further acidified for the next chosen pH value. For later work involving the best candidate acid and the control acid, set amounts of acid were added to a small sample of resin, the pH read, and a drop taken for a DSC scan. A new sample of resin was used for each acid concentration.

Extraction of Acid

The amount of acid that could be extracted from the cured resin was measured on ground-up resin cakes. After a one-shot addition of the precalculated amount of acid to a weighed portion of liquid resin, the sample was stirred vigorously for 1 minute with a paddle, usually divided into approximately 10 g samples in aluminum pans, weighed, and then put into an oven at a preset temperature. After the selected cure time, the samples were taken out, cooled 5 minutes in a desiccator, and weighed. If these were to be stored thereafter, it was always in a resealable polyethylene bag that was then kept refrigerated to prevent further cure. Next the resin cakes were ground in a Wiley mill to pass a 40-mesh screen, i.e., smaller than 0.42 mm. This gave

particles whose diameters approximate the thickness of a plywood glue-line. The grinding was done in successive short periods to keep the sample from getting too warm. A weighed sample of the ground resin was put in a vial, and a volume of distilled water equal to 10 times the resin weight was added. The capped vial was put on a shaker, and the pH of the mixture was monitored at 1- to 3-day intervals. As soon as the pH readings on successive measurements agreed within ± 0.01 , the extraction was considered complete. Then the contents were filtered and the vial and solids washed with distilled water. The acid content of the liquid extract was determined by filtrating with 0.0992 N sodium hydroxide solution.

Strength Durability Tests

Durability of acid-phenolic-bonded wood laminates was evaluated by shear testing after accelerated aging at 60° C and 67 percent relative humidity. The adherends were rotary-peeled yellow birch veneer, 3.2 mm thick, 150 by 150 mm panels, equilibrated at 6 percent moisture content. Resin containing an added 10 percent by weight of walnut shell flour was acidified, stirred, and brushed onto both pieces of three pairs of panels. After 10 minutes open assembly time and 15 minutes closed, the panels were individually pressed under selected temperatures and times at 1.0 MPa (150 psi). From each panel 14 single lap shear specimens, 18.0 mm wide by 62 mm long with an overlap distance of 10.0 mm, were cut. Ten specimens were randomly chosen for each aging time from among the total of 42 specimens derived from each resin mix. Besides samples tested in the initial condition, others were tested after being aged for 14, 28, or 56 days. The aging specimens were hung on small racks inside jars containing saturated sodium nitrate solutions at the bottom. When these are sealed and put in ovens at 60° C, the relative humidity inside the jars is 67 percent.

Before testing, all specimens are put through a vacuum-pressure-soak cycle, 1/2 hour for each condition. The specimens were tested wet in tensile shear at ambient temperature until the maximum force was determined. Data from 10 specimens were averaged, and the standard deviations were calculated.

RESULTS AND DISCUSSION

Rates of Reaction

A typical series of DSC scans on phenolic resins having different levels of acidity is shown in Figure 2. This figure shows that

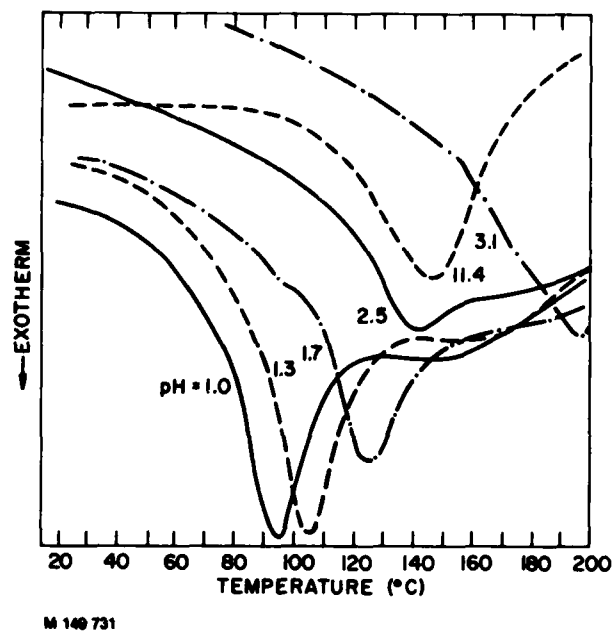


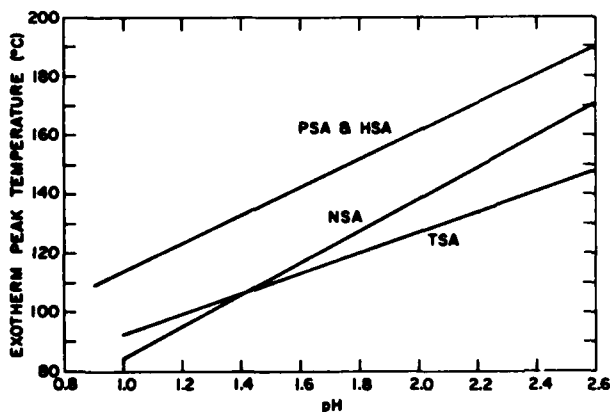
Figure 2.--Typical series of DSC scans on phenolic resins at various pH levels. Acidic resins contained TSA as catalyst, the alkaline resin was a commercial adhesive. The heating rates were 10° C/min.

TSA-catalyzed phenolic resin reacts faster than the alkaline phenolic only at pH values below about 2.5.

The exotherm peak temperatures plotted against pH values allow comparisons of the various acids' ability to increase the cure rate of the phenolic resin. For monomeric acids, this comparison is made in Figure 3. Phenol sulfonic acid (PSA) and hydroquinone sulfonic acid (HSA) showed essentially identical behavior of the exotherm temperature as a function of pH. The naphthalene sulfonic acid (NSA) showed better catalytic activity than the first two acids. However, the control toluene sulfonic acid (TSA) showed better catalytic activity than any of the other monomeric acids tried, except that NSA appeared to gain a slight advantage at pH values near 1.0.

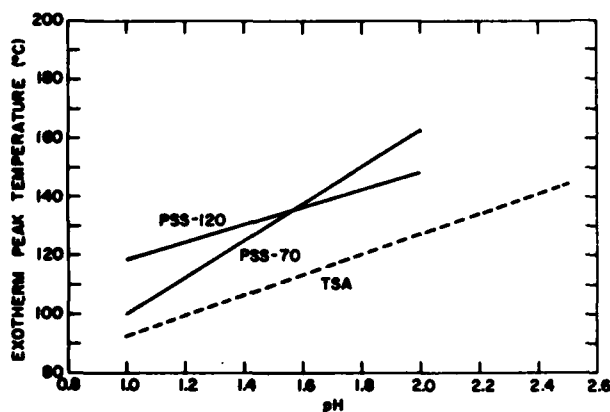
The results for the two polymeric acids and the control are compared in Figure 4. The PSS-70 did not give nearly the reactivity to the phenolic resin as did the TSA at high pH values. But at the lower pH values near where an acid catalyst would be used in practice, their catalytic abilities seemed to come much closer. The higher molecular weight PSS-120 consistently provided much less reactivity than

TSA. Based just on reactivity at a certain pH, only NSA and PSS-70 would be competitive with TSA.



M 149 732

Figure 3.--The effect of pH on the DSC exotherm peak temperature for phenolic resin catalyzed by four different monomeric acids. The heating rates were 10° C/min.

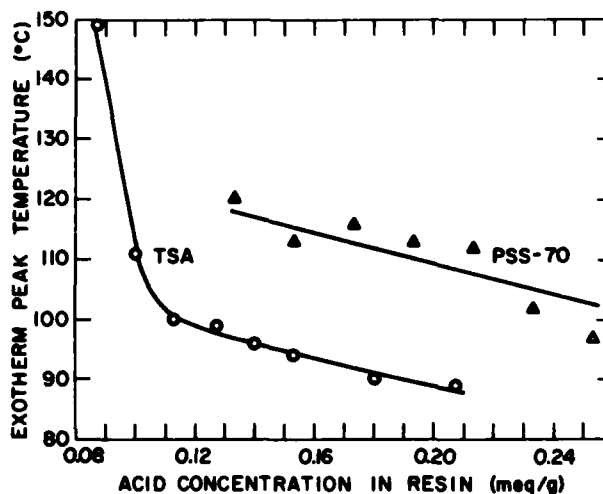


M 149 733

Figure 4.--The effect of pH on the DSC exotherm peak temperature for two polymeric acids and the TSA control. The heating rates were 10° C/min.

One other element is important to the question of catalytic reactivity: The amount of acid needed to reach a given pH and, therefore, to achieve a certain reduction in the exotherm peak temperature. At the same concentration (normality) of the acid solution, it takes about as much NSA or PSA to reach a given resin pH as it does TSA. But larger quantities of the polymeric acids are necessary, quite possibly because the acid groups on a polymer chain cannot disperse as widely as can monomeric acid molecules. This limitation

creates a bigger discrepancy between the efficiencies of PSS-70 and the control TSA, as shown in Figure 5. In this case, each point represents a separate batch of acidified resin. This plot indicates a fairly consistent 20° C disadvantage, i.e., higher temperatures are required to produce equally speedy cures for PSS-70 relative to TSA at the same concentration levels. For comparison in terms of pH rather than concentration batches of resin, each with a measured pH of 1.28, correspond in this figure to the TSA point at a concentration of 0.14 meq/g and to the PSS-70 point at 0.23 meq/g.



M 149 734

Figure 5.--The dependence of the DSC exotherm peak temperature for phenolic resin cure on acid concentration in the liquid resin for PSS-70 and for TSA. The heating rates were 10° C/min.

Extraction Results

Usually extraction experiments were run with three acids concurrently, two of the trial acids and the control acid, TSA. This seemed necessary after preliminary results indicated that the fraction of acid extractable from cured resin could vary considerably for the same acid and same cure conditions in several supposedly similar batches. Though an explanation for this has not been discovered, this variability does not invalidate the overall conclusion.

Table 1 shows the results of two sets of experiments. In the first set, all three acids were added in concentrations to give essentially equal pH. The two polymeric acids did not set hard at room temperature in the 7 days allowed for cure at room temperature.

Table 1.--Extractability of various acid catalysts from phenolic resin

Acid	Percentage extracted ^{a/}	
	23° C Cure	150° C Cure
	meq/g ^{b/}	
TSA	0.134	c/89
PSS-70	0.133	d/--
PSS-120	0.133	d/--
TSA	0.186	e/37
PSA	0.186	e/32
NSA	0.186	e/29
		f/106
		f/94
		f/98
		f/44
		f/77
		f/47

a/ Based on concentrations of acid per unit weight of solids. The numerator is based on the total weight of sample extracted. The denominator is the amount of acid added beyond that needed to neutralize initial alkali.

b/ Total meq of acid used per gram of total initial solids in the acidified liquid resin.

c/ Cured for over 4 months before extraction.

d/ Not hardened after 6 days.

e/ Cured for 3 weeks before extraction.

f/ Cured for 30 minutes.

Using the results only for the high temperature cure and comparing acid levels for equal weights of resin solid, the calculated values indicated that almost all the acid was extracted, and that the two polymeric acids extracted as easily as the control.

A comparison of two other monomeric acids with the control is shown in the lower half of table 1. Here the fraction of acid extracted is less, but still much higher than the 10 percent that had been set as a maximum limit. Once again, the trial acids were extracted as much as TSA.

One question resulting from this latter experiment was the possibility that lower temperature cures might allow less extraction than high temperature cures. This question, as well as the effect of longer cure times, was checked in experiments using four cure temperatures and different periods of cure time. Table 2 shows the results of those experiments. There is no obvious effect of temperature on extractability, and a large increase in cure time did not seem to significantly decrease extractability. The amounts

Table 2.--Effect of curing conditions on extraction of toluene sulfonic acid catalyst from cured phenolic resin

Test group	Acid concentration	Cure temperature	Cure time	Acid extracted ^{a/}
				Pct
	meq/g ^{b/}	°C		
A	0.186	23	3 weeks	39
B	0.185	65	2 hours	56
B	0.185	65	18 hours	57
C	0.185	65	2 hours	42
C	0.185	65	18 hours	45
C	0.185	105	12 minutes	46
C	0.185	105	60 minutes	46
C	0.185	150	6 minutes	44
B	0.185	150	30 minutes	55
B	0.185	150	30 minutes	57
B	0.185	150	30 minutes	52
A	0.186	150	30 minutes	57

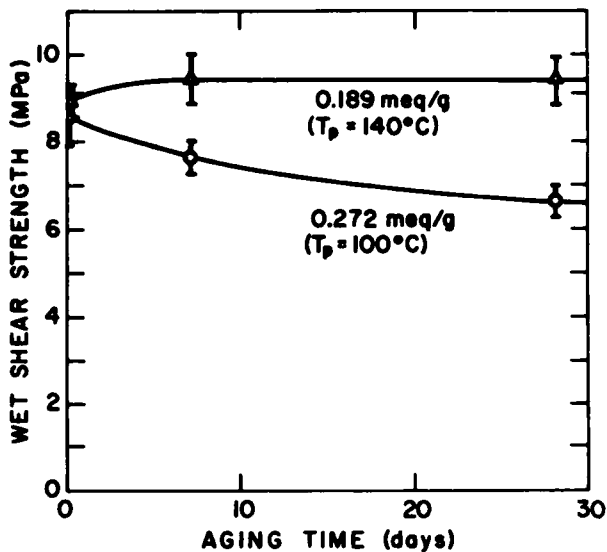
a/ Based on concentrations of acid per unit weight of solids. The numerator is based on the calculated weight of solids in the sample extracted. The denominator is the amount of acid added beyond that needed to neutralize the alkali present.

b/ Units are total meq of acid used per gram of total initial solids in the acidified liquid resin.

of acid extracted in all these cases were still much higher than the 10 percent maximum set as a guide. The present results agree with those of earlier studies. Plath's experiments (11) showed that from 30 to over 60 percent of TSA was extracted from thin films, and other scientists (1) report that the equivalent of 70 percent of the TSA added beyond neutralization of initial alkali was extractable from a resin.

Accelerated Aging

The extent of degradation of acid-catalyzed bonds was a direct consequence of the amount of acid that was added to the liquid resin. Figure 6 shows that 0.189 meq/g of TSA added to the phenolic resin did not cause any noticeable degradation of strength during 4 weeks of accelerated aging, but that an additional 50 percent acid caused considerable loss of strength in bonds made from

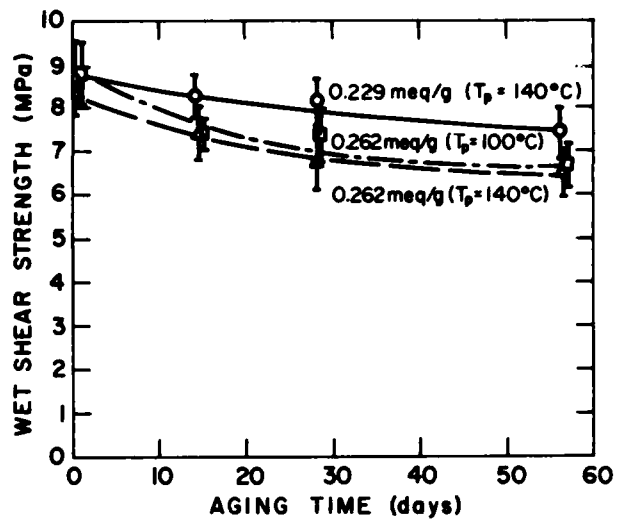


M 149 735

Figure 6.--Effect of accelerated aging at 60° C and 67 percent relative humidity on the strength of TSA-catalyzed phenolic joints, at two concentration levels.

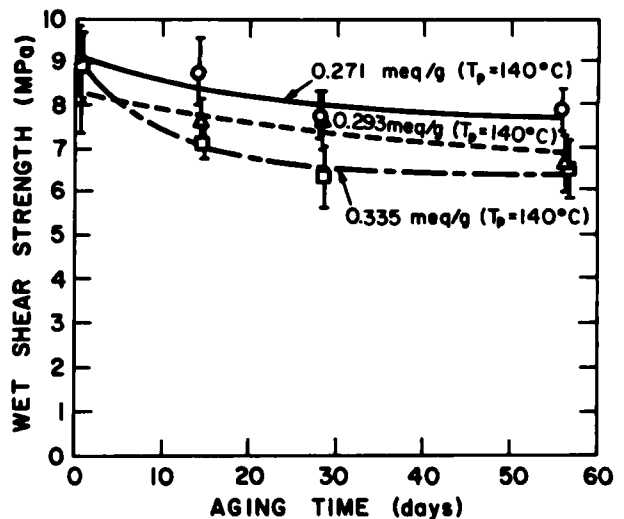
another glue mix. (The difference in press temperatures would tend to lessen expected differences, if it had any effect.)

Both TSA and PSS-70 show the progressive deterioration of bond durability as a function of acid strength. The acid levels were chosen for both acids to span a range from where acid levels had little or no effect to levels estimated to give a pH near 1.0 in the liquid resin. Figure 7 shows accelerated aging experiments on three sets of panels bonded with TSA-catalyzed resin. The 0.229 meq/g TSA sample had a measured pH of 1.08, and the two at 0.262 meq/g had measured pH values of 0.90 and 0.91. The set catalyzed with just 0.229 meq/g did show degradation, but less than with 0.262 meq/g. The different press temperature used for the two sets at 0.262 meq/g made little difference in strength retained after 8 weeks. Panels bonded with PSS-70 catalyzed resin behaved similarly, Figure 8. The three PSS-70 samples had measured pH values of 1.88 for 0.271 meq/g, 1.57 for 0.293 meq/g, and 0.92 for 0.335 meq/g. Higher levels of this acid led to progressively greater degradation after accelerated aging. These durability tests confirm the problem of excessive acid migration indicated by the extraction tests.



M 149 736

Figure 7.--The effect of two acid concentration levels and two press temperatures on the strength of TSA-catalyzed phenolic joints during accelerated aging at 60° C and 67 percent relative humidity.



M 149 737

Figure 8.--The effect of three concentration levels on the strength of PSS-70-catalyzed phenolic joints during accelerated aging at 60° C and 67 percent relative humidity.

SUMMARY

None of the acids specially chosen to provide desired better entrapment in the cured phenolic resin performed better than one of the standard commercial catalysts for acid-catalyzed phenolics, i.e., toluene sulfonic acid. This acid speeds the cure of a phenolic resin as well as any other tried, and less TSA is needed than of the polymeric sulfonic acids to reach the same low pH values or reactivity. In comparison tests the extractability of TSA was no worse than any of the other acids tried. In the phenolic resin used, bond durability after 8 weeks accelerated aging at 60° C and 67 percent relative humidity shows definite deterioration by TSA concentrations in the resin as low as 0.229 meq/g of solids. The PSS-70-catalyzed resin behaved similarly.

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EFFECT OF RESIN TYPES AND FORMULATION ON INTERNAL BOND

STRENGTH AND DIMENSIONAL STABILITY OF HARDWOOD FLAKEBOARD

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ABSTRACT

A series of experiments was conducted to develop effective and economical resin systems to improve dimensional stability of southern hardwood flakeboards. First, boards 0.5 inch thick were made from 3-inch-long flakes of nine species of southern hardwoods. Dimensional stability was measured following 5-hour boil, vacuum-pressure soak, and 50 to 90 percent RH exposure test. Within the range of the experiment, all species except white oak and post oak yielded boards of acceptable dimensional stability at board density of 44.5 pounds per cubic foot or less.

To improve dimensional stability, a resorcinol modified phenolic system was developed and tested. Although resorcinol adhesives have outstanding durability under severe test conditions, a resorcinol modified phenolic system resulted in little improvement in dimensional stability of hardwood flakeboard.

To produce a flakeboard of acceptably high durability from wood of high density species, a phenolic alloy of phenol-formaldehyde resin and polyisocyanate was developed. The key to this alloying process is to first apply minor amounts of polyisocyanate before application of major amounts of phenolic resin on wood furnish. Next would be to react to the combined adhesive in situ to obtain an improved thermosetting adhesive resin suitable for hardwood flakeboard. The performance of the new phenolic alloy is superior to phenolic resin under high flake moisture content, low resin content, and low panel density. The internal bond strength of all white oak and southern red oak panels with application of polyisocyanate before phenolic resin is more than 500 percent greater than the one with phenolic alone. Since IB is one of the most critical factors controlling the acceptable minimum panel density, the substantially greater IB is considered a favorable factor for reducing panel density to improve dimensional stability.

INTRODUCTION

The market for reconstituted wood panels for structural exterior application is potentially very large. Interest in the development of such panels has generated much recent research by corporations, university labora-

tories, government agencies, and trade associations. (See Literature Cited.)

The Pineville, Louisiana, laboratory of the Southern Forest Experiment Station has concentrated its research on making panels of flakes cut from southern hardwoods. This paper is one of a series describing efforts to develop an effective and economical resin system to improve dimensional stability of such southern hardwood flakeboards. The study involves three experiments: (1) Dimensional stability of flakeboards made from southern hardwood; (2) formulation of resorcinol-modified phenolic resin adhesives; and (3) development of a new adhesive system to improve internal bond strength and dimensional stability.

Experiment 1.--Dimensional stability of Flakeboards from Southern Hardwoods

Physical and mechanical properties of wood vary widely among hardwood species; dimensional stability of flakeboard as affected by wood species is therefore an important consideration. Nine hardwood species were selected on the basis of their abundance and wide range of properties. Flakeboards were produced from them and linear expansion and thickness swelling were determined. Details of the results were published previously (Hse 1975a).

All boards were prepared in the laboratory with flakes 3 inches long, 3/8-inch wide, and 0.015 inch thick. The flakes were from rotary-peeled veneer cut to thickness on a metal-working lathe and then accurately clipped to length and width.

The general conditions for board manufacture were:

Panel size: 19 x 20 inches
Flake moisture content: 3 percent
Resin content: 4 percent of liquid phenolic resin based on oven-dry weight of flakes
Hot press temperature: 335°F
Hot press time: 5 minutes

Ranges of average thickness swelling in the three exposure tests were:

50 to 90 percent RH---13 to 32 percent
5-hour boil---20 to 112 percent
VPS---20 to 57 percent

Thickness swelling varied from test to test. The 5-hour boil consistently resulted in the greatest swelling, followed in order by the VPS and 50- to 90-percent RH exposure test.

In 5-hour-boil and VPS tests, swelling for all species increased as panel density increased. This result was anticipated, since increase in density is achieved by increasing compaction.

In the 50- to 90-percent RH test, there was little difference in swelling between panel densities of 39.5 and 44.5 pcf. Swelling increased slightly as panel density increased to 49.5 pcf.

White oak panels swelled significantly more than those of other species. They were also notable for their substantial interparticle delamination after the 5-hour boil. In no species could a relationship be found between initial bond strength and swelling.

Ranges for average linear expansion in the three exposure tests were:

50 to 90 percent RH---0.068 to .351 percent
5-hour boil---.045 to .443 percent
VPS---.027 to .480 percent

On average, the low-density species were slightly more stable than the high-density ones. As in the test of swelling, white oak panels were the least stable.

All 49.5-pcf boards, except hickory and post oak, expanded more than either 44.5- or 39.5-pcf boards of the same species. Red maple, sweetbay, and sweetgum were the most stable of the 44.5-pcf boards. Among 39.5-pcf boards, sweetgum, and sweetbay were the most stable.

The Forest Service Task Group charged with setting performed targets for structural flakeboard¹ specified a maximum of 0.250 percent linear expansion as determined by a 30- to 90-percent RH exposure test. In the three exposure tests reported here, all 39.5-pcf boards met the specification. In the 44.5-pcf class, post oak and white oak failed. In the 45.5-pcf group, five species failed--post, white, and southern red oak, white ash, and black tupelo.

¹USDA Forest Service Task Group on Panel Product Specifications (John Zerbe, Chairman). 1973. (The national program has been described by Schaffer, E. L. 1974. Forest residue into structural particleboard: A Forest Service national program. Paper No. 74-1548, presented at 1974 Winter Meeting, Amer. Soc. Agric. Eng., Chicago, Ill., Dec. 10-13, 1974. 21 p.)

Table 1.--Dimensional stability properties of flakeboard as measured by vacuum-pressure-soak, 5-hour-boil, and RH tests

Species	Board weight	Internal bond	Vacuum-pressure soak		5-hour-boil		50-90% RH	
			Thickness swelling	Linear expansion	Thickness swelling	Linear expansion	Thickness swelling	Linear expansion
			psi		Percent			
Sweetbay	39.5	109	27.8	0.127	36.9	0.067	20.3	0.094
	44.5	260	29.3	.047	47.8	.061	16.4	.088
	49.5	236	30.1	.214	47.1	.168	21.1	.153
Red maple	39.5	97	20.3	.134	20.5	.145	13.3	.156
	44.5	284	27.1	.027	31.5	.053	13.9	.090
	49.5	315	27.8	.144	47.6	.146	20.8	.176
Sweetgum	39.5	81	23.6	.059	32.0	.095	21.6	.068
	44.5	171	31.9	.093	47.1	.045	20.8	.083
	49.5	196	42.6	.126	58.2	.164	31.8	.195
Black tupelo	39.5	113	22.3	.130	24.2	.128	15.4	.154
	44.5	239	23.4	.222	31.2	.177	14.6	.219
	49.5	385	25.7	.225	39.2	.199	21.6	.252
White ash	39.5	83	21.2	.198	23.3	.194	13.7	.204
	44.5	148	21.4	.149	28.1	.181	13.5	.174
	49.5	273	24.6	.227	40.0	.204	22.2	.259
Red oak	44.5	55	20.7	.171	26.4	.173	14.9	.169
	49.5	146	27.4	.253	51.5	.175	23.2	.251
Hickory	44.5	65	22.1	.245	27.3	.238	15.7	.212
	49.5	107	23.0	.171	33.5	.213	16.0	.172
Post oak	44.5	58	27.5	.296	63.7	.241	14.6	.270
	49.5	119	28.0	.306	65.2	.189	18.9	.268
White oak	44.5	51	48.5	.379	80.1	.314	20.1	.296
	49.5	88	56.8	.480	112.3	.443	25.6	.351

Experiment 2.--Formulation of Resorcinol Modified Phenolic Resin Adhesive

It was noted in the previous experiment that satisfactory dimensional stability (i.e., linear expansion) of panels fabricated from several hardwood species was not attained at board densities meeting strength requirements. Therefore, the objective of this experiment was to determine if a resorcinol modified phenolic system could be developed for hardwood flakeboard to improve dimensional stability. Resorcinol was chosen because it satisfies the highest requirements for glued assemblies of wood. Resorcinol adhesives have proved to be very durable under extreme test conditions and are widely used in marine plywood.

Optimizing Reaction Conditions

Basic resin formulation variables for the phenolic resin in the experiment were:

Formaldehyde to phenol molar ratio---1.9
Sodium hydroxide to phenol molar ratio---0.45
Reaction concentration---47.5 percent

Resin preparation and testing procedures were generally the same as in the previous study (Hse 1975b). To modify the phenolic resin, the selected methods of resorcinol addition were:

- (1) Phenol and formaldehyde added at beginning of cook, then resorcinol was added 1 hour later.
- (2) Resorcinol and formaldehyde added at beginning of the cook, then phenol was added 45 minutes later.
- (3) Phenol, resorcinol, and formaldehyde all were added at beginning of the cook schedule.

The total substitution of phenol by resorcinol was 10 percent.

General gluing conditions for fabrication of the three-ply, 3/8-inch southern pine plywood were:

Panel size---20 x 20 inches
 Glue spread---80 pounds per 1,000 sq ft
 of double glueline
 Closed assembly time---25 minutes
 Hot press temperature---285°F
 Hot press time---2.5 minutes
 Specific pressure---175 psi

Average percent wood failure was as follows:

Method of resorcinol addition	Percent wood failure
1. Phenol and formaldehyde at beginning of the cook, then resorcinol was added 1 hour later	71
2. Resorcinol and formaldehyde added at beginning of the cook, then phenol was added 45 minutes later.	79
3. Phenol, resorcinol, and formaldehyde all were added at beginning of the cook schedule.	85

These results indicate that blending all the phenol, formaldehyde, and resorcinol at the beginning of the reaction results in slightly better performance than adding either phenol or resorcinol separately.

Effects of Resorcinol Content on Glue Bond

Because resorcinol costs almost five times more than phenol, the amount of resorcinol in the phenolic resin strongly affects manufacturing economics of modified phenolic resins. In the subexperiment, three levels of resorcinol content (i.e., 5, 10, and 15 percent) were tested. Also included in the experiment were two formaldehyde to phenol ratios (i.e., 1.9 and 2.5). All the phenol, resorcinol, and formaldehyde were blended at the beginning of the reaction. Panel preparation and testing procedures were similar to those of the previous experiment.

Resorcinol content, formaldehyde to phenol ratio, and average percentage wood failure were:

Molar ratio formaldehyde/phenol	Resorcinol content Percent	Bond Quality	
		2.5 min. Cure time	3.5 min. Cure time
		Percent wood failure	
1.9	0	83.4	90.5
	5	75.9	87.9
	10	78.3	83.4
	15	78.8	83.0
2.5	0	87.1	90.5
	5	90.7	92.9
	10	85.0	91.1
	15	88.6	92.4

Variance analysis indicated that the percentage of wood failure differed significantly (0.05 level) with two of the three primary variables, i.e., cure time and molar ratio of formaldehyde and phenol. The significant interaction involved molar ratio of formaldehyde to phenol and resorcinol content.

As expected, bond qualities of the resin with longer cure time were significantly higher (89.0 percent average) than those with shorter cure time (83.5 percent).

On the average, 2.5 molar ratio of formaldehyde to phenol yields better glue bond (89.8 percent) than 1.9 molar ratio of formaldehyde to phenol (82.7 percent).

Resorcinol content interacted with formaldehyde to phenol ratio to affect bond quality. At a ratio of 1.9, resin without resorcinol performed better. But at ratio of 2.5, small gains in bonding accompanied resorcinol addition--the sole exception being the 10 percent resorcinol substitution of phenol. These results are graphed in figure 1.

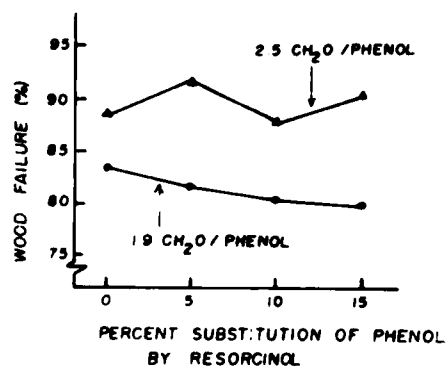


Figure 1.--Interactions of wood failure with formaldehyde to phenol ratio and resorcinol content.

Although a ratio of 2.5 formaldehyde to each phenol is not a common choice in manufacturing standard phenolic resin, it improved bonding quality of resin subjected to resorcinol modification. The conclusion was that blending phenol, resorcinol, and formaldehyde at the beginning of the reaction and 2.5 molar ratio of formaldehyde to phenol should be used for subsequent experiments.

Effects of Resorcinol Modified Phenolic Resin of Dimensional Stability

Resorcinol-modified phenolic resins were tested as possible binders for hardwood flakeboard to improve dimensional stability. In addition, resorcinol resin was formulated and applied as mixed resin system in situ with phenolic resin. Variables considered in the experiment were:

1. Resin factors
 - a. Phenolic resin without modification
 - b. Phenolic resin with 5% of phenol substituted with resorcinol
 - c. Phenolic resin with 10% of phenol substituted with resorcinol
 - d. Mixed resin of 50% phenolic resin and 50% resorcinol resin
 - e. Mixed resin of 75% phenolic resin and 25% resorcinol resin
2. Wood species
 - a. Southern red oak (Quercus falcata Michx.)
 - b. White oak (Quercus alba L.)
3. Flake moisture content
 - a. 3%
 - b. 7%

Resin Preparation

For phenolic resin, the molar ratio of formaldehyde to phenol was 1.9, reaction concentration was 47.5 percent, and molar ratio of sodium hydroxide to phenol was 0.45.

Preparation procedures for the resorcinol modified phenolic resins were generally the same as described in previous experiments. Molar ratio of formaldehyde to phenol was 2.5. All chemicals (i.e., phenol, resorcinol, and formaldehyde) were blended at the beginning of the reaction.

The basis formulation variables for resorcinol resin were:

1. Molar ratio of formaldehyde to resorcinol---0.6

2. Reaction concentration---46%
3. Initial reaction pH was 4.1 and final pH was 7.1

To prepare the resorcinol resin, all the formaldehyde, resorcinol, and water was placed in the reaction kettle. Sodium hydroxide was added to gradually increase the pH from 4.5 to 7.1 in 60 minutes. Reaction temperature was maintained initially at 75°C and increased to 90°C at 60 minutes. When viscosity reached Gardner-Holt viscosity G (\approx 300 centipoise), the reaction was terminated by rapidly cooling the mixture to 25°C.

Panel Preparation

All panels were prepared in the laboratory with flakes about 3 inches long, 0.015 inch thick, and variable in width. Both southern red oak and white oak flakes cut on a Koch shaping-lathe headrig were dried to an average moisture content of 3 percent and 7 percent before adhesive was added. General conditions for panel preparation were:

Panel size: 1/2 x 16 x 21 inches
Panel density: 45 lbs/cu ft
Resin content: Resin solid equaled 5% of the oven-dry weight of the wood furnish
Hot press temperature: 335°F
Press closing time: 45 seconds
Hot press time: 5 minutes
Replication: 3

Sampling and Testing

Boards were trimmed to 19- by 14-inch panels before cutting into 2- by 14-inch test specimens. Two specimens each were selected from each panel for vacuum-pressure-soak, dimensional stability, static bending, and creep tests. After static bending test, the specimens were cut to yield two 2- by 2-inch samples for tensile strength perpendicular to the face (internal bond).

The dimensional stability test measured changes in length and thickness when the specimens were brought from equilibrium at 90 percent RH at 80°F.

The vacuum-pressure-soak test consisted of soaking specimens in water under vacuum (25 in Hg) for one hour and then under 85 psi pressure (at room temperature) for 2 hours. Lengths and thicknesses were measured before and after soaking.

A special optical linear micrometer as described by Suchsland (1970) was fabricated

in the study for measuring the length. The device is a modified microscope featuring two microscope tubes with eyepieces and objective lenses, a stage with specimen support, and a dial gage reading to 1/10,000-inch (fig. 2).

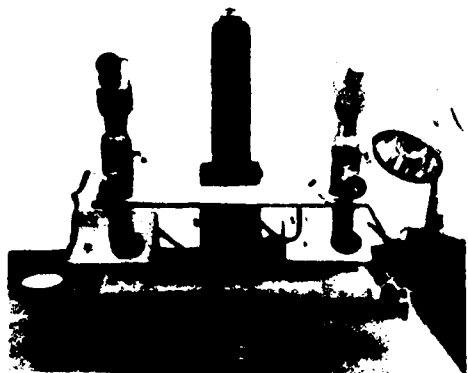


Figure 2.--Optical linear micrometer showing two microscopes, dial gage, and specimen on stage with knobs for lateral X-Y stage movement.

Results and Discussion

Table 2 summarizes average internal bond (IB) strength, linear expansion, and thickness, and resin variables.

Thickness swelling.--Average thickness swell ranged from 20.1 to 95.4 percent in the VPS and from 15.2 to 84.2 percent in 30-90 percent RH test. The VPS consistently caused more swelling than did the 30-90 percent RH test, the exception being resins with 5 or 10 percent resorcinol substitution at 30-90 percent RH with 7 percent flake moisture content.

On average, resorcinol addition, whether as direct substitution of phenol or as mixed resin *in situ* resulted in greater thickness swell, the sole exception being the white oak panels with mixed resin system. These results are graphed in figures 3 and 4.

As shown in table 2, the panels fabricated with flakes at 7 percent moisture content consistently yielded smaller thickness swell than did those fabricated at 3 percent moisture content. It is possible that higher moisture content of flakes provides more favorable conditions for wood to quickly set in a deformed shape due to plastic flow during pressing. This deformed set, in turn, results in less springback and better thickness stability.

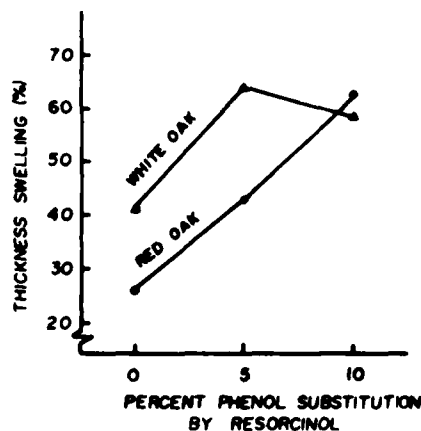


Figure 3.--Effect of resorcinol substitution of phenol on thickness swelling.

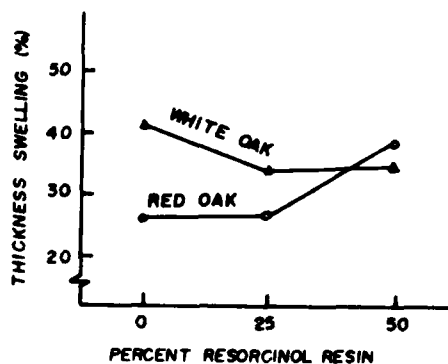


Figure 4.--Effect of mixed resin *in situ* system on thickness swelling.

It is also possible that higher flake moisture content enhances resin mobility and penetration. A study by Haygreen and Gertjensen (1971) indicated that impregnating flakes with phenolic resin produced greater dimensional stability than the same percentage of resin applied entirely as bonding resin. When the impregnating phenolic resin was applied to green flakes, the dimensional stabilizing effect was greater than if sprayed at lower moisture contents.

Linear expansion.--Average linear expansion ranged from 0.246 to 0.607 percent in the VPS and from 0.070 to 0.578 percent in 30-90 percent RH test. The VPS consistently resulted in slightly more swelling than did the 30-90 percent RH test.

Table 2.--Effect of modified phenolic resin on dimensional stability of flakeboard

Wood species and resin ¹	Vacuum-pressure-soak						30-90% RH			
	IB		Thickness swelling		Linear expansion		Thickness swelling		Linear expansion	
	3	7	3	7	3	7	3	7	3	7
	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.	percent flake M.C.
-----Percent-----										
Southern red oak										
A	64	29	26.4	26.0	0.251	0.358	22.6	15.7	0.177	0.158
B	27	49	57.8	29.6	.365	.321	50.7	30.2	.210	.134
C	9	35	92.9	33.1	.480	.302	81.5	37.6	.527	.132
D	56	69	43.5	36.0	.356	.289	37.2	33.1	.289	.214
E	71	59	33.7	18.9	.286	.276	32.6	17.9	.282	.113
White oak										
A	58	30	42.2	41.4	.444	.530	31.9	26.6	.296	.280
B	30	Delaminated	64.9	----	.474	----	43.9	----	.394	----
C	28	Delaminated	59.2	----	.570	----	46.7	----	.488	----
D	61	36	40.3	30.3	.327	.334	23.9	22.7	.261	.262
E	70	Delaminated	34.1	----	.336	----	20.5	----	.287	----

¹Resin A is a straight phenolic resin. Resin B is phenolic resin with 5% of the phenol substituted with resorcinol. Resin C is phenolic resin with 10% of the phenol substitution with resorcinol. Resin D is mixed resin *in situ* of 50% phenolic and 50% resorcinol resin. Resin E is mixed resin *in situ* of 75% phenolic acid and 25% resorcinol resin.

By analysis of variance, the effect of fortified phenolic resin, either by mixing resorcinol resin or by partial resorcinol substitution of phenol at resin formulation, on linear expansion was not significant.

As in the test of thickness swelling, white oak panels were less stable than red oak. Dimensional stability of the white oak panels made at 7 percent flake moisture content were not measured because of substantial interparticle delamination at panel fabrication.

Experiment 3.--Development of a New Adhesive System

Experiment 2 showed that a resorcinol modified phenolic system resulted in little improvement on dimensional stability of hardwood flakeboard. Thus, a series of studies were conducted to develop a phenolic alloy which would not only yield specification-grade flakeboard over a broad range of wood species and densities at an acceptable panel density, but would also tolerate high flake moisture content and temperature, high temperature and humidity in the working area, low resin application, and conditions conducive to pre-cure.

Formation of Phenolic Alloys

A commercially available polymethylene polyphenol isocyanate with functionality of 2.7 and viscosity of 200 to 275 cps at 25°C was chosen to react with phenolic resin *in situ* to form a combined adhesive system. Five flakeboards were fabricated by each of the following adhesive blending processes.

- (A-1) Applied polyisocyanate before the phenol-formaldehyde resin adhesive
- (A-2) Applied polyisocyanate and phenol-formaldehyde resin adhesive simultaneously
- (A-3) Applied phenol-formaldehyde resin adhesive before the polyisocyanate.

Both phenol-formaldehyde resin and polyisocyanate were applied by conventional air-atomizing nozzles in a rotating drum-type blender. The phenol-formaldehyde resin was 75 percent of the total amount of adhesive and the polyisocyanate constituted 25 percent.

All flakes were produced by a shaping-lathe headrig to average 3 inches long 0.015-inch thick, and were of random width. The mixed hardwood flakes were 40 percent sweetgum and 60 percent southern red oak.

The panel fabrication and testing were similar to that of experiment 1. The general conditions for panel preparation were:

Panel density---46 pcf
 Panel thickness---1/2 in.
 Resin content---4%
 Hot press temperature---300°F
 Hot press time---4.5 minutes

Average IB was as follows:

Test	Adhesive blending process	Internal bond
		psi
A-1	Polyisocyanate before phenolic	127
A-2	Polyisocyanate and phenolic simultaneously	89
A-3	Phenolic before polyisocyanate	67

These results indicate that an improved adhesive system can be achieved by applying minor components of polyisocyanate before the major component of phenolic resin on wood furnish and then reacting the combined adhesive in situ to obtain an improved thermo-setting adhesive resin suitable for hardwood flakeboard. The polyisocyanate reacts readily with hydroxy groups or water on the surface of or among the wood fibers to form strong adhesion. Subsequently, a cross-link reaction between isocyanate and phenolic resin occurs to reinforce the properties of phenolic adhesive.

Effects of Polyisocyanate:Phenolic Resin Ratio

Evidence of the superior performance of an adhesive system in which polyisocyanate is applied before phenol formaldehyde resin led to a study to determine the best ratio of polyisocyanate to phenol formaldehyde resin.

The panel fabrication and testing were as in earlier tests except the hot press time was 5.5 minutes and total resin content was 5 percent.

Polyisocyanate:resin ratio and average internal bond strengths were:

Test	Polyisocyanate phenolic resin ratio	Internal bond		
		$\frac{B^2}{A^2}$	$\frac{S^2}{A^2}$	$\frac{A^2}{A^2}$
-----psi-----				
B-1	0/100	72	72	72
B-2	10/90	99	72	72
B-3	20/80	152	97	80

2/B is application of polyisocyanate before phenolic resin. S is application of polyisocyanate and phenolic simultaneously. A is application of polyisocyanate after phenolic resin.

B-4	30/70	192	112	83
B-5	40/60	208	125	92
B-6	50/50	216	131	100
B-7	60/40	173	139	113

The superiority of applying polyisocyanate before phenolic resin is again apparent. Also, increasing the ratio of polyisocyanate to phenolic resin to 50/50 resulted in increased bond strength.

Effects of Flake Moisture Content

To measure the tolerance of applying polyisocyanate before phenolic resin when wood furnish has a high moisture content, new test conditions were chosen. The panels were prepared as previously described, again using a hot press time of 5.5 minutes and resin content of 5 percent.

Test conditions and average internal bond strengths of the panels were:

Flake moisture content (percent) and resin	Polyisocyanate:phenolic resin ratio	IB
	Percent	psi
4 percent		
C-1	0/100	72
C-2	10/90	104
C-3	30/70	169
C-4	50/50	208
11 percent		
C-5	0/100	0
C-6	10/90	72
C-7	30/70	135
C-8	50/50	174

Results again clearly demonstrate the efficiency of applying polyisocyanate before phenolic resin. Flakes having 11 percent moisture content were satisfactorily bonded by applying as little as 10 percent of polyisocyanate before the phenolic resin. In the conventional phenolic resin system, steam generated from flakes with high moisture content causes panel delamination during hot pressing.

Effects of Panel Density

The high wood density of hardwood species such as the oaks and hickories makes fabrication of low density panels from these species difficult. To measure the tolerance of the new adhesive system to high-density hardwood species, southern red oak was made into panels.

Half the panels (D-1, D-3, and D-5) were fabricated with conventional phenolic-formaldehyde resin adhesive without polyisocyanate. Panels D-2, D-4, and D-6 were fabricated by applying polyisocyanate before phenolic resin. Hot press time and total resin content were again 5.5 minutes and 5 percent. The panels were prepared and tested as described previously. Flake moisture content was 7 percent.

Panel characteristics were:

<u>Panel density and test</u>	<u>Polyisocyanate:phenolic resin ratio</u>		<u>IB</u>
	<u>Percent</u>		
41 pcf			
D-1	0/100		21
D-2	20/80		84
45 pcf			
D-3	0/100		44
D-4	20/80		124
49 pcf			
D-5	0/100		92
D-6	20/80		116

The panels fabricated with initial application of polyisocyanate had consistently higher internal bonds. Satisfactory panels were produced even at 41 pcf, which was not possible with the conventional phenolic resin.

Effects of Resin Content

In the manufacture of flakeboard panels, resin content strongly affects panel performance and manufacturing economics. Resin is the most expensive item in manufacturing cost. To measure the efficiency of the new adhesive system, resin content was varied in the series E panels.

The E-1, E-3, and E-5 panels were fabricated with conventional phenolic-formaldehyde resin adhesive without polyisocyanate; for E-2, E-4, and E-6 panels, polyisocyanate was applied before phenolic resin. The hot press time and panel density were 5.5 minutes and 44 pcf. The panels were prepared and tested as described previously.

Resin content and internal bond strengths were:

<u>Resin</u>	<u>Polyisocyanate:phenolic resin ratio</u>		<u>IB</u>
	<u>Percent</u>		
Three percent			
E-1	0/100		43
E-2	20/80		71
Four percent			
E-3	0/100		56
E-4	20/80		139
Five percent			
E-5	0/100		68
E-6	20/80		152

The superiority of the resin system containing polyisocyanate is again apparent for all resin content levels in the test.

These tests confirm that applying polyisocyanate before phenolic resin is superior to phenolic resin alone when used at high flake moisture contents and low resin content levels. Satisfactory flakeboards were formed from high-density species such as southern red oak at significantly lower panel density than that attainable with conventional phenolic resin systems.

Effects of Polyisocyanate-Phenolic Resin System on Dimensional Stability

To examine the effects of polyisocyanate-phenolic resin system on dimensional stability, the variables considered in the experiments were:

1. Resin variables
 - a. Straight phenolic resin
 - b. Mixed resin in situ of 50% phenolic and 50% polyisocyanate
 - c. Mixed resin in situ of 75% phenolic and 25% polyisocyanate
2. Wood species
 - a. Southern red oak
 - b. White oak

Panel preparation, sampling, and testing were as described in experiment 2. All flakes were conditioned to 7 percent moisture content. Panel density was 45 lb/cu ft (basis of panel weight and volume at 6 percent moisture content).

Average internal bond strength, thickness swelling, and linear expansion following vacuum pressure soak treatment are summarized in table 3.

Table 3.--Effect of polyisocyanate on dimensional stability

Wood species and resin ¹	IB	Thickness swelling ²	Linear expansion ²
		psi	Percent
Southern red oak			
A	29	26.0	0.358
B	147	27.2	.370
C	158	28.0	.343
White oak			
A	30	41.4	.528
B	176	31.8	.329
C	149	30.8	.375

¹Resin A is a straight phenolic resin.
Resin B is 50% phenolic and 50% isocyanate mix.
Resin C is 75% phenolic and 25% isocyanate mix.

²/Vacuum pressure soak treatment.

For white oak panels, application of polyisocyanate before phenolic resin resulted in substantial improvement in dimensional stability.

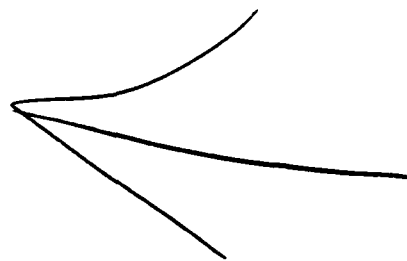
It is noted that the internal bond strength of all panels with application of polyisocyanate before phenolic resin is more than 500 percent greater than the one with phenolic alone. Since IB is one of the most critical factors controlling the acceptable minimum panel density, the substantially greater IB is therefore considered a favorable factor for reducing panel density to improve dimensional stability.

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THE USE OF FOREST AND AGRICULTURAL RESIDUE EXTRACTS IN THE PRODUCTION OF
EXTERIOR PHENOLIC RESIN ADHESIVES.

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ABSTRACT

Four types of residue materials, namely: southern pine bark, oak bark, pecan nut pith, and peanut hulls, were treated via sixteen extraction processes, yielding sixty-four kinds of extracts.

Reactivities of the extracts with formaldehyde were investigated. Some of the extracts reacted vigorously with the formaldehyde and exhibited a high degree of exothermic reaction.

In plywood and particleboard bond tests, several copolymer resins having 40 weight percent of the standard phenol replaced by the natural residue extracts, proved successful even at shorter press times than these required for commercial P-F resins. Some of the copolymer resins retain their fast curing characteristics even when 60 percent by weight of the standard phenol was replaced by the extract.

INTRODUCTION

For more than thirty years, we have known that lignin, tannin, and other polyphenols obtained from renewable sources can be used to make resins. In spite of extensive laboratory research and numerous publications, only a few actual uses have been developed so far. These investigations have resulted in the issuance of numerous U.S. and foreign patents, yet there seem to have been little in the way of industrial application of these discoveries on a commercial scale. Possible reasons for the lack of application of this technology are because of (1) the lignin or residue resins seem to require excessive cure times, (2) the reproducibility of bonding results is often not good, and/or (3) economic factors in the basic resin cost.

A series of experiments was carried out aimed at investigating the practicability of using several bark and agricultural residue components as substitutes for portions of the phenol in phenol-formaldehyde resins. This work was designed both to study opportunities for waste material utilization and to explore possible new sources of raw materials for resins and glue mixes. The primary criterion was to develop resins capable of producing acceptable bond quality as determined by industrial specifications.

EXPERIMENTS

Four kinds of residue materials, namely southern pine bark, oak bark, pecan nut pith, and peanut hulls, were extracted and treated via sixteen different treatments producing sixty-four extracts for study.

The reactivities of different phenols have been compared by several authors, by measuring the rate of disappearance of formaldehyde (e.g., Sprung, 1941), and it was felt that such information would be a good first step in evaluating the resin making potential of these extracts. Therefore, the relative reactivities of the extracts toward formaldehyde were first investigated.

Some of the extract components reacted vigorously toward formaldehyde and with a high degree of exothermic reaction at the beginning. On the other hand, some did not show this type of reaction vigor.

Several bark and residue extracts, which had been found to consume (i.e., react with) more than 50% of the available formaldehyde at the end of 120 minutes of reaction time (at 85°C), were used to prepare copolymer resins with phenol and formaldehyde.

The resultant copolymer resins were evaluated for their bond quality in southern pine plywood. The levels of 20% and 40% (weight basis) replacement of standard phenol were examined, and furthermore, press time requirements were evaluated for copolymer resins at the 40% phenol replacement level.

Some copolymer resins, involving replacement of 20% by weight of the standard phenol and a moderate level of sodium hydroxide in the resin, were comparable to the commercial phenol-formaldehyde control resin with respect to the bond quality they produced in southern pine plywood.

Several of the copolymer resins involving 40% by weight replacement of the standard phenol by extracts proved to be superior to the commercial phenol-formaldehyde control resin, especially at short press times. Of particular interest is the fact that several of these resins exhibited good bond quality even at a press time of 2 minutes (3-ply, 3/8" thick panels, pressed one panel per opening at 300°F platen temperature).

The commercial phenol-formaldehyde resin was unsatisfactory at the shortest press time of 2 minutes, although it provided satisfactory bond quality at the manufacturer's recommended 3 minutes press time and did very well at the longer press time of 4 minutes.

The copolymer resins using extracts of natural products in combination with phenol, and formaldehyde were also evaluated for their bonding qualities in particleboards and in composite panels involving flakeboard cores with veneer faces and backs.

In bonding the 5/8" homogeneous southern pine particleboards, two of the five experimental copolymer resins, namely those having 40% by weight of the standard phenol replaced by the sodium hydroxide extracts of (a) peanut hulls and (b) pecan nut pith, exhibited better bonding qualities than the resorcinol resin catalyzed commercial phenol-formaldehyde control resin. These two copolymer resins provided more than 200 psi internal bond and 2200 psi MOR with a press time of 5 minutes at 360° F platen temperature on 5/8" thick panels, whereas the commercial control resin needed longer than 6 minutes press time to achieve similar board properties.

In bonding the composite panels, the most significant and important result was that the copolymer resins involving peanut hull extracts passed the APA 6-cycle test used either in composite bonds with oak flakeboard cores and southern pine veneer surfaces or in oak or

southern pine flakeboard core materials. In composite panels, testing involves both the plywood and the particleboard bonds. Press times for the 1/4" thick flakeboard core of as short as 75 seconds were successful. However similar 1/4" thick boards made with the resorcinol catalyzed, commercial phenol-formaldehyde control resin failed the APA 6-cycle test, even at the longer press time of 120 seconds.

Two copolymer resins, with more than 50% by weight of the standard phenol replaced by the extracts of (a) peanut hulls and (b) pecan nut pith were evaluated in gluing southern pine plywood. These copolymer resins retained their fast curing characteristics, even though 60 weight percent of the standard phenol was replaced by the extracts of these natural products.

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CARBOHYDRATE TRANSFORMATION BONDINGOF LIGNOCELLULOSIC MATERIALS¹

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ABSTRACT

A study has been carried out to assess whether sugars and/or starches can be used as binders for wood. It has been found that they can be transformed by heat and suitable catalysts to solids insoluble in water and this transformation can be used for bonding wood.

INTRODUCTION

Sugars and starches are being used as adhesives in special applications where a waterproof bond is not required; mostly for bonding paper. As agricultural products, they are abundant and relatively cheap. The problem is how to transform them to polymers resistant to water at sufficiently mild conditions and short time so that they could be used as adhesives for wood.

It has been shown that sugars and starches can be transformed into furanes, which react with phenols to produce phenol-furfural resin. I have carried out a rather large study to assess whether furanes could be made to react with wood lignin in situ in a similar way as with phenol or to homopolymerize in the glue line to produce bonding of wood.

A first, quite logical approach in pursuing this idea was to try to transform wood carbohydrates at the interface into furanes and couple them with lignin. It was found that transformation of cellulosic carbohydrates requires more drastic conditions than transformation of simple sugars or starches. Easily hydrolysable sugars such as sucrose, sugar cane molasses or starches such as wheat flour can be transformed into furanes much faster; therefore, these carbohydrates were used in the study.

¹Paper presented at the Wood Adhesives--Research, Application, and Needs symposium, The Wisconsin Center, Madison, Wis., Sept. 23-25, 1980.

As catalysts, several inorganic and organic acids, several acidic salts, and a combination of acidic salts with alkalis from all three groups--hydroxides, carbonates, and amines--have been examined.

It has been found that sugars and starches can be transformed by heat and suitable catalysts to substances which either react with wood or homopolymerize to produce bonding of wood (Stofko, 1978). The main problem in this reaction is that it takes place at acidic conditions and higher temperatures that lead to cellulose degradation resulting in reduced wood strength.

It appears, however, that there are formulations of catalysts and conditions at which this reaction can be performed at a pH close to the pH of wood without serious hydrolytic degradation of wood. There are also methods of producing the necessary heat for this transformation in a reasonable short period of time.

THE ASSUMED CHEMISTRY OF BONDING

When sucrose, starch or other polymeric carbohydrates are heated under acidic conditions, they hydrolyze to monomers. Further heating at elevated temperatures results in internal dehydration of pentoses to furfural and of hexoses to HMF (hydroxymethyl-furfural) as shown in Figure 1.

HMF is an unstable compound which can rehydrate to levulinic acid (Fig. 2) or homopolymerize to a black, intractable resin, depending on the reaction conditions.

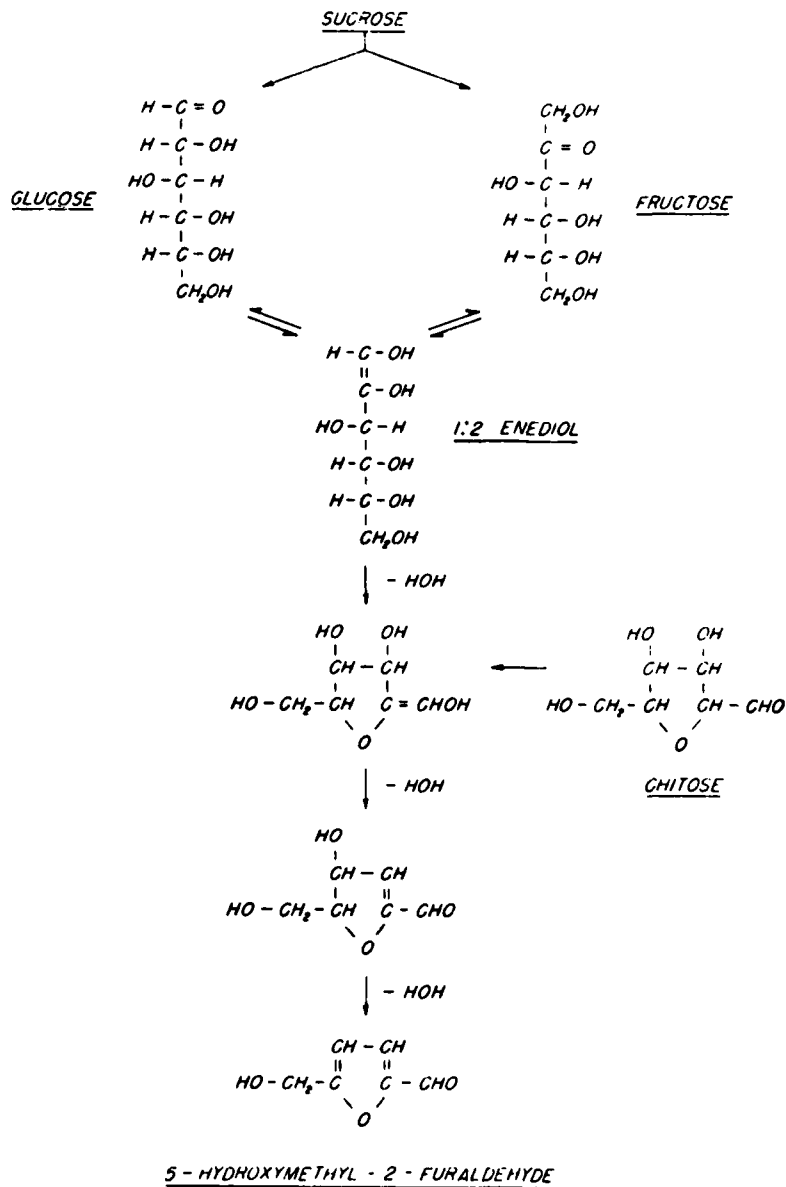


Figure 1.--Mechanism for formation of 5-hydroxymethyl - 2-furaldehyde from sucrose (U.S. F.P.L., 1967)

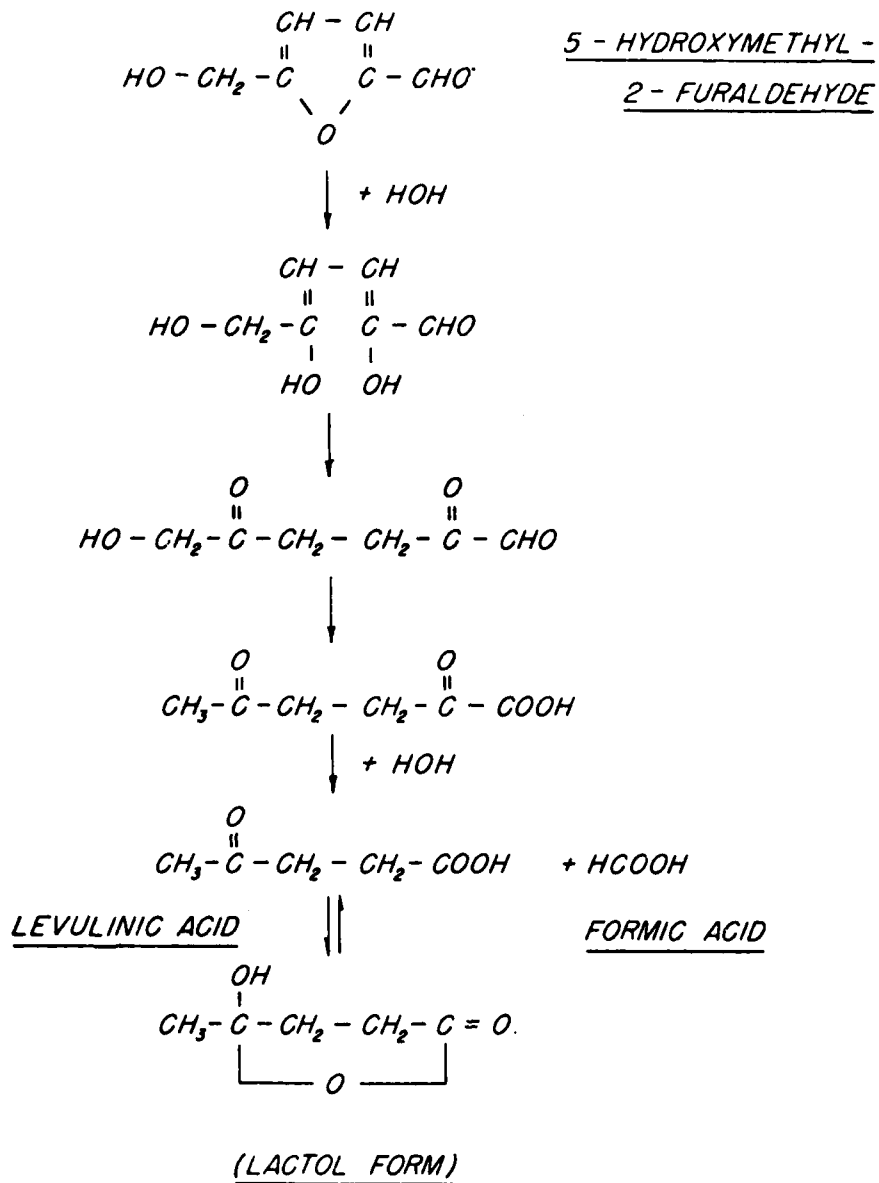


Figure 2.--Mechanism for formation of levulinic acid from 5-hydroxymethyl - 2-furaldehyde (U.S. F.P.L., 1967)

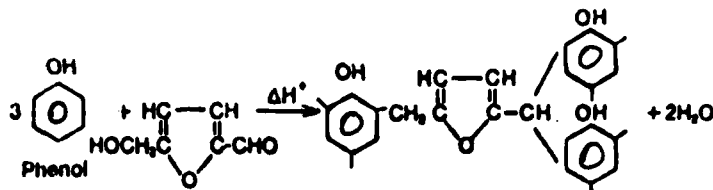


Figure 3.--Formation of Phenol-Furfural Resin

However, if HMF is formed in the presence of reactive compounds such as phenolics, it is trapped and homopolymerization to polymeric humines or rehydration of HMF to levulinic acid is prevented. The reaction of HMF with phenol under proper conditions to Novolak-type phenol-furfural resins can be visualized as shown in Figure 3.

In my system, no phenol was used, but there are wood phenolics present on the wood surface, primarily lignin. It has been reported (Nikitin, 1968) that lignin activated by acids is a reactive substance that, in the presence of suitable compounds, may react with them. Thus, in an acidic medium, lignin was found to react with phenols, alcohols, mercaptans, oxidants, and reducing agents to form derivatives. In the absence of acids, the lignin does not react with these substances. It may be assumed that acidic catalysts used to catalyze carbohydrate transformation to furanes also catalyze lignin activation and coupling with HMF. It would be very difficult to present the mechanism of such coupling at the present time.

The necessity of using acidic catalysts in the process creates a serious problem of two-stage hydrolytic degradation of wood: first, during pressing and second, a slow, long-term degradation by remnants of acids present in the products. Unless such side effects of the bonding reaction are prevented, the process cannot be accepted as a viable bonding method.

CATALYSIS OF CARBOHYDRATE TRANSFORMATION

I have examined as catalysts: (1) acids; (2) acidic salts; and (3) acidic salts in mixture with alkalis.

Acids as Catalysts

Acids were used to assess whether wood carbohydrates at the interface could be transformed to binders as well as for assessing the difference in bonding strength produced by wood carbohydrates and by sugars and starches added to the interface.

Two series of three-ply plywood of ten-inch square size were made from 1/8-, 1/16-, and 1/10-inch Douglas-Fir veneers of 4 to 6 percent moisture content. Bond properties were evaluated using standard shear tests in dry conditions and after four hours boiling in water and tested wet.

In Series I, only acidic catalysts were added to the surface to be bonded. Veneer surfaces were sprayed with the solution of either hydrochloric acid or ferric chloride so that from 0.2 to 1.2 grams of 100 percent equivalent was deposited per square foot area of the surface. Veneers were pressed at 285° to 300°F press platen temperature for five to eight minutes to plywood.

In Series II, wheat flour as starch with sulphuric or hydrochloric acids as catalysts were used. The amounts were 5 to 18 grams of solution containing 2.5 to 9 grams of carbohydrates and 0.25 to 2.5 grams of acid per square foot of surface area. Plywood was pressed at 350°F platen temperature for five to seven minutes.

The average shear strength in dry conditions and after boil-dry-boil from 51 (Series I) or 24 (Series II) specimens is presented in Table 1. Wood failure is not indicated because it is meaningless. High wood failure that may have been caused by wood degradation is not a good indicator of bond quality.

Table 1.--Bond strength produced by transformation of wood carbohydrates, sugars, and/or starches

Carbohydrates	Shear strength psi	
	Dry	After Boil-Dry-Boil
Wood Carbohydrates	81	11.5
Wheat Flour	165	67.0

Table 2.--Shear strength of plywood made of red and white Lauan using wheat flour and sucrose with NH_4Cl catalyst

Wood Species		Dry			After 3 hrs. soaking in H_2O at 140°F		
		\bar{X}	S	n	\bar{X}	S	n
White and red Lauan	psi	140.8	20.05	8	94.6	20.15	8
3-ply - .35" thick	ZWA	80.0	24.00	8	49.0	36.0	8

Table 3.--Bond strength of particleboard made of Ocoume wood and sucrose with NH_4NO_3 catalyst

		\bar{X}	S	n
Specific gravity		.675	.022	8
Internal bond - psi	Dry	120.400	8.500	8
	2 Hr. Boil	21.800	9.950	8
Thickness swelling %	24 Hr. Soak	12.400	1.350	8
	2 Hr. Boil	22.100	1.810	8
Water absorption	24 Hr. Soak	34.100	7.320	4
	2 Hr. Boil	117.000	16.000	4

Bond strength produced by transformation of wheat flour is more than two to six times higher than that produced by transformation of wood carbohydrates. This can be explained by insufficient amounts of "carbohydrate binders" in the bonding surface if only wood carbohydrates are used. It is very likely that mostly easily hydrosable hemicelluloses participate in this transformation and their amount per unit area of the surface may not be adequate.

Sugars and starches form a continuous film on the wood surface which acts as a "glue line" and provides a typical adhesive bonding similar to that of conventional adhesives. After pressing, the interface is a dark, hard solid. Wood failure is quite high, 80 to 100 percent, but not very deep, indicating that there is a wood layer close to the interface which is weaker than the rest of the wood because cellulose has been degraded.

Shear strength at dry conditions and after boil-dry-boil represents a strength which has

been reduced by first-stage degradation in the press. Series of tests performed after about 60 days have shown second-stage degradation from acids retained in the glue line. The pH of plywood after pressing was 2.5

Acidic Salts

Acidic salts were assumed to react differently than acids at carbohydrate transformation to furanes. First of all, they act only in a dissociated state. Cations are always present in the reaction medium and they may, to some degree, protect wood against hydrolytic degradation. I have examined ammonium, sodium, and potassium salts of several inorganic and organic acids. Three-ply plywood made of 0.04- to 0.094-inch veneers of red and white Lauan using the formulation of: 35 percent wheat flour, 15 percent sucrose, and NH_4Cl catalyst gave results shown in Table 2. Results did not

pass requirements of the Japanese standard that requires minimum shear strength of 99 psi.

Particleboards of 5/8- and 3/4-inch thickness were made of Ocoume wood using 8 percent sucrose (oven dry base) and NH_4NO_3 catalyst. Properties are presented in Table 3. These properties were considered satisfactory.

The measurement of pH, according to ASTM D-1583-61, of solid cured adhesive films of several formulations gave results shown in Table 4. As seen in this table, ammonium nitrate produces less acidic glue lines than ammonium chloride. The examination of other nitrates has shown that sodium or potassium nitrates cause less degradation than ammonium nitrate does. In general, however, although acidic salts were found to degrade wood less than the acids, some first-stage degradation does occur. Since pH of products was lower than pH of untreated wood, some second-stage degradation should also be expected in time.

Table 4.--Hydrogen ion concentration in cured adhesive film (according to ASTM D-1584-61)

Binder solution	Solution	Cured adhesive film
35% sucrose NH_4NO_3 catalyst	3.5	2.4
35% wheat flour 15% sucrose NH_4Cl catalyst	5.65	1.7
35% wheat flour 15% sucrose NH_4NO_3 catalyst	5.5	3.35
35% wheat flour 15% sucrose NH_4NO_3 catalyst Alkali	6.85	4.9

Acidic Salts and Alkalis

In order to reduce or eliminate the hydrolytic effect of acidic salts on wood, pretreatment of the surface to be bonded by alkali prior to applying the binder solution was examined. Such pretreatment was supposed to deposit a layer of alkali onto the surface which would act as a barrier to penetration of acidic ions from the glue line into the wood.

It was found that pretreatment as well as

admixing alkali to the binder solution reduces or eliminates wood degradation. This effect is demonstrated as the effect of board pH after pressing on physical properties of fiberboards made using 5 percent of sucrose (to oven dry weight base) at two levels of NH_4Cl and one level of NH_4NO_3 with alkali and without alkali (Table 5). Impact strength and MOR are strongly affected by pH, while internal bond is not. At reduced pH, lower MOR, tensile strength, and impact were obtained. It is obvious that NH_4Cl reduces board pH more than NH_4NO_3 . From these and other data, it appears that if pH of the board is lower than the pH of wood the board is made of, some degradation takes place. If some acid is left in the board, second-stage degradation should be expected in time. If pH of the board is equal to or higher than pH of wood, no second-stage degradation should be expected, except probably from oxidation by air oxygen if the board is of higher pH than 7.0.

However, pH of the board after pressing is not fully indicative of first-stage degradation. Dissociation of acidic salts is reversible. The pH in the board during pressing might be lower than after pressing. If pH during pressing drops too low, first-stage degradation might take place. The only way first-stage degradation can be detected is by indirect evidence from the affect on physical properties.

The addition of compatible alkalis for the purpose of protecting wood against degradation eliminates or significantly reduces the first-stage degradation during pressing. If pH of boards after pressing is close to the natural pH of wood, there are no conditions for second-stage degradation in time.

Table 6 shows shear in tension of three-ply plywood made of Japanese hardwood veneers of 0.04- to 0.094-inch thicknesses using a formulation containing wheat flour, sucrose, NH_4Cl and alkali. Bond properties achieved were considered equal to or better than properties obtained with phenol as melamine formaldehyde resins.

Figure 4 demonstrates the affect of the addition level of molasses solids on basic physical properties of medium density fiberboards. The level of potassium nitrate catalyst and alkali was kept constant. Statistical analysis has shown that differences between 10 and 15 percent add levels as well as in most properties between 5 and 10 percent are statistically insignificant.

Table 5.--The effect of pH on basic properties of fiberboards

Additives % O. D.	Board pH	Specific gravity	MOR psi	Internal bond psi	Impact ² lb.in./in. ²
5% sucrose + 1.5% NH ₄ Cl	2.4	.801	1717	77	4.9
5% sucrose + .33% NH ₄ Cl	3.5	.816	1900	108	13.0
5% sucrose + 1% NH ₄ NO ₃	2.8	.796	1728	109	7.0
5% sucrose + 1% NaNO ₃	3.9	.810	2080	85	21.0
5% sucrose + .5% NH ₄ Cl + alkali	3.8	.772	2789	76	15.2
5% sucrose + 1% NH ₄ NO ₃ + alkali	5.2	.788	2823	141	23.0
5% sucrose + 1% NaNO ₃ + alkali	7.2	.798	3113	117	26.0

Table 6.--Shear strength of plywood made of tropical hardwoods using wheat flour-sucrose with NH₄Cl catalyst and alkali

Shear strength psi											
Dry			Soaked in H ₂ O 77 hrs. at 77 ^o F			Soaked in H ₂ O 3 hrs. at 140 ^o F			Boiled in H ₂ O 4 hrs. Dried at 143 F 20 hrs. Boiled in H ₂ O 4 hrs.		
\bar{X}	S	n	\bar{X}	S	n	\bar{X}	S	n	\bar{X}	S	n
397.5	64.26	8	308	48.8	8	266	53.76	8	160.3	58.38	8
Wood Failure											
79.0	25.30	8	74	38.9	8	80	24.50	8	61.0	33.60	8

Table 7.--Basic properties of particleboards (single-layer boards of core hardwood furnish 3/4", no sizing)

	Specific gravity	MOR psi		MOE X 10 ³ psi		IB psi	24 hr. soak in H ₂ O		2 hr. boil in H ₂ O		Board pH
		Dry	Boiled	Dry	Boiled		% Swell	% ABS	% Swell	% ABS	
Interior											
\bar{X}	.729	1704.0	--	322.0	--	107.0	15.2	65.2	25.1	95.4	4.25
S	.022	142.0	--	38.4	--	26.4	6.2	12.1	9.25	22.4	
n	5	5	--	5	--	5	5	5	5	5	
8% UF Control											
	.739	1833.0		341.0		114.0	11.3	69.2	0	0	4.45
Exterior											
\bar{X}	.698	1179.0	621.0	251.0	134.0	77.0	11.27	63.6	15.08	98.7	4.20
S	.032	191.3	103.9	33.9	23.3	23.0	1.11	2.52	2.37	3.38	
n	5	5	5	5	5	5	5	5	5	5	
5.9% PF Control											
	.698	1214.0	540.0	234.0	77.0	56.0	9.85	54.17	10.88	90.8	5.90

In Table 7, properties of one-layer, interior and exterior particleboards made of coarse, core, mixed hardwood particles using sucrose, wheat flour, NH₄NO₃, and alkali are shown. Interior particleboard formulation produces a bond which does not disintegrate in boiling water, but retention of strength after two hours boiling is not sufficient. Exterior formulation does produce a boil-resistant bond and about 50 percent retention of MOR and MOE (modulus of elasticity) after two hours boiling.

CONDITIONS OF APPLICATION

Since this bonding system is only in the process of development, definite conditions and parameters cannot be presented at this time. However, some aspects of bonding reaction can be discussed here. Because of the lack of evidence, I am not in a position to say whether the original assumption of furanes coupling with lignin is valid or not. It appears that bonding taking place is chemical in nature and there are some reasons to assume that wood constituents do participate in bonding reaction. Bond formation by carbohydrates added to wood is effected by catalysts, alkali, temperature, and time, but also by chemical composition of wood itself. Because of differences in chemistry among wood species, more adjustments of the basic formulas of wood species is necessary than with conventional adhesives.

Because at dehydration of sugars to furanes, three molecules of water are eliminated from one molecule of sugar: this bonding reaction is more sensitive to moisture than phenol formaldehyde resin. Little bonding is developed at high moisture content--above 16 percent. The lower the moisture content, the higher level of bonding achieved. In fact, wood particles or veneers covered with bonding solution can be dried to very low moisture contents, close to zero, prior to pressing and still obtain good bonding. Moisture contents of 3 to 5 percent prior to spreading and 10 to 16 percent after spreading produce satisfactory results.

Amounts of bonding solution to be used have not been definitely established, but it appears that 1.2 parts of carbohydrate binder solids can be substituted for about one part of phenol formaldehyde resin solids. About 30 grams of binder solution containing about 21 grams of solids per square foot of double glue line was found producing satisfactory results in plywood. The pH of the solution is between 5 and 9, depending on the formulation, and pH of the product, between 3.8 and 5.5, depending on the formulation and pH of wood.

The most important difference to conventional adhesives is the curing temperature. At pH levels which are acceptable from

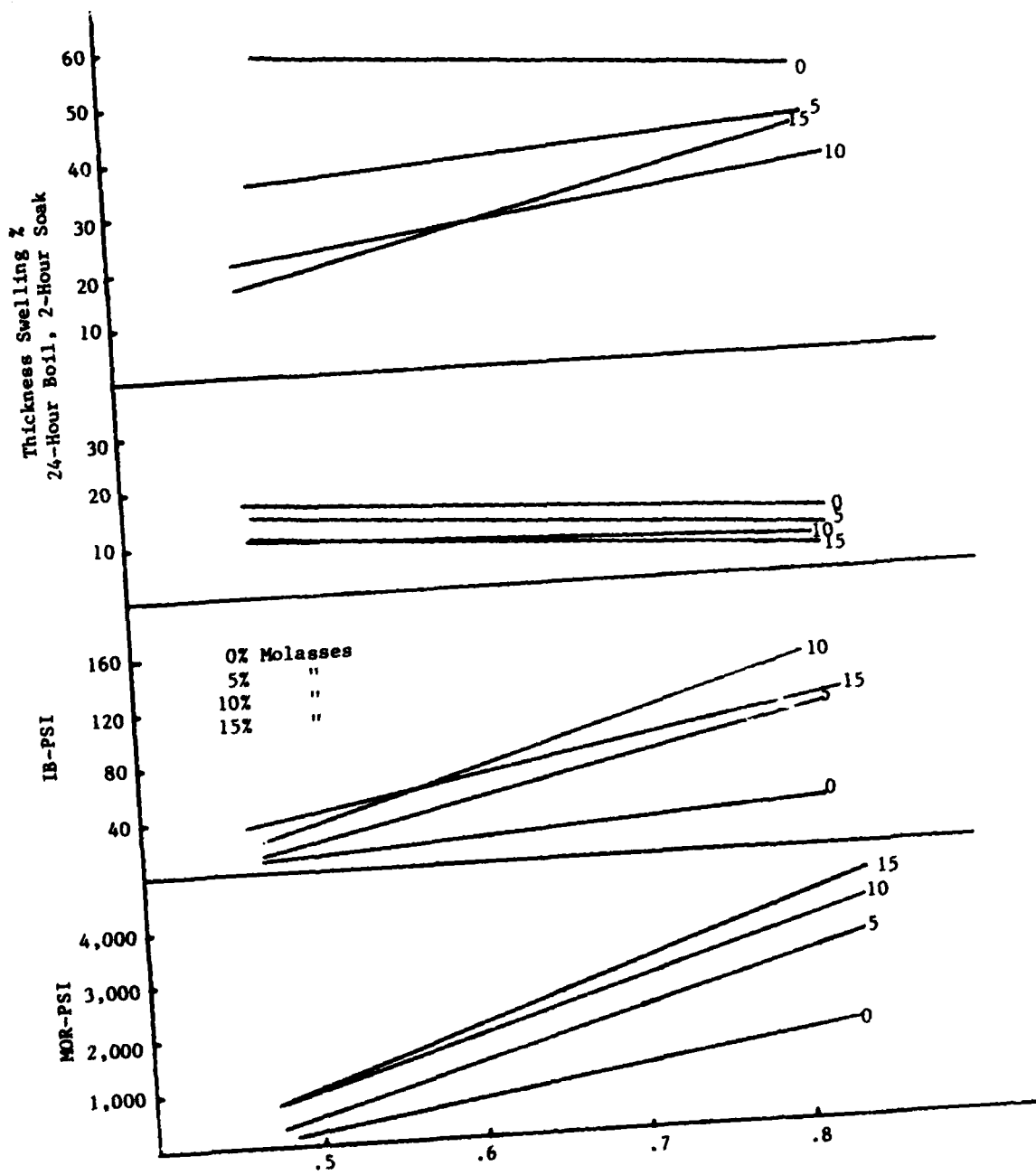


Figure 4.--Comparison of Selected Board Properties at 0 to 15 Percent Add of Molasses with KNO₃ and Alkali 1/2-Inch Fiberboards

the standpoint of degradation, transformation of sugars or starches to binders requires temperatures of 350° to 420°F. At 400°F, transformation is completed in about two minutes. At high temperatures, curing is achieved at times which are not higher than conventional pressing times. There are methods of pressing producing such acceptable press times.

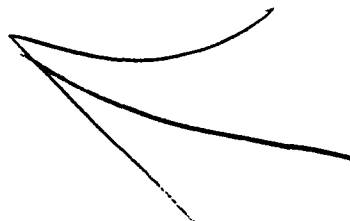
Plywood glue line produced by this process is of dark brown color, and the color of particleboard is brown, which is darker than that of phenolic particleboards.

CONCLUSION

It has been found that sugars or starches can be transformed in situ by heat and suitable catalysts to solids insoluble in water, and this transformation can be used for bonding wood. If a suitable acidic salt in the presence of a compatible alkali is used as a catalyst, bonding reactions are completed at pH levels close to the natural pH of wood without significant wood degradation. Application of the process to bonding plywood, particleboards, and fiberboards gave quite promising results.

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AD P 002420

EXTERIOR ADHESIVE FROM SULFITE

MILL EFFLUENT

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ABSTRACT

Poplar waferboards bonded with ammonium-based spent sulfite liquor (SSL) binder and properly hot pressed could readily meet the CAN 3-0188.2-M78 requirements. The abundance of SSL at low cost allows the massive use of SSL binder in waferboard production, resulting in a better quality waferboard, yet at a low production cost.

INTRODUCTION

The development of wood adhesive from spent sulfite liquor (SSL or lignosulfonate) has long been a goal for research. There are two major incentives for this: the abundant availability of SSL as a low-cost waste product and the need to reduce the pollution caused if SSL is discharged as effluent. The recent worldwide energy shortages and price increases for the synthetic resin binders commonly used in composite wood products certainly make this goal more attractive from the economic and environmental points of view.

Since the early seventies, research work has been carried out at the Eastern Forest Products Laboratory (now Forintek Canada Corp.) in Ottawa on utilizing SSL as a binder for waferboard production. As a result, we have developed several SSL binder systems. At the 1975 Wood Adhesive Symposium I presented a paper describing the bonding characteristics of acidified spent sulfite liquor (Shen 1978). The system as reported required a simple addition of sulfuric acid and was applicable to SSL of all bases. Since the binder was highly acidic some concern was expressed as to its long term durability. However, subsequent laboratory studies indicated that the acidic content of SSL binder had no adverse effect on its long term durability (Shen 1978).

In 1977, while we continued work in SSL binders, we found that ammonium-based SSL could be used as a thermosetting binder without the acidification. However, this crude SSL binder required a much longer press time and a higher platen temperature to cure. Further improvement was later obtained by fractionation of the original SSL. As a consequence, we found that the low molecular weight fraction was more reactive and hence shortened the press

time. Detailed information may be found in our previous publications (Shen and Calvé 1979, 1980, Trivedi, Fung, and Shen 1978).

Since 1979, the ammonium-based SSL binder system has been under industrial development jointly carried out by the Eastern Laboratory of Forintek Canada Corp. and Tembec Inc. This report summarizes the routine monitoring and evaluation of raw SSL from Tembec's sulfite mill as a binder for waferboard manufacture. Optimum process parameters are being developed for both SSL binder production and SSL waferboard manufacture at pilot plant scale to be carried out in the near future. In addition, both the technical and economic feasibilities of using this new SSL binder system for waferboard manufacture are briefly discussed.

PROCEDURES

Materials

1. Ammonium-Based SSL

Once every month, a few hundred gallons of raw SSL were collected directly from the cooking digesters of the Tembec Mill at the end of cooking operations. The raw SSL was shipped to Forintek for testing. The raw SSL was first concentrated by evaporation to about 45-50% solids. This concentrate could be used directly as a crude liquid SSL binder or further processed into a fine powder by spray drying (Shen, Fung and Calvé 1979). One percent of aluminum stearate by weight was added to the dried powder as a dust arrester. The powder was then ball-milled for 2 hours to obtain uniform fine particles (90% passed 200 mesh Tyler screen). The brownish powder normally contains 4-6% moisture content and has a shelf life of a few years if kept dry. The powder is somewhat hygroscopic and readily dissolves in water.

Poplar wafers 1-1/2-inch (38.1 mm) long, 0.028-inch (0.71 mm) thick and of random width used in this study were supplied by a Canadian waferboard manufacturer. Some waferboard were made with laboratory prepared poplar wafers 2-1/2-inch (63.5 mm) long, 3/4-inch (19 mm) wide and 0.018-inch (0.45 mm) thick.

Waferboard Making

Waferboard of 18 x 18 x 7/16-inch (457 x 457 x 11.1 mm) and density of 659 kg/m³ (41 pcf) were made from industrial and laboratory prepared wafers. SSL binders varying in content from 4 to 12 percent in powdered form were used. For comparison, a commercial powdered phenol formaldehyde (PF) resin was included. This phenolic resin is currently being used in Canada for waferboard manufacture. Two percent of slack wax (Esso 778) was sprayed on the wafers before they were blended with the powdered resin. The moisture content of wafers was controlled at 3% before resin blending. For board pressing, a 24 x 24-inch (610 x 610 mm) hydraulic press heated with steam to platen temperature of 210, 220 and 230°C (410, 427 and 448°F) was used. The closing pressure was 500 psi (3.45 MPa) and the press was closed to stops.

Board Evaluation

The boards were tested for mechanical properties: modulus of elasticity (MOE); modulus of rupture (MOR, both dry and wet); torsion-shear (TS, both dry and wet); and physical properties such as thickness change, springback and water absorption. The wet strength was obtained from the specimens after immersion in boiling water for 2 hours followed by immersion in cold water for one hour before testing. The boil test is specified by CAN 3-0188.2-M78 as an accelerated aging test for exterior grade composite panels (Canadian Standards Association 1978). In addition, the wet strength was measured by torsion-shear and is presented as an indication of the degree of resin binder cure. Thickness change and water absorption were also obtained from the boiled torsion-shear specimens. The springback, known as permanent set, was derived from the boiled MOR specimens after being tested and reconditioned.

The pH of waferboard was determined in a solution of 10 g of board (milled to 40 mesh particles) in 100 ml of distilled water. The solution was boiled for 4 hours, cooled, and the pH determined.

RESULTS AND DISCUSSION

Bonding Efficiency of the Crude SSL Binder

The table shows the general bonding efficiency of the 6 batches of SSL binders collected from Tembec's mill during 1979-80. Each figure represents test results from 72 waferboards equally divided into 2 press temperature and 3 press time groups. Statistical analysis indicates no significant difference in either mechanical or physical properties of waferboards, produced under similar pressing conditions, attributable to the 6 batches of the raw SSL.

TABLE Poplar waferboards bonded with 4% powdered SSL resin

Batch	Press		Density (pcf)*	MOR (psi)		MOE 1,000 (psi)	Torsion-Shear (in-lb)		Thick Exp.	Water Absorb.
	Temp (°C)	Time (min)		Dry Wet			Dry	Wet		
1	210	8	42.2	2940	0	655	66.1	0	D	D
		10	41.0	3100	1080	634	66.1	12.7	64	165
		12	43.0	3220	1640	640	72.7	20.0	54	157
1	220	8	42.6	3080	1530	753	66.1	10.9	62	166
		10	42.5	3470	1630	691	70.0	26.8	41	147
		12	42.5	2920	1500	664	71.9	34.8	36	135
2	210	8	43.1	3270	540	639	65.4	0	D	D
		10	42.8	3370	1280	691	65.9	14.7	57	164
		12	42.6	2910	1640	655	76.5	24.5	52	153
2	220	8	42.6	2840	1360	690	65.5	13.4	57	165
		10	42.0	3480	1800	719	70.3	25.8	46	144
		12	41.7	2700	1630	703	73.9	38.4	40	134
3	210	8	43.5	3310	480	693	67.1	0	D	D
		10	44.0	3650	1660	711	71.8	17.4	61	169
		12	42.2	3430	1760	659	74.4	28.4	50	143
3	220	8	43.2	3550	1790	799	52.2	1.9	73	172
		10	42.1	2710	1740	602	51.6	22.7	49	147
		12	42.9	3120	1970	709	60.6	28.3	41	140
4	210	8	43.3	3140	0	685	64.7	0	D	D
		10	42.6	2920	1350	691	75.2	9.5	72	163
		12	42.0	2820	1430	664	69.3	15.7	52	162
4	220	8	41.8	2830	800	656	65.3	30	D	D
		10	42.9	2940	1670	674	68.4	20.6	49	158
		12	42.3	2710	1730	601	68.7	30.0	38	140
5	210	8	40.0	2670	480	693	67.1	0	D	D
		10	42.2	3010	1660	711	71.8	17.4	61	169
		12	41.7	2650	1760	659	74.4	28.4	50	143
5	220	8	43.2	3550	1790	799	73.4	15.2	61	152
		10	42.1	2710	1740	602	69.8	26.4	41	142
		12	42.9	3120	1970	709	77.6	40.3	37	135
6	210	8	41.4	2750	0	615	54	0	D	D
		10	41.2	2400	1060	535	53	13	77	181
		12	43.6	3010	1650	595	50	24	46	162
6	220	8	41.5	2440	1080	560	55	9	61	166
		10	42.5	2550	1620	640	50	18	49	150
		12	41.8	2480	1770	625	63	29	48	138
CSA MINIMUM				2000	1000	400	35**			

* Density based on condition weight and volume.

** CSA requires a minimum 18 of 40 psi or equivalent to 35 in-lb torsion shear.

Press temperature and time appear to have no effect on dry board strength but they have great influence on wet strength and dimensional stability. Longer press time and higher platen temperature always yield waferboard with greater wet strength and improved dimensional stability. Each of the 6 SSL binders reacted in a similar manner to press time and temperature.

All these 6 crude SSL binders applied at a 4% level require a minimum of 10 minutes press time at a platen temperature of 210°C (410°F), or a minimum of 8 minutes press time at a platen temperature of 220°C (428°F), to cure a 7/16-inch (11.1 mm) board that would withstand

the boiling test. Incidentally, all the 72 boards made with these 6 crude SSL powders considerably surpassed CAN 3-0188.2-M78 requirements with the exception of those boards hot pressed at 210°C (410°F) with the shortest press time of 8 minutes. A separate study indicated that press time could be further shortened if a higher platen temperature of 230°C (446°F) were used. With this high platen temperature a press time of 7 minutes is adequate to cure a 7/16-inch (11.1 mm) board that will pass the boiling test.

Unfortunately this inexpensive crude SSL binder may not be practically suitable for use in some of the existing Canadian waferboard mills because it requires a long press time or a higher-than-conventional platen temperature [210°C (410°F)]. However, for a new waferboard mill to be designed and built specifically to accommodate this slower curing SSL binder, the economic advantage is indeed very attractive.

Waferboards Bonded with Higher Resin Contents

Figures 1, 2, 3 and 4 show the mechanical and physical properties of poplar waferboards made with laboratory wafers of 0.018-inch thickness and bonded with both powdered phenolic and SSL resin at various levels of loading. The phenolic bonded boards were made with 2.5, 3.5 and 4.5% resin and pressed at 210°C (410°F) for 6.5 minutes. The SSL bonded boards were made with 6, 8, 10 and 12% binder and pressed at 220°C (428°F) for 8 minutes. Since waferboard quality is directly related to the amount of resin used, the overall properties of waferboard improve as resin content of both phenolic and SSL increases. There appears to be a linear relationship between resin content and board property; in the range studied the more the resin, the better the board.

The overall properties of waferboards bonded with 6% SSL were better than the boards bonded with 2.5% phenolic resin and were close to those bonded with 3.5% phenol. It is interesting to note that phenol-bonded boards yielded higher Modulus of Rupture and lower Modulus of Elasticity relative to boards bonded with SSL binder. However, the dimensional stability measured by thickness change and springback of SSL bonded waferboard after boiling was much better than that of phenolic bonded boards. This superiority in dimensional stability may be attributed, apart from the combined effect of higher resin content and more rigorous pressing conditions, to the nature of the binder. Ammonium ion is well known for its high diffusivity and plasticization which may result in uniform penetration of SSL resin into wafers, thus plasticizing the mat under heat and pressure during hot press operation. The penetration of SSL binder into wa-

fers may allow us to speculate that the bonding efficiency of SSL binder is relatively lower than phenol-formaldehyde resin commonly used in conventional waferboard manufacturing.

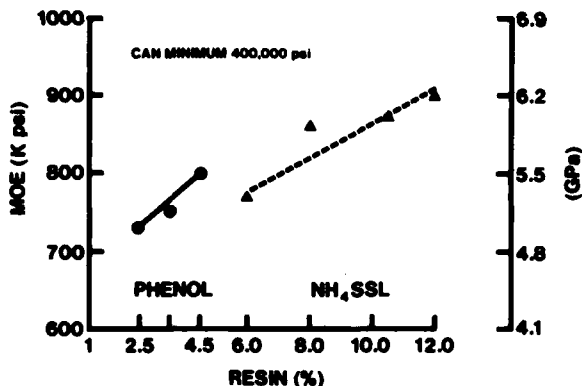


Figure 1.--Effect of Resin Content on MOE (lab wafers 0.018").

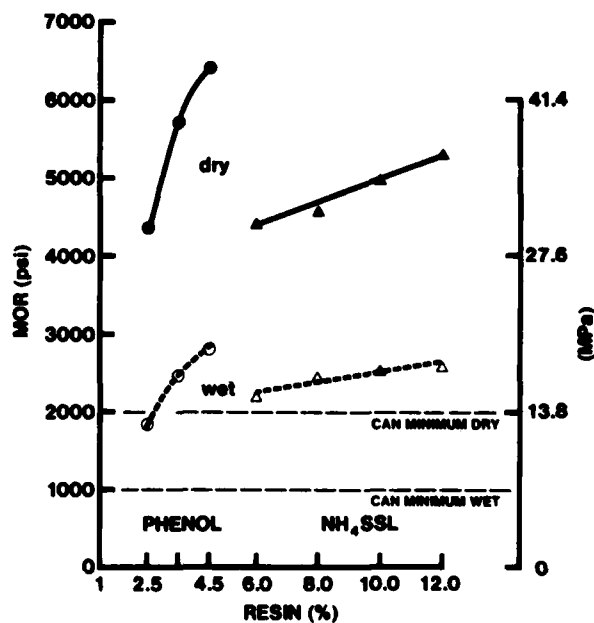


Figure 2.--Effect of Resin Content on MOR (lab wafers 0.018").

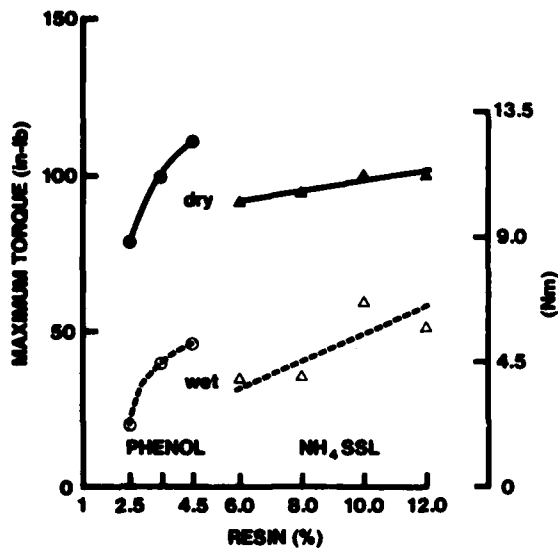


Figure 3.--Effect of Resin Content on Torsion-Shear (lab wafers 0.018").

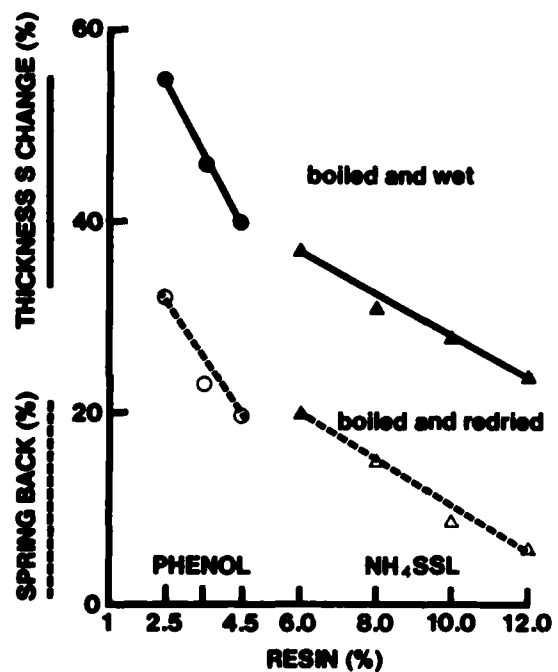


Figure 4.--Effect of Resin Content on Dimensional Stability (lab wafers 0.018").

Board pH

The pH of the finished board ranged from 4.6 to 5.0 for phenolic waferboards and from 3.7 to 4.4 for SSL waferboards, for comparison, two commercial waferboards and one commercial red cedar, urea resin-bonded boards were included in this study.

Figure 5 shows the relationship between board pH and resin content in board bonded with both phenolic and SSL binder. Since both phenolic and SSL binder (raw SSL pH 1.0) are acidic, board pH appears to directly relate to the amount of binder in the board: the higher the resin content, the lower the pH.

High acidity in the board could have a long term effect on the strength of composite products and also a corrosive effect on nails and other hardware used to fabricate the panels. For these reasons, some users specify a minimum pH of about 3 for composite panels (MacFarlane 1964). Others state that acidity at a pH above 2 has little degradation effect upon wood (Hoffman 1972, Kollmann 1936). This is consistent with the practice of using wood tanks to store acid. Since western red cedar and oak are known to have a pH of 2.5 and 3.5 respectively and a Canadian commercial urea formaldehyde particleboard made from western red cedar is known to have a pH of 3.3 (Campbell & Bryant 1941), ammonium-based SSL boards with a pH above 3.3 may not have any long-term adverse effect on wood or metal. However, further study of this is being planned.

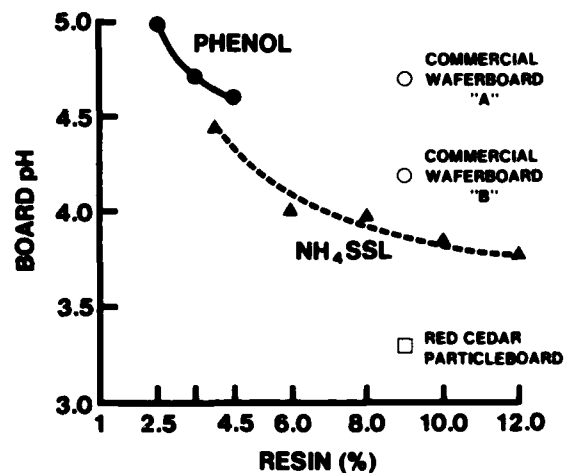


Figure 5.--Relationship Between Resin Content and pH of the Finished Boards. (The pH of three commercial boards are also included for comparison).

Economics

Conventional Canadian waferboards are being made with about 2.5% to 3.0% powdered phenolic resin, currently priced at about 70 cents per pound. Ammonium lignosulfonate in liquid form (50% concentration) has been sold in the U.S. in the past few years at 3.0 to 3.5 cents per solid pound. According to Tembec Inc., the licensed Canadian Manufacturer of this new SSL

binder, the crude powdered SSL binder will be marketed at about 10 cents per pound. Based on these figures, a simple comparison between the conventional phenolic resin system and the SSL binder system demonstrates considerable saving on resin cost. Conventional waferboard bonded with 2.5% phenolic resin requires 50 pounds of resin at an approximate cost of \$35.00 to produce one ton of waferboard. For the new SSL system, which requires 6% SSL binder or 120 pounds SSL binder, the cost is \$12.00 to make one ton of waferboard. The difference in resin cost between these two systems is \$23.00 per ton of waferboard. Similarly, the saving in resin cost between the application of 4.5% phenolic and 12% SSL binder would be \$39.00 per ton of waferboard. Another advantage of using higher SSL binder content is the relatively lower consumption of wood furnish in waferboard production. Theoretically, there is about 9.5% difference in wood consumption between waferboard bonded with 2.5% phenolic resin and 12% SSL binder. This saving in wood consumption can certainly be considered economically attractive. Of course, these figures must be adjusted slightly downward to reflect the extra consumption of energy required by the SSL binder system due to its longer press time and higher platen temperature.

CONCLUSION

Ammonium-based spent sulfite liquor from a sulfite pulping mill was evaluated as a thermosetting binder in powdered form for bonding waferboard. The six raw SSL were found to have similar bonding characteristics and quality.

The crude SSL is slow in curing and requires a minimum of 10 minutes press time at 210°C (410°F) or 8 minutes at 220°C (428°F) to produce a 7/16-inch (11.1 mm) waferboard to pass the CSA boiling test. However, higher platen temperature appears more effective in reducing press time and in stabilizing boards.

Since the SSL is very inexpensive, it is economically feasible to use higher resin content to produce a waferboard superior in mechanical strength and dimensional stability.

Based on this initial laboratory evaluation, the raw SSL produced at Tembec's mill has the potential to be fully developed as an inexpensive thermosetting binder for industrial production of waferboard. As part of commercialization of this new binder system, continuing tests and evaluations are underway. Pilot plant production of this SSL binder and full-scale waferboard plant trials will be carried out in the near future.

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WATER DILUTABLE FURAN RESIN BINDER FOR PARTICLEBOARD¹

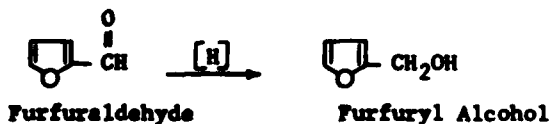
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FaRes[®] B-260, a water dilutable furan resin, can be used as a binder for particleboard. Board properties obtained were comparable to those obtained with commercial phenolic binders. Board costs can be significantly reduced by using low cost ammonium liginosulfonate as a resin extender. Also to be considered is that furan resins are derived from renewable agricultural residues, hence will be relatively unaffected by future actions of the OPEC countries.

The forest products industry in the United States consumes approximately one billion pounds annually of urea-formaldehyde and phenol-formaldehyde resins. Scarcity of quality round wood is forcing greater usage of bonded wood products, especially for exterior grade applications. This increased exterior use of bonded wood products will require the use of larger quantities of more moisture resistant resin binders in the future.

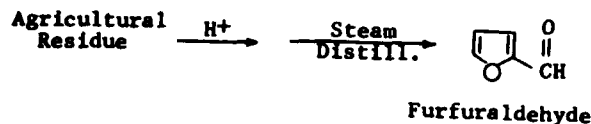
The oil embargo of 1974 and the recent rapid escalation of crude oil prices of OPEC nations, as well as the current political instability in many of the oil producing countries, appear to mandate the development of alternate resinous binders not dependent on uncertain supplies of increasingly more costly crude oil. The objective of this work was to demonstrate the suitability of furan resin binders which are derived from renewable resources such as agricultural residues.

Furan Resin Chemistry. The starting material for furan resins is furfuryl alcohol which is prepared by the hydrogenation of furfuraldehyde.

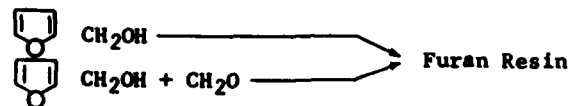


¹Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

Furfuraldehyde is prepared from agricultural residues such as corn cobs, rice hulls, oat hulls or sugarcane bagasse by digestion with acid followed by steam distillation. Agricultural residues are rich in C₅ sugars; hence, they are preferred raw materials.



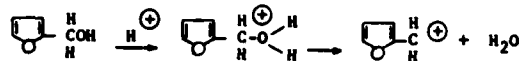
Furan resins are prepared by the homopolymerization of furfuryl alcohol or by the copolymerization of furfuryl alcohol with formaldehyde under mildly acidic conditions (pH 2.0-2.5).



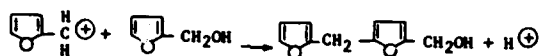
Note: Under strongly acidic conditions furfuryl alcohol can polymerize with explosive violence.

Since resins prepared in this fashion contain low levels of hydroxyl (~6%), they are relatively nonreactive and require a crosslinker such as furfuryl alcohol or furfuraldehyde to effect cure, especially at room temperature.

The commonly accepted mechanism for the polymerization of furfuryl alcohol is initial protonation of the furfuryl alcohol followed by the splitting off of a molecule of water to give a carbonium ion.

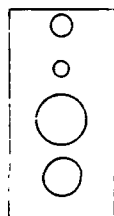


Nucleophilic attachment via the 5-position of a second furfuryl alcohol molecule gives a higher homolog of furfuryl alcohol and regeneration of a proton as shown below.



This process is repeated to give increasingly higher homologs until the reaction is terminated by neutralization of the acid catalyst when the desired viscosity is reached.

It is readily apparent that this reaction scheme is too simplistic to explain the polymerization of furfuryl alcohol if one prepares a TLC (Thin Layer Chromatographic) plate of a conventional furan resin.



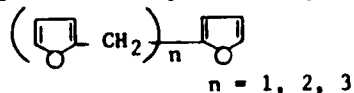
Type I Compounds
Type II Compounds
Type III Compounds
Type IV Compounds

By using a Kontes Model K-4 95000 Densitometer, the amount of the various types of compounds is determined to be as follows:

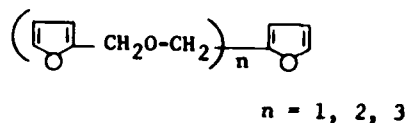
Type I	✓	10%
Type II	✓	5%
Type III	✓	45%
Type IV	✓	40%

By using larger samples, sufficient quantities of the various types of compounds can be separated by Column Chromatography and each type can be further separated by Gel Permeation Chromatography or Size Exclusion Chromatography so that identification of individual oligomers can be made by using NMR (Nuclear Magnetic Resonance), IR (Infrared) and other analytical techniques. Identification of Type I through IV is as follows:

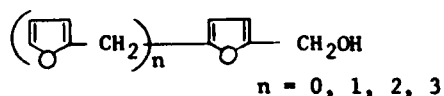
Type I Homologs of Difurymethane



Type II Homologs of Difurfuryl Ether

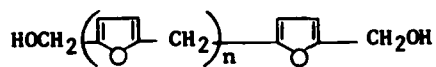


Type III Homologs of Furfuryl Alcohol

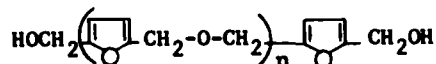


Type IV Polyfunctional Resin

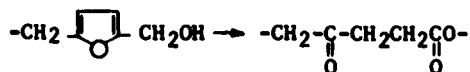
This material did not migrate from the origin because of high polarity; therefore it could not be separated into components for characterization. Based on NMR, IR and other data, it is believed to consist primarily of polymer terminated on both ends by hydroxyl groups such as:



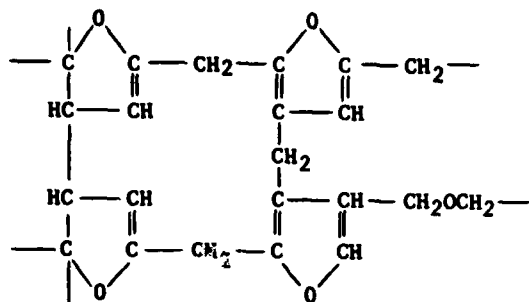
or



The Type IV polymer contains some carbonyl groups suggesting opening the furan ring to make derivatives of levulinic acid:

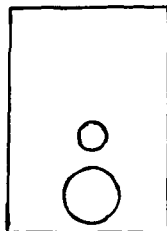


These results confirm the work of Wewerka, Loughran and Walters (1971) who separated and identified compounds of Types I, II and III from acid-polymerized furan resins. While these linear condensation reactions accomplished under mild acid catalysis generate liquid thermoplastic resins, subsequent cross-linking under strong acid catalysis gives a highly intractable, solvent-resistant resin. Schmitt (1974) postulated that ring-ring interaction occurs through double bond polymerization as well as methylene bridging between the 2 and 3 positions on the furan rings to give polymers of the following structure:



Conventional furan resins, whether homopolymers of furfuryl alcohol or copolymers of furfuryl alcohol with formaldehyde, give the same type of TLC analysis.

Recently, a proprietary procedure was developed at The Quaker Oats Company for making reactive, self-polymerizable resin which contains approximately 16% hydroxyl by reacting furfuryl alcohol and formaldehyde under proprietary conditions. This resin is quite different in composition from a conventional furan resin as is illustrated by the separation of the resin using techniques described above. A TLC chromatogram shows the following:



Type I Compounds
 Type II Compounds
 Type III Compounds
 Type IV Compounds

There is an absence of non-functional, non-polar Type I and Type II compounds and only 5-15% of the monofunctional furfuryl alcohol homologues. The majority of the resin (85-95%) consists of the highly polar, polyfunctional Type IV compounds.

As a result of the high hydroxyl content, a unique property of this type of resin, being offered commercially as FaRez® B-260, is its ready dilutability with water. The resin itself is not soluble in water; however, up to 50% water by weight can be stirred into the resin, resulting in a dramatic reduction in viscosity as shown in figure 1.

Particleboard Screening Studies. The ready dilutability and chemical reactivity of FaRez® B-260 resin suggested its use as a particleboard binder. FaRez® B-260 resin was evaluated for use in this application at the Washington State University and in the laboratories of The Quaker Oats Company. Initial screening studies showed that FaRez® B-260 resin could be easily applied from a water solution by spraying onto chips in a rotating drum and the resultant chips could be molded into a board with acceptable internal bond strength and water boil resistance (table 1).

A number of latent catalysts were studied. The catalysts of choice, from a safety handling and performance point of view, were 50% water solutions of either maleic or oxalic acid. As can be seen from table 1, IB's, MOR's, wet MOR's, (2 hr water boil), % swell and % MOR retentions were comparable to the phenolic resin controls. One item to note is the last example in table 1 where properties, especially water boil resistance properties, were dramatically improved as a result of better resin distribution on the chips by increasing air atomization pressure. This effect of resin application efficiency needs further study.

Initial screening studies at WSU demonstrated that addition of 10% ammonium lignosulfonate (50% water solution of Orzan A from Crown Zellerbach) to a water dilution of FaRez® B-260 resin gave a dramatic improvement in board properties as compared to the use of FaRez® B-260 resin alone without added catalyst. Although subsequent studies showed that the use of other acid catalysts such as maleic anhydride and oxalic acid gave similar increases in board properties, there was continued interest in the use of ammonium lignosulfonate as catalyst and extender because of its low cost. Consequently, a series of boards were made using different ratios of ALS to FaRez® B-260 resin. As can be seen in table 2, up to 14% of the FaRez® B-260 resin can be replaced with ALS without any significant effect on properties, and up to 21% can be replaced with minor effects other than a reduction in IB. At 29% replacement, initial MOR shows little decrease, but IB and moisture resistance are significantly reduced. Water resistance is still much better than that of UF bonded boards in that the samples survived the water boil test.

Effect of Press Time. The enhanced chemical reactivity of FaRez® B-260 type resins suggested the opportunity for higher production rates and lower press temperatures than is achieved with commercial boards bonded with phenolic resins. In order to verify enhanced production rates a series of boards bonded

TABLE 1

FaRez® B-260 Boards

FaRez B-260 %	Catalyst	%	M.C. to Press	Spec. Grav.	IB	MOE, x10 ⁶	MOR	2 hr WB Wet MOR	% Swell	% MOR Ret.	Data Source
7	--	--	--	--	21	--	850	--	--	--	WSU
7	MA ⁽¹⁾	.2	--	--	130	.28	1840	688	--	39	WSU
7	MA ⁽²⁾	.5	10.0	.68	94	--	2531	1067	42	42	OO
7	"	1	9.9	.67	124	--	2557	961	44	38	OO
7	Ox ⁽³⁾	.5	9.8	.67	95	--	2358	1046	39	44	OO
7	"	1	9.9	.69	101	--	2226	992	35	45	OO
7 ⁽⁴⁾	MA ⁽²⁾	1	9.8	.68	135	--	2762	1879	20	68	OO
Borden ⁽⁶⁾	--	--	--	--	108	--	2381	1032	45	43	OO
Geo. Pac. ⁽⁷⁾	--	--	--	--	100	--	2551	1027	40	40	OO

(1) 50/50 MA/PCHO

(2) 50/50 MA/H₂O

(3) 50/50 Oxalic Acid/Water

(4) Atomization pressure increased to give better resin distribution on wood chips.

(5) Borden - Cascophen PV-65

(6) Georgia Pacific - GP 91/49

TABLE 2

FaRez® B-260/ALS* Boards

FaRez B-260 %	ALS %	M.C. to Press	Spec. Grav.	IB	MOR	Wet MOR	% Swell	% MOR Ret.	Data Source
6.3	0.7	--	--	120	2300	--	--	--	WSU
6.0	1.0	--	--	147	1965	710	--	36	WSU
6.0	1.0	9.6	.68	97	2518	1072	46	42	OO
5.5	1.5	9.9	.69	64	2364	1220	56	52	OO
5.0	2.0	9.6	.69	58	2233	608	85	27	OO

* 50% solution of Crown Zellerbach Orsan A in water

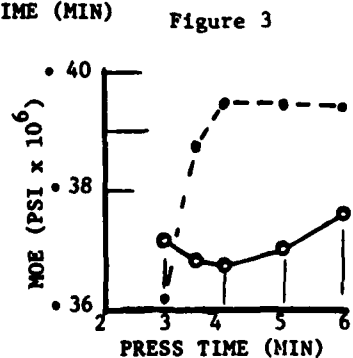
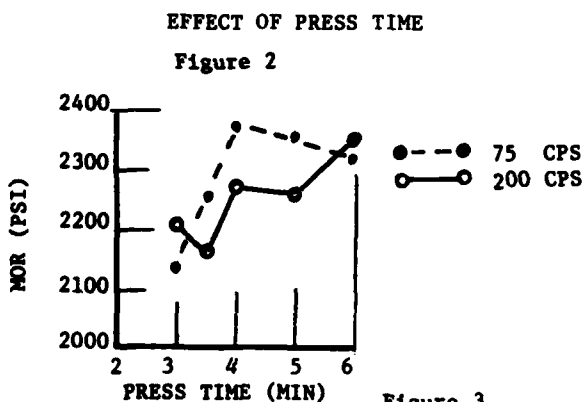
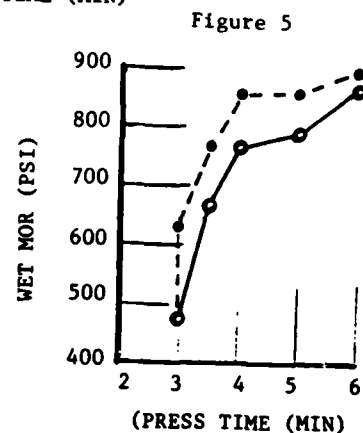
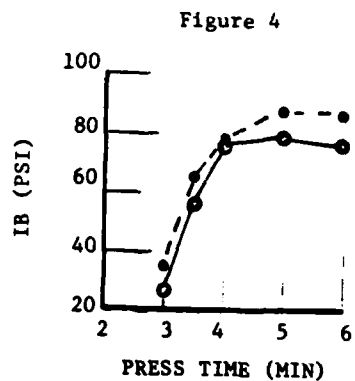
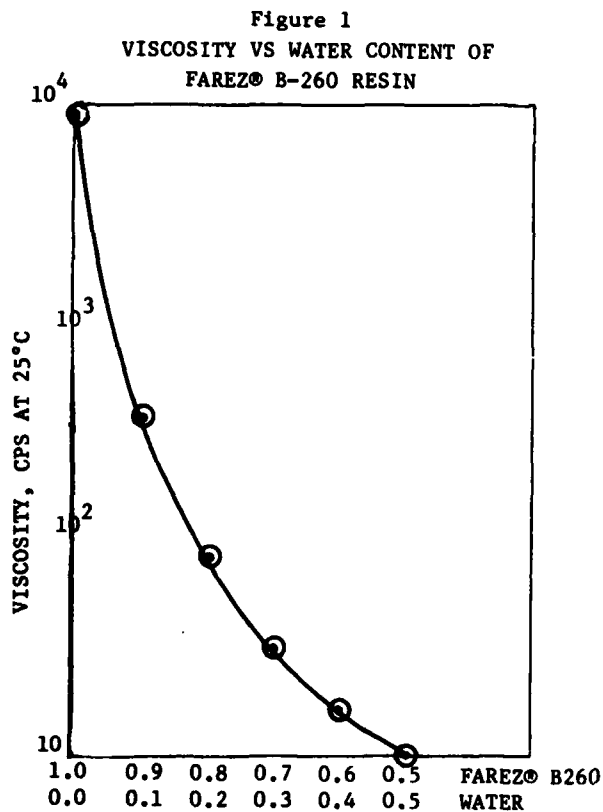


Figure 6
EDGE EFFECT
INTERNAL BOND
(16" X 16" BOARD)

108	122	113	A 99	151	170	78
129	123	105	B	142	130	124
156	179	165	C	133	156	108
164	184	189	D	156	142	92
131	202	168	131	107	144	130
88	153	162	124	100	145	153
126	150	90	120	104	152	142

AV: A = 125 B = 143 C = 145 D = 158
 OVERALL AVERAGE = 135

with FaRez® B-260 resin were run at varying press times. Preliminary results from this study being done at WSU are given in figures 2 to 5. As in the previous studies, press temperature was kept at 350°F but the press time was varied from 2.5 to 6 minutes. In earlier experiments press times were kept constant at 7 minutes. Two viscosity levels (200 cps and 75 cps as achieved by dilution of FaRez® B-260 resin with water) were tested. As can be seen from the figures, significantly better results were achieved with the 75 cps resin solution, presumably because of better resin distribution on the chips. From these results a press time of 4 minutes would appear to be optimum with only IB increasing after 5 and 6 minutes and wet MOR only after 6 minutes in the press.

Figure 6 data suggest a minor edge effect on manufactured particleboards as shown by the results of IB tests for a 16" x 16" board.

Conclusions. Based on results obtained to date we have reached the following conclusions:

1. Furan resins can be used to make exterior grade particleboard.
2. FaRez® B-260 resin seems uniquely suited for use as a particleboard binder because of ready dilutability with water to give low viscosity solutions for spray application.
3. Initial results indicate that FaRez® B-260 resin and commercial phenolic binders give comparable board properties.
4. Ammonium lignosulfonate is usable as a low cost catalyst/ extender for FaRez® B-260 resin. The usable level of ALS will be determined by level of water resistance needed in the final board.
5. FaRez® B-260 resin can be easily applied using conventional equipment.
6. Initial results suggest that a shorter press cycle can be used with FaRez® B-260 resin compared to that used with phenolic binders.
7. Furan resins are derived from renewable resources rather than petroleum and will be less affected by pricing and supply policies of the OPEC countries.

ACKNOWLEDGMENT

We would like to thank Dr. William E. Johns, Assistant Professor; Thomas M. Maloney, Head; Walter Plagemann, Graduate Research Assistant; and other members of the Washington State Wood Technology Section for permission to use data generated at WSU in this paper as well as for advice and assistance in setting up laboratory facilities for making particleboard at The Quaker Oats Company Research Laboratory in Barrington, Illinois.

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Schmitt, C. R. 1974. Furfuryl Alcohol Resins. *Poly. Plast. Tech. Eng.* 3(2):121-158.

AD P 002422

ADHESIVE REQUIREMENTS FOR OVERLAYING PLYWOOD¹

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ABSTRACT

This paper discusses: (1) Development of phenol formaldehyde based adhesives for bonding medium density overlays to veneers of Douglas-fir, lauan, meranti, and southern pine, (2) Requirements for application of the adhesive to the overlays, (3) Conditions for bonding the overlays to veneers; and (4) Performance and testing of the adhesives.

INTRODUCTION

Plywood is covered with resin-impregnated papers, called overlays, to improve the surface characteristics of the plywood (Seidl 1955). The overlays are used to improve the print performance of siding products, the surface finish of concrete poured against overlaid plywood, or decorative prints are used to surface plywood used in cabinets and boat bulkheads (fig. 1). Many interstate highway signs are fabricated from overlaid plywood that is either painted or covered with reflective tape (fig. 2).

BACKGROUND

Medium density overlays have been used for approximately 40 years to upgrade the surface performance of plywood. The weight of the overlay is sixty pounds per thousand square feet, exclusive of glue line. When made by the saturating process, the overlay contains a minimum of 22 per cent resin, more usually 27 to 33 per cent resin. When applied to the plywood by hot pressing, the thickness of the overlay is 0.012 to 0.014 inch.

¹Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

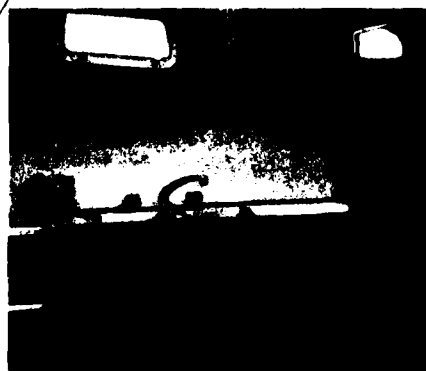


Figure 1.--Decorative print and cushion sheet used for boat cabinets and bulkhead.

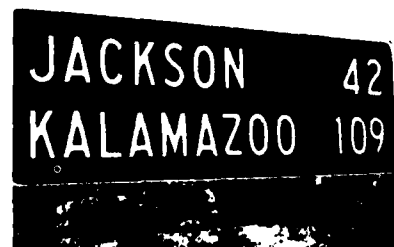


Figure 2.--Overlaid plywood highway sign.

Medium density overlays are also used between the decorative print and the plywood to improve smoothness and to reduce the transmission of defects and repairs through the decorative print. The decorative print contains enough resin to be self bonding to the medium density overlay. Sufficient flow must be left in the decorative resin and medium density overlay resin to achieve a bond between the two overlays. Medium density overlays used under the decorative prints are commonly referred to as cushion sheets.

FORMULATION OF THE ADHESIVE

Medium density overlays are not self-bonding and require an adhesive to bond the overlay to the plywood. Generally, a glue line is coated and dried on the back of the overlay, allowing the overlay to be stored until needed. Other methods of bonding the medium density overlay to plywood include use of a paper glue line or an application of an adhesive to the face veneer.

Application of the adhesive to the overlay may be accomplished by the usual paper coating techniques such as use of a roll coater, air knife, or a die fountain coater. For a direct roll coating application, the viscosity of the adhesive is generally controlled at 1000 to 4000 cps. measured at the application temperature. Lower viscosity adhesives will promote excessive penetration into the overlay. The result of excessive penetration is a glue starved glue line and a poor bond between the overlay and the veneer. Higher viscosity adhesives applied by direct roll coating yield a rivuleted and nonuniform coating. Poor bonds are found between the rivulets. The rivulets penetrate the overlay and "bleed through" to the surface of the overlay during hot pressing (fig. 3). This causes an unsatisfactory overlay surface with poor adhesion to paint films or discoloration of concrete poured against the overlay.

A die fountain coater is an excellent way to achieve uniformity in the film thickness of the adhesive (fig. 4).

The drying and advancement or "B" staging of the resin is more easily accomplished with a uniform film thickness when compared to the drying requirements of a rivuleted film. The solids of the adhesive formulations may range from 45% to 70% solids content. The drying rate must be controlled to prevent disruption of the film by the removal of the water and the solvents.

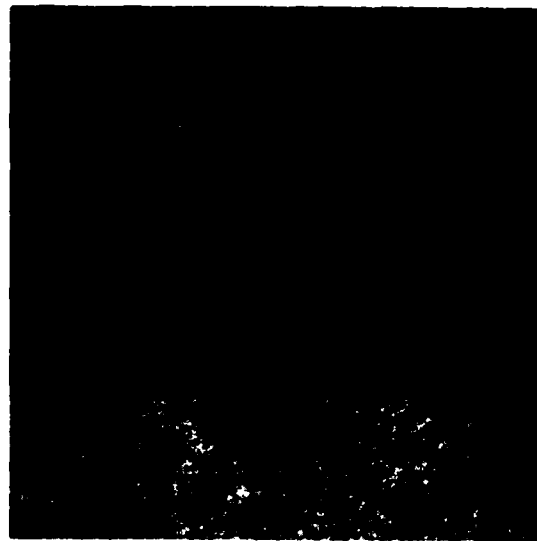


Figure 3.--Overlay face showing glue line bleed-through from rivuleted coating and dense summer wood.

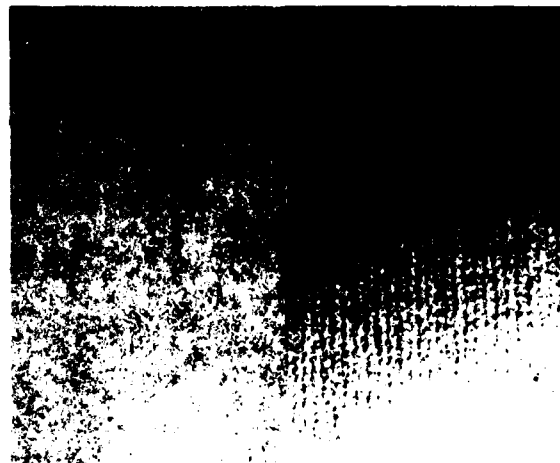


Figure 4.--Contrast in smoothness of the die fountain coater application and the direct roll coating application.

The adhesive film must be dried to the point where the overlay will not block when rolled up or stacked in sheet form. Flow tests are used to monitor the degree of "B" staging and prevent over-curing of the glue line. The relationship between the quantity of adhesive applied and the flow properties of the adhesive must be established before the flow test can be used to determine the proper curing or staging of the glue line (fig. 5). To prevent undercuring of the glue line, a blocking and a hot pressed bond test are used.

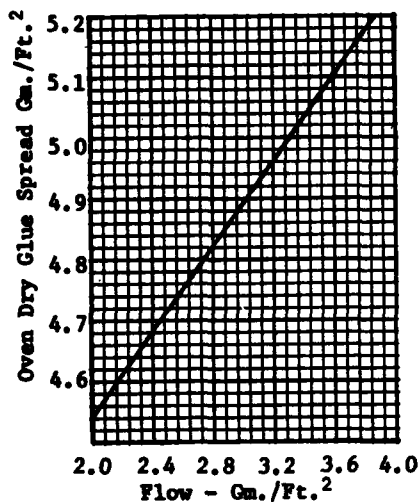


Figure 5.--Spread weight versus flow.

Storage requirements for the coated overlay include wrapping the overlay bundles with a vapor barrier material such as a polyethylene film to prevent absorption of moisture by the overlay and coating. Absorption of moisture by the overlay may cause the overlay to stick to the press platen when hot pressed. Absorption of moisture by the overlay and glue line will cause blocking of the glue line to the adjacent overlay face. Storage temperatures for the phenolic glue line should be room temperature or less. High storage temperatures will result in advancing the cure of the glue line to the point where it will not have sufficient flow to bond to the veneer. Storage life of the glue line is approximately one year at 70° F. The appearance of the phenolic glue line is changed from a pink or brownish color to a purple color when the storage life of the glue line has been exceeded.

Steam heated hot presses are used to bond the overlay to the plywood. The hot presses contain a number of openings, usually 16 to 24, allowing 16 to 24 panels to be made at each pressing.

Thinner plywood constructions with an overlay on one face may be pressed with two panels in each opening.

The press time and temperature are related to: (1) the cure of the overlay, (2) the cure of the overlay glue line, (3) the thickness of the panel, (4) the resulting rate of heat transfer to the plywood glue lines, and (5) the cure rate of the plywood adhesive. Press temperatures vary from 275° F. to 300° F. depending on the thickness of the panel, moisture content of the veneer and the amount of water in the plywood glue line. Excessive moisture combined with higher press temperatures will cause steam pockets which rupture the wood in the panel when the press is opened. Press times usually run from 5 to 10 minutes, depending on the press temperature and thickness of the plywood.

Hand loaded presses may take as long as two to three minutes to load. Thus, the overlay glue line may be in contact with the hot press platen for as long as 3 minutes before the application of pressure. This interval is known as the precure time and is the longest for the panel loaded first.

The rate of cure of the overlay glue line must be fast enough that the glue line is fully cross linked at a 7 minute press cycle at 275° F. or a 5 minute cycle at 300° F. The cure rate of the glue line must be slow enough that there is sufficient flow after exposure to 3 minutes of precure to bond to the veneer. In practice, the best glue line we have developed has slightly over 2 minutes precure resistance at the 285° F. press temperature.

The industry requires an 85% average wood failure for the bond of the overlay to the wood substrate. The size of the test specimen is 1 square inch. The number of test specimens per panel varies from 5 to 16 for each panel face. The samples are subjected to a vacuum-pressure and a boil test to stress the bond by swelling and shrinking the wood. These tests are described in U. S. Product Standard PS 1-74.

The face veneer must be solid. Knot holes and splits must be repaired. The face veneer must be relatively smooth to insure contact between the overlay glue line and the veneer at the pressures used, usually 175 to 225 psi. Rough veneer causes poor bonds,

even delamination, and an unsightly surface (fig. 6). Table 1 compares the influence of roughness and moisture content on the bonds achieved with a low flow glue line.



Figure 6.--Overlay glue line delamination caused by dry, rough veneer and a low flow glue line.

The moisture content of Douglas-fir veneer should be within a range of 2% to 7%. With a glue line containing sufficient flow to bond rough veneer, higher moisture content causes over penetration of the glue into the wood, giving a glue starved glue line and a poor bond (Bergin 1965). Lower moisture content causes a reduction in the flow of the glue, giving poor, shallow bonds. Variations

in veneer density contribute to either over-penetration in low density wood or shallow bonds in dense woods.

The formulation for bonding the overlay to Douglas-fir veneers also works well with veneer of southern pine, lauan, meranti, and mersawa (fig. 7).



Figure 7.--Overlay bond to meranti veneer, 100% wood failure.

The main component of the adhesive formulation is a thermosetting phenolic resole. This is an alkaline catalyzed condensation product of phenol and formaldehyde. The mole ratio of the formaldehyde to phenol is lower than the 2 moles of formaldehyde to 1 mole of phenol found in the typical plywood resin.

Table 1.--MDO Bond Quality After Vacuum-Pressure Cold Soak Test on 3/8" MDO 2-Side Panels % Wood Failure (Dunbar 1976)

Face Veneer Surface	Face Veneer Moisture Content		
	0.5-0.9%	4-5%	9-9.5%
Smooth	83%/81%	93%/92%	82%/83%
Medium	68%/67%	58%/63%	82%/77%
Rough	42%/40%	50%/70%	82%/80%

Wood failure results are averages of 3 panels at each condition.

Sodium hydroxide is used as the catalyst. The amount of sodium hydroxide that can be used as catalyst is limited due to the hygroscopic properties imparted to the glue line on the overlay and the resulting tendency for the glue line to block in bundle form.

A stroke cure test is used to relate the cure time of the resin to the required press time of 7 minutes at 275° F. (Chow 1975). The stroke cure test consists of placing a sample of resin on a hot plate set at 285° F. A spatula is used to stroke the resin until the resin gels and the resin strings break when the spatula is lifted from the hot plate. A resin with a stroke cure time of 40 to 45 seconds will meet the required press cycle of 7 minutes at 275° F. Resins with shorter stroke cure times will reduce the precure tolerance and the storage life of the glue line. Resins with a longer stroke cure will be undercured in the lower temperature, shorter press time press cycles.

The cure rate of the resin is determined by the ratio of the formaldehyde to phenol and the ratio of the catalyst to the phenol. The cure time of the resin is a function of the cure rate and the degree of advancement of the resin. The resin is advanced in the reaction vessel by cooking at a specific temperature to a predetermined viscosity. For a given charge of sodium hydroxide, phenol and formaldehyde, the solids content remains constant. The reaction rate of the resin may also be determined by plotting the viscosity of reactants versus the reaction time. The following graph (fig. 8) demonstrates the change in reaction rate obtained by changing the ratio of formaldehyde to phenol, using equivalent amounts of catalyst.

The resin must be advanced far enough to react the lower molecular weight fraction which otherwise will cause excessive penetration into both the overlay and the lower density veneer (Herscher 1962). Another problem with the low molecular fraction is the tack found in the glue line and the increased propensity for blocking. Lower reaction temperatures favor a more uniform molecular weight distribution.

The resin must not be advanced to the extent that it is no longer dilutable by water, although addition of a small amount of one of the lower alcohols will improve the dilutability. Dilution is required to achieve the viscosity range in the mixed adhesive for the roll coating application. The die fountain coater will allow use of higher viscosity adhesives.

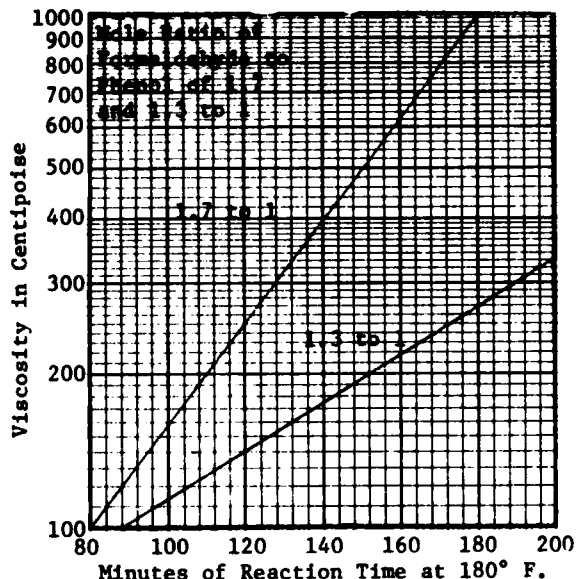


Figure 8.—Determination of the phenolic resin cure rate obtained by plotting the resin viscosity versus the reaction time in a reaction vessel.

The other components of the mixed adhesive include flow promoting additives, higher molecular weight thermoplastic resins such as acrylics, polyacrylamides, polyamides, polyvinyl acetates and polystyrenes, extenders and fillers.

Flow promoting additives such as ethylene glycol, polyethylene glycol and polypropylene glycol improve the wettability of the adhesive on dry veneer.

The high molecular thermoplastic resins reduce the penetration of the glue line into the overlay, increase blocking resistance by migration to the glue line surface, and improve precure resistance.

Starches, wheat flours and other amyloseous materials contribute some adhesive properties while preventing over-penetration of the adhesive into the more porous veneers.

Bark, wood and nut shell flours are used as fillers. The fillers do not contribute to the adhesive properties of the glue line but help prevent penetration into the overlay and veneer.

Spread weights vary from 4 grams to 6 grams per square foot on a solids basis. The higher spread weights are useful in bonding rough, dry veneer and more absorptive veneers and contribute to precure resistance.

For a two-step operation, where the panel is made and sanded before the overlay is bonded in a second pressing operation, less glue is required.

TESTING THE ADHESIVE

Testing the overlay bonds at the plywood plant is accomplished by cutting at an angle through the overlay and into the face veneer. Another cut is made an inch away from the angled cut. A knife is slipped under the angled cut, and a section of the overlay and part of the face veneer is removed. The wood is removed from the back of the overlay and the bond is evaluated. Testing right out of the hot press can detect excessive precure times or incorrect press temperature settings.

The American Plywood Association standard for overlay bond quality is 85% wood failure. Two tests are used, a vacuum-pressure and a boiling test. Both tests involve stressing the glue line by expanding and contracting the wood. Five samples are obtained from each panel tested. The samples are kerfed just through the overlay one inch from the edge of the sample. For the vacuum-pressure test, the samples are placed in a pressure vessel and covered with cold water. A vacuum of 25 inches of mercury is drawn for 30 minutes followed by a 30 minute application of 65 to 70 pounds per square inch of pressure. The boiling test consists of boiling 4 hours, drying for 20 hours at 145° F., and boiling for an additional 4 hours. The samples are then cooled in water and the wood removed from the back of the overlay samples. The samples are dried and the wood failure is estimated (APA 1980).

Observation of the samples will indicate the causes for adhesive failure. Precure failure or lack of pressure is indicated by a darkened glue line which does not transfer to the veneer (fig. 9). Wet or porous veneers are detected by excessive transfer of the glue to the veneer (fig. 10). The face of the veneer is discolored by the adhesive with little adhesive remaining on the overlay. When the glue line has not changed color and there is glue on both the overlay and veneer, undercure is indicated (fig. 11).

Samples exposed to the Weatherometer and exterior exposure demonstrate that the vacuum-pressure and boil tests are good indicators of long-term durability for product performance in the field.



Figure 9.—Overlay bond to Douglas-fir veneer of samples precured for 2, 2-1/2 and 3 minutes. The wood failure is estimated at 85%, 25% and 20%.

FUTURE REQUIREMENTS

In the Pacific Northwest, the old-growth Douglas-fir is being replaced by second-growth Douglas-fir approximately 80 years old. The result is a reduction in the supply of smooth face veneers. Steaming the blocks before the peeling of the veneers does gain some improvement in smoothness and an increase in the yield of face grade veneers (Lickess 1957). Additional volume can be gained by two-stepping; two-step panels are much more labor intensive and, under past market conditions, are not an economically feasible way to go. The panel blanks are repaired and sanded before the overlay is applied in a second pressing operation.

Use of lauan, meranti, mersawa, and other Asian veneers as faces offers further opportunities for market expansion. Superior smoothness is obtained by the use of these Asian veneers.

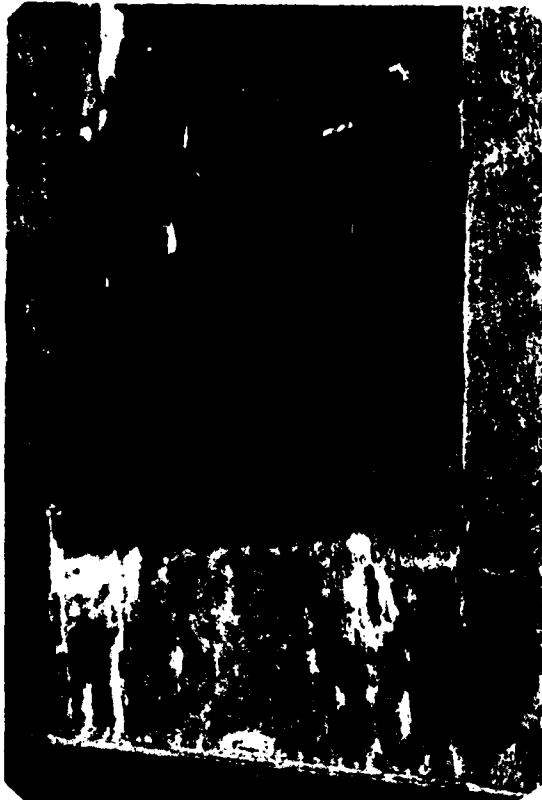


Figure 10.--Delamination caused by wet veneer.

Use of press chargers upgrades product quality by eliminating fall-down from precure.

Areas of improving the performance of the adhesive include: (1) longer precure tolerance, (2) better specific adhesion to different species of veneers, and (3) reduced penetration of the adhesive into the overlay.

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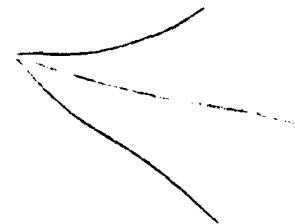


Figure 11.--Delamination caused by undercure.

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AD P 002423

ALTERNATIVES TO SOLVENT-BORNE ADHESIVES¹

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ABSTRACT

Rapidly escalating costs of solvent borne adhesives have now given water borne adhesives a significant economic advantage to further advance the environmental and OSHA forces already acting to reduce solvent usage.

Water borne adhesive systems based on chloroprene to polyvinylacetate copolymers are contrasted to solvent borne adhesives in areas of application processing, end use performance and economics.

To understand the rapidly escalating cost of solvent-borne adhesives, one needs only to recall the last time you filled up your gas tank. Figure 1 shows the price of gasoline over the past 20 months.

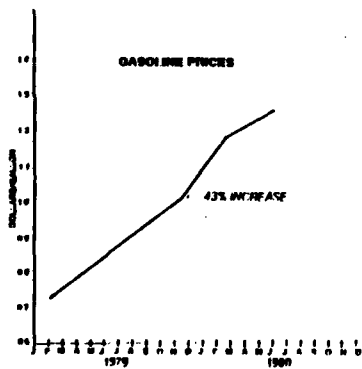


Figure 1.

Contact cement is the dominant solvent-borne adhesive system we see in the wood products industry. The rising costs of solvents used in these adhesives is seen in Figure 2; note the slope similarity to gasoline prices. Then you translate this into glue line costs, Figure 3, we see a similarly increasing slope. The twin lines representing flammable solvent costs reflect both the upper and lower tier of the market.

¹Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

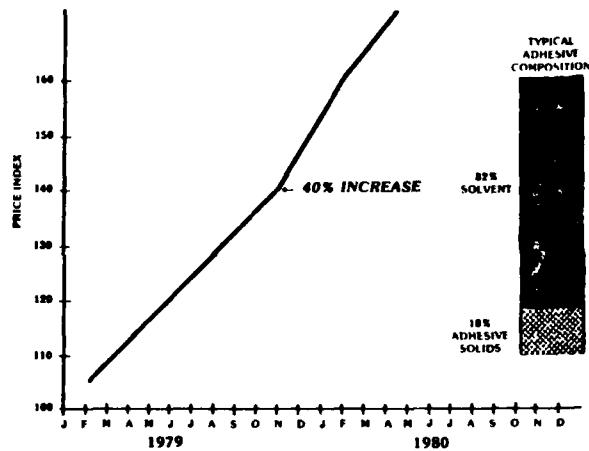


Figure 2.

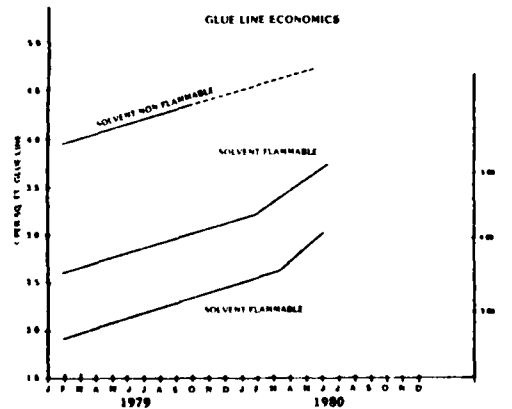


Figure 3.

When we superimpose onto Figure 3 cost of a water borne contact cement, Figure 4, one can see we are at the economic threshold at both tiers. Since we know oil price increases aren't a question of whether, but how much, the need for a more cost effective adhesive is an economic necessity.

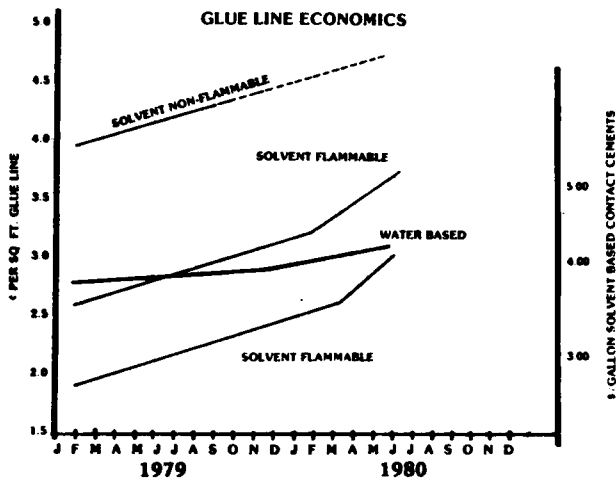


Figure 4.

What are our alternatives? Obviously, water borne systems are a first consideration. Systems based on polyvinyl copolymers are available and well known and won't be discussed here. Another alternative is hot melt in film form (heat activated) or in molten form. In brief, hot melt's economic and performance levels are rather limited and will not be considered in this paper. Since the contact cement (neoprene based) systems dominate, we'll restrict this discussion to the water borne version of contact cement as the most probable alternative.

The cost of water borne contact adhesives have not been stagnant in our inflationary world today, but as Figure 5 shows, there's a radical difference on a relative scale when compared to solvent borne. Water borne adhesives are much less sensitive to petrochemical escalation. Though your dollar per gallon price tag, water vs. solvent, is much higher, it is so because of its composition. Figure 6 shows there's more adhesive in a gallon!

When adjusted for coverage, Figure 7, and a given \$/gallon price tag, the cost to cover a common area is, in this example, 16% more. One could readily use other price tags to position your particular operation.

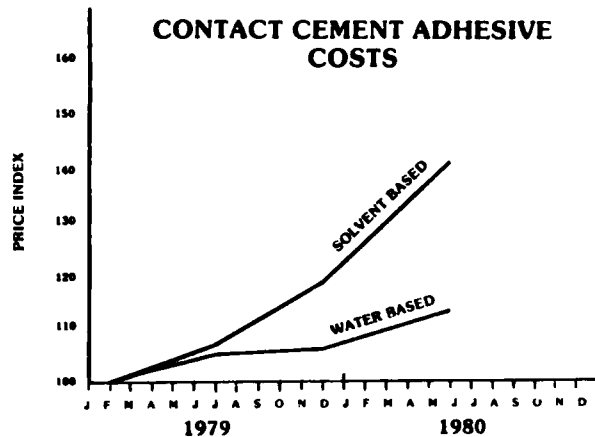


Figure 5.

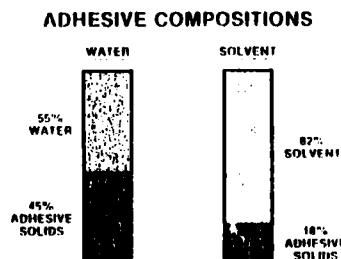


Figure 6.

ADHESIVE COSTS

	<u>\$/GALLON</u>	<u>COVERAGE FACTOR</u>	<u>TRUE COST</u>
SOLVENT:	4.30	2.23	\$9.59
WATER BASED:	8.25	1.00	\$8.25
		DIFFERENCE	\$1.34

Figure 7.

When you add the dollar impact of current and future EPA regulations, OSHA, and insurance costs, the cost effectiveness of non-solvent borne adhesive systems becomes rather apparent.

The water borne contact adhesives (neoprene based) differ in use from solvent form in several ways:

In the area of application, they can be sprayed, roller coated or curtain coated. The

latter two methods are not too common with solvent borne, mainly due to viscosity control, penetration and high amounts of wet film thickness used. These problems are virtually nonexistent with a water borne system and now can often be a more effective application method.

Spraying equipment needs to be modified via rust resistant plumbing. Nozzles and tips are also different, but readily available. Atomization and fluid pressures are about a third of those encountered with solvent.

The quantity of dry adhesive needed to make a proper adhesive bond is slightly higher (about 20%) for the water borne. This is most evident on a water absorbant surface as particleboard.

To properly dry a water borne contact cement, additional oven capacity will be needed. Current technology, namely in high intensity infra-red ovens, permits drying 3-4 wet mils of water borne adhesive in less than one minute at line speeds of 16-24 feet per minute. The added expense of these ovens would be offset by savings in the cost of the adhesive, plant insurance and easier and less costly compliance to EPA and OSHA regulations.

The combining (nip roll) operation isn't different and requires no special comment.

End Use Performance of currently available water borne contact cement can meet virtually all needs which are presently being handled with solvent borne.

Historically, water borne contact cements have been around over twenty years. These earlier versions had poor mechanical stability (pumping ease), misted badly when sprayed, and had no metal adhesion. The recent technology has solved these problems and now can produce a "pebbly" surfaced spray pattern not unlike one now achieves with solvent. The latter characteristic insures better surface contact when dealing with irregular surfaces.

The advanced water borne contact cement technology (catalyst added; 48 hr. pot life) has shown a significant improvement in heat and water resistance which, of course, spells durability. In addition, good deflection and recovery values can be achieved so that virtually every construction and end use needs now serviced by solvent borne contact adhesives can be handled.

AD P 002424

ADHESIVE TROUBLE SHOOTING IN THE WOOD INDUSTRY

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ABSTRACT

Many of the problems encountered in using wood adhesives are related to effect of moisture on wood, effect of water in structural adhesives and substrate preparation. A quality control program can reduce the adverse effect of bonding problems.

Many of the problems involved in wood gluing are caused by the lack of recognition of the importance of the effect of 1) moisture on wood, 2) water content of wood adhesives and 3) condition of the surface to be glued.

EFFECT OF MOISTURE ON WOOD

In contrast to many substrates, wood is more heterogeneous than most. In the range where most gluing is done, wood changes in dimension unequally in each of the three directions - radially, tangentially and longitudinally upon the absorption or loss of water.

Figures 1 and 2 show the effect of moisture loss on the dimensional stability of wood in the tangential and radial direction. Since the shrinkage in a tangential direction is almost twice that in a radial direction, moisture change affects the cross-section depending on its relative location in the log. Cupping and bowing are a result of the differential dimensional effect due to difference of movement with moisture change. This also sets up severe stresses in a board as post shown in Figure 2 so that, in some cases, the internal strength of the board is exceeded, causing a split.

The relative amount of shrinkage is shown for various woods in Table I.

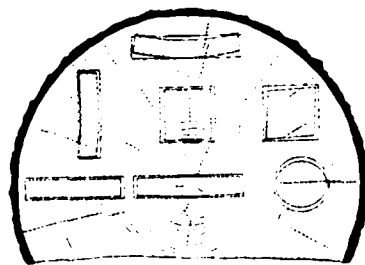


Figure 1.

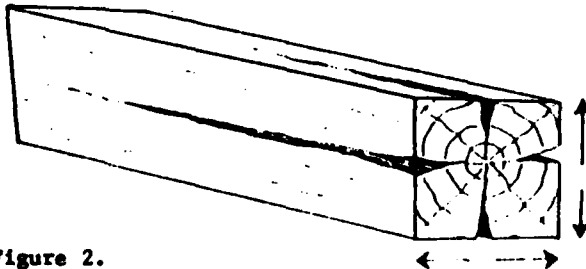


Figure 2.

Species	% Dimensional Change per % Moisture Change		
	Radial	Tangential	Volumetric
Alder, red	.15	.24	.48
Ash, white	.16	.26	.45
Basswood, American	.22	.31	.53
Beech, American	.17	.37	.54
Birch, yellow	.24	.31	.56
Cherry, black	.12	.24	.38
Cherry, Pin	.09	.34	.43
Cottonwood	.13	.31	.47
Elm, American	.14	.32	.49
Elm, Rock	.16	.27	.47
Elm, Slippery	.16	.30	.46
Hackberry	.16	.30	.56
Hickory, Pecan	.16	.30	.45
Luan, red	.11	.27	.39
Mahogany	.12	.17	.27
Maple, silver	.10	.24	.40
Maple, sugar	.16	.32	.50
Oak, black	.15	.32	.47
Oak, bur	.15	.29	.42
Oak, Southern Red	.15	.29	.54
Oak, white	.18	.30	.53
Sweetgum	.17	.33	.50
Sycamore, American	.17	.25	.47
Teak	.08	.14	.23
Tupelo, black	.15	.26	.46
Tupelo, water	.14	.25	.42
Walnut, black	.18	.26	.43
Willow, black	.09	.27	.46
Willow, Pacific	.10	.30	.46
Poplar, yellow	.13	.24	.41

Table I.

It will be noticed that mahogany is one of the most stable of the common woods and that beech varies considerably between the tangential and radial shrinkage. Several illustrations of the effects of this are as follows:

A change of 4% moisture content in a table top 36" wide made from tangential beech boards will change about 1/2" in width.

Gluing a 1" tangential-faced board to a 1" thick radially-faced board and with a 4% moisture change will cause a difference in thickness of 8 mils or 4 mils per side. This occurred in Figures 3 - 5. Visually, such a difference becomes readily apparent.



Figure 3.



Figure 4.



Figure 5.

On the other hand, mahogany in Illustration 1 would have only increased in width 1/4" while in Illustration 2, the difference in board thickness would have been only 1 mil per side.

It is important that lumber used in panels have equal moisture content. Figure 6 shows panels made of boards which had unequal moisture contents at gluing. When these boards in the panel equalized to the same moisture content, (the panel was sanded to the same thickness) the thickness of the wettest board became much less than the others.

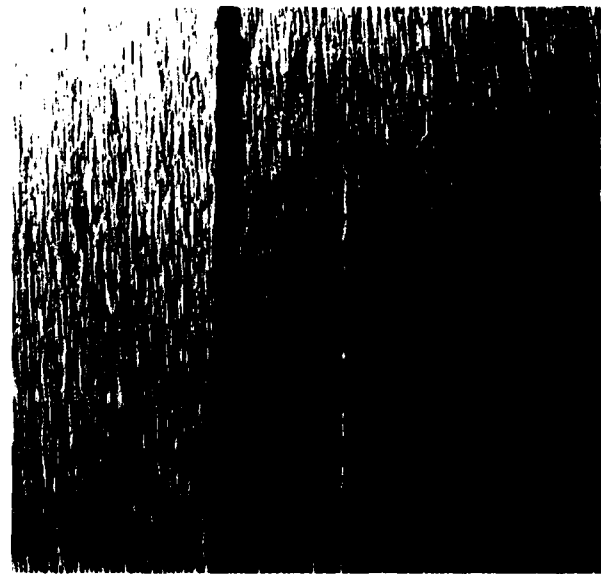


Figure 6.

Since the average relative moisture content varies by season and by region, the moisture content of furniture parts will also vary in a parallel fashion. Average moisture content is shown by Figure 7.

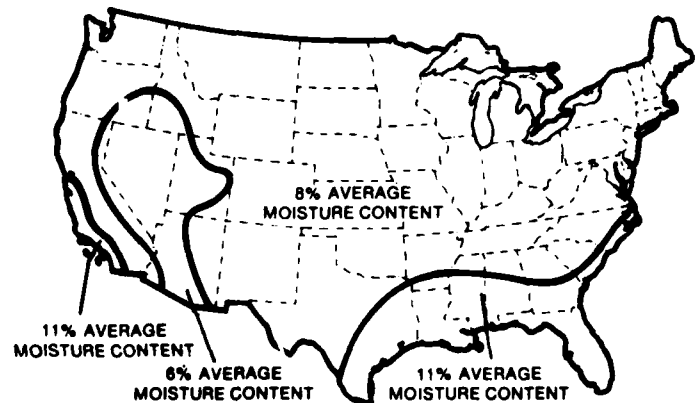


Figure 7.

Normally, 6-8% is a good moisture content for wood from which to manufacture furniture. For mobile home sidewalls and floors, a higher moisture content not to exceed 15% is more suitable.

Shrinkage, with moisture change, in the direction of the grain is comparatively very small - between 0.1 and 0.2% for most wood species between green and oven dry.

It can be readily seen that flat bonding boards cross grain causes a high stress concentration with moisture change. An example is shown in Figure 8.

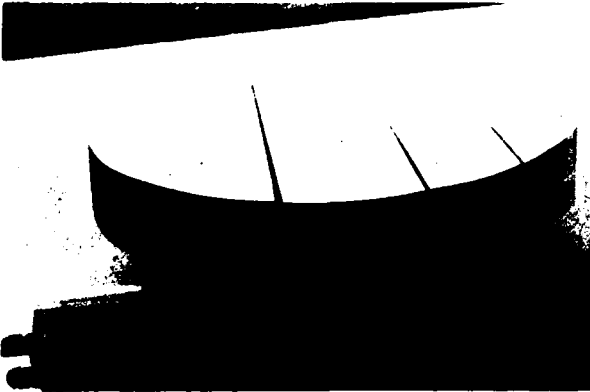


Figure 8.

The chair arm (glued to the post) did not change in length when the post became thicker, rupturing the joint. Figure 9.



Figure 9.

In Figure 10, the lumber band is evident as the differential expansion tore the face veneer apart. Figure 11 shows a failure from bonding end grain to side grain.



Figure 10.



Figure 11.

Miter joints are also highly stressed by moisture change as the width changes dimension while the length does not. An illustration is Figure 12.

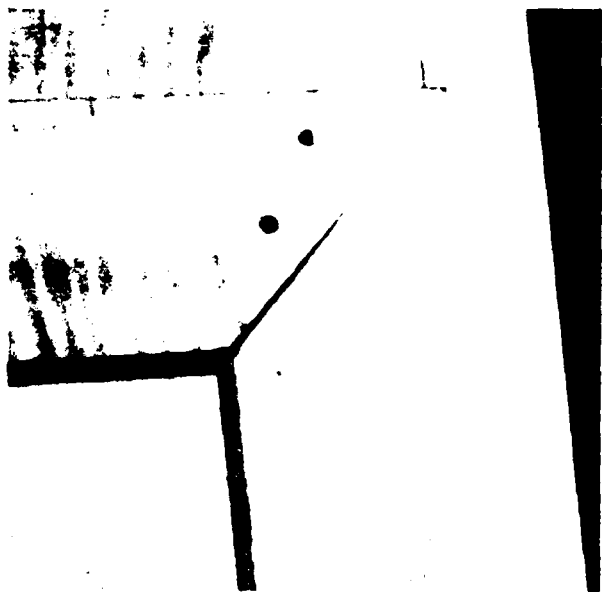


Figure 12.

Bonding wood to other materials with different moisture absorption and consequent dimensional change is shown in Figure 13. Here the honeycomb core did not change in the same way as the lumber band, which shows in the veneer facing.



Figure 13.

Differences in thermal expansion between two unlike materials will also set up similar stresses.

The changes occurring from moisture change are not only evident as visual defects but, also, from joint strength obtained.

The strength obtained in a joint is that normally registered in a perfect non-stressed one less the stresses in the joint and, also, that due to lack of attaining an ideal joint.

Figures 14 and 15 show collapsed boards. The internal stresses exceeded the cohesion of the wood and, therefore, cracked. This collapse was caused by improper drying. Bonded joints made from this lumber would be less than that for unstressed lumber. This would also be true of joints with lesser internal stress.



Figure 14.



Figure 15.

A test for lumber stress can be made as in Figures 16 and 17.



Figure 16.



Figure 17.

If the fingers are parallel, there is little residual stress incorporated into the wood. If, either immediately or on aging 24 hours, the fingers pinch or bend outward, the lumber has a built-in stress.

Pocket moisture meters, such as shown in Figure 18, are valuable for carrying by a supervisor, so that lumber can be randomly inspected, particularly at points in the plant where there is a suspicion of wood moisture content being out of control.



Figure 18.

EFFECT OF WATER IN WATER-DISPERSED ADHESIVES

Most structural adhesives used in the wood industry are water based. They are dispersed in water usually to make them liquid at the time of bonding. Water may also be present to allow a chemical reaction to occur. In any event, after the bond is made, the water leaves the glue line. In other words, an adhesive with 60% solids has 40% water. After the water leaves, this 40% may be evident as voids. In the above example, in a thick glue line, the adhesive film covering the substrates will be 100% solids, leaving less than 60% solids in the center of a thick glue line. This is shown in Figure 19, where the dowel did not fit the hole tightly enough.

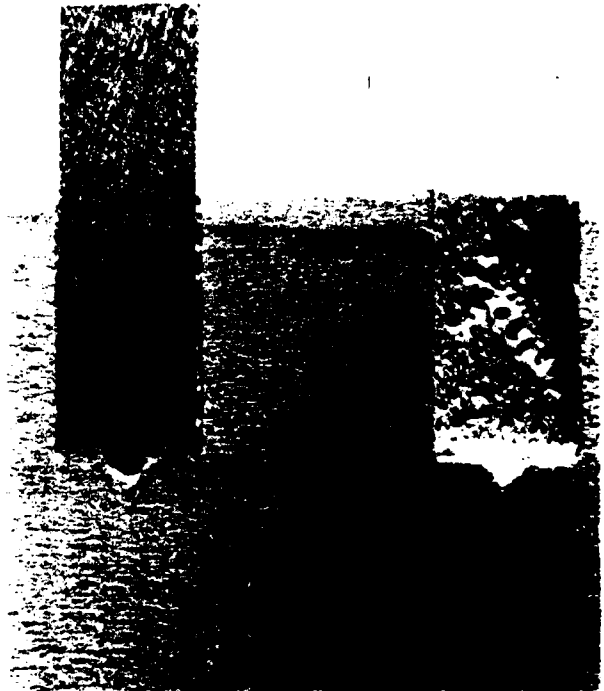


Figure 19.

Dowels should not fit the hole so tightly that the glue is pushed to the bottom, neither should they fit as loosely as illustrated. If a dowel must be hammered into place, it is too tight. Finger pressure should be adequate. However, it should not wobble in the hole.

Sometimes dowel diameter variation can be due to exposing dowels to the changing relative humidity in the environment. Putting the dowels in a heated box before use can reduce the size variation. Such an arrangement is shown in Figure 20.



Figure 20.

Complete adhesive coverage between the dowel and hole is important both for speed of strength development and ultimate strength. Application to both the dowel and hole improves this possibility. Too frequently, application, such as in Figure 21, is obtained.

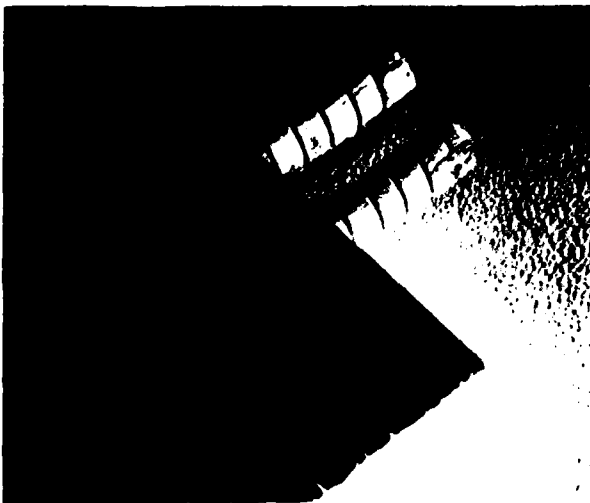


Figure 21.

Inadequate dowel length, even if properly glued, will yield weak joints, as in Figures 22 and 23.

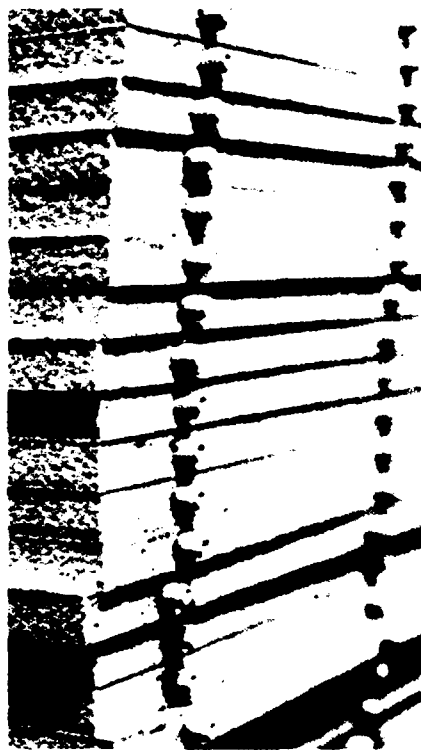


Figure 22.



Figure 23.

Unfortunately, some automatic dowellers apply glue to the bottom of the hole and expect the dowel to bottom, forcing the adhesive up around the dowel. Frequently, coverage from this application method is incomplete, resulting in a joint not as strong as it might be.

Figures 24 and 25 are caused by inadequate pressure giving a thick bond line.



Figure 24.



Figure 25.

Figure 26 is a thick glue line as a result of a machining problem.

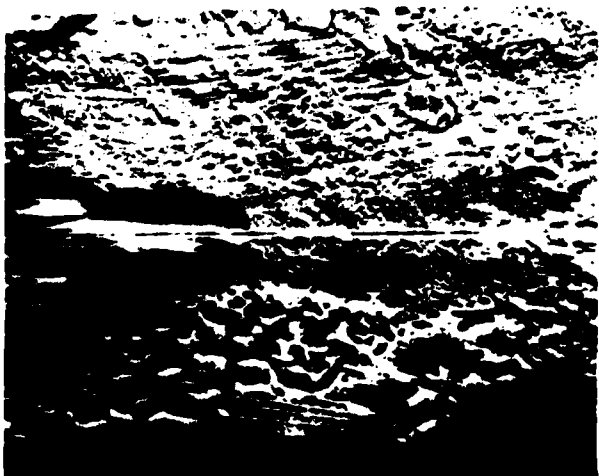


Figure 26.

Figures 27 and 28 result from improper clamping. The pressure did not pull both sides of the panel together with equal pressure, leaving one side open.



Figure 27.

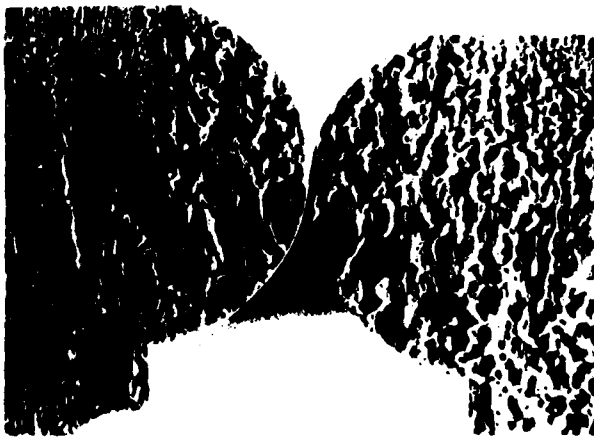


Figure 28.

Some remedies due to clamping can be made by re-spacing clamps. Figure 29 shows an exaggeration of poor clamp arrangement. The total pressure applied is not as important as the uniformity of pressure.

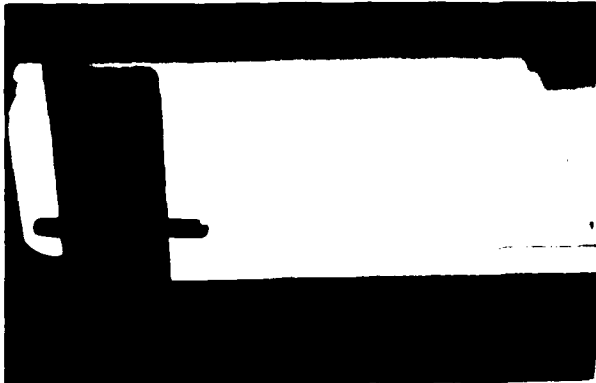


Figure 29.

Open joints on edge glued panels will frequently show through the face veneer, defecting the appearance of the face as in Figure 30.

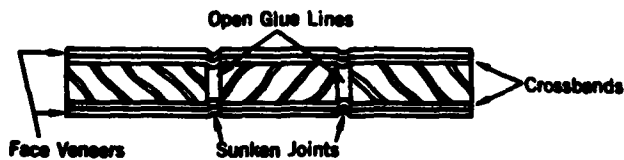


Figure 30.

When post gluing, it is important that equal pressure be applied to the bond line. With high jaw clamps, measurement of the distance between the jaws - top and bottom - will insure even pressure. See Figure 31. Figure 32 shows a clamp carrier for post gluing.



Figure 31.

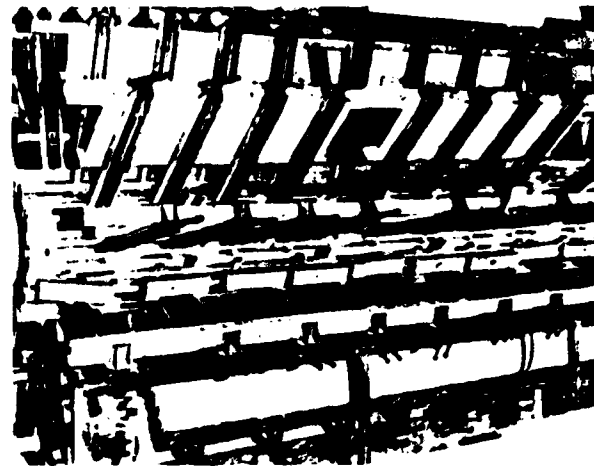


Figure 32.

Torque wrenches and panel hold-downs, as in Figure 33, will aid the evenness of pressure, regardless of the operator or his motivation on a particular day. However, poor maintenance of torque wrenches may cause uneven pressure. They should be calibrated at regular intervals with a compressometer (Figure 34).



Figure 33.

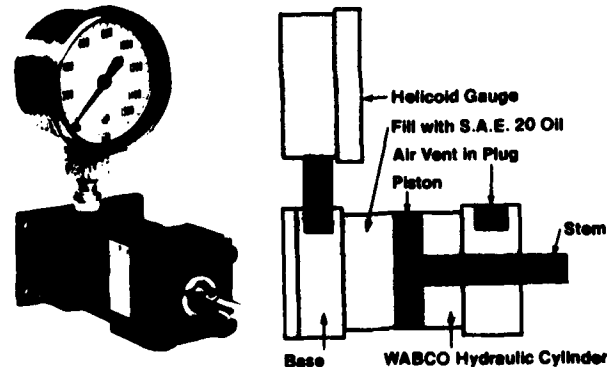


Figure 34.

Since water-based adhesives add water to the wood adjacent to the glue line, the wood in the vicinity of the bond is swelled more than the rest of the panel as shown in Figure 35.

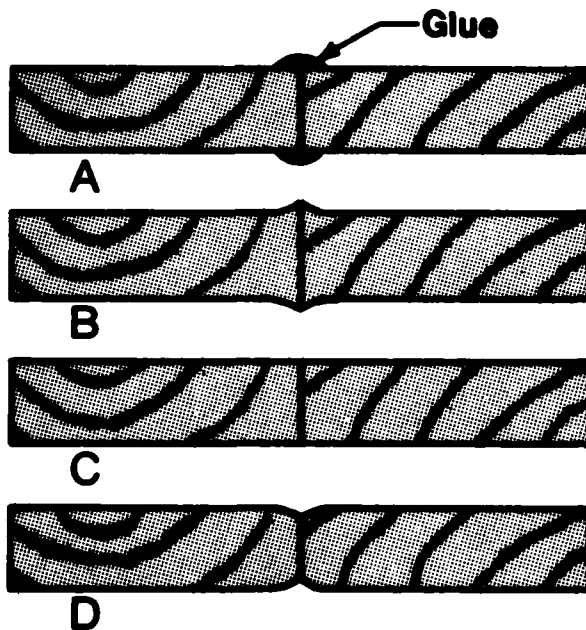


Figure 35.

If the panel is planed smooth immediately on removal from the press, the swelled wood will be planed to the same thickness as the drier material. When the moisture content of the panel equalizes, there will be a valley at each glue line. (Figure 36).



Figure 36.

This sunken joint will be more obvious with a shiny finish than a matte one.

The time of seasoning to eliminate sunken joints should be at least 24 hours and may need to be 72 hours. Seasoning panels in a heated chamber can reduce this time.

EFFECT OF SUBSTRATE CONDITION

The condition of surface of the wood substrate is important to joint strength. Wood adhesives are designed to minimize penetration into the wood in order to eliminate "starved" joints. Since this penetration is only a few thousandths of an inch, this outer layer is important. Almost any preparation method can make good or bad surface layers, depending on the conditions.

Figure 37 shows a good saw joint made with a sharp saw mounted on good equipment.

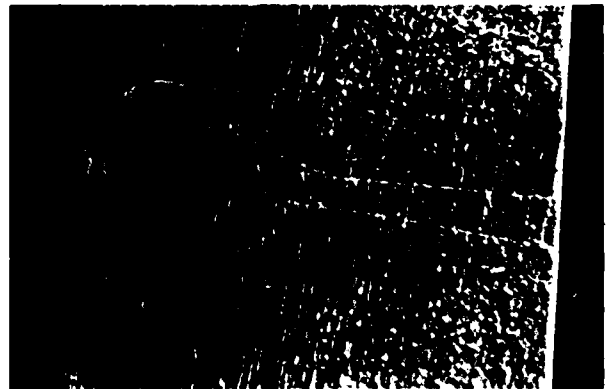


Figure 37.

Figures 38, 39 and 40 show joints made with a dull saw. The surface fibers adjacent to the kerf were loosened but not removed. These form a weak bond layer. Some of these surfaces are emphasized visually with a crayon. (Figure 41).

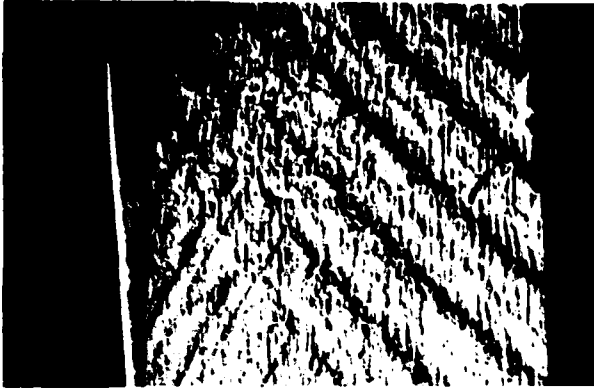


Figure 38.

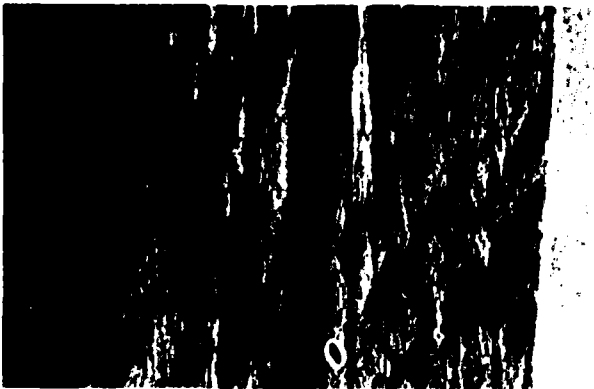


Figure 39.

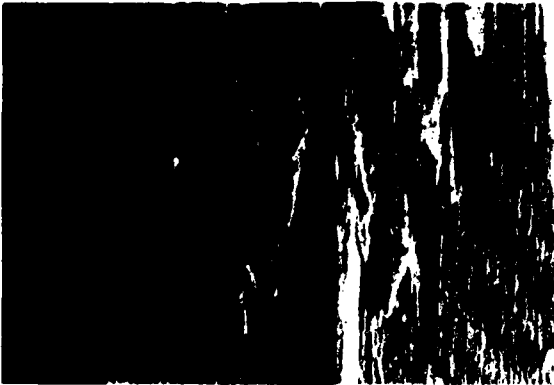


Figure 40.



Figure 41.

Figure 42 shows a poorly prepared abrasive planer joint. This is likely to occur with coarser grits. Wood species and moisture content also affects the fineness of grit needed to make a satisfactory glue joint.



Figure 42.

Burned surfaces are difficult for conventional wood adhesives to adhere to. Figure 43 illustrates this for a dowel. The same effect occurs with edge joints.

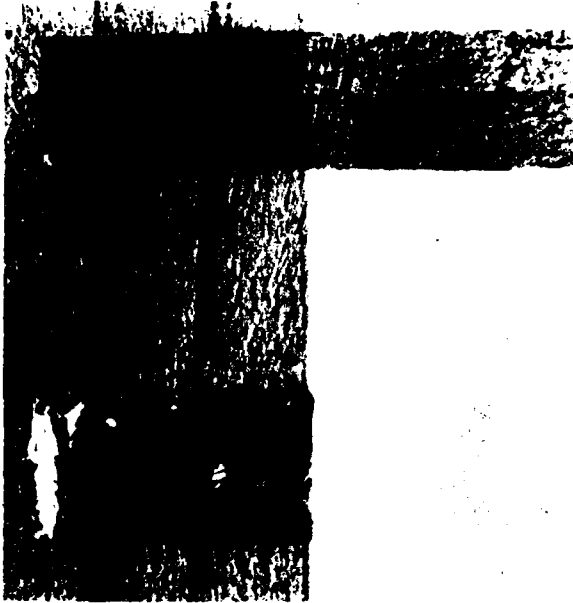


Figure 43.

Figure 44 shows a dowel hole with a poor gluing surface. This can be caused by advancing a drill too rapidly.

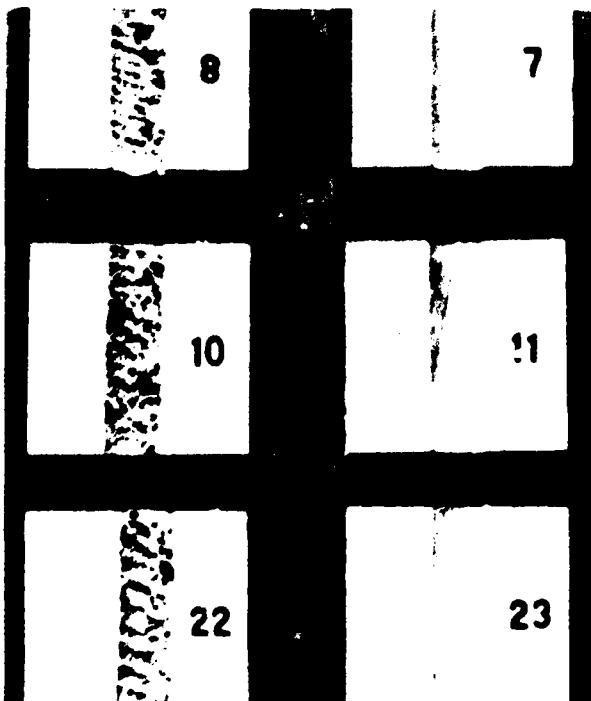


Figure 44.

Sometimes, bleed-through with a veneer, as in Figure 45, may cause a finishing problem or difficulty in breaking down a stack of panels. A change of adhesives, reduction of spread rate or reduction of pressure will usually cure the problem.



Figure 45.

Surfaces need to be clean before gluing. This is particularly true of flat surfaces to be laminated with face veneer or high pressure laminates. Particles left on the surface will telegraph through, as in Figure 46.

Figure 46.

A vacuum brush cleaner, as in Figure 47, will eliminate most particles.

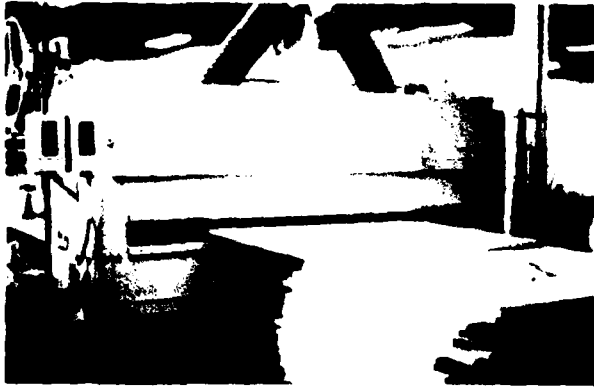


Figure 47.

Sometimes, wood chips may get into the adhesive and cause trouble. A pump fitting into the drum and equipped with a filter can reduce this problem. (Figure 48).

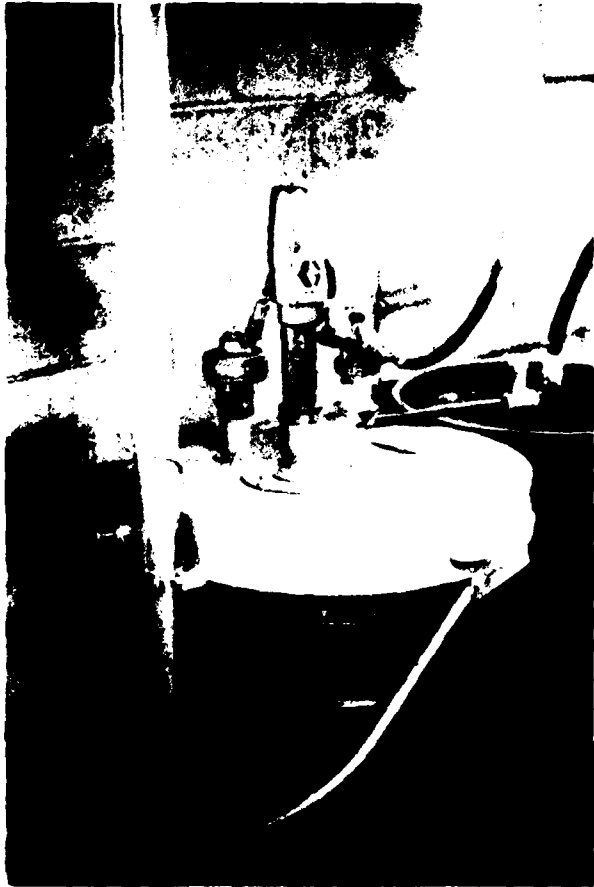


Figure 48.

MISCELLANEOUS CAUSES OF PROBLEM

Joint failures can also be caused by a number of other errors.

Figure 49 illustrates a lack of adequate pressure to get transfer in the joint.



Figure 49.

Figure 50 shows a lack of spread to obtain transfer to the opposing joint face.



Figure 50.

Figures 51 and 52 illustrate high pressure laminate which was cold pressed with only a small area where contact was made, which show up as particleboard and wood failure.

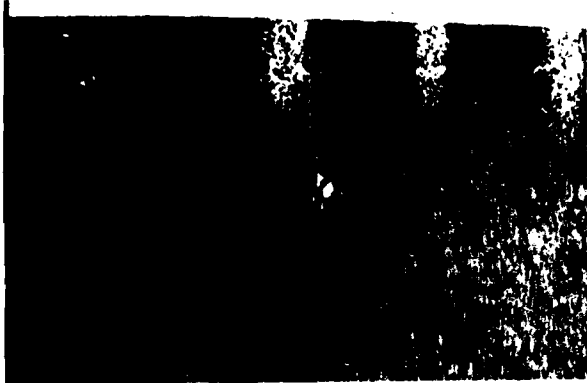


Figure 51.



Figure 52.

Figure 53 shows a pre-dried joint. The thicker ridges of glue (made by grooves in roller coater) were still wet enough to transfer and make some bond. The thinner part of the film was dry at assembly.



Figure 53.

Figure 54 shows a wet film from a roller coater which would make a good joint if pressed in this condition.



Figure 54.

Certain adhesives are swelled by the solvents in the finish. See Figures 55 and 56. This defect will not disappear with time. To correct, choose either an adhesive not affected by the finish or change finishes.

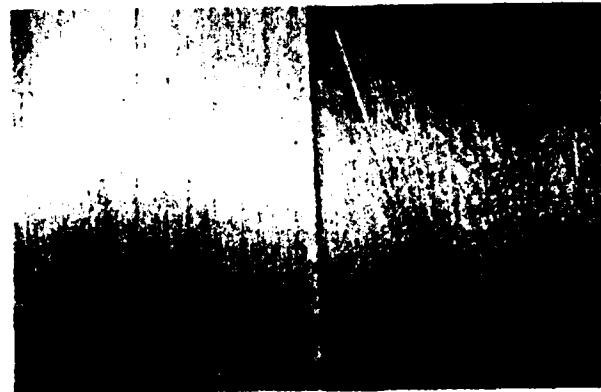


Figure 55.

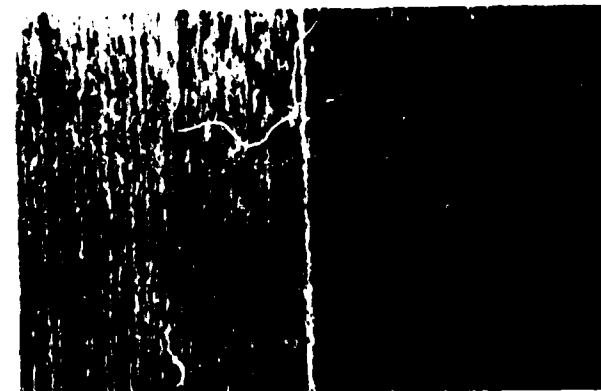


Figure 56.

If the glue fills the wood pores, the finish applied later cannot go into the pores, yielding a white appearance under the finish, as in Figure 57. To prevent this, it is necessary either to prevent the adhesive from filling the pores or to sand off this glue before finishing.



Figure 57.

Acid glues pick up a stain from contact with iron. This may come from piping, valves on drums, iron clamps or coffee cans. Lesser amounts of iron do not discolor the adhesive but may stain certain woods such as oak, cedar, walnut, mahogany, etc. (See Figure 58).

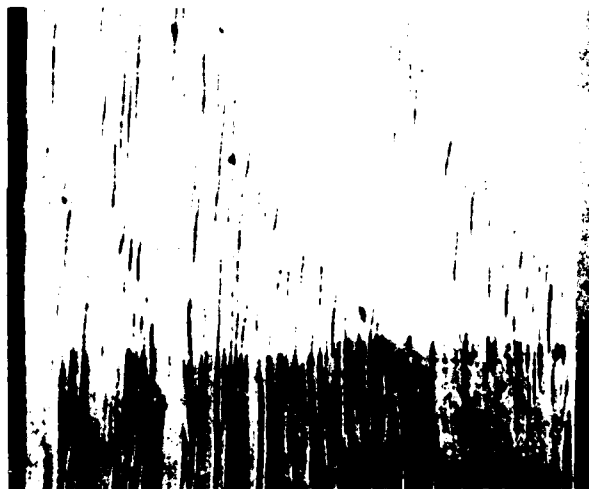


Figure 58.

Gluing with temperatures below the chalk point with polyvinyl acetate glues will give a weak, unusually white colored glue line. Figure 59 shows a glue which has chalked but would normally dry clear.

Figure 59.

Figure 60 shows another chalked bond line. If a chalked joint occurs, the joint must be re-made, with the room and wood at temperatures above the chalk point.

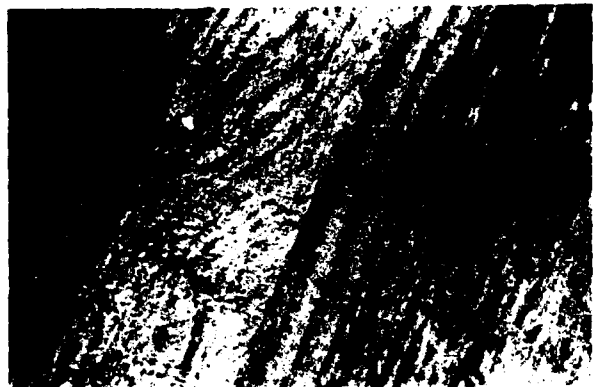
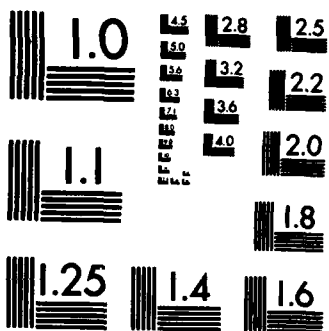


Figure 60.

The presence of stain in the glued joint indicates that the joint was open prior to finishing. (See Figure 61).



Figure 61.



MICROCOPY RESOLUTION TEST CHART
 NATIONAL BUREAU OF STANDARDS-1963-A

QUALITY CONTROL METHODS

If suitable testing equipment is not available, a chisel test can give comparative results, but only if used on a minimum of 10 joints per test. Figures 62 and 63 show what can happen to a chisel test depending on grain direction.

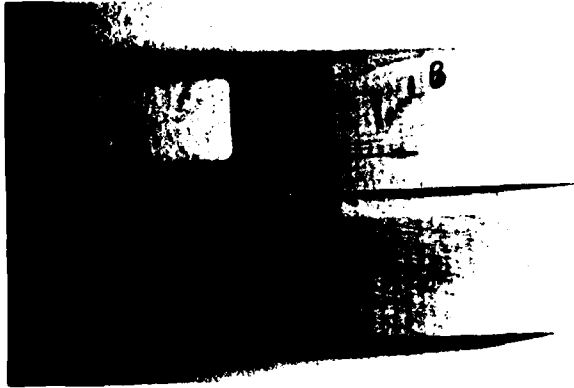


Figure 62.

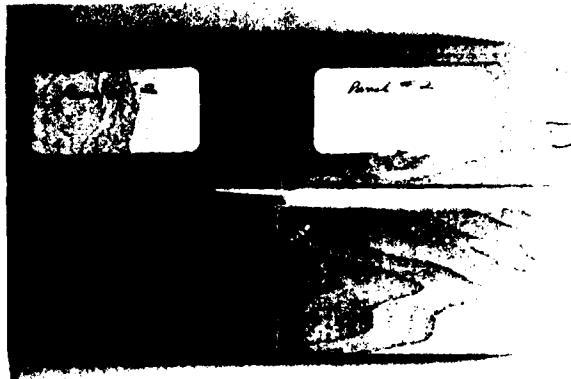


Figure 63.

In Figure 62, a panel was sawed in two parts with the chisel direction in opposite directions. In one case, 100% wood failure occurred and in the opposite direction, 0% wood failure resulted. In Figure 63, the same process and same result was obtained. In addition, a chisel was used in the opposite direction on the part with 100% wood failure with 0% wood failure observed. Grain direction is an important factor, in addition to joint strength, in the amount of wood failure obtained from a chisel test. Therefore, at least 10 bonds must be averaged to be meaningful.

Every woodworking operation doing gluing should institute a quality control program. This will allow corrective action to be taken, if the bonding operation gets out of control, before too much defective product is made.

To make a quality control effective, several things need to be done:

1. One person needs to assume responsibility for it.
2. This person should not report to manufacturing, shipping or sales.
3. Quality control needs to be done on a regular basis.
4. Suitable tools need to be provided. We use those in Figure 63 for trouble shooting. These are suitable for quality control.
5. Records need to be kept of
 - a. inspection results.
 - b. manufacturing processes (see Figures 64 - 68).
 - c. product being manufactured.

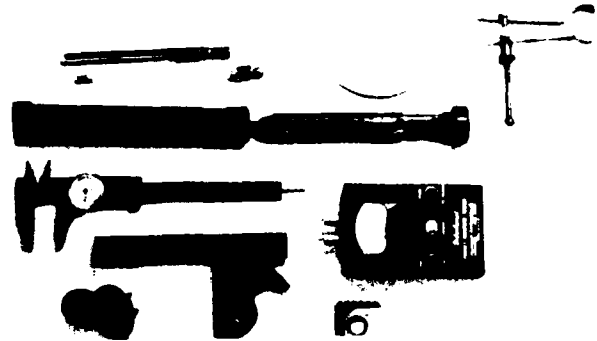


Figure 64.

M. C. LUMBER FROM KILNS

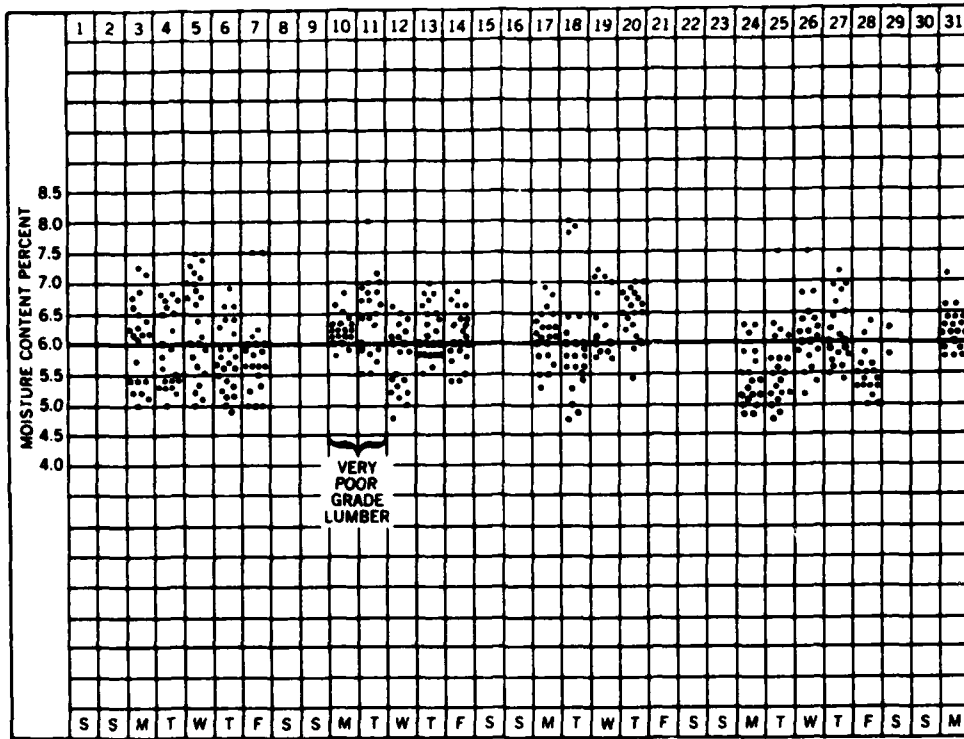


Figure 65.

M. C. LUMBER FROM KILNS—E. M. C. IN PANEL DEPARTMENT

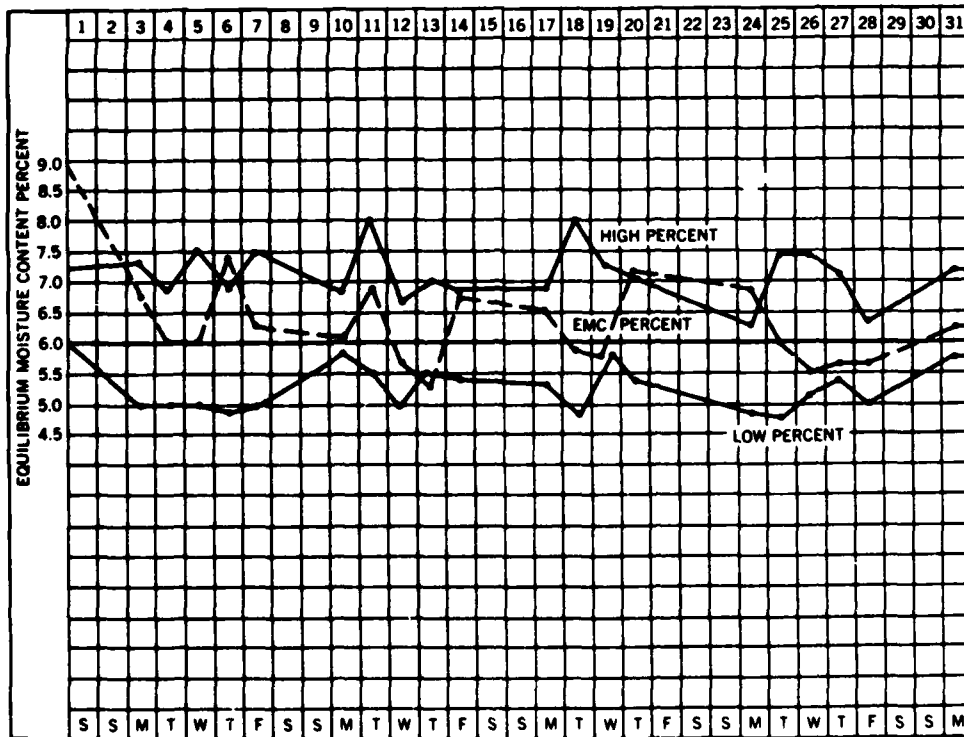


Figure 66.

JOINT FAILURE SUMMARY % PRODUCTION IN 1000 PANELS

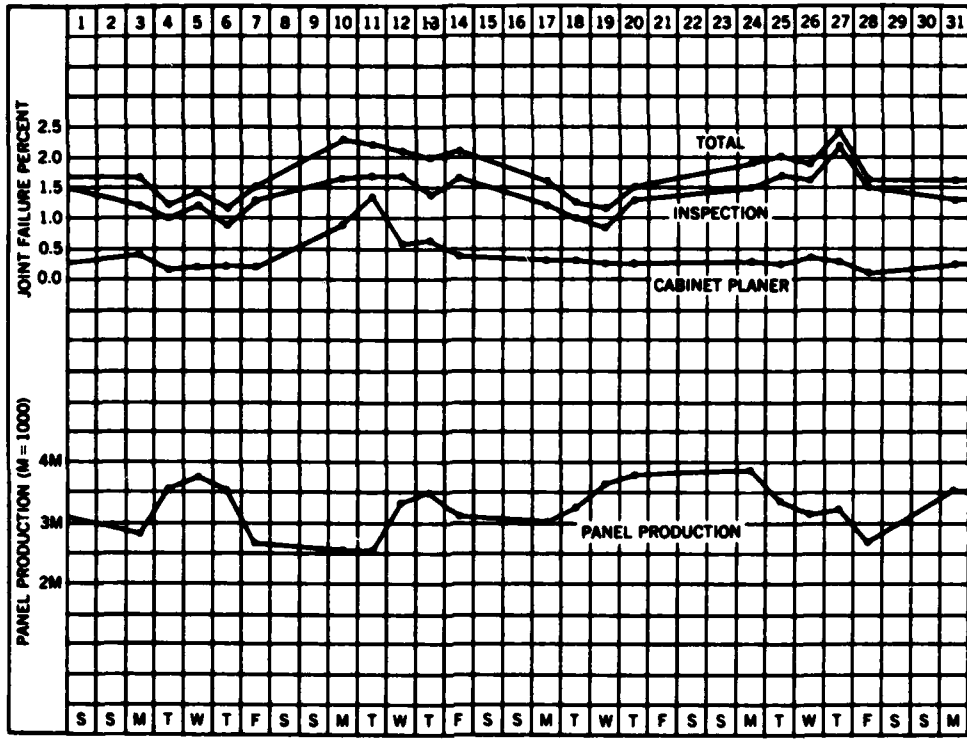


Figure 67.

DAILY REPORT—GLUE AND PANEL DEPARTMENT

(date)

HUMIDITY CONDITIONS IN GLUE AND PANEL AREA:						OUTSIDE WEATHER CONDITIONS:	
HYGROMETER READINGS			EQUALS IN LUMBER M.C.			TEMP.	HUMIDITY
STATION—	1	2	Av.	1	2	Av.	
Morning							Morning
Afternoon							Afternoon
Comments:							Average
							Comments:

GLUE USED:

MANUFACTURED BY	A Mfrs. No.	B Catalyst	C Extender	D Water	Proportions
Clamp No. 1					
Clamp No. 2					
Clamp No. 3					
Clamp No. 4					
If proportions changed from preceding report or through day, state why:					
Pounds glue used			Equals pounds per 100 sq. ft.		

ELECTRONIC PRESS DATA AND OUTPUT ALL CLAMPS:

Clamp N	P.S.I.		NO. PANELS	SQUARE FEET	MAN HOURS	SQUARE FEET PER MAN HOUR
	Top	Edge				
Clamp No. 1 (Elec.)						
Clamp No. 2 (Elec.)						
Clamp No. 3 (Wheel)						
Clamp No. 4 (Wheel)						
TOTALS			AVERAGE			

CABINET PLANNER REPORT:

NO. PANELS PLANNED	SQUARE FEET	MAN HOURS	JOINT FAILURES		OTHER REJECT REASONS		
			No. Panels	Sq. Ft.	% Total	No. Panels	Sq. Ft.

CONDITION OF LUMBER FROM ROUGH MILL:

	M.C.	Saw Joint	Afternoon	M.C.	Saw Joint	Comments
Morning						
Afternoon						

JOINT FAILURE SUMMARY:

	CABINET PLANNER	PANEL TEST	AT CLAMPS	INSPECTION DEPARTMENT	TOTAL
Number of panels					
% of Total panels planned for day					
% of Total panels glued for day					

Figure 68.

AD P 002425

FORMALDEHYDE FROM UF-BONDED PANELS--ITS MEASUREMENT

AND ITS RELATION TO AIR CONTAMINATION¹

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ABSTRACT

The formaldehyde emission behavior of a variety of particleboards and hardwood plywoods has been measured using six test methods: a Dynamic test which measures steady state air concentrations of formaldehyde under controlled ventilation rate and board loading, two Desiccator tests, a Paper Sorption test, the Equilibrium Jar test, and the Perforator test. Data from all six methods correlate approximately with one another but, as expected, large deviations occur. The Dynamic procedure is regarded as a primary board characterization test since it models actual use conditions; it is probably too complex for rapid screening purposes, however. For that purpose a Desiccator test is considered to be the most satisfactory of the methods examined.

INTRODUCTION

A major emphasis of the experimental work at the Forest Products Laboratory on the formaldehyde emission problem has been the characterization of board emission behavior under dynamic (air ventilating) conditions. That effort has included a quantification of the effects of ventilation rate and loading (board area per chamber volume) upon observed air concentrations of formaldehyde (11,12). It was our feeling that emphasis upon dynamic behavior was warranted because such tests represented an approach toward actual use conditions and, therefore, should constitute a primary performance characterization of urea-

formaldehyde-bonded boards. However, dynamic tests are too exacting and time consuming to be employed generally for screening or quality control purposes. Consequently, we have also examined several simpler screening or quality control test methods in order to establish: (1) Whether the test results from such methods bear any direct relation to dynamic steady state formaldehyde/air concentrations, and (2) whether any of these simple methods offer obvious advantages over the others. This paper summarizes the findings from these studies, some of which are published elsewhere in greater detail (11,12).

EXPERIMENTAL

Details of the various test methods are already available and only brief descriptions are given here. These methods include: (1) the Dynamic test, (2) the JIS Desiccator test, (3) the NPA-modified Desiccator test, (4) the Equilibrium Jar test, (5) the Perforator test, and (6) the Paper Sorption test.

In the Dynamic test, particleboard specimens, 16 x 50 x 100 mm with sealed edges, were placed in a glass vessel which was capped and stored in a temperature- and humidity-controlled

¹ Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

² Supported by Mitsui Toatsu Chemicals, Inc. Present address is: Mitsui Toatsu Chemicals, Inc., Hokkaido Factory Division, Toyonumas 1, Sunagawa, Hokkaido 073-01, Japan.

chamber (11,12). Conditioned air was pulled through the vessel at a constant rate. The formaldehyde concentration in the exiting-air stream was determined at intervals by scrubbing through water and subsequently analyzing the water solution using Purpald or acetylacetone reagents (11). After a time, the measured concentrations varied randomly about a mean value and this is termed the steady state concentration C_s (ppm formaldehyde in air). Such C_s values were determined as a function of air exchange rate N (hr^{-1}) and loading L (m^2 of exposed board area per m^3 free air volume in the vessel).

In the JIS Desiccator test (7,11), specimens 50 x 150 mm are placed on end in a 9-liter desiccator which also contains 300 ml H_2O in a crystallizing dish. The desiccator is capped and allowed to stand at $22.5 \pm 2.5^\circ \text{C}$ for 24 hours, after which the water in the crystallizing dish is analyzed for formaldehyde using acetylacetone reagent (7,11). In conformance with the JIS procedure, nine specimens of 16-mm-thick particleboard and 10 specimens of < 10 mm plywood were used. In contrast, the NPA-modified desiccator test (3) calls for the use of eight specimens, 70 x 127 mm, when the thickness is < 16 mm; it also employs a 400-ml beaker in place of the crystallizing dish and chromotropic acid in place of the acetylacetone.

For the Equilibrium Jar method (5), specimens 70 x 127 mm are placed singly into eight 32-oz, wide-mouth jars. A second jar is placed mouth-to-mouth over each of the sample jars and the joint is taped with parafilm. After standing for 25 hours at $22.5 \pm 2.5^\circ \text{C}$, each jar set is separated, the air from the upper jar is purged into sodium bisulfite solution, and that solution is analyzed for formaldehyde using chromotropic acid. When the formaldehyde content is very low, all eight upper jars may be purged into one sodium bisulfite solution. At sufficiently high levels, each upper jar is purged and analyzed separately and the resultant values averaged.

In the Perforator test (13,14), a number of 25 x 25 mm specimens are refluxed in toluene for 2 hours. The condensing toluene is bubbled through a column of water which absorbs the formaldehyde. In this study, the resulting water solution was analyzed for formaldehyde using acetylacetone reagent and fluorescence measurements (11).

The Paper Sorption test (11) intersperses sheets of filter paper between six specimens, 50 x 150 mm, which are stacked, weighted down, and allowed to sit at ambient temperature for 16 hours. The central area of each sheet was then moistened with Purpald reagent; when dry,

the intensity of the purple color was determined by measuring the reflectance at 540 nm with a brightness meter.

A wide variety of plywood and particleboard panels were studied. One group of four UF and two phenolic particleboards was prepared at the FPL (11). These were characterized by the Dynamic, the JIS, and the Paper Sorption tests. Two of the urea-formaldehyde (UF) boards were aged at 60°C for 30 days and retested by the Dynamic method. A second group of particleboard and plywood panels was obtained from Mead and Hunt. Weyerhaeuser Corporation supplied several particleboards and the Hardwood Plywood Manufacturers Association supplied a number of plywood panels as part of a round robin sponsored by the Formaldehyde Institute. These last three groups of boards were characterized by the JIS and NPA-modified Desiccator tests, the Perforator, and the Equilibrium Jar.

Prior to testing, the specimens were not pre-equilibrated under a specific air-flow, temperature, or humidity condition. Since a major goal was to compare values obtained from the different methods, the specimens from a given panel were instead kept under identical conditions insofar as possible and the various tests to be performed upon those specimens were all initiated within 1 to 3 days. The 25 mm-square Perforator specimens, for example, were minimally exposed to the atmosphere during their preparation from panels and then immediately sealed in jars until they could be tested.

RESULTS AND DISCUSSION

The Dynamic test data are presented and analyzed first. This presentation is followed by a brief discussion of the screening methods, which includes their observed cross correlations and comments regarding their advantages and disadvantages. Table 1 summarizes the linear regression data for the methods' correlations, and table 2 summarizes rather subjectively the relative advantages and disadvantages of the methods examined.

Dynamic Testing

The observed steady state air concentrations of formaldehyde at $40^\circ \text{C}/75\%$ relative humidity (RH) are reproduced from another publication (12) in figure 1 as a plot of $1/C_s$ versus N/L , the ratio of ventilation rate to loading. The lines through the data result from linear regression analysis according to equation (1), the form of which has been proposed by several investigators (1,4,6).

Table 1.--Parameters from methods correlations

Tests correlated ^{a/}	Type of correlation	Linear Regression Parameters			
		Intercept	Slope	Correlation coefficient, r^2	Percentage error in predicted mean, $\frac{b/}{100 \frac{s_y \cdot x}{y}}$
JIS Desiccator vs C_s	Cartesian	-0.14	4.50	0.965	24
NPA Desiccator vs JIS Desiccator	Cartesian	0.027	0.462	0.990	7
Paper Sorption vs C_s	Cartesian	70.5	-3.92	0.990	2
Equilibrium Jar vs NPA Desiccator	Double logarithmic	-0.199	0.831	0.964	64
Perforator vs NPA Desiccator (particleboard)	Double logarithmic	0.909	1.041	0.933	8
Perforator vs NPA Desiccator (plywood)	Double logarithmic	0.653	0.914	0.854	15

a/ Dependent vs independent variables.

b/ 100 x Standard error in predicted mean of dependent variable ÷ observed mean of dependent variable.

$$\frac{1}{C_s} = \frac{1}{C_{eq}} + \frac{1}{KC_{eq}} \cdot \frac{N}{L} \quad (1)$$

This is stated in Hoetjer's terminology (6) where C_{eq} is the formaldehyde concentration under equilibrium conditions, i.e., in the absence of air ventilation, and K represents a material transfer coefficient intended to characterize the formaldehyde permeation rate through the board-air interphase region.

Equation (1) provides an excellent fit to the particleboard data. The regression parameters are summarized in table 3 and were used to calculate the C_s versus N/L curves shown in figure 2. Considering current usage of UF boards in mobile homes (2), for example, and the energy constraints upon ventilation rates, the practical limits of the curves in figure 2 lie between N/L 0.2 and 1.5 (12). Within that range, however, there is about a fourfold decrease in C_s .

The utility of dynamic testing combined with equation (1) is illustrated in table 4 which presents some calculated C_s values at

25° C/75% RH for the best of the three particleboards, the aged D set. These C_s values were calculated using the 40° C/75% RH parameters in table 3 plus the fact that C_s is reduced approximately fourfold by changing from 40° C to 25° C (11). The loading values of 0.5 and 1.2 m^2/m^3 generally cover the range anticipated in mobile homes (2); observed ventilation rates are in the span 0.2 to about 1.0 hr^{-1} but 0.5 hr^{-1} is apparently regarded as a reasonable goal (10). If, for purposes of discussion, we set 0.1 ppm formaldehyde as a desirable air contamination standard, table 4 indicates that the ventilation rate of 0.5 hr^{-1} would have to be raised to about 1.2 hr^{-1} at the lower loading and to 3.0 at the higher loading. These increased ventilation rates of 1.2 and 3.0 hr^{-1} would in turn about double and quadruple, respectively, the infiltration heat losses (10).

Assuming such energy losses to be unacceptable, what degree of improvement in the aged D board would be required to meet the 0.1 ppm standard at 0.5 hr^{-1} ventilation rate?

Table 2.--Method evaluation summary^{a/}

Criterion	Method				
	Dynamic steady state concentration, C _s	Desiccator	Paper sorption	Equilibrium Jar	Perforator
	ppm	µg/ml	Brightness	ppm	mg/100g
Reproducibility	~ 10% ^{b/}	< 10% ^{c/}	< 5% ^{c/}	~ 10% ^{d/}	~ 5%
Ease and simplicity	5	1	1	3	2
Conducted under controlled temperature-RH conditions	1	4 (changing board, MC nonequilibrium)	3 (nonequilibrium)	2 (affected by board MC)	2 (affected by board MC)
Range of applicability	2	1	3	3	4
Results should be affected by both free formaldehyde and hydrolytic formaldehyde	1	2	3	3	5
Proximity to actual use conditions	1	3	3	2-3	5
Correlates with C _s		2 ^{e/}	2 ^{e/}	3	4

a/ Except for reproducibility, expressed on relative scale of 1-5 where 1 is best.

b/ References (11,12).

c/ Reference (11).

d/ Measured for values > 2 ppm. Error much larger below 1 ppm.

e/ Not examined for plywood.

The calculations in table 4 indicate the need for at least a twofold board improvement at $L = 0.5 \text{ m}^2/\text{m}^3$ and a fivefold improvement at $L = 1.2 \text{ m}^2/\text{m}^3$.

Screening Methods

Desiccator Test.--Figure 3, which is taken from reference (11), indicates that dynamic steady state concentrations, C_s, at 25° C/75% RH for five particleboards are linearly related to the corresponding JIS Desiccator values. The correlation coefficient of the regression is 0.965 and the prediction error for the Desiccator values is 24% (table 1). These particular dynamic measurements were conducted at one N/L (0.060 m/hr) and for C_s values from about 0.2 to 7 ppm. There seems to be no reason to doubt that

similar relations would be approximated for other N/L and other boards, as long as the boards possessed a formaldehyde supply adequate to maintain steady state values for periods of days to a few weeks (12). Additional data would be desirable to confirm such extensions as well as the applicability to plywood.

The JIS Desiccator values are also directly related to the NPA Desiccator values, as would be expected from the similarity of the two tests. This can be seen in figure 4 to be true for a variety of boards, with a correlation coefficient of 0.990 and a prediction error for the NPA values of 7% (table 1). For JIS values up to 6 µg/ml, the NPA values are approximately 46% of the JIS values. Interestingly, the 46% relationship is within 10% of that calculated from the equations given by Kubota, *et al.* (9) for the effects of differences in board and water surface areas. The existence of a fixed relationship between

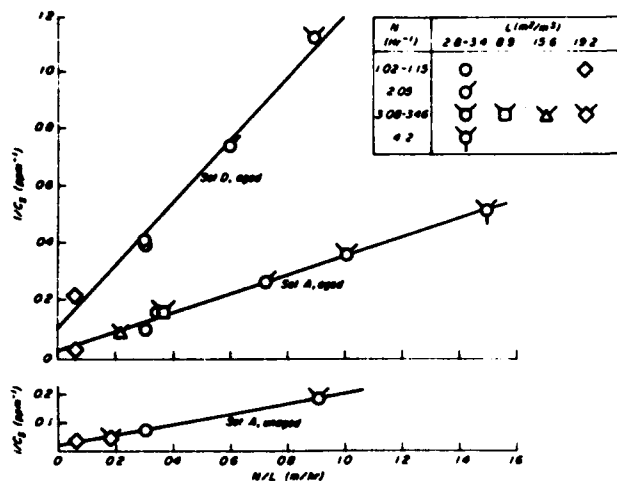


Figure 1.--Test of equation (1) [N, ventilation rate (air exchange/h); L, loading (m² of panel/m³ free air volume); and C_s, steady state level of formaldehyde contamination in air (ppm).]

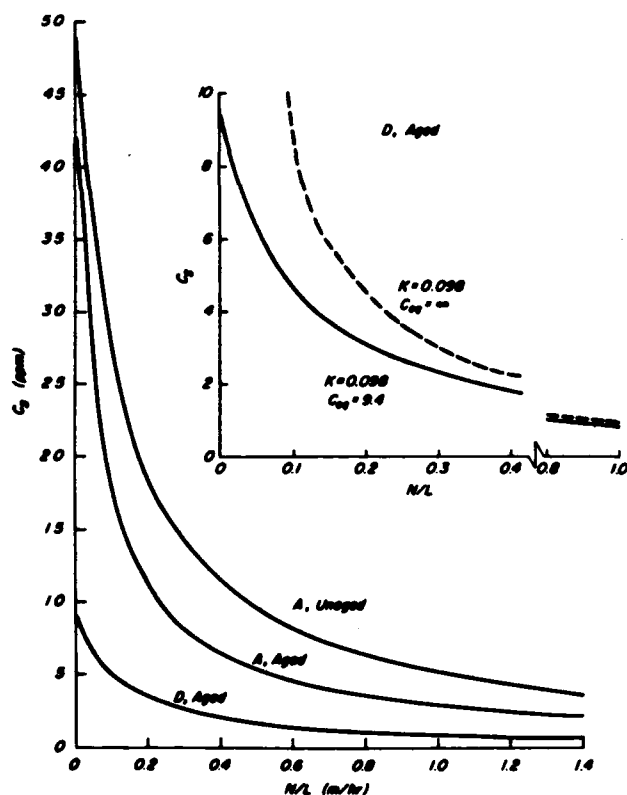


Figure 2.--Calculated dependence of C_s on N/L [N, ventilation rate (air exchange/h); L, loading (m² of panel/m³ free air volume); and C_s, steady state level of formaldehyde contamination in air (ppm)].

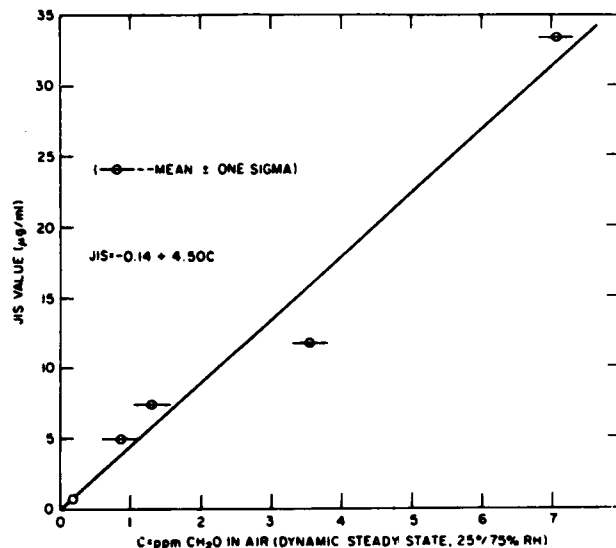


Figure 3.--Correlation between JIS Desiccator and Dynamic methods.

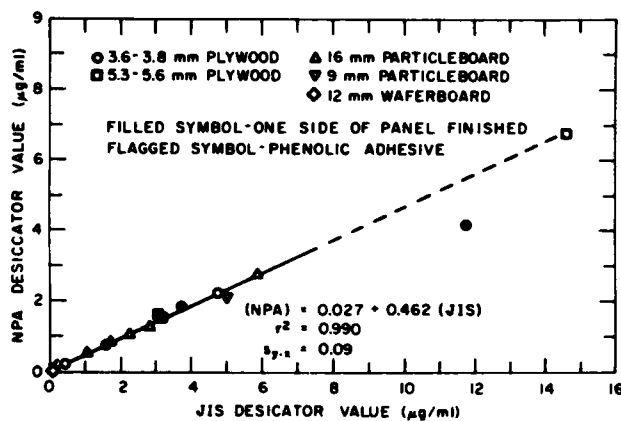


Figure 4.--Correlation between Desiccator methods.

Table 3.--Parameters from equation (1)^{a/}

Board set	K	C _{eq}
	m/hr	ppm
A, unaged	0.109	51.0
A, aged	0.079	43.7
D, aged	0.098	9.4

$$\frac{a/}{C_s} \frac{1}{C_s} = \frac{1}{C_{eq}} + \frac{1}{KC_{eq}} \cdot \frac{N}{L}$$

C_s = steady state formaldehyde concentration in air (ppm)

N = ventilation rate (air exchanges per hour)

L = loading (m² board per m³ chamber volume).

Table 4.--Calculated air contamination levels at 25° C/75% RH for aged D boards

Loading, L	Ventilation rate, N	Steady state formaldehyde concentration, C _s
m ² /m ³	hr ⁻¹	ppm
0.5	0.2	0.46
	0.5	0.21
	1.2	0.09
1.2	0.2	0.87
	0.5	0.45
	3.0	0.09

these two test versions will permit meaningful comparisons of board quality between Japan and the United States since the NPA Desiccator may become the standard quality control test in this country (3).

The two methods are considered together in the evaluation summary in table 2. The Desiccator tests are distinguished by their simplicity and broad applicability range. This is, however, inherently a nonequilibrium test and is conducted under rather unrealistic conditions; some implications of these properties will be discussed later.

Paper Sorption Test.--The same dynamic data employed above also correlate linearly with the intensity of the purple color developed in the Paper Sorption test. Figure 5,

taken from reference (11), illustrates the correlation in a plot of spot brightness (low brightness = high purple intensity = high formaldehyde) against C_s at 25° C/75% RH.

The correlation coefficient of the regression is 0.987 and the prediction error is 2% (table 1). This test is very simply performed and may offer some advantages in plant quality control since it could be carried out nondestructively, i.e., with entire panels instead of small specimens.

Equilibrium Jar Test.--The jar values from a variety of boards are plotted against the corresponding NPA Desiccator values in figure 6. A double logarithmic plot was used in order to spread out the lower range of the scale. The regression possesses a correlation coefficient of 0.964 and yields a prediction error in jar values of 64% (table 1). However, due to the large scatter at the low end and the lack of data in the middle region, this correlation should be regarded as tentative. Because of sensitivity problems at the low end and its relative complexity, the jar test in our judgement is much less satisfactory than the desiccator method (cf. table 2).

Perforator Test.--The Perforator and Desiccator data are plotted on a double logarithmic scale for particleboard and one waferboard in figure 7 and for plywoods in figure 8. In figure 7 an approximate correlation exists for Perforator values from about 0.2 to 50 mg/100 g board despite the fact that values below about 10 mg/100 g are usually (13,14) considered unreliable due to artifacts introduced by extractibles from the wood itself. Nevertheless, the regression line possesses a correlation coefficient of 0.933 (table 1) and a prediction error in the Perforator value of 8%. The data point for the waferboard sample was not used in the regression analysis since that sample possessed a moisture content of only 2% compared to values between 6 to 8% for all other samples. (Board moisture content has been shown to have a small influence upon both Perforator (14) and Desiccator (11) results.) In figure 8 more scatter is seen in the plywood data which also extend well below 10 mg/100 g. The correlation coefficient in this case is only 0.854 and the prediction error is 15% (table 1). Possibly the reason for the correlations extending to very low values is an insensitivity of the acetylacetone fluorometric analysis procedure to wood extractibles, but this has not been verified.

The Perforator test is believed to measure the total free (chemically unbound) formaldehyde within a board, although a small dependence upon board moisture content does indicate that a certain amount of hydrolytically produced formaldehyde can contribute to the Perforator values (13,14). Unlike the

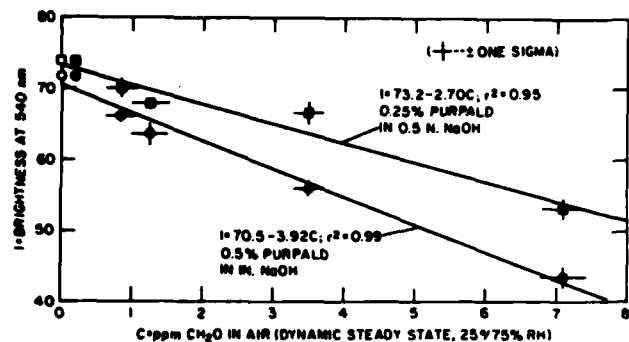


Figure 5.--Correlation between Paper Sorption and Dynamic methods.

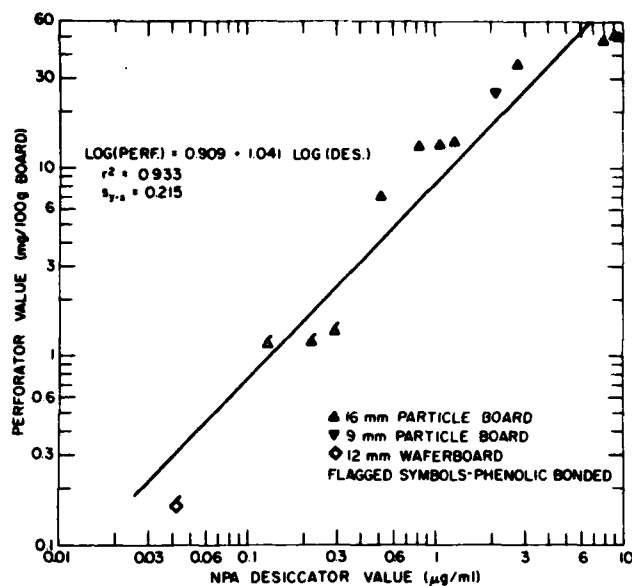


Figure 7.--Correlation between Perforator and Desiccator for particleboard.

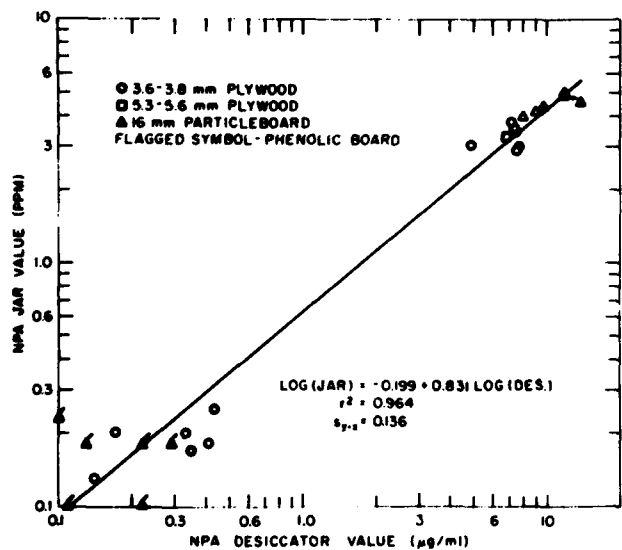


Figure 6.--Correlation between Jar and Desiccator methods.

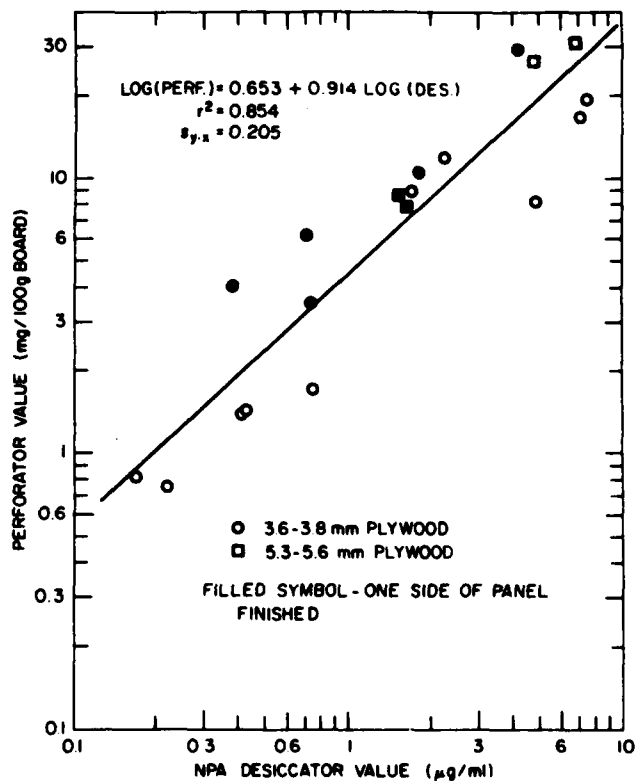


Figure 8.--Correlation between Perforator and Desiccator for plywood.

other methods examined here, the Perforator method does not directly measure the board's ability to emit or retain the formaldehyde contained within it. Consequently, while Perforator values will be little influenced by board physical characteristics, e.g., surface coatings or whether the board is plywood or particleboard, the other methods should be influenced by such factors and to similar extents. For example, in figure 8 it can be seen that the finished plywoods (filled symbols) generally have a lower Desiccator value than the unfinished boards at the same Perforator value. The coating, of course, reduces the emission rate as well as the moisture uptake and therefore results in a lower Desiccator value. Moreover, the plywood regression line is displaced towards higher Desiccator values relative to the particleboard line (Figure 7), e.g., at a Perforator value of 10 mg/100 g board the predicted Desiccator values are 1.2 µg/ml for particleboard and 2.4 µg/ml for plywood. Therefore, it appears that particleboard either emits its formaldehyde less readily than does the plywood, or the plywood absorbs moisture faster than the particleboard.

Thus, comparisons between Perforator and other test values can provide some insights into differences in the formaldehyde emission process. In addition, the Perforator method possesses the advantages of good reproducibility (cf., table 2), comparative simplicity, and widespread use in other countries. As detailed in table 2, however, it suffers from some serious deficiencies as an exclusive screening procedure, e.g., there are questions about its lower limit, it is primarily sensitive to free formaldehyde, it is conducted under totally artificial conditions, and it is only correlated in a limited manner with board emission behavior.

SUMMARY AND CONCLUSIONS

Dynamic (air ventilating) experiments were performed on three particleboards over a range of ventilation rates (N) and loadings (L). The steady state concentrations of formaldehyde in air were fit by a two-parameter equation, the parameter values being dependent upon the particular board set. Such experiments are rather complex and lengthy. They do, however, afford a characterization of the effect a board's emission behavior has upon air contamination under conditions which model those in actual application. Moreover, they provide a means of estimating the advantages or disadvantages of changes in ventilation rate and loading.

A limited evaluation of several rapid screening methods has been conducted. These included two minor variants of a Desiccator procedure, a Paper Sorption test, the Equilibrium Jar test, and the Perforator method. It was concluded that the most satisfactory of these is a Desiccator method. This choice was based upon the fact that such a method (1) is very easily performed, (2) has satisfactory reproducibility, (3) can measure a very wide range of board emissivity, and (4) should generally, though not always, respond to board variations in much the same way that dynamic testing does.

Criterion 4 above implies that there should be a direct correlation between Desiccator and C_s values. This was in fact demonstrated for several particleboards but needs to be verified for a greater variety of boards, including plywoods. Interestingly, all the methods examined here appear to give results which can at least be approximately correlated with one another. For some boards, however, rather large deviations from a correlation are observed. These deviations may be due to errors in methods, e.g., perhaps Equilibrium Jar data at low emissivities, or to the fact that different methods do not respond in quite the same manner to board variables. The Perforator test, for example, appears to measure the total free formaldehyde content of a board. However, the Desiccator value reflects the tendency of the board to lose its formaldehyde content (presumably free and bound) in the presence of water which acts both as a strongly attracting sink for formaldehyde and as a hydrolysis stimulator.

The Desiccator value also represents a transient condition established in the absence of air circulation, and may therefore be influenced by the necessity for formaldehyde permeation through a stagnant gas layer adjacent to the board surface (8). The dynamic C_s measurement is made under steady state conditions at fixed humidity, and the presence of air circulation may alter the nature and effect of any stagnant gas layer.

Thus, an exact one-to-one correspondence between the various methods should not be expected. Although the simpler tests can be extremely useful for screening and quality control purposes, it will be desirable, perhaps essential, to employ a controlled Dynamic test for final, critical board emission characterization.

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AD P 002426

REDUCTION OF FORMALDEHYDE LEVELS IN MOBILE HOMES¹

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ABSTRACT

This is a preliminary report on investigations into methods of reducing airborne formaldehyde levels in existing mobile homes.

Two effective techniques for reducing formaldehyde levels have been identified. Fumigation of mobile homes with ammonia appears to produce long-term reductions of approximately 61-73%. Use of a high capacity air recirculation device in which formaldehyde is removed from the air by a filter bed of potassium permanganate impregnated alumina pellets produced reductions of approximately 74% during operation.

INTRODUCTION

In recent years there have been an increasing number of complaints by mobile home dwellers about indoor air quality. This trend has sharply accelerated since mid-year 1976 when the Federal Mobile Home Construction and Safety Standards became effective, resulting in a significant tightening up of the mobile home structure. Lower air infiltration rates would be expected from these homes than those manufactured prior to the federal standards.

The majority of the complaints are associated with formaldehyde, although it should be borne in mind that there are a number of other indoor air pollutants, some of which can produce similar symptoms. Hollowell, et al. (1979) has identified carbon monoxide, nitrogen dioxide, and radon in addition to formaldehyde as common indoor-generated contaminants whose levels are elevated by decreased air infiltration resulting from energy conservation measures in residential buildings. Moschandreas

(1978) identified carbon monoxide, carbon dioxide, nitric oxide, hydrocarbons, aldehydes, total suspended particulates and respirable suspended particulates pollution levels as often being higher indoors than outdoors. He discussed their dependence on infiltration-exfiltration rates and how they are increased in "tight" houses. Without minimizing the importance of formaldehyde, the indoor air quality problem in mobile homes is more than simply a formaldehyde problem and should be addressed as such by the federal regulatory agencies involved.

There can be a number of formaldehyde sources in mobile homes including UF-bonded particleboards, UF-bonded plywood wall paneling, furniture with UF-bonded veneers, certain textiles and combustion processes such as gas stoves and cigarettes. Intensive R&D efforts by a number of forest products companies and UF resin producers are beginning to result in UF-bonded building materials with substantially lowered formaldehyde emissions. Some of these have recently begun to appear in the marketplace. Although the outlook for reduced formaldehyde levels in newly constructed mobile homes will improve, reliable techniques are needed to reduce the levels in existing mobile homes where appropriate. The purpose of this research is to identify and develop the most effective of these techniques.

¹Paper presented at the Symposium, "Wood Adhesives - Research, Applications, and Needs," Madison, Wisconsin, September 23-25, 1980.

VARIABLES AFFECTING FORMALDEHYDE LEVELS

The major variables determining the formaldehyde levels in a given mobile home with a given variety of formaldehyde emitters are temperature, infiltration rate (ventilation), relative humidity, and age. The loading rate or quantity of UF-bonded building materials is also a very important factor, but for the purposes of this discussion, only environmental variables are being considered.

Temperature has a substantial effect on formaldehyde levels in mobile homes. Increasing temperatures increase the level of formaldehyde as illustrated by figure 1. This is a general effect also observed in test chamber measurements of UF-bonded particleboards (Neusser and Zentner 1968) and plywood wall paneling.

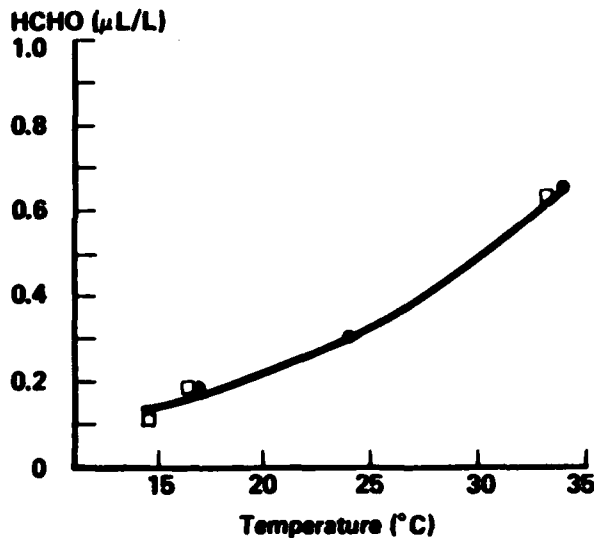


Figure 1

Variation of formaldehyde levels with temperature in a mobile home. Formaldehyde measurements made in a 8.4 x 14.6 m double-wide mobile home over a two day period.

- Data from a modified NIOSH chromatropic acid method
 - Data from a CEA 555 Analyzer
- μL/L is equivalent to ppm (v/v)

The infiltration rate, or fresh air ventilation rate, of a mobile home is another important variable. It depends not only on the tightness of construction and living habits of the occupants, but

also on weather factors such as wind velocity and temperature. Infiltration rates are commonly expressed in air changes per hour and are on the order of 0.5-1.5 air changes per hour for typical U.S. homes (Handley and Barton 1973). In a limited number of mobile homes, we have measured infiltration rates by the carbon monoxide decay rate method (Goldschmidt 1978) and found a range of 0.14-0.5 air changes per hour under calm weather conditions. The lower figure represents only one air change every seven hours. This can be compared with recommended ventilation rates of 0.4-0.6 air changes per hour of outdoor air for mobile homes calculated from ASHRAE² Standard 62-73. Figure 2 shows the relationship for formaldehyde level with infiltration in a mobile home.

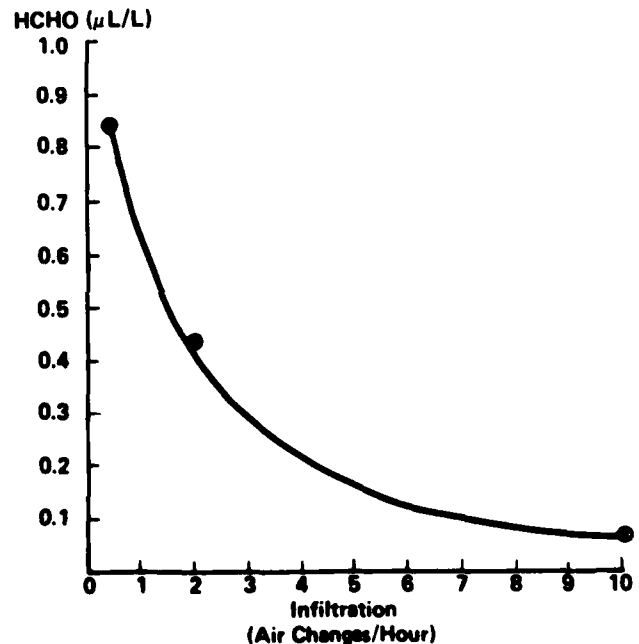


Figure 2

Variation of formaldehyde levels with infiltration in a mobile home. Formaldehyde measurements made in a 4.25 x 20.15 m single-wide mobile home using a modified NIOSH chromatropic acid method. Infiltration rates were determined by a carbon monoxide decay rate method. The two higher infiltration rates were obtained using exhaust fans and open windows. The mobile home was allowed to remain 24 hours at each infiltration rate before the formaldehyde measurement was made.

²The American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

Air humidity also has an effect on formaldehyde level. Andersen (1976) and others have established that increasing relative humidity results in higher formaldehyde levels in test chambers and rooms containing UF particleboard. Berge, et al. (1980) have recently published a mathematical model for relating formaldehyde levels at different temperatures and humidities in a climate chamber containing particleboard.

The age of a mobile home has an influence on its formaldehyde level. Although there is little definitive mobile home data to support this statement, it is generally agreed that new mobile homes have the highest formaldehyde levels and that these levels decrease over time. There have been few formaldehyde-related complaints concerning mobile homes more than three years old.

FORMALDEHYDE ABATEMENT TECHNIQUES

Ineffective Measures

The subject of effective measures for reducing airborne formaldehyde levels in mobile homes has been a very confused one. Many "retrofit" techniques have been recommended, but very few have any convincing data to support their efficacy. For example, there have been a number of liquid products put on the market that are sprayed into the air, onto walls and carpets, or are evaporated from wick bottles and claim to neutralize or eliminate formaldehyde odors in mobile homes. Although we have not tested all of these, the ones we have tested were either not effective in lowering formaldehyde levels or at best were somewhat effective only for a few minutes. We were able to demonstrate equal or better short-term effectiveness by misting the air in a room with the same quantity of water. It is believed that as a group these materials have no long-term effect on formaldehyde levels and act only as odor-masking agents.

Ozone treatment has been recommended as a formaldehyde abatement technique by some, but without any data supporting its long-term effectiveness. Our experience has been that while ozone may reduce formaldehyde levels while actually present, it has little, if any, effect once the treatment is finished. The high toxicity of ozone prevents its continuous use in occupied homes in any quantities that might be effective.

A Rationale for Formaldehyde Abatement

One can attack the problem of formaldehyde abatement in an existing mobile home in two general ways: by lowering the formaldehyde emission rate or by removing the formaldehyde from the air after it has been emitted. Listed below are the techniques that we are aware of that have some degree of effectiveness in reducing indoor formaldehyde levels:

Methods of Formaldehyde Reduction

<u>Reduction of Emission Rate</u>	<u>Removal from Air</u>
Ammonia fumigation	Ventilation
Sealing of particleboard	Absorbent systems

Ventilation has already been discussed. Ammonia fumigation and absorbent systems, the two most effective techniques, are the main subjects of this paper and will be discussed after particleboard sealing.

A technique that has met with limited success in long-term reduction of formaldehyde levels is the careful coating of all exposed particleboard surfaces and edges with a good quality sealer. This includes the particleboard decking under the carpets and all particleboard in cabinets and shelving. This is an expensive treatment and is limited in effectiveness because the unexposed surfaces cannot be sealed, the plywood wall paneling cannot be sealed without altering its appearance, and there may be other formaldehyde emitters present.

Ammonia Fumigation

Ammonia fumigation, in our experience, is the most cost-effective "retrofit" measure for reducing indoor formaldehyde levels. Ammonia fumigation of mobile homes has the advantage of reaching most of the formaldehyde emitters, except of course, combustion sources. Neusser and Zentner (1968) reported good results from ammonia fumigations in homes containing particleboard in Austria and Norway, using 25% aqueous ammonia. No damage was detected to fittings, armatures or electrical contacts. Sundin (1978 and 1980) reported that ammonia gas treatment of homes containing particleboard resulted in long-term formaldehyde reductions of approximately two thirds. There have been recently developed at least two manufacturing plant ammonia gas treatment processes for particleboard, one by RY AB in Sweden

Table 1
RESULTS OF AMMONIA FUMIGATIONS OF 12 MOBILE HOMES¹

Type of Mobile Home	Location	Before Fum. HCHO ($\mu\text{L/L}$)	After Fumigation HCHO ($\mu\text{L/L}$)									
			Weeks									
			0	4	8	12	16	20	24	28	32	
1. Single-W	Alabama	1.0	0.28*	0.26			0.24				0.27*	
2. Double-W	Wash.	1.1	0.20*	0.23	0.20							
3. Single-W	Wash.	0.84*	0.07*			0.17			0.19*			
4. Single-W	Wash.	0.99	0.16*		0.29*							
5. Single-W	Kentucky	0.65	0.24*									
6. Single-W	Florida	0.41	0.11									
7. Single-W	Wash.	0.98*		0.16*	0.32*		0.31					
8. Single-W Office	Illinois	0.56		0.31*					0.22*			
9. Double-W	Oregon	0.88	0.24*									
10. Single-W	Oregon	1.0	0.13									
11. Double-W	Florida	0.51	0.15*									
12.	Florida	0.41	0.12									

¹Formaldehyde Measurements Made Using a Modified NIOSH Chromotropic Acid Method

*Data Temperature Corrected According to Figure 1

(Smedberg 1979) and the Verkor FD-EX process. These processes are claimed to substantially reduce the free formaldehyde content (analyzed by the Perforator Method) of UF particleboards.³

In aqueous solution ammonia reacts readily with formaldehyde to form hexamethylenetetramine, a relatively stable adduct. A number of workers in this field have attributed ammonia's ability to lower free formaldehyde contents and reduce formaldehyde emissions of UF-bonded wood products to this chemical reaction, although the presence of hexamethylenetetramine in ammonia-treated particleboard or other products has apparently not yet been demonstrated.

³Weyerhaeuser has developed other, more cost-effective techniques for substantially lowering the formaldehyde emission of particleboard and hardwood plywood wall paneling.

The major questions at the beginning of this research program were how effective is ammonia fumigation in mobile homes and what precautions are necessary in order to safely carry out the procedure. It is believed now that ammonia fumigation will in most cases give long-term formaldehyde level reductions of approximately two thirds and that the procedure can be carried out safely by trained personnel with no damage to the mobile home. Work is continuing on this procedure to better define the optimum fumigation conditions, obtain longer-term data and to identify any deleterious effects to the mobile homes.

Weyerhaeuser has ammonia-fumigated a number of mobile homes during the past year in which the occupants complained of formaldehyde problems. Table 1 shows the formaldehyde levels before fumigation and at various times after fumigation for these mobile homes. For most of the mobile homes it was not possible to make all measurements at the same temperature. Since temperature differences can have a substantial effect on formaldehyde levels,

the data in table 1 has been temperature-corrected according to figure 1 so that the before- and after-fumigation formaldehyde levels reflect the same temperature for any one home.⁴ Mobile homes 1, 3, 7, and 8 have formaldehyde data for 13-28 weeks after fumigation and show long-term reductions of 61-73%.

The ammonia fumigation procedure itself involves the use of approximately 3.8 L (1 gal.) of 28% ammonium hydroxide per 194 m³ (6930 ft³) of mobile home volume. This is the volume of a typical 4.25x20.15 m (14x66 ft) single-wide mobile home. The ammonium hydroxide is placed in shallow plastic pans in each major room and the home is sealed for a minimum of 12 hours with the thermostat set at a minimum of 27°C. Precautions are taken to protect the person carrying out the fumigation, food, clothing, pets, house plants and light-colored oak. The mobile home is then thoroughly ventilated. A residual ammonia odor, initially less than two parts per million after ventilation, disappears completely within several days.

Absorbent Systems

An absorbent system used in combination with an air recirculation fan appeared to be a possible solution to indoor formaldehyde problems. Mathematics, familiar to heating and ventilating engineers, indicate that a formaldehyde curve similar to figure 2 should be obtained when using a hypothetical formaldehyde-removal device. The horizontal axis of figure 2 in this case would be efficiency of removal multiplied by the air recirculation rate instead of infiltration. This behavior assumes a constant formaldehyde emission rate. The main point of this is that while it would not be possible to reach zero formaldehyde even with a high-capacity, high-efficiency device, much can still be done to lower the formaldehyde levels.

Our first step was to test potential formaldehyde absorbents and oxidation catalysts for formaldehyde removal efficiency. Activated carbon was not tested because available literature (Stakavich 1969)

⁴The ability to temperature-correct formaldehyde data for mobile homes is almost a necessity. It is recognized here that the use of figure 1 for this purpose is only an approximation and that further refinement in this area is needed.

indicated that it has very low capacity for retaining formaldehyde in the range below 1 ppm. The following materials were tested in a small chamber for rate of formaldehyde disappearance at 25°C:

<u>Materials Tested</u>	<u>Formaldehyde Disappearance Rate</u>
Automobile Catalytic Converter Catalyst I	None
Automobile Catalytic Converter Catalyst II	Fast
Hydrocarbon Oxidation Catalyst	None
Impregnated Activated Carbon	Slow
Potassium Permanganate Impregnated Alumina (PIA)	Fast
Tungsten Carbide	None
Cerium Dioxide	None
Quartz Mercury U.V. Lamp	Slow (Ozone produced)
Quartz Mercury U.V. Lamp Filtered	None

From this screening of potential candidates, two were selected for scaled-up testing. The first, catalytic converter catalyst II, which is a catalyst containing platinum, palladium, rhodium, and cerium dioxide, and the second, commercial potassium permanganate impregnated alumina pellets (PIA).

A prototype air recirculation test device was constructed in the shape of a large box on the top of which a 50 m³/min (1800 CFM) fan was mounted. The four vertical faces of the box could each hold a 100x60x3.5-cm filter or could be closed off as desired. The fan pulled room air into the box and forced it out through the filters.

Figure 3 shows the results of tests conducted with this recirculation device in a 4.25x20.15 m (14x66 ft) single-wide mobile home. The device was operated at maximum recirculation capacity (44 m³/min or 13.6 air changes per hour) using two filters containing a total of 36 kg PIA. Formaldehyde level reductions were approximately 74% in the early part of the test.

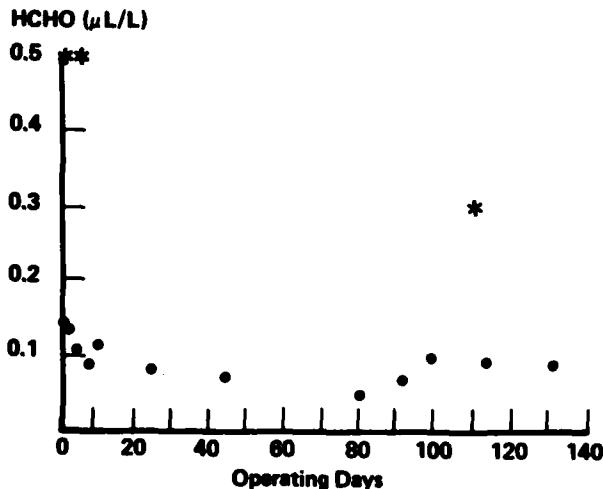


Figure 3
Reduction of formaldehyde levels in a 4.25 x 20.15 m mobile home using the air recirculation test device with PIA. The recirculation device was operated at 44 m³/min. with two filters containing a total of 36 kg PIA.

* Control (Device Off) • Device On

Similar formaldehyde reductions were obtained using the same volume of catalytic converter catalyst II. However, in this test an unidentified irritant was produced in the air and this catalyst was dropped from consideration. Formic acid seemed to be a likely candidate for the irritant, but a test for this was negative.

To give an idea of the approximate costs involved in this approach, our recirculation device and filters cost \$165 for materials. Fabrication costs are difficult to estimate, but might be an equal amount. The 36 kg of PIA cost \$112 for a total of \$442. Other costs would be for power consumption and replacement of the PIA when exhausted.

CONCLUSION

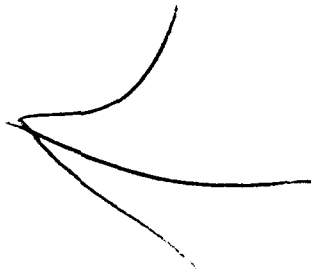
We have demonstrated and offered preliminary data on two methods of substantially reducing formaldehyde levels in existing mobile homes. In our opinion ammonia fumigation offers the more cost-effective and acceptable approach. We are continuing to gather and refine data on the effectiveness and the best procedure for ammonia fumigation.

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AD P 002427

FORMALDEHYDE TESTING IN MOBILE HOMES:

SOURCE MATERIALS, TEST METHODS AND CONDITIONS¹

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ABSTRACT

The current emphasis on the irritant and possible health effects of atmospheric formaldehyde in manufactured housing has placed an additional burden on the industry to reduce formaldehyde liberation to a reasonable level. The extensive use of materials containing formaldehyde in manufactured housing compounds the problem and demands a broad testing program. To meet the needs of this program, a colorimetric method of determining formaldehyde levels using Purpald reagent was modified for field testing. This method produces fast, accurate, on-the-spot readings, which provides a valuable tool in determining the sources and conditions of formaldehyde liberation in mobile homes.

This test method is described and its advantages and limits are discussed. Data gathered by this method are also presented, including the relationship of vapor pressure to the migration patterns of atmospheric formaldehyde in a conventional mobile home. Extensive testing has also been very helpful in determining the effectiveness of various retrofit methods of formaldehyde reduction where complaints exist. The effectiveness of coating or sealing materials, reduction with ammonium hydroxide, and increased ventilation are also discussed.

TEST METHODS

To date, the most common and universally recognized method of determining atmospheric formaldehyde is a procedure recommended by the National Institute for Occupational Safety and Health (NIOSH). The procedure calls for a minimum of 30 liters of air drawn through glass impingers containing 20 ml of distilled water. If other aldehydes are present, 20 ml of 1% sodium bisulfite is recommended. The formaldehyde concentration absorbed into the water is determined colorimetrically using chromotropic acid.

Although the method is specific and accurate, it requires laboratory analysis which is time-consuming and does not offer on-the-spot readings. Our firm has had extensive experience with another method that we have found suitable for field applications. The method utilizes an alkaline solution of Purpald which reacts with a carbonyl compound to form an aminal, which can then undergo air oxidation to produce a chromophore only if the carbonyl is an aldehyde. Under standard conditions a plot of absorbance versus formaldehyde concentration is linear from 50 to 600 nanograms per milliliter. This is more sensitive than p-rosaniline or chromotropic acid (2).

The method is based upon one developed at Georgia-Pacific and patterned after that suggested by HPMA/NPA (3,5).

¹Presented at the 1980 Wood Adhesives Symposium. Research, Applications and Needs. Madison, Wis., September 23-25, 1980.

This procedure calls for impinging a maximum of 10 liters of air (one l/minute) in the Purpald reagent (0.25% Purpald in 0.5N NaOH) or into distilled water with later addition of reagent. To further develop the color, the reagent is shaken in a wrist-action shaker for 30 minutes. We have had comparably accurate results by scrubbing with clean air through a second impinger with a Hydroxy lamine Hydrochloride solution, as the wrist-action shaker was difficult and awkward to use in the field. The Bausch-Lomb Mini 20 spectrophotometer designed for field applications was used to determine the color absorbance. We have found it sufficiently accurate for our field tests.

In our laboratory and field tests, we have periodically run comparison tests with the NIOSH chromotropic acid method and consistently have found the Purpald method to indicate lower levels of concentration. We feel this may be the result of the difference in specific gravity between the Purpald reagent and distilled water. We have not found this to be true when distilled water is used with later addition of reagent. This conversion factor has been found to be consistent at 1.35.

In sampling levels of atmospheric formaldehyde with levels greater than 1.0 PPM, we found that shortening the sampling time was much more accurate than dilution. Sampling time as low as one minute (one liter) has been sampled with a minimal loss of accuracy. The formula for calculating levels of formaldehyde from the absorbance is shown in Fig. 1. Periodic standardization of the Purpald reagent is also necessary, especially during lot changes. A sample of the standardization curve is shown in Fig. 2.

$$\text{PPM (CH}_2\text{O)} = \frac{A \times F \times 20 \times 24.47 \times 760 \times T}{V \times P \times 30.03 \times 298} \times 1.35$$

Where:

- A - Absorbance
- F - Absorbance Factor (From Wet Standardization)
- 20 - ML of Reagent in Impinger
- 24.47 - UL of CH₂O Gas in one Micromole
@ 760MM hg and 25°C
- T - Absolute Temperature in Degrees Kelvin
(K = C° + 273)
- V - Volume of Air in Liters
- P - Atmospheric Pressure in MM of Hg
(To convert inches of Hg to MM multiply
inches x 25.4)
- 30.03 - Molecular Weight of CH₂O
- 1.35 - Conversion Factor to NIOSH P+CAM125

FIG. 1

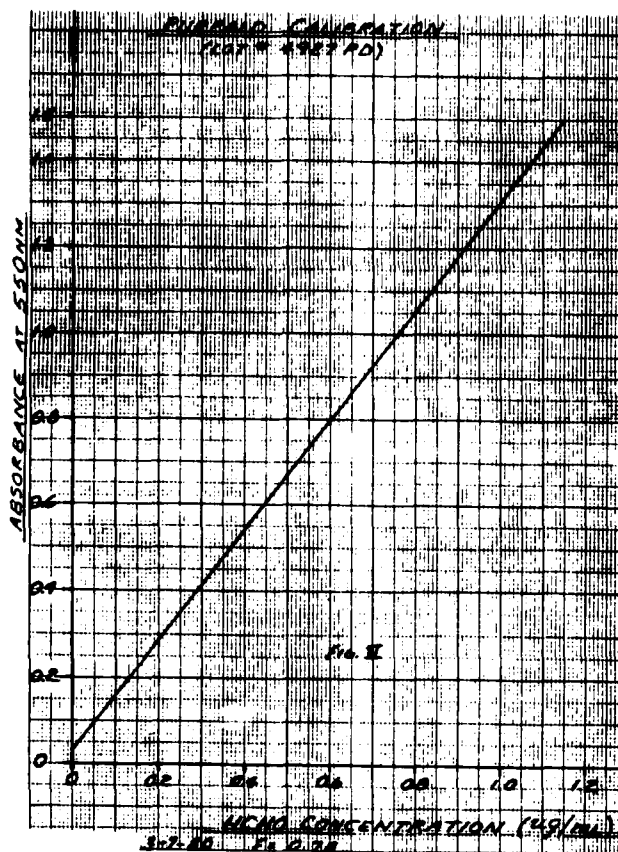


FIG. 2--Purpald Calibration

Another test method we have found useful as a screening device is the Lion Formaldemeter. The meter uses an electrochemical fuel cell containing two platinum electrodes. When air is drawn into the fuel cell a small voltage is generated which is directly proportional in magnitude to the formaldehyde vapor concentration. This voltage is displayed on a liquid crystal digital meter and reads in tenths from .1 to 100 PPM. The unit operates similar to the breath analyzer used by law enforcement officials for the detection of alcohol. We found the unit is not totally specific for formaldehyde. Literature received with the instrument states that the presence of methanol, ethanol, phenol, formic acid, furfuryl alcohol and resorcinol will cause additive readings. If a person is able to recognize these interferences and deal with them accordingly, the instrument can be a valuable tool.

TEST CONDITIONS

One of the most serious problems in testing ambient levels of atmospheric formaldehyde in mobile homes is that formaldehyde

liberation is directly proportional to atmospheric conditions. "Spot" or "grab" sampling methods are not representative of average levels in the home. Wide variations in levels are common even in a 24-hour period. Many State agencies have adopted the practice of closing up the home for a 24-hour period previous to testing. This practice is logical during the heating season, or if the home is air conditioned, but cannot be considered representative in the summer when it is normal to have a few windows open. Closing up the home can create differential pressures, causing the source materials to liberate much higher levels of atmospheric formaldehyde than could ever be expected under normal conditions. We feel the most effective method of determining if a formaldehyde problem exists in a dwelling is to test levels at the known sources as well as the ambient. This can be accomplished by sampling the air within cabinets and wall cavities. If these source levels are considerably higher than the ambient, it is logical to assume that they are the major contributor.

FIELD RETROFITS

Currently it is a popular belief that particleboard is a major construction material used in mobile homes and consequently would be the main source of formaldehyde emission (4). As this is a logical assumption, field retrofits concentrated on sealing all exposed particleboard in a mobile home. Effective sealants were developed and applied to the decking and other exposed particleboard in the home. In many cases the complaints still persisted. As plywood paneling has been considered another major source of formaldehyde (1), testing had concentrated in this area. Air samples drawn from exterior and partition wall cavities in many mobile homes indicated levels high enough to cause concern, but in most cases sealing or replacing the paneling would be a drastic step. Other methods of formaldehyde reduction such as fumigation of the total home with ammonium hydroxide or injecting formaldehyde scavengers into the wall cavities appear to be effective methods of ambient formaldehyde reduction.

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AD P 002428

POLYMERIC ISOCYANATE AS WOOD PRODUCT BINDERS¹

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ABSTRACT

Polymeric isocyanates are receiving a great deal of attention as binders for the wood products industry due to their excellent bonding efficiency, fast press cycles, low binder requirements, long resin storage stability, and absence of formaldehyde. Polymeric isocyanates, being solvent-free liquids, may be utilized as is or emulsified with water in spray or centrifugal blender applications.

Data are presented showing the rate of bond formation, though minimum press time, with polymeric isocyanate bound board is similar to that of a urea-formaldehyde binder. Mat moisture content has little effect on the reaction stoichiometry although it will change the density profile of the board significantly. And, the use of Fourier transform infrared shows the presence of both polyurethane and polyurea in the core of a polymeric isocyanate bound waferboard.

INTRODUCTION

Polymeric isocyanates have attracted a great deal of attention as binders for wood products. European manufacturers have been using polymeric isocyanate for a number of years although the North American market, for the most part, is just beginning to consider polymeric isocyanates as a viable binder. These isocyanates offer a number of advantages over existing resins such as excellent binding efficiency, fast press cycles, and low binder requirement.

A major problem with polymeric isocyanates is their tenacious adhesion to the metal cauls and platens. To avert this problem it has been necessary to prepare composite boards,

i.e., an isocyanate bound core but a different resin used in the face layers. This method of manufacture will yield boards with excellent internal bond characteristics of the isocyanate, but the faces will have the bond and durability characteristics of the other resin (8).

To prepare a 100% isocyanate bound board in single or multiopening presses, it has been necessary to release the cauls and platens prior to pressing. This method has been adequate, but in the event the release application is omitted, the boards will have a tendency to adhere to the cauls and platens and possibly cause a halt to production.

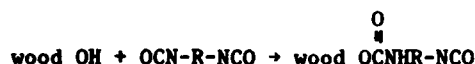
The Upjohn Company has recently announced the availability of a novel, self-releasing polymeric isocyanate, Isobind[®]100 that has been designed specifically for the reconstituted wood products industry. Isobind[®]100 may allow the manufacture of single or multilayer

¹Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

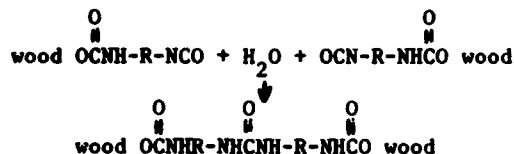
all isocyanate boards without the problems associated with caul release, provided recommended procedures are followed.

The polymeric isocyanate will react with a broad spectrum of compounds containing "active hydrogen," such as water, phenols, alcohols, and acids, all of which exist in one form or another in wood (1).

The superior properties achievable with low levels of polymeric isocyanate binders presumably arise, in part, from the reaction of the isocyanate with the hydroxyl groups of the lignocellulosic substrate to form a polyurethane.



These isocyanate terminated wood-urethanes can be joined and crosslinked by water by the formation of aromatic urea and biuret.



A recent study (3) has shown that the isocyanates will react with lignin and the polysaccharides to form wood-isocyanate polyurethanes, which confirms the previous hypothesis.

Our experiments on this area were conducted to determine 1) the minimum press time, which would indicate the rate of bond formation under press conditions, 2) the possible shift in reaction towards higher polyurea content through the use of various moisture content mats, and 3) the use of instrumentation to determine the presence of polyureas and polyurethanes.

To determine the rate of reaction via minimum press time we used our standard conditions of a 350°F press, a mat moisture content of 12%, a one minute closing speed (end of "daylight" to stops), bound the mat with 5% Isobind® 100, and placed a thermocouple in the core of the board to measure temperature vs. cure. Hammermilled (3/8") Ponderosa pine was the furnish.

We found the mat core reached 100°C in 70 seconds after entering the press. Removing a board from the press at 85 seconds, Figure 1, yielded delamination. After 90 seconds in the press 70% of the final properties were realized.

One hundred seconds provided 88% of the final properties and at 110 seconds, or 50 seconds after close, the board had reached its final properties and showed no change with further pressing.

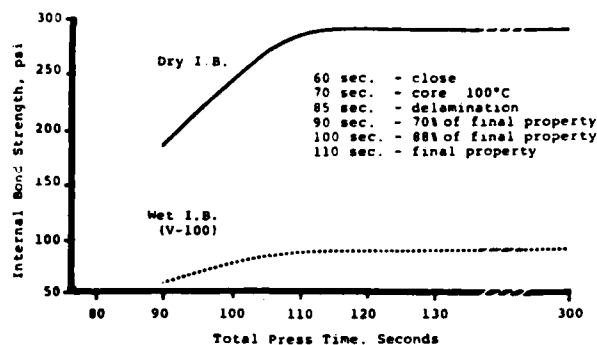


Figure 1.--Internal bond strength vs. press time.

This data shows the minimum press time, under these conditions, to be 40 seconds after a core temperature of 100°C is reached. This is similar to the temperature requirement for a U-F binder to cure but much lower than the published (2) requirements of 150°C or greater for P-F resin to cure.

The stoichiometry during board preparation, e.g. the ratio of isocyanate groups to available lignocellulosic groups to water, is difficult to calculate. A mat containing 5% isocyanate and 5% water contains approximately 0.05 equivalents of isocyanate per 1.0 equivalent of water or 20 times the amount of water necessary to totally react all of the isocyanate groups to urea. The quantity of lignocellulosic groups available under press conditions is unknown but one would assume that as the mat moisture content was increased, the reaction would favor the formation of lower molecular weight ureas and a loss in bonding efficiency.

To study this, boards were prepared where the total mat moisture content range evaluated was from 5% water to 25% water based on the weight of the dried furnish (Table I). MOR, MOE, and the thickness change during 2 hour boil show only slight variation over this range of moisture contents. The MOR values show a high of 2,800 psi at 5% moisture and a low of 2,570 psi at 25% moisture, while the 9% moisture to 20% moisture samples fall within this range. MOE values follow this pattern with a high of 380 kpsi at the 5% moisture level and a low of 355 kpsi at the 25% moisture level.

Table I.--Properties at various moisture contents

% Water total	5	9	12	16	20	25
% Isobind [®] 100	5	5	5	5	5	5
Density, overall, pcf	42	42	42	42	42	42
MOR, psi	2800	2750	2660	2600	2570	2570
MOE, kpsi	380	375	370	370	365	355
I.B., psi	370	304	280	264	253	230
Wet I.B., psi, (V-100)	97	79	65	62	57	55
Swelling, 2 hr. boil, %	33	33	34	34	35	36

The properties which appear to be influenced by moisture content are the internal bond strengths, both wet and dry. The dry IB with 5% moisture content is 370 psi and is reduced as the moisture content increases to a low of 230 psi at 25% moisture. Shown graphically, Figure 2, a decrease of 22% in IB is realized when the moisture content is increased from 5% to 9% and a decrease of approximately 15% is shown by raising the moisture content from 9% to 16%. The addition of higher levels of water show a continuing decrease with a loss of approximately 15% in properties from the 16% moisture level to the 25% moisture level. Although there is an obvious decrease in IB values with increasing moisture, there was a question of whether the decrease was due to a loss in bonding efficiency of Isobind[®]100 via a change in the reaction mechanism or to a physical property change due to a density gradient in the board.

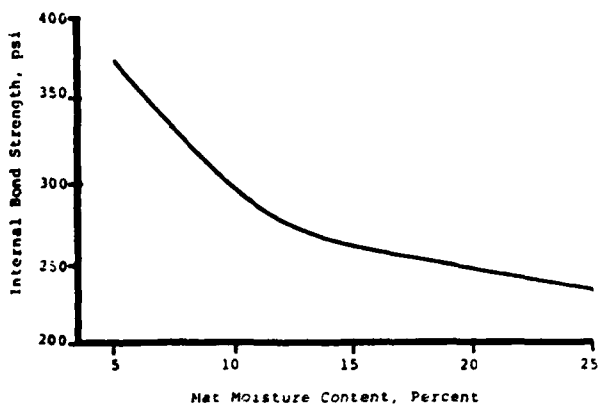


Figure 2.--Internal bond strength vs. mat moisture content.

To answer that question, samples were milled at 0.025 in. intervals to plot a density profile through the boards (Table II). As was expected (7), the 42 pcf board containing 5% moisture had a maximum density

Table II.--Density gradient vs. mat moisture content 3/8 inch board, 42 pcf overall density

% Moisture, total	Density, pcf face	Density, pcf core
5	44.0	40.3
9	45.2	37.2
12	46.2	36.2
16	46.8	35.6
20	49.7	34.9
25	50.5	33.1

of 44 pcf and a core density of 40 pcf. As the mat moisture content was increased, the variance between high density and low density increased to a maximum of 17 pcf at the 25% moisture level, from 50 pcf near the face to 33 pcf in the core. Therefore, the loss in IB properties is attributed to the lowering of core density, and any loss in bonding efficiency is minimal. The anomaly in MOR and MOE is a function of particle geometry and furnish.

Instrumental data on the reaction of polymeric isocyanates with wood has been difficult to accumulate under press conditions. One problem with analysis is the small quantity of binder (1.5% to 5%) used in relationship to the mass of wood. If a higher binder level were used it would not duplicate the press situation and, with excess isocyanate, the presence of other products such as polyisocyanurate, polycarbodiimide, allophanate, etc., are possible.

Work has been done on the use of infrared with wood (4-6) but a problem with analyzing this data is the close proximity, in the 1500 to 1800 cm^{-1} region, of polyurethanes, polyureas, and many wood components.

In order to identify the bonding of polymeric isocyanates and wood, through I.R., we felt the spectra of wood had to be withdrawn or negated and only the spectra of any changes shown.

Our initial efforts in this area, using a Nicolet 7000 Fourier transform infrared with an ATR cell, were positive. A waferboard was prepared using 5% Isobind[®]100 as the binder under our standard waferboard conditions of a 400°F press temperature, 5% mat moisture content, with a one minute closing time. After pressing, the board was trimmed and thin sections of the core were removed for FTIR scans. A control board was also prepared.

Once the IRs had been run, recorded and stored, the control spectrum was subtracted from the sample spectrum using transmission subtraction techniques of the Fourier transform and the region from 1485 cm^{-1} to 1800 cm^{-1} were expanded, Figure 3. As shown,

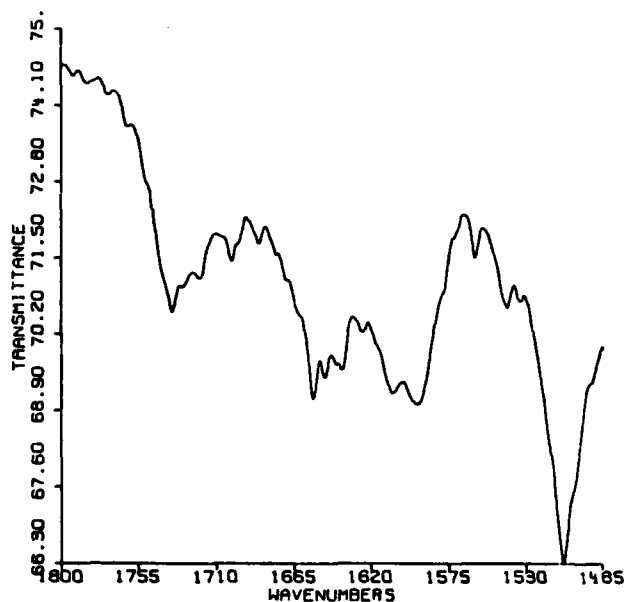


Figure 3.—FTIR, bound core minus unbound core.

the spectrum shows numerous peaks that would be expected through the aromaticity of the polymeric isocyanate plus peaks that would be expected from both polyurethane and polyurea present in the sample.

To definitely label these peaks as lignin polyurethane, cellulose polyurethane, etc., at this time, would be premature.

We are continuing our work in this area and will report our findings when concluded.

We have presented, through operating parameters and instrumental analysis, data to further substantiate the reaction of a polymeric isocyanate with wood.

Isobind[®]100 bound products are subject to system variables as is any other current binder, but it will process at the speed of a U-F binder yet yield properties equivalent or superior to a P-F binder. Under press conditions, Isobind[®]100 will reach its final properties after 40 seconds at a $\geq 100^\circ\text{C}$ core temperature, although it must be understood that large boards, high moisture content, etc., will require a press time adequate to relieve internal pressures.

The influence of mat moisture on the stoichiometry of the reaction is minimal although a significant density gradient at high moisture levels reduces internal bond properties. The use of instrumental analysis as a tool to investigate the products formed with normal levels of Isobind[®]100 in a pressed board is opening a new avenue of analysis, one that is being more deeply explored by the Upjohn Company.

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AD P 002429

ISOCYANATE ADHESIVES AS BINDERS FOR COMPOSITION BOARD¹

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ABSTRACT

Comparison of urea- and phenol-formaldehyde adhesives with various isocyanates and isocyanate-polyols as binders for composition board indicates that the latter are more costly but generally result in improved board properties, as well as increased efficiency of processing.

Manufacturers of wood composition boards continue to search for supplements or replacements for presently used adhesives of urea- and phenol-formaldehyde. Because of environmental and health concerns, these manufacturers are seeking to reduce the amount of free formaldehyde emitted from their products, which are made by consolidating mats of resin-coated particles under heat and pressure. Such reduction can be accomplished by altering resin chemistry or by adopting resin components or new adhesives such as isocyanates that do not emit formaldehyde.

Adhesives presently used by board manufacturers include urea-, phenol-, and melamine-formaldehyde (UF, PF, and MF), and polymeric isocyanate (PMDI). These adhesives are used in the following types of composition boards:

<u>Board type</u>	<u>Adhesive</u>	<u>Board use</u>
Particleboard	UF, PF	Furniture stock, underlayment, mobile home decking.
Medium-density fiberboard	UF, PF, MF/UF, PF/MF/UF	Furniture stock, siding
Structural composite board	PF, PMDI	Sheathing, underlayment, siding, concrete forms
Waferboard	PF (Powdered)	Sheathing, siding, underlayment, decking

Before adopting a new adhesive, manufacturers must consider its ease of formulation and application, its effect on board physical properties, its effect on the environment and human health, and its relative costs. The objective of this study is to compare the use of isocyanates with that of UF and PF as binders for composition board on the basis of these factors. The types of isocyanates to be considered include monomeric (MDI), polymeric (PMDI), emulsifiable polymeric (EMDI), and a urethane adhesive of polymeric isocyanate-polyol (PMDI-polyol), all of which are diphenylmethane diisocyanates.

ADVANTAGES AND DISADVANTAGES

There are a number of advantages in using isocyanate adhesives:

- * High adhesive and cohesive strength--isocyanates will chemically bond to themselves and wood in addition to a number of other materials, whereas UF and PF form weaker mechanical bonds with wood.
- * Flexibility in formulation--isocyanates can be made emulsifiable to mix with UF, PF, or a number of other water-based adhesives, and they can be formulated with almost any member of the diverse family of alcohols to make urethanes, thus providing a wide range of adhesive properties and, consequently, end uses.
- * Ability to be water-based--unlike UF and PF resins, isocyanates can be liquids at 100 percent resin, or they can be made as oil-in-water emulsions.

¹Paper presented at the Symposium on Wood Adhesives, Madison, Wisconsin, September 23-25, 1980.

- * Versatility of cure temperature and rate--isocyanates can be cured at room temperatures with catalyst or at elevated temperatures; catalysts such as amines can be used to accelerate the cure rate.
- * Excellent structural properties--these properties are due to the bonding characteristics of isocyanates and their ability to be formulated into different polymers with the potential to crosslink and become a network.
- * Ability to bond with furnish having high moisture content--isocyanates react readily with hydroxyl groups in water and wood during bonding, thus tying up water molecules and eliminating the tendency of boards having high moisture contents to blow during hot pressing. Isocyanate can form suitable bonds with wood furnish at moisture contents up to 25 percent before strength begins to diminish, resulting in potential savings in drying cost.
- * No formaldehyde emissions--no toxic fumes have been detected from isocyanate curing under normal pressing conditions or from cured isocyanate-bonded boards.

However, there are also disadvantages that must be considered when using isocyanate adhesives:

- * High reactivity--the feature that makes isocyanates so desirable as bonding agents can also cause manufacturing problems and potential health risks. Isocyanates can bond to metals (i.e., caul plates and presses) and can have a shorter pot life than UF or PF. They can also react with moisture on the skin or with moisture in the lungs if inhaled as atomized isocyanate or isocyanate-coated wood dust. The greatest potential hazard would occur during the period from resin application to hot pressing. Therefore, proper precautions are necessary when handling uncured isocyanates; adequate ventilation must be provided, and skin must be promptly cleansed after contact with them.
- * High cost--in comparison with UF and PF, isocyanates are expensive. In order to determine overall costs, however, other factors should be examined: the ability of isocyanates to reduce pressing times, to bond with smaller amounts of resin, and to reduce drying time of furnish. Comparative resin costs are as follows:

<u>Adhesive type</u>	<u>\$/lb of solids</u>
UF	.13
PF	.30
PF (powdered)	.60
MDI	1.25
PMDI	.85
EMDI	.93

- * Lack of tack--some manufacturing processes incorporating UF are designed to take advantage of its tack; therefore, a tackless PMDI would present difficulties. PF, however, does not have tack. Thus, switching from PF to a PMDI would not present problems as far as tack is concerned.
- * Need for special storage--PMDI must be stored with a blanket of dry air over it and at room temperature or slightly higher.

COMPARISON OF MDI AND PMDI

From the standpoint of cost and ease of use, PMDI is a better binder for composition board than is nearly pure MDI. Particleboard formulated with 5 percent resin by weight and a density of 42 lb/ft³ had a higher internal bond strength (IB) and modulus of rupture (MOR) when bonded with PMDI than with MDI (fig. 1). These boards had curing times of about 3 minutes at 350°F. Faster cures could be achieved by using a catalyst; however, pot life would accordingly decrease.

COMPARISON OF PMDI, EMDI, PF, AND UF

A similar analysis can be made by comparing particleboards of identical densities but bonded with PMDI, EMDI, PF, or UF. Boards bonded with isocyanate adhesives were dramatically higher in IB and MOR than were those bonded with either UF or PF (fig. 2 top, middle). However, when the specimens were boiled for 2 hours and tested wet for MOR, the values for those bonded with isocyanates were not appreciably higher than those for boards bonded with PF (fig. 2, bottom). This loss in durability after boiling could be a limiting factor if we want to reduce the amount of isocyanate resin in order to offset its higher cost. Currently, the durability of an adhesive is measured by how well it retains its initial dry strength when wet, not by its absolute strength. Because isocyanates react with hydroxyl groups in wood, they adsorb less water; consequently, linear expansion and thickness swelling are less than for PF or UF (Wilson 1980).

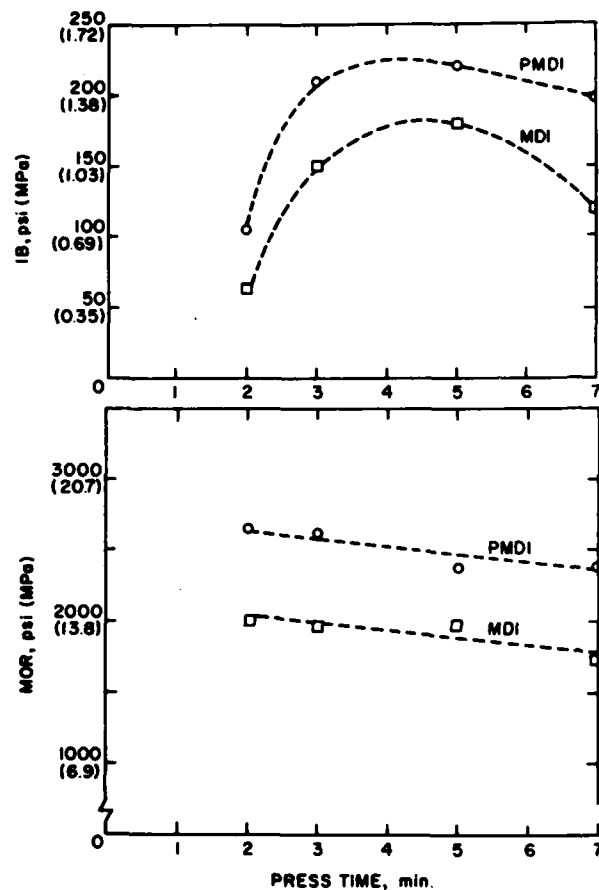
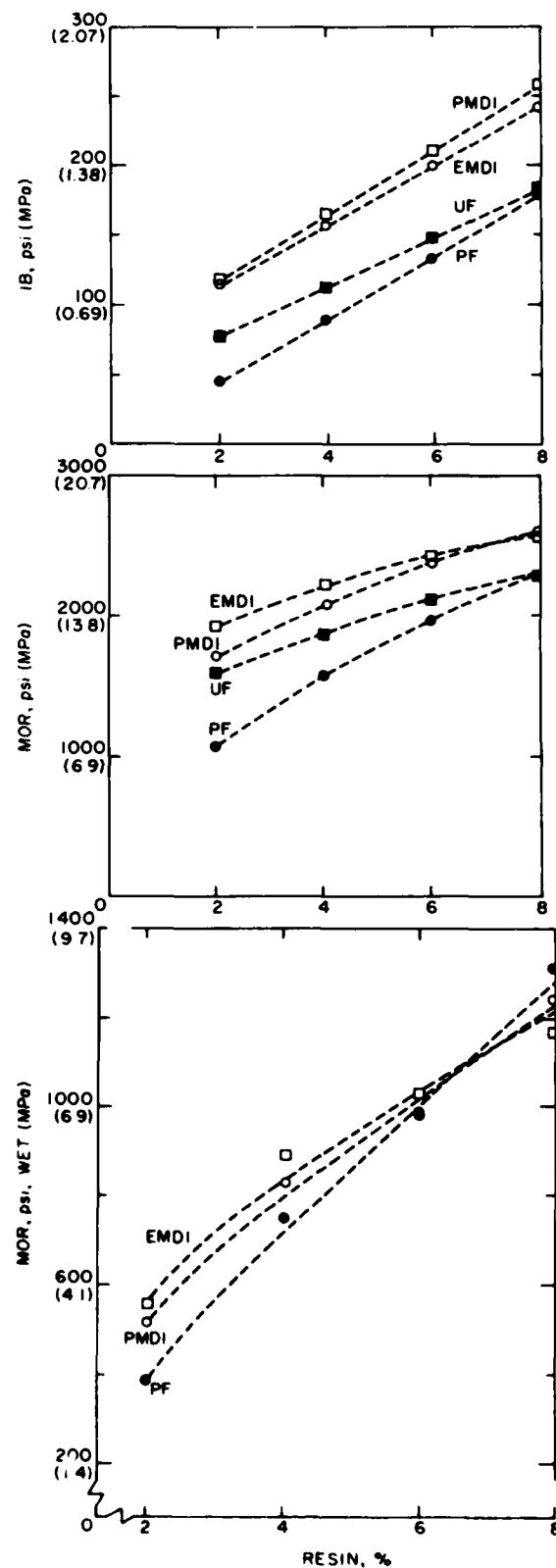


Figure 1.--(Top) Internal bond strength (IB) and (bottom) modulus of rupture (MOR) of particleboard bonded with 5 percent PMDI and MDI adhesives.

Properties of boards bonded with PMDI and EMDI were equivalent. It is noteworthy, however, that the EMDI was applied as essentially a 100 percent solid with a small amount of emulsifying agent. If it had been applied as an emulsion in water at about 50 percent solids, board properties might have improved because of better resin distribution.

Figure 2.--Effect of type and percentage of resin on (top) internal bond strength (IB), on (middle) modulus of rupture (MOR), and on (bottom) MOR of boiled specimens of particleboard. (UF not boil-tested.) From Wilson (1980).



USE OF PMDI-POLYOLS

There are several advantages to using polyols with isocyanates. Polyols of various molecular weights or functionalities can be selected, thereby providing adhesives with a wide range of properties. Furthermore, polyols can be selected that are cheaper than isocyanates and that can possibly improve the performance of the board. For example, Milota (1981) found that when particleboard with a density of 40 lb/ft³ was bonded with PMDI-polyol (5 percent by weight) containing varying amounts of polyethylene glycol with a molecular weight of 1000 (PEG 1000), maximum IB occurred when between 20 and 40 percent PEG 1000 was substituted for PMDI (fig. 3 top). Similar results were noted for MOR.

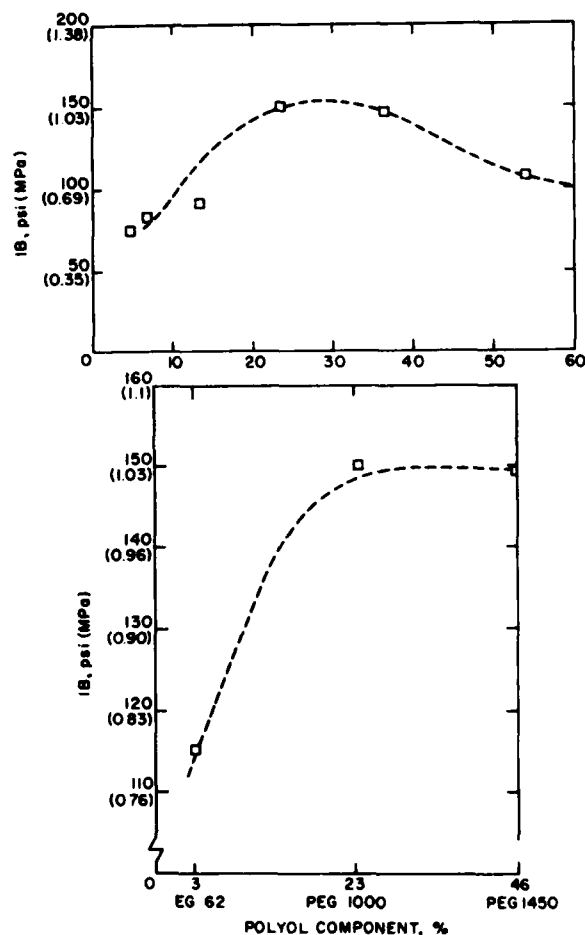


Figure 3.--(Top) internal bond strength (IB) of particleboard bonded with PMDI-polyol containing various percentages of polyethylene glycol (PEG) 1000 and (bottom) with PMDI plus ethylene glycol 62, PEG 1000, or PEG 1450. (Percentages are on a weight basis.) Adapted from Milota (1981).

Molecular weight of the polyol can also affect adhesive bonding strength. Milota (1981) also found, for example, that when particleboard was bonded with PMDI to which polyol was added at an equivalent weight ratio of 1:12, IB increased as the molecular weight of the polyol increased: from ethylene glycol (EG) 62 to PEG 1000 to PEG 1450 (fig. 3 bottom). Although IB was similar for boards bonded with PMDI plus PEG 1000 or PEG 1450, the amount of polyol was greater in the formulation with 1450, which had a lesser amount of PMDI. Similar gains in performance would also occur with EMDI-polyols.

Addition of polyols to isocyanates can also improve durability. Taki and others (1979) have reported that a wetted board bonded with PMDI plus polyvinyl alcohol regains much of its original strength after it is redried.

SUMMARY

Isocyanate adhesives have many advantages over presently used adhesives of UF and PF as binders for composition board. Their high bonding strength, ability to cure at room or elevated temperatures, ability to bond wood at high moisture contents, ease of formulation, and freedom from emission of formaldehyde all contribute to their potential as useful adhesives. However, the fact that they are highly reactive can be a disadvantage when considering production practices and environmental concerns. This reactivity necessitates certain handling precautions prior to curing. Their high cost can be offset by the need to use less resin, faster cure times, reduced drying of furnish, and by the capability of making higher priced products. Wet strength of boards bonded with isocyanates is not much higher than for those bonded with PF adhesives. With some types of isocyanates, however, much of the original bonding strength is regained once the board is redried.

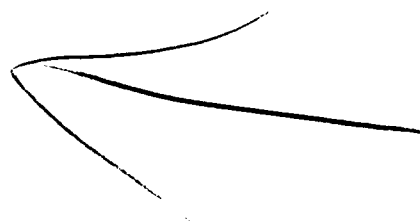
PMDI and EMDI are the resins usually considered for use in formulating composition board. However, PMDI-polyol or EMDI-polyol offer greater potential advantages in improved bonding strength, wet strength, and durability, and in lower costs. Thus, isocyanate adhesives have potential as binders for selected products when specific types of performance are required that cannot be met by either UF or PF or when increased manufacturing efficiencies offset the higher adhesive costs.

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AD P 002430

EPI - A NEW STRUCTURAL ADHESIVE¹

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ABSTRACT

Ashland Chemical Company is marketing a new family of structural adhesives under the trademark Megabond[®]. These adhesives are referred to by the generic term Emulsion Polymer/Isocyanate (EPI). The EPI adhesives were evaluated under the recognized ASTM standards for structural durable adhesives. They meet or exceed the requirements of these standards which tells us that we do have a new structural adhesive. Test data are presented which prove the superior qualities of EPI adhesives in terms of strength, creep resistance, accelerated aging and working properties. These EPI adhesives have earned the name "forgiving adhesives."

INTRODUCTION

During the 1960 symposium on adhesives for the wood industry, the two areas which received the most attention were the need for continued research on durability prediction, and the need for better communication and information exchange between all parties concerned for the development and use of adhesive technology.

While much good work has been done and progress has been made along the lines of these recommendations, the adhesive manufacturer commercializing a new structural adhesive is still confronted with essentially the same questions asked 20 years ago. There is still a lack of consensus on how to prove "durability" short of long term weather exposure.

Ashland Chemical Company is marketing a new family of structural adhesives under the trademark Megabond[™]. These are referred to by the generic term Emulsion Polymer/Isocyanate (EPI) adhesives.

The EPI adhesives were evaluated under the recognized ASTM and industry standards for structural durable adhesives. They met or exceeded the requirements of these standards which tells us that we do have a new structural adhesive.

In the 1975 symposium on adhesives for the wood industry, R. F. Blomquist stated in his keynote address, "Although many new adhesive systems have been used in the wood industry. We are still using the same types of adhesives for plywood, laminated timber, furniture, and particleboard binders as before. There has been a trend to the more durable adhesives for severe service and many technical improvements have been made to meet individual plant production needs. The wood industry still needs adhesive systems that are faster curing, simpler to use, more durable and economical than those currently available. Identification of specific properties needed in adhesives for new processes and products is vital in developing the necessary new systems." He also stated, "The adhesives industry has grown extensively since 1960 and public confidence in bonded construction has increased significantly." (Blomquist 1976)

¹Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

Perhaps this lack of actual introduction of basically new structural adhesives as opposed to modifications and improvements of existing systems explains the absence of

provisions to deal with a truly new system. There was no immediate and pressing need for such provisions.

T. E. Brassell in his presentation on Adhesives for Glued-Laminated Timber stated, "The current standards for adhesives for glued-laminated timber do not limit the chemical formulations of wet-use adhesives. At the present time, no new adhesives have been made available to the laminating industry as a result of these standards. The standards contain a number of performance requirements, but some additional tests need to be developed for these adhesives such as for fire resistance, impact resistance, and durability." He also stated, "The adhesives used for laminated timbers are of the same generic types that have been proved by years of experience. These are phenol-resorcinol, resorcinol, melamine-urea and melamine. The currently used ASTM specification for wet-use adhesives will permit adhesives of other chemical formulations to be used." (Brassell 1976)

This is true only in theory because whenever we contact a new prospective user with our excellent data, this fact is acknowledged with a "yes, but" and a long list of more or less defined "other" specifications and requirements are enumerated which vary widely by individuals; among these are:

Have you tested the vibration resistance, the mold resistance, compatibility with a myriad of materials or conditions, will pests like the glue, etc.? The most frequently asked question however, is something like: What will the glue do after 10 years exterior service in Florida or Saudia Arabia?

Again, this problem had been recognized because in the chairman's wrap-up of the 1975 symposium on adhesives for products from wood, we find the following: "If we had a new adhesive at 2 cents a pound that worked well in production and produced high quality bonds with ease, no one would use it until its long-term durability were assured." (Gillespie 1976)

In response to the same need, P. Krueger proposes about 15 durability factors for evaluating structural adhesives; (Krueger 1980) this is part of his approach to determine working stresses for structural adhesives which will be presented later in this symposium. This appears to be the first comprehensive approach to include all practical parameters into a single test method to classify adhesives in our industry.

EPI ADHESIVES

Here are findings about Ashland's new Emulsion Polymer/Isocyanate Adhesives. These EPI's are the result of research directed at the development of water-based, formaldehyde-free adhesives exhibiting a high degree of durability.

While Ashland has a long history of success in adhesive technology as demonstrated by 55 patents in this field it has never been a major supplier to the wood industry. However, Ashland became a dominant binder supplier to the foundry core business over the short time span of only seven years. Our isocyanate technology revolutionized that industry by solving several basic problems in providing extremely fast setting, cold curing and environmentally desirable binders. The successful use of two-component systems in the foundry core business encouraged Ashland to acquire the related basic technology of EPI adhesives.

These new adhesives are in most cases two-component systems, consisting of a base emulsion polymer and a crosslinking agent containing a protected polymeric isocyanate. The crosslinker is mixed with the base emulsion to provide an adhesive with a working life of up to several hours. When the adhesive is applied to the wood, water migrates from the glue line and the crosslinker is free to react with components of the base emulsion, the bound water in the wood, and also with the cellulose substrate, forming a highly durable bond.

EPI adhesives cure at ambient temperatures as low as 40° F. Naturally, the use of heat will accelerate the reaction. This two-component system gives the adhesive technologist an enormous flexibility to formulate for a myriad of conditions encountered by the adhesive in the marketplace.

The tested Ashland Megabond™ formulation meets all the conditions of ASTM D-2559-76, "Standard Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions," the generally recognized standard for structural durable adhesives (ASTM 1979, Rice 1980). It is also meeting all the conditions of D-3110-72 "Standard Specification for Adhesives Used in Nonstructural Glued Lumber Products," the primary standard for nonstructural adhesives in the wood industry. (ASTM 1979, Rice 1980)

APPLICATION

Since 1975, EPI adhesives have been used in Japan for fabricating stressed-skin panels for prefabricated homes. Conventional PRF adhesives were replaced with EPI for greater flexibility in operating temperatures, more acceptable appearance of the glue line, ease of handling the adhesive, and faster production rates. Approximately 50,000 homes have been constructed with EPI adhesives with its performance equivalent to PRF in various Japanese environments--cold and hot weather, high humidity areas etc. EPI bonded panels have performed well in roof, floor and wall applications for single and multiple story dwellings.

In the USA, EPI adhesives have found industrial applications in the door industry. They are used for type I and fire door constructions where the adhesive requirements are high. The "forgiving" nature of the EPI has reduced reject rates caused formerly by chalking and precure; it has eliminated sizing steps on highly porous substrates such as mineral core; it allows one-step processing of nonporous substrates such as lead liners for x-ray doors.

A small scale test for fire doors exposes samples to 400° F and establishes the shear strength under this condition. Test data indicate that some EPI adhesives have an unusually high temperature resistance. Average values as high as 750 psi were measured with appropriate formulations and substrates.

EPI adhesives have been tested by an independent testing laboratory against the California test standard for mobile home adhesives (CA-25-4) along with several adhesives presently being used in manufactured home construction. The selected Megabond™ Formulation easily passed all the tests; this was not the case with several of the other adhesives. Ed Starostovic's final conclusion was that "in 25 years of research in the application of structural adhesives, never before have I felt so certain that we are about to confirm that a replacement for phenol resorcinol has been found." (Starostovic 1979)

EPI adhesives have been used at laminated beam manufacturing facilities to evaluate in-plant processing parameters and performance against daily quality control tests. Results indicate that the tested EPI adhesive is well within required limits and comparable to typical results with PRF.

The tough accelerated aging portion of the ASTM 1037 particleboard test method was used, among others, to evaluate COM-PLY lumber

bonded with EPI adhesive. Southern pine veneer was applied to the highly porous edge of thick exterior particleboard in preparation to the construction of an experimental house for HUD (U.S. Department of Housing and Urban Development). The test results are favorable, however, they have not been released for publication. (Vick 1980)

EPI adhesives also have a good affinity to substrates other than wood; presently they are used for the bonding of aluminum skins to plywood with or without use of a wash-coat on the aluminum.

TEST DATA

ASTM D2559-76

Tests were run on EPI adhesives containing WD2-A320 base emulsion with 20 parts (pph, by weight based on emulsion) of cross-linker CX-10. Tests were also run on phenol-resorcinol adhesive (PRF) for comparative purposes. In all cases, cure was carried out at room temperature (70-75°) with both Douglas-fir and Southern yellow pine being tested. The specific bonding parameters are included in Table 1. As called for in D2559-76 (and related method D3535-76) three different tests were run:

- A. Shear strength test for both strength and wood failure.
- B. Accelerated aging test which can predict the tendency to delaminate during weathering, and
- C. Deformation test to indicate any tendency of the adhesive to "creep" under sustained load.

The shear strength results are given in Table 2, while delamination and creep test results are given in Tables 3 and 4, respectively. As can be seen from the test results, EPI adhesives meet and exceed the requirements of D2559 and perform similarly to PRF adhesive. These results indicate that EPI adhesive is indeed structural giving shear strength at least 90% of the strength of the wood itself with almost no tendency to deform under sustained load conditions. Also, as required of structural adhesives in wet use conditions, EPI adhesives exhibit excellent durability as indicated by delamination test results.

The results of two evaluation runs in industrial glulam plants are shown in Tables 5 and 6. All values are above the requirements except in plant 2 where one of the beams

Table 1.--Bonding Parameters in Preparing Specimens for ASTM D2559-76

<u>Wood Species</u>	
Douglas-Fir	$S_m \geq 0.43^1$, $M = 12\%^2$
Southern Yellow Pine	$S_m \geq 0.51$, $M = 12.5\%$
<u>Emulsion Polymer/Isocyanate Adhesive</u>	
Emulsion	Megabond WD2-A320
Crosslinker	Megabond CX-10
Adhesive Mix	20 parts CX-10 per 100 parts WD2-A320 by weight uniformly blended
Spread Rate	80 lbs./MSGSL applied by hand roller
Age of Mixed Adhesive before Use	15-45 minutes @ 70-75°F
Assembly Times (70-75°F & 35-50% RH)	
Open Assembly/Closed Assembly	0 min./0 min. 0 min./60 min. 5 min./60 min.
<u>PRF Control Adhesive</u>	
Adhesive & Mix	Commercial PRF resin with 20 pph (by wt.) of hardener uniformly blended
Spread Rate	70 lbs./MSGSL (Douglas-Fir) and 80 lbs./MSGSL (Southern Pine) applied by hand roller
Age of Mixed Adhesive before Use	30-45 min. @ 70-75°F
Assembly Time	Open Assembly - 0 min.; Closed Assembly - 45 min.
<u>Pressing and Conditioning Factors</u>	
Clamping Temperature	70-75°F
Clamping Pressure Used	125 psi
Clamping Time	24 hrs.
Post Conditioning Time	≥ 6 days at 70-75°F and 65% RH

¹ Specific gravity based on oven dry weight and volume.

² Moisture Content in % based on oven dry weight.

Table 2.--ASTM D2559 Step Shear Strength Test Results

Adhesive	Assembly Times (minutes) ¹ (OAT/CAT)	Average Step Shear (psi)	Average Wood Failure (%)	Average Step Shear (psi)	Average Wood Failure (%)
		Douglas-Fir	Douglas-Fir	Southern Pine	Southern Pine
EPI	0/0	1520	89	1671	83
	0/60	1498	86	1431	82
	5/60	1324	82	1389	78
PRF	0/45	1063	77	1431	68
Minimum Required per ASTM D2559 ²		1070	75	1290	75

¹ OAT = Open Assembly Time (mins.); CAT = Closed Assembly time (mins.).
² Minimum Required Shear Strength Adjusted for Moisture Content.

Table 3.--ASTM D2559 Delamination Test Results

Adhesive	Assembly Times (minutes) (OAT/CAT)	Average Delamination (%)	
		Douglas-Fir	Southern Pine
EPI	0/0	2.2	1.6
	0/60	3.9	3.6
	5/60	4.0	3.2
PRF	0/45	1.1	1.6
Maximum Delamination Allowed per ASTM D2559		5.0	5.0

Table 4.--ASTM D2559/D3535 Creep Test Results

Adhesive	Species Bonded	Total Deformation (in.)	
		160°F	80°F, 90% RH
EPI	Douglas-Fir	.0110	.0130
	Southern Yellow Pine	.0085	.0055
PRF	Southern Yellow Pine	.0040	.0035
Maximum Deformation Allowed per D2559		.1390	0.1390

Table 5.--Laminated Timber Plant Trial Test Results

Adhesive	Assembly Times (minutes) (OAT/CAT)	Average Step Shear (psi)	Average Wood Failure (%)	Average Step Shear (psi)	Average Wood Failure (%)
		Douglas-Fir	Douglas-Fir	Southern Pine	Southern Pine
<u>Plant I</u> (clamp time 16 hrs)					
EPI	5/60	1390	86	--	--
EPI	30/30	1436	81	--	--
PRF (typical)	--	1300	--	--	--
Requirement	--	1170	70	--	--
<u>Plant II</u> (clamp time 2 hrs)					
EPI	5/15	979	79	1385	80
Requirement	--	1100	75	1100	75

Table 6.--Laminated Timber Plant Test Results

Adhesive	Assembly Times (minutes) (OAT/CAT)	Clamp Time (hrs)	Average Delamination (%)	
			Douglas-Fir	Southern Pine
<u>Plant I</u>				
EPI	5/60	16	2	--
EPI	30/30	16	1.5	--
PRF (typical)	--	16	2	2
<u>Plant II</u>				
EPI	5/15	2	0	0
EPI	5/15	2	--	--
Requirement	--	--	5	5

showed low shear values combined with high wood failure and "0" delamination. This clearly indicates low wood strength and good performance of the EPI adhesive.

ASTM D3110-72

Tests were run on EPI adhesives using Megabond™ base emulsion WD2-A320 with different levels of crosslinker CX-10. (Rice 1980). Tests were also run on crosslinking polyvinyl acetate control adhesive. Ponderosa pine was used as the substrate. ASTM D3110 wet use tests on laminate bonds were run using 10, 15, and 20 pph of crosslinker. Specific bonding parameters are in Table 7.

Test results are given in Table 8. It can be seen that the EPI adhesives met or exceeded the requirements of ASTM D3110. In almost all cases, the EPI adhesives gave superior performance compared to the crosslinking PVAc adhesives. The crosslinking

PVAc adhesives are of the type used for non-structural applications in the wood industry.

CA 25-4

The California Mobile Home Standard CA 25-4 served as the model for a comparative evaluation of the EPI versus other adhesives commonly used in the manufactured housing industry. Again, the EPI formulations surpass all the requirements by a safe margin and prove superior to most of the competitive formulations. Test results are given in Table 9.

WHI-1980-08-08

This proposed test standard for Adhesives for Use in Fire Doors by Warnock Hersey Professional Services exposes materials qualifying for 90 minute fire doors to 400°F temperatures measured by a thermocouple in the center of the glue line. The specimens

Table 7.--Material and Bonding Parameters for D3110 Specimens

<u>Wood Species Used</u>	
Ponderosa Pine	Moisture Content 9-12%
<u>Emulsion Polymer/Isocyanate Adhesive</u>	
Emulsion	Megabond WD2-A320
Crosslinker	Megabond CX-10
Adhesive Mix	Crosslinker level varied from 10 to 20 parts of WD2-A320 by weight uniformly blended
<u>Phenolic Modified Crosslinking PVAc Control Adhesive</u>	
Commercial product designated as xPVAc with 5 pph catalyst, uniformly blended was used as the control adhesive.	
<u>Spreading, Bonding and Conditioning Parameters</u>	
Spread Rate	60 lbs./MSGL applied by hand roller
Assembly Time	Open Assembly Time - 0 min. Closed Assembly Time - 5-20 min.
Clamp Temperature	70-75°F
Clamp Pressure	125 psi
Clamp Time	24 hours
Post Clamp Conditioning Time (70-75°F and 65%)	≥ 6 days

Table 8.--ASTM D 3110 (Wet Use) Test Results on Ponderosa Pine

Adhesive	Crosslinker (or Catalyst) Level (pph)	Dry (10.2) ¹		Boil (10.2) ¹		Vacuum Pressure (10.2.1.2)	
		(psi)	(%) WF	(psi)	(%) WF	(psi)	(%) WF
EPI	10	1424	87	697	65	756	60
	15	1311	82	634	73	706	70
	20	1364	85	640	82	690	75
xPVAc	5 ²	1561	73	543	74	605	9
Minimum Requirement per D 3110		678	60	565	50	565	50

¹ Test Description Paragraph No. from D3110-72.
² Catalyst Addition Level Recommended by Supplier.

Table 9.--California Mobile Home Standard CA25-4 Test Results¹

Adhesive	Dry Shear ASTM D-905		Hot Shear 15 hr @ 150°F		Shear at 90°/85% RH	3 Cycl. Soak/O. dry		Mold Resistance		Creep Res.		
	(psi)	(% WF)	(psi)	(% WF)		(psi)	(psi)	(psi)	(psi)	Control	Inoculated	Hot
					DF/ply							
EPI ¹	3082	55	2819	67	2011	568	446	3149	3291	Pass	Pass	
EPI ²	2994	63	1777	58	2379	758	438	2833	2822	Pass	Pass	
Casein	2752	43	2623	38	2592	529	444	1192	0	Pass	Pass	
PRF	2352	24	2411	33	2348	792	537	2830	2963	Pass	Pass	
PVA	2269	18	2186	16	2259	641	413	999	943	Pass	Pass	
PVA	2528	56	2500	26	2814	732	564	3371	3398	Pass	Pass	
Required	2800	--	1000	--	1000	375	375	90% of Control		<.003"	<.001"	

Samples prepared and tested per CA25-4 Procedure. Press Cure 24 hrs. at room temperature followed by conditioning 17 days at room temperature and 50% RH.

¹ Megabond Emulsion WD2-A220 plus 5 pph CX-10.
² Megabond Emulsion WD2-A220 plus 20 pph CX-10.

are tested hot in shear in a manner similar to ASTM D906-76.

Table 10 gives test results of fire door stile materials bonded with EPI adhesive, the average value of 763 psi for one of these combinations attests to the excellent heat resistance of EPI adhesives.

Time/Temperature Study

To characterize some of the working properties of EPI adhesives we are presenting tests run with EPI adhesive to determine press time required at various cure temperatures.

Megabond™ emulsion WD2-A320 with 15 pph

Table 10.--Test Results of 90 Minute Fire Doors Bonded with EPI Adhesives

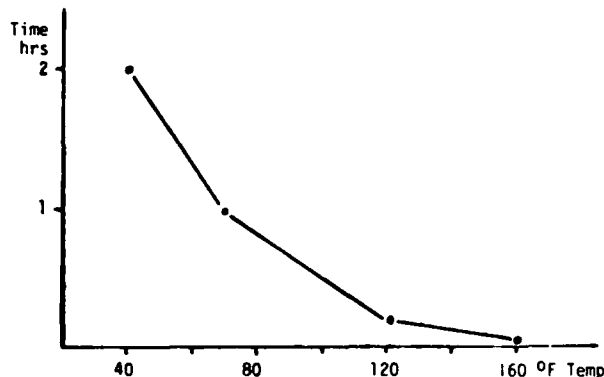
Adhesive	Test Specimen	400°F Shear Strength (psi)
EPI ¹	FR laminated hardboard ⁴	540
	Composite FR stile	532
EPI ²	FR laminated hardboard	512
	Composite FR stile	520
EPI ³	FR laminated hardboard	763
	Composite FR stile	572
Minimum required:		500

- ¹ Megabond Emulsion WD2-A320 plus 5 pph CX-10.
- ² Megabond Emulsion WD2-A320 plus 10 pph CX-10.
- ³ Megabond Emulsion WD2-A320 plus 15 pph CX-10.
- ⁴ FR - Fire Retardant.

Tests conducted per Warnock-Hersey Test Program.

crosslinker CX-10 was used. Testing was done according to ASTM D905 (strength properties of adhesive bonds in shear by compression loading). Douglas-fir plywood (1/2 inch, 5 ply, A-D sanded) was used as the substrate with a moisture content of 8-10%. The spread rate was 50 lb/MSF with combined assembly time of 10 minutes.

Test results are given in Figure 1. It can be seen that EPI adhesives can be used at temperatures ranging from 40°F to 160°F. Superior performance of the same adhesive over such a wide temperature range is remarkable. The press times are considerably shorter than these commonly used with PRF adhesives.



Press time is measured from the time the glueline reaches the specified temperature. Specimens were aged 16 hours before testing.

Spread Rate/Temperature Study

In order to optimize plant conditions over the wide range of operating conditions determined in the time/temperature study, shear tests were run to determine required spread rate as the ambient air temperature varies from 40°F to 120°F. Ponderosa pine was used as the substrate (moisture content 8-10%). EPI adhesive used was WD2-A320 emulsion plus 15 pph CX-10 crosslinker. Spread rate was varied from 40 to 80 lb/MSGL. Test results are given in Figure 2. It can be seen that EPI adhesive can be used efficiently at ambient temperatures from 40 to 120°F by simply adjusting the spread rate.

Temperature (°F)	Press Time (min)	Shear Strength (psi)	(%WF)
160	0.5	713	89
120	5.0	556	91
70	60	566	65
40	120	606	85

Figure 1.--Press time vs. temperature, Megabond WD2-A320 with 15 pph CX-10.

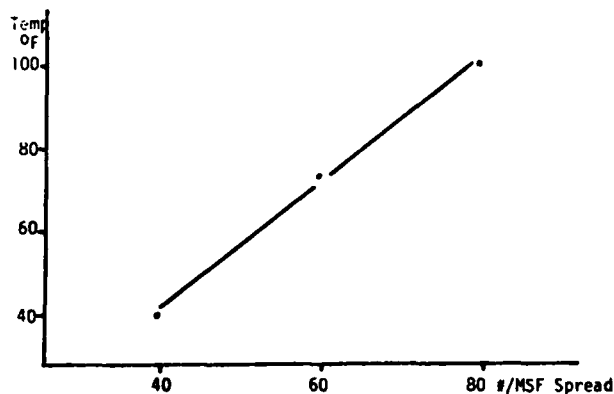


Figure 2.--Spread rate vs. assembly temperature, Megabond WD2-A320 with 10 pph CX-30.

Temperature (°F)	Spread Rate (lb/MSF)	Dry Shear (psi) (%)WF	Boil (psi) (%)WF
40	40	1194 40	728 40
75	60	761 40	546 35
100	80	478 67	756 53

Figure 2.--Spread rate vs. assembly temperature, Megabond WD2-A320 with 10 pph CX-30.

If a constant rate of spread is required, Figure 3 shows the maximum recommended assembly times for higher ambient temperatures. At 120°F closed assembly times up to 10 minutes gave good strength values. Because of these most flexible characteristics the EPI adhesives are rightfully termed "forgiving adhesives."

Conclusions

Since adhesives of the EPI type meet the conditions of ASTM D2559, D3110, CA 25-14, fire door qualification, and laminated timber quality control tests, this indicates that we indeed do have a new structural adhesive equivalent to phenol resorcinol and cross-linking polyvinyl acetate adhesives in their respective applications.

EPI adhesives give the user the added advantages of shorter press times, no chalking temperature, low temperature curing, no formaldehyde emission, better resistance to high temperatures and accelerated aging tests than the xPVA adhesives, environmental attractiveness, ability to determine performance by adjusting hardener level and more tolerance to variations in process conditions such as temperature or moisture content.

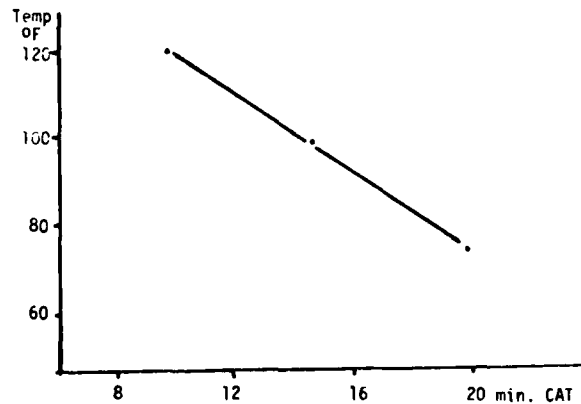


Figure 3.--Assembly time vs. temperature, Megabond WD2-A320 with 10 pph CX-30.

Temperature (°F)	Maximum CAT (min.)	Dry Shear (psi) (%)WF	Boil (psi) (%)WF
40	20	1121 33	730 25
75	20	831 73	523 50
100	15	897 78	667 45
120	10	1064 70	589 23

Figure 3.--Assembly time vs. temperature, Megabond WD2-A320 with 10 pph CX-30.

Still, in our commercialization efforts to the structural wood industry, we are confronted with the practical side of those prophetic words about the new two cent adhesive that worked well and produced high quality bonds and still nobody will use it until its long-term durability is proven.

The research community for 15 years has recognized and talked about the need for a test to assure long-term durability. Still, there is no generally accepted method for correlating accelerated test data with actual exterior exposures, thus assuring long-term durability. Although a method such as the automatic boil test (ASTM D3434) does a good job in indicating long-term durability for glued wood specimens, it does not assure actual exterior exposure performance. (Caster, Kulenkamp 1976) We are working with the industry organization for structural assemblies, AITC, and have proposed a test program to prove structural and exterior qualities of new adhesive systems. They have responded well and will work with the adhesives committee of ASTM, SCATA, universities and others.

Hopefully, we can merge the many different opinions on what measures "durability"

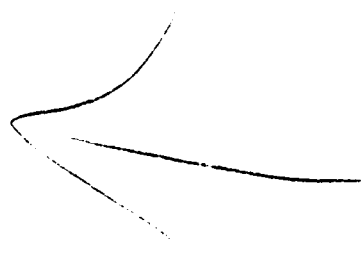
and "structural" properties into a generally acceptable set of rules, which will allow the introduction of new promising adhesives in a more efficient way than is now possible.

Summary

Ashland Chemical Company has a new family of durable and structural adhesives for the wood industry. We have evaluated our Megabond™ adhesive formulations by the recognized ASTM standards. We have met or exceeded these standards. In spite of this, industry is reluctant to use EPI adhesives in structural application because we do not have a long term performance history. Still, EPI adhesives are used commercially in Japan, Europe and America on an increasing scale based on this superior performance. To allow a more rapid transfer of the fruits of successful new adhesive research, a generally acceptable test method is needed classifying adhesives as to degree of durability and structural qualities. This would allow the fast introduction of such an adhesive with confidence and a minimum of risk to the user.

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AD P 002431

PROPERTIES OF ELASTOMER-BASED CONSTRUCTION ADHESIVE

AT SERVICE TEMPERATURES IN WOOD BUILDINGS¹

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ABSTRACT

Strength, elastic properties, load duration and creep were measured following exposure to temperatures and stresses expected during service life. Temperature-stress exposure reduced strength properties. High testing temperature reduced strength and low temperature raised strength. Shear elastic modulus was quite stable in the range 10 to 160°F (-12 to 71°C) but increased markedly at lower temperatures. Long time loading caused a larger strength reduction for the adhesive than we expect to observe for wood. This load duration effect was larger at elevated temperature. Adhesive creep was similar to wood creep but greater at 70°F (21°C), increasing more at 160°F (71°C).

INTRODUCTION

Conventional synthetic resin structural adhesives have shear stiffness properties much higher than wood. In designing bonded wood structures, it has been possible to ignore the elastic properties of these adhesives because of this high stiffness and the very thin bond lines. Elastomer-based construction adhesives form relatively thick bond lines with low shear moduli. Their shear-slip properties must be considered in design work.

The shear strength of conventional adhesives exceeds wood shear strength and is not highly taxed by the design loads applied to bonded wood systems. The load duration and creep properties of those adhesives have not been critical. Elastomer-based adhesives, being lower in strength, are stressed to a higher percent of their ultimate shear strength and it has been necessary to examine load duration properties and creep.

This research examines the effect of temperature in service on the properties of a

particular elastomer-based construction adhesive. We chose this adhesive because it seemed to have generally desirable structural properties and good potential, in our independent research. We sought and obtained the financial support of the 3M Company, manufacturer of 3M5230 Scotch Grip Wood Adhesive.

Design methods that consider adhesive elastic properties have been published (2,4,5,6,7,9,13). Shear strength, shear modulus, creep, and recovery information at 70°F have been investigated and results published (3,8,14). One unexplored question has been the effect of temperature and periods of stress in service upon adhesive behavior.

In this study, wood-adhesive bonds were exposed to a history of temperature and stress, then tested to determine the shear strength, shear modulus, and tension strength at -10°F, 70°F, and 160°F. The load duration and creep behavior were studied at 70°F and 160°F.

EXPERIMENTAL PROCEDURE

Adhesives perform structurally by resisting shearing loads. The ultimate shear strength and the shear load-slip properties are needed for design work. The tensile strength perpendicular to the bond line is

¹Paper presented at the Wood Adhesives--Research, Application and Needs Symposium, Madison, Wisconsin, Sept. 23-25, 1980.

also of interest, although to a lesser degree than the shear properties. Usually shear parallel and tension perpendicular to the bond line occur simultaneously. This study was planned to measure these three properties.

We are interested in these properties for bond lines which have a history of service, as well as for those which are made in the laboratory and tested without any particular record of service history.

Obtaining test material with a real known history of service in wood buildings at this time for this adhesive was not possible. Based on information found in the building materials literature (10,11,15), the following exposure schedule was devised to simulate the more extreme stress and temperature periods which might be encountered in real service.

Temperature, °F	Relative Humidity %	Applied Stress psi	Duration Hours
-10	80+	20	150
0	80+	35	450
70	65	10	100
120	15	10	450
160	5	10	200

The hours at each condition are continuous. In real service this would occur intermittently, and these would be the cumulative time at or near the condition. Also, in real service there would be periods of slowly, as well as rapidly, changing temperature and stress. So, there are some legitimate differences between real and simulated exposure. Effects are believed to be cumulative.

The stresses applied during the exposure are values which would occur in such structural members as stress-skin panels, I- or box-beams, panel-on-frame systems and possibly gussets, designed for shear stress of about 35 or 40 psi at maximum load. Such maximum stress is likely to occur in the winter in northern regions. At temperatures above freezing, stresses will seldom be large except for very short time periods.

Shear Strength and Shear Modulus

Shear strength and shear modulus can be measured from the same specimen by recording the load-slip response as well as the ultimate load. A modified Douglas-fir shear block specimen, ASTM D143 (1) shown in figure 1, was used. The adhesive bond was made with the wood at 12% moisture content (MC) using spacer shims to control the thickness (0.03 in.). Shear blocks were cured 30 days or more in a

12% equilibrium moisture content (EMC) chamber. Bond line thickness was measured after cure and used to compute shear modulus values from load-slip data.

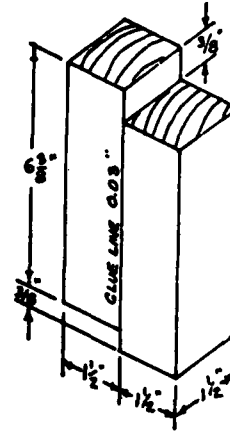


Figure 1.--Shear specimen.

Five groups of ten specimens were made, conditioned, and tested for shear strength and shear modulus, as follows:

Group	Exposure	Test Temperature
Controls	12% EMC @ 70°F	70°F
TRO	Temperature regime only, no stress applied	70°F
TS	Temperature-stress regime	160°F
TS	Temperature-stress regime	70°F
TS	Temperature-stress regime	-10°F

Specimens under exposure are shown in figure 2.

Tension Perpendicular to Grain Strength

The tension test specimens were the type recommended for wood in ASTM Standard Method D143, modified by a thin reinforcement lamination to force the failure into the bond line region. They are described in figure 3. The specimens were fabricated from shear blocks of the type described above and exposed to the same series of conditions, resulting in five similar groups for tension perpendicular to

grain testing.

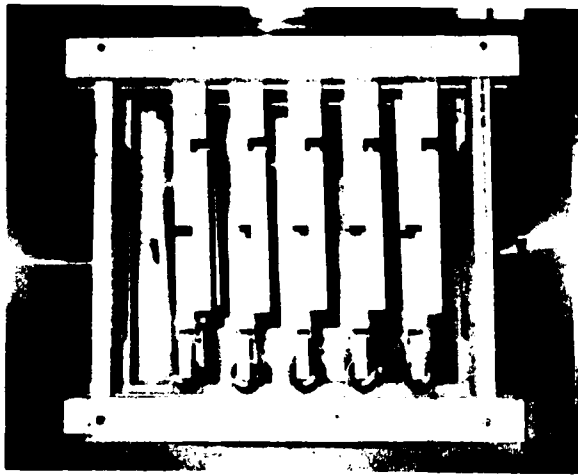


Figure 2.--Temperature-stress exposure chamber.

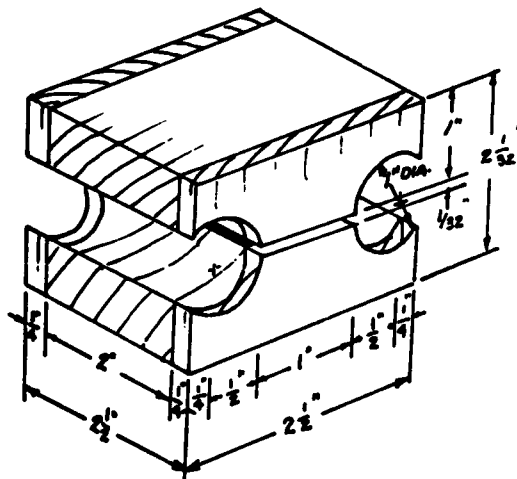


Figure 3.--Tension specimen.

Testing Shear and Tension Specimens

Prior to exposure, the specimens were subjected to ten cycles of load to 50 psi to produce the initial stress aging described in the literature (8,14). Elastomer-based adhesives change their stress-strain behavior during the early stages of loading, but after ten cycles they appear to repeatedly follow the same stress-strain curve. Whether this is characteristic of all elastomer-based adhesives or only the few we have tested is unknown.

The rate of loading for the shear specimens was 0.015 inch per minute. For the tension perpendicular to grain tests, the rate was 0.1 inch per minute. These rates produce failure in five to ten minutes, which is the short-term loading duration commonly recommended (ASTM D143) for wood products testing. We sought to place the adhesive properties evaluation in the same context as the wood properties evaluation for the adherend of the wood-adhesive systems.

The specimens were loaded to failure using a universal testing machine. The load-slip curves for the shear modulus measurements were obtained with a linearly variable differential transformer mounted on a yoke attached to the specimens to constrain the specimen to parallel movement of the two halves of the shear blocks.

Load Duration and Creep

The ability of the adhesive to maintain its strength under periods of constant loads of various intensities was measured by using specimens of the type shown in figure 4. By supporting the outer layers and loading the central layer, the bond line was subjected to shear stress. By measuring the slip between the layers, the shearing deflection was measured periodically to provide information on

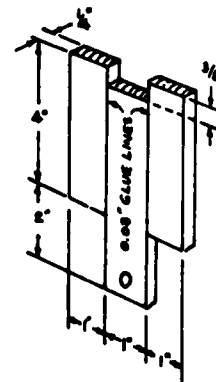


Figure 4.--Load duration specimen.

creep of the adhesive. These specimens were not subjected to temperature-stress exposures of the type previously described. They were made of 12% MC Douglas-fir wood with carefully controlled bond line thickness, averaging 0.03 inch.

Loading was performed on test fixtures shown schematically in figure 5.

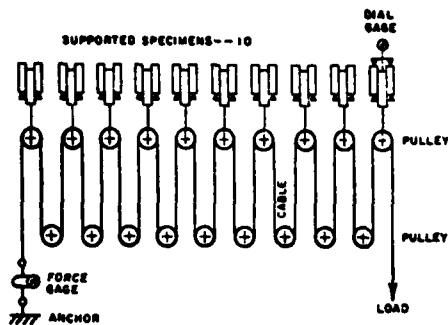


Figure 5.--Load duration test schematic.

Five groups of ten specimens were placed under loads in a controlled environment of 70°F, 12% EMC, at bond line stresses of 120, 105, 90, 75, and 25 psi.

Four groups of ten specimens were placed in a 160°F, dry atmosphere, at 90, 75, 50, and 25 psi bond line stress. Higher loads were not used because the performance at 90 psi and 160°F indicated that the life at higher stress would be too short to justify measurement.

In these load duration studies, the time-to-failure was recorded for each specimen until at least six specimens failed or until at least six months had elapsed. Deflection information provided a measure of creep. The median time-to-failure for each group was the property of interest in constructing load duration curves of the adhesive.

The degree to which specimens that survived the tests recovered their slip deformation after release of load was also noted.

RESULTS

Results from the shear and tension tests appear in table 1.

Shear Strength

At 70°F the control specimens were stronger than those exposed to the simulated service temperature and temperature-stress histories.

Strength of controls averaged 213 psi. Specimens exposed to the temperature history at no load averaged 158 psi, a strength reduction of 26 percent.

Exposure to both temperature and stress conditions resulted in 148 psi average shear strength, a further strength reduction of 5 percent.

These average values showed statistical significance by t-test at or below the 5 percent level of confidence. Variance was examined by the F-test. The variances, as indicated by the standard deviations in table 1, were not significant of a difference at the 2.5 percent level. We are thus assured that the differences are real and variability is not changed by the exposures.

The strength of the adhesive after exposure to the temperature-stress history is especially useful as a basis for allowable design values. Table 1 lists strengths at three temperatures within the service range. These are plotted in figure 6. As might be expected, high temperature reduces the shear strength and low temperature increases the value. The low temperature sample, through an error in controlling test temperature, provided some values at +10°F and some at -10°F. This resulted in an extra point on the curve and indicated an abrupt increase in strength between 70°F and 10°F and a uniform strength in the 10°F to -10°F range. Values at 160°F, 10°F, and -10°F were significantly different from those at 70°F. The values at 10 and -10°F were not different. Standard deviations, shown in parentheses, were a larger portion of the means at 160°F temperature than at the lower temperatures. All of these measures of variation are similar to those for wood properties (10 to 20 percent of the mean).

Shear failures were largely cohesive, occurring in the bond line. They were characteristically rough-textured, showing the cellular anatomy of the adhesive. Failures at the wood-adhesive interface were occasional, and seemed to take place when the adherend was dense latewood (summerwood). Shear surfaces showing a high percentage of interface failures were not related to the ultimate strength value. Equally strong bonds were associated with both types of failure surface. True "wood failure" was almost totally absent, probably because

Table 1.--Shear strength, shear modulus and tension strength results.

Exposure ¹	No.	Shear Strength psi	Shear Modulus		No.	Tension Strength psi
			0-25 psi	0-50 psi		
Controls, 70°F	10	213(20) ²	58(12)	55(11)	12	236(33)
TRO, 70°F	12	158(11)	57(9)	60(7)	12	157(39)
TS, 160°F	10	107(20)	52(7)	53(7)	10	102(27)
TS, 70°F	10	148(10)	58(5)	54(5)	10	125(13)
TS, 10°F	4	348(35)	57(15)	57(16)	--	-----
TS, -10°F	6	344(28)	174(29)	187(33)	9	229(35)

¹TRO = Temperature regime only; TS = Temperature-stress regime.

²Numbers in parentheses are standard deviations.

adhesive shear strength is considerably below wood shear strength (500 psi or more).

Shear Modulus

The shear modulus was measured for the 0-25 psi and the 0-50 psi stress ranges. Wood structural systems may perform at loads which cause shear stress throughout these ranges and if the strain behavior is not linearly elastic, we need to know. Linear elastic behavior in the working range is indicated by agreement in the two G-values we measured.

The values in table 1 are secant shear moduli and there is good agreement at the two ranges of shear stress.

Shear moduli of specimens exposed to the temperature-stress history and tested at 10, 70, and 160°F were not significantly different from one another or from the control group. The capacity of the adhesive to maintain a uniform shear modulus over this broad range of conditions (fig. 6) means that designs will not be temperature sensitive in terms of the load-deflection behavior. The higher shear modulus for the specimens exposed only to the temperature history did not prove to have any real significance, when compared to the controls, but was definitely better than those values for the temperature-stress exposure. Possibly the improvement at zero stress and elevated temperature during the exposure was due to advancing cure. The low temperature treatment did not impair the adhesive.

A distinct improvement in adhesive stiffness at -10°F was observed. Due to a temperature control problem, four of the low temperature test group specimens were tested at 10°F instead of -10°F. This provided another point on the temperature versus shear modulus curve

(fig. 6) and revealed a marked increase in shear modulus between 10 and -10°F. The increased ratio of standard deviation to mean value for the specimens at the two low temperatures is probably due to the reduced sample size in these groups, rather than any real change.

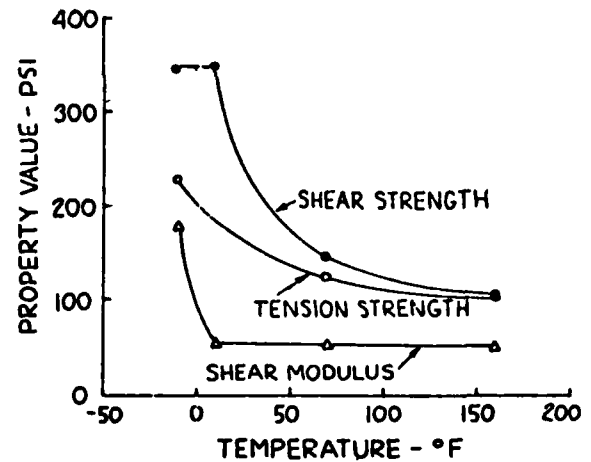


Figure 6.--Shear strength, shear modulus, and tension strength versus temperature.

Tension Strength

Table 1 summarizes the mean tension strengths. Control specimens were strongest at 236 psi. Exposure to the temperature history at zero stress produced a 33 percent loss in strength. The combined temperature-stress exposure produced an added 14 percent loss in strength for performance at 70°F.

The effect of temperature on the performance of specimens exposed to the temperature-stress history followed the pattern observed for shear strength, high temperature reducing tension strength and low temperature causing an increase (fig. 6).

Over the range of service temperature the tension strengths indicate useful allowable properties can be established.

In terms of physical appearance, wood failure was more frequent for the control specimens, which were the strongest. Lower strength specimens in the other groups usually displayed cohesive failure, but a few high wood failures occurred. Instances of wood failure were usually associated with strong tension values and weak wood in the specimens. Tension perpendicular to grain is not a strong wood property. The control group, with its high wood failure results, is a test of wood properties rather than adhesive properties. The results are useful since we are concerned with wood-adhesive system performance.

Load Duration

Some materials experience a loss of strength when placed under stress for long periods of time. At constant stress levels above 50 or 60 percent of its ultimate, as measured in short duration tests with continuously increasing load, wood for example, loses enough strength as time passes to fail. Some materials scientists refer to this as static fatigue, to differentiate it from the more common phenomenon of cyclic fatigue.

During this process the materials creep. At lower stresses the materials creep but do not lose enough of their strength to fail, at least not in any reasonable period of time. In such cases the creep reaches a maximum and appears to stabilize.

Published load duration information on wood has usually been for flexural stress in beams, which includes the effects of shearing creep since beams in flexure, unless loaded in pure bending, are also stressed in shear.

Since the adhesive of this study would be used to bond composite beams, among other uses, its load duration and creep properties are of much interest.

The load duration behavior is usually presented graphically. The time-to-failure at different levels of sustained stress is plotted on a horizontal axis, usually on a logarithmic scale, and the stress is plotted on a vertical axis. The median time-to-failure for groups of specimens subject to each stress level gives points on the load duration curve.

Figures 7 and 8 are the results obtained at 70 and 160°F in this study. Over half the specimens in a group must fail to obtain these points. In this study, which was limited to load durations of six to twelve months, there was insufficient time to obtain the median times for specimens at the low stress levels.

The results show that the adhesive loses shear strength in shorter time periods than wood at the same percentages of their ultimate

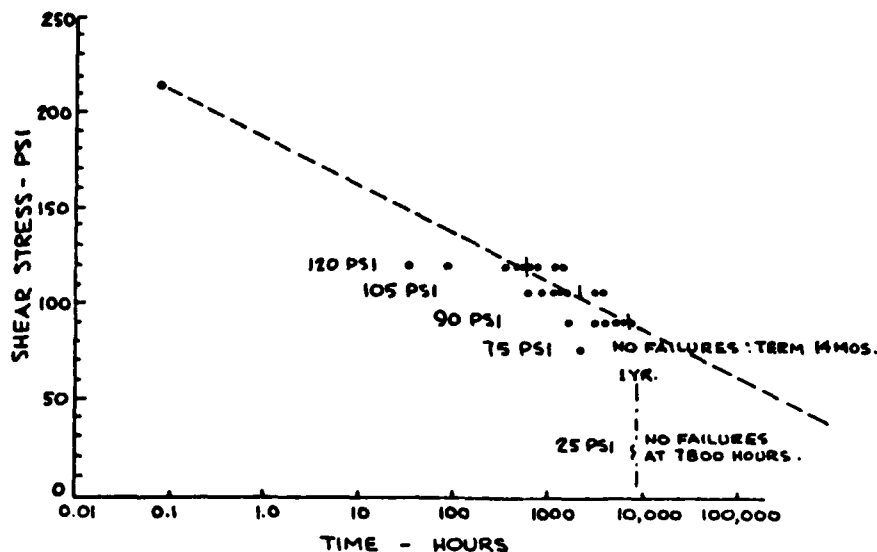


Figure 7.--Load duration at 70°F.

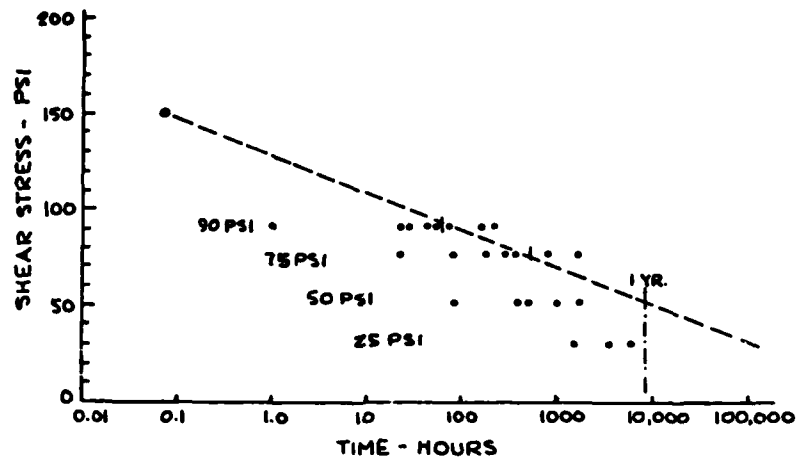


Figure 8.--Load duration at 160°F.

stress. If the stresses to cause median time to failure of ten years could be determined, load duration adjustments for adhesive strength could be established.

While these tests were too short in duration to provide this information, they do show that at stresses below 50 psi, creep seems to stabilize and the ten-year median times-to-failure would probably be reached. This is shown more clearly in the creep curves, figures 9 and 10.

Creep is a problem mainly under permanent stress. Short periods of stress at higher levels cause creep that is partially recovered when the load returns to normal. In these creep curves, deflection is the average of the specimens which have survived up to any point in time along the curves. When a specimen fails, the average deflection of the remaining specimens often decreases.

In most ordinary wood buildings the permanent load is between 15 and 33 percent of

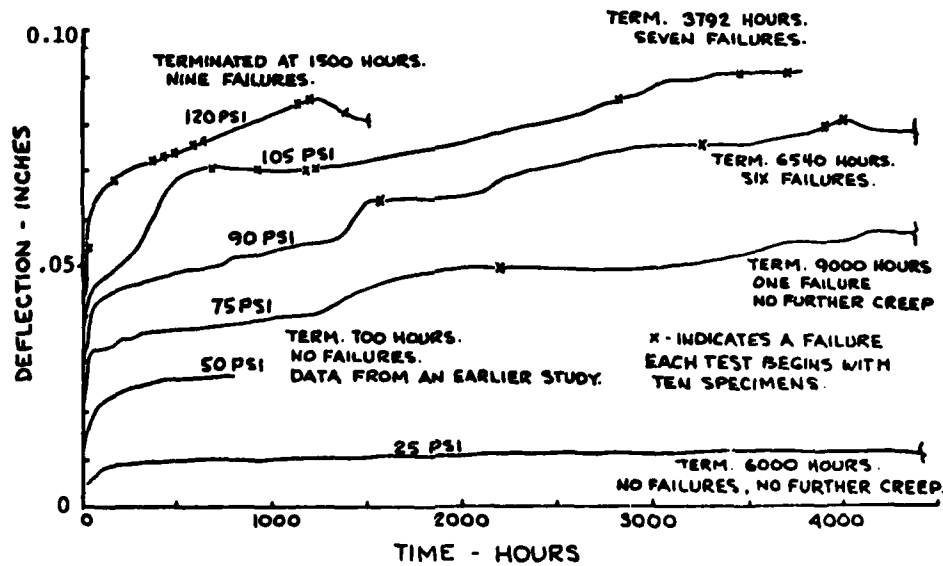


Figure 9.--Creep at 70°F.

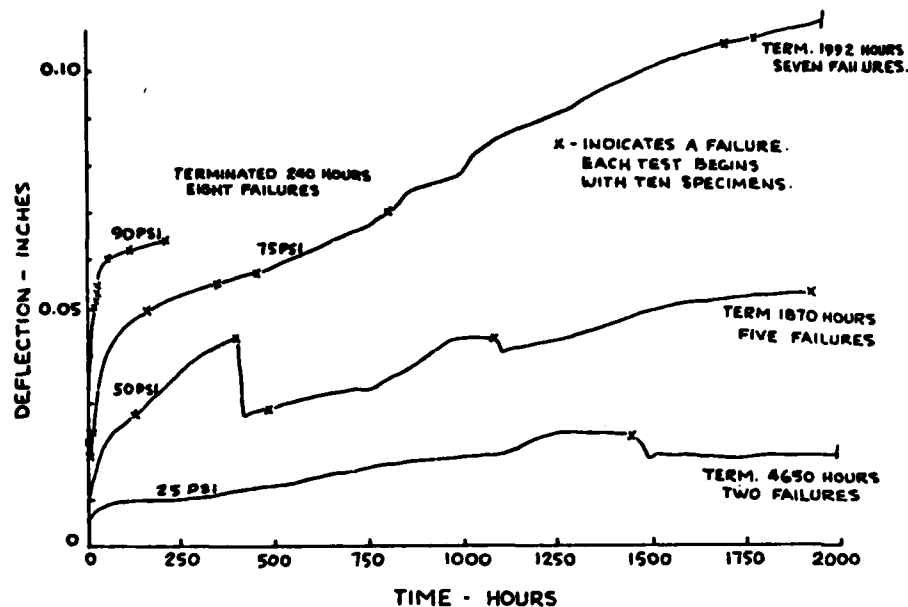


Figure 10.--Creep at 160°F.

the total load for which the building is designed. Therefore, if a structure is designed for an allowable adhesive shear stress of 50 psi, the permanent shear stress will be 7.5 to 13.3 psi. Figures 9 and 10 show that creep is stable at those low levels.

The effect of elevated temperatures was to reduce the time-to-failure at any stress level, or to reduce the stress level for any given time-to-failure. Creep, at these permanent stress levels, was found to be 100 percent of initial elastic deflection for the 70°F condition and 200 percent for the 160°F condition. These values are comparable to those customarily accepted for wood, of 50 to 100 percent. Creep data on wood at 160°F is not found in the literature.

CONCLUSIONS

The shear strength for an adhesive bond of 0.03-inch thickness, following a temperature-stress history of the type used in this research, is described by the equation:

$$\sigma_v = 330 - 66T^{0.24}$$

Where: σ_v = shear strength, psi

T = temperature, °F

The temperature-stress history reduced the shear strength at 70°F by 31 percent,

compared to controls kept at 70°F and 65% relative humidity.

Exposure of the adhesive bond to the temperature regime, at zero stress caused a 26 percent reduction in shear strength compared to controls.

The difference between the effect of temperature regime only and temperature-stress regime is significant at the 5 percent probability level.

The tension strength perpendicular to the adhesive bond displays a similar relationship to temperature for bonds exposed to the temperature-stress regime.

$$\sigma_t = 205 - 22.4T^{0.3}$$

Where: σ_t = tension strength perpendicular to bond, psi

T = temperature, °F

The temperature-stress history reduced the tension strength by 48 percent compared to controls kept at 70°F and 65% relative humidity. The temperature regime at zero stress caused only a 31 percent reduction in strength. These differences were significant at the 5 percent probability level, or less.

The shear modulus is uniform in the shear stress range 0 to 50 psi. The shear stress

versus shear strain curve is therefore linear in this range, which simplifies its design use.

This study showed that the shear modulus was not significantly affected by a temperature or temperature-stress history of the type imposed over a range from 160°F down to the region of about 10°F. Below this temperature the shear modulus increases very greatly, tripling in value at -10°F. There is no evidence that the temperature-stress experience is harmful to shear modulus.

The time-dependent nature of 3M5230 adhesive resembles that of wood in flexure more closely than that of wood in shear. The shear strength of wood is not much affected by time under load, according to the information available to us in the literature (12). Although 3M5230 behaves somewhat like wood in flexure, the reduction in strength with time under load is larger for the adhesive. Furthermore, the effect is larger yet at the elevated temperature. This is interesting because there is little information about the effect of temperature on the load duration properties of wood.

Creep of 3M5230 adhesive is similar to wood creep but larger. At shear stress levels for permanent loading, creep at 70°F is about twice that for wood in flexure, and four times as great at 160°F. Despite these larger creep effects, the characteristic is manageable, since the adhesive is such a small element in the combined wood and glue creep effect in most structures.

The conclusion about recovery can be stated very simply. Recovery occurs. It is in the region of 40 to 80 percent. It depends on the prior history of loading, the stress level and the temperature, and probably should be investigated further if the need for the information appears to be important.

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AD P 002432

STRUCTURAL BONDING OF CCA-TREATED WOOD FOUNDATIONS¹

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chromated copper arsenate

ABSTRACT

These experiments indicate that CCA-treated lumber and plywood can be structurally bonded into foundations with a gap-filling phenol-resorcinol adhesive, providing the wood surfaces are brushed with a dilute aqueous solution of sodium hydroxide before applying the adhesive. Foundation walls constructed by these bonding techniques withstand extremely high racking loads, eliminate costly corrosion-resistant fasteners, and permit more efficient structural use of wood.

INTRODUCTION

Wood foundations, constructed of preservative-treated plywood and lumber and engineered to withstand foundation loads, are finding greater acceptance among builders and homeowners. Since the first foundations were constructed in 1969, approximately 40,000 units have been built in the U.S. and Canada. Wood foundations are now approved by the Federal Housing Administration, Veteran's Administration, Farmer's Home Administration, and major building codes.

Wood foundations must be constructed with corrosion-resistant fasteners. Approved fasteners are stainless steel nails and staples, silicon bronze, copper, and hot-dipped zinc-coated nails. Stainless steel fasteners are the most durable, but they are very expensive --at least six times the cost of galvanized nails. Stainless steel nails greatly increase foundation wall costs when required nailing schedules are followed, particularly when walls must withstand high racking loads. A structural adhesive offers an alternative means of fastening walls which can eliminate costly nails and

nailing. A structural adhesive can also impart much greater strength and stiffness to walls than nails, thereby enabling foundations to resist high racking loads from soil backfill and wind. Finally, the composite action of adhesive-bonded plywood and lumber makes it possible for fewer pieces of lumber to effectively share greater loads, thereby reducing the costs of lumber.

Earlier research (Vick 1973a, 1973b, Zornig & Vick 1974) demonstrated that an effective gap-filling structural adhesive could be made from phenol-resorcinol resin and various thickening agents. These adhesives exceeded the strength of untreated exterior grade southern pine plywood. The surfaces did not require planing to ensure adequate bonding. However, wood treated with chromated copper arsenate (CCA) preservative could not be bonded satisfactorily. Several resorcinol and phenol-resorcinol formulations were tested on unplanned surfaces, but none produced bonds equal to the integrity of CCA-treated plywood.

The literature indicated that CCA preservatives inhibited resorcinolic-type adhesives from normal bond development. Poor bondability has been related to hydrogen ion concentration of CCA treating solutions (Thompson 1961). Even weakly acidic natural woods have been shown to affect bondability (Freeman 1959). Surface aging factors, including surface contaminants, are known to inhibit wetting and penetration of these adhesives (Herczeg 1965). Planing these surfaces improves bondability. Hexavalent chromium which is present in the preservative

¹Paper presented at 1980 Symposium on "Wood Adhesives--Research, Applications, and Needs," sponsored by the U.S. Forest Products Laboratory and Washington State University, at the University of Wisconsin, Madison, Wis., Sept. 23-25, 1980. Paper also presented at the 34th Annual Meeting of the Forest Products Res. Society, Boston, Mass., July 7, 1980.

imparts water repellancy to wood surfaces. Its presence may inhibit water-loss from the adhesive thereby interfering with the rate and amount of resin cross-linking (Moult 1977).

These experiences indicated that a chemical surface treatment might be a solution to bonding CCA-treated wood with a phenol-resorcinol construction adhesive. The potential benefits from structural bonding of treated-wood foundations led to the following three experiments. The purpose of the first two was to find an effective chemical surface treatment for the wood. The third experiment was designed to demonstrate the effectiveness of the treatment, and the gap-filling adhesive, as they contributed to the racking strength of shear walls.

MATERIALS

Adhesive

The adhesive used in Experiments I and II was a mixture of a commercial phenol-resorcinol-formaldehyde resin, paraformaldehyde hardener, and attapulgite clay as thickening agent. By mixing 100 parts (weight basis) resin, 10 parts paraformaldehyde and 13 parts attapulgite, the requisite gap-filling and slump characteristics were achieved. The adhesive mixture's apparent viscosity at a very low rate of shear was approximately 500,000 cP. Resistance to sagging was indicated by extruding adhesive beads 1/4 to 1/2 inch in diameter and 6 inches long on vertical wood surfaces. No sagging was observed after 10 minutes.

ASTM Specification D 2559 (ASTM 1977) was used to test the structural capabilities of this adhesive on untreated southern pine lumber (two laminates). In these tests, bondlines averaged 0.030 inch in thickness after curing. Average dry shear strength was 1,301 lbs/in² with wood failure of 80 percent. Delamination of bondlines was 2.3 percent after three cycles of soaking and drying. When subjected to the static loading test, joints did not creep after 1 week exposure to either 90 percent relative humidity, or 160° F. These tests indicated the adhesive in thick bondlines would be only marginally acceptable for use in exterior structural laminates; however, in plywood-to-lumber joints, the adhesive exceeded the structural capability of exterior softwood plywood.

In Experiment III, the adhesive formulation was changed to reduce brittleness of the film, and to improve resistance to spatter when nailing. The mixture by weight was 100 parts phenol-resorcinol resin, 10 parts paraformaldehyde, 10 parts walnut shell flour, and 3 parts of a special grade of chrysotile asbestos. The viscosity,

slump characteristics, working properties, and structural capabilities were approximately the same as for the attapulgite-filled adhesive.

Lumber and Plywood

Lumber and plywood were pressure-treated with CCA-preservative to a minimum retention of 0.60 lbs/ft³, according to specifications of the American Wood Preservers Bureau Standard AWPB-FDN. Type C preservative was used in Experiments I, II, and III, except in the second series of racking tests in Experiment III where Type A was used.

The lumber was No. 1 southern pine in nominal 2- x 6-inch sizes. The plywood was southern pine, 4-ply, Structural I, C-C grade. The 1/2-inch thickness was used in all experiments, except 5/8 inch was used to construct racking walls in the first series of tests in Experiment III.

EXPERIMENT I--CHEMICAL SURFACE TREATMENTS

Design

Preliminary experiments were conducted to search for chemicals that could improve the wettability and penetrability of unplanned CCA-treated wood surfaces. Chemicals were selected (a) to cause a drop of water to spontaneously wet the wood's surface, (b) to raise the alkalinity of the surface to or above the pH of the adhesive, (c) to dissolve contaminants present on the wood's surface, and (d) to increase the amount of resin penetration. Of the many chemicals screened, aqueous solutions of sodium hydroxide, sodium carbonate, and tri-sodium phosphate seemed to improve resin wetting and penetration. To determine which of these chemicals could best improve bondability, they were prepared in two concentrations, and applied by brush to plywood and lumber surfaces. Since the amount of drying time between applying the chemical and the adhesive might affect strength, drying time was included as a third factor. Experimental factors in this experiment were:

<u>Experimental factors</u>	<u>Levels of factor</u>
Chemicals	(1) Sodium hydroxide (2) Sodium carbonate (3) Tri-sodium phosphate
Chemical concentrations	(1) 1 Normal (2) 3 Normal
Drying times	(1) 1 Hour (2) 24 Hours

This experiment was designed as a completely randomized model with 3 x 2 x 2 factorial arrangement of the above levels of factors.

Procedures

A typical test joint was prepared by bonding a 1-1/2-inch-wide by 20-inch-long piece of CCA-treated plywood to a similar size piece of lumber with each of the chemical treatments applied to both surfaces. After the chemical had dried for a prescribed time, the adhesive was extruded in a bead on one surface, then the pieces of wood were nailed together. The bondlines were intended to be thick and of variable thickness to simulate actual application conditions. They averaged 0.030 inch in thickness when cured.

The effects of the 12 combinations of treatments were evaluated for shear strength and wood failure, in both dry and water-soaked conditions. These properties were determined from block-shear specimens that were cut from the above described joints. All specimens were tested according to PFS specifications (PFS 1971).

Results and Conclusions

The significance of experimental factors and their interactions, as determined by analysis of variance, are shown in table 1. Chemical was a very strong main effect which influenced all four strength properties. Further comparisons between chemicals (not shown here), clearly indicated sodium hydroxide contributed more to improving all strength properties than either sodium carbonate or tri-sodium phosphate.

Chemical concentration was a significant factor only in determining dry shear strength,

where the 3N concentration contributed more to strength than the 1N.

Drying time was not a significant main effect, although it was a component in two interactions, i.e., Conc x Time and Chem x Conc x Time. It was very close to being a significant influence on wet shear strength. The effect of drying time was not clear in this experiment.

In view of these results, and the importance of some interactions, more thorough testing of sodium hydroxide in both concentrations with intermediate drying times was considered essential.

EXPERIMENT II--SODIUM HYDROXIDE SURFACE TREATMENTS

Design

This experiment was designed to test sodium hydroxide in two concentrations, with an expanded number of drying times, based on an increased number of experimental units. Factors included in this experiment were:

Experimental factors	Levels of factor
Chemical concentrations	(1) 1 Normal (40 g/l NaOH) (2) 3 Normal (120 g/l NaOH)
Drying times	(1) 0 Hours (2) 1 Hour (3) 4 Hours (4) 8 Hours (5) 24 Hours
Control	(1) No surface treatment

Table 1.--Significance level of experimental factors and their interactions on shear strength and wood failure of dry and wet specimens, Experiment I

Source of variation	Degrees of freedom	Dry specimens		Wet specimens	
		Shear strength	Wood failure	Shear strength	Wood failure
Chemical Concentration	2	.032 ¹	.0008 ¹	.0001 ¹	.0007 ¹
ChemxConc	1	.004 ¹	.866	.141	.821
Drying time	2	.005 ¹	.258	.156	.757
ChemxTime	1	.160	.637	.053	.118
ConcxTime	2	.081 ¹	.404	.036 ¹	.222
ChemxConcxTime	1	.003 ¹	.672	.093	.719
Replication (ChemxConcxTime)	2	.019 ¹	.381	.166	.904
Determination (ChemxConcxTimexRep)	144	.0001	.0001	.0001	.0001
Total	312				
	467				

¹Significant at or above the 0.05 level of probability.

Treatments were completely randomized with 2 x 5 factorial arrangement of factor levels. Each treatment combination was replicated 58 times with a single determination of each physical property within a replication. Shear strength and wood failure, in both dry and water-soaked conditions, and resistance to delamination were the properties measured in each replication.

Procedures

The test joints were prepared in the same manner described in Experiment I. These joints were also nailed together. The resultant cured bondlines varied greatly in thickness, and averaged 0.030 inch as in the previous experiments.

Block-shear specimens (dry and water soaked) were cut and tested according to the PFS specifications (PFS 1971). Delamination specimens were subjected to cyclic vacuum-pressure soaking and drying, as described in Test 109 of AITC 201-73 (AITC 1973). This procedure is a severe test of an adhesive's ability to resist delamination under accelerated exterior weathering conditions in laminated wood products.

Results and Conclusions

The analysis of variance (table 2) indicated concentration was a highly significant effect for all five strength properties. The 3N concentration was significantly better than 1N in dry shear strength, dry wood failure, wet wood failure, and resistance to delamination. The exception was wet shear strength which was limited more by the wet rolling-shear strength of the plywood than by the strength of the adhesive bond under test. All the above effects can be observed from the average test values reported in table 3. Note the differences in

property values between control specimens (without any chemical treatments) and the surface treated specimens. These differences are shown as statistical comparisons with the controls in table 3.

Drying time had statistically significant effects on some properties at the 0.05 level of probability (table 2). These properties were dry shear strength, wet wood failure, and resistance to delamination. On close study of table 3, it is apparent how drying time became a significant factor. At 0 hours drying time, test values for dry shear strength, wet wood failure and delamination clearly differed from the remaining values at the other drying times.

When results from the 3N sodium hydroxide treatment (table 3) were compared with the PFS quality control specification (PFS 1971), the requirements were easily satisfied. The minimum dry shear strength is 650 lbs/in², and minimum wet wood failure is 85 percent. Although delamination didn't quite meet the 5 percent requirement of ASTM Specification D 2559 (ASTM 1977), the highest value of 10.6 percent at 0 hours drying time was not severe. When delamination occurred, it invariably developed at the plywood-adhesive interface where wide bands of summerwood covered most or all of the bonding face of the plywood. Wood failure within the summerwood bands is virtually impossible, so stress was relieved at the summerwood-adhesive interface as delamination.

These experiments indicate that the bondability of unplanned, CCA-treated wood can be improved dramatically by surface brushing the wood with aqueous 3N (120 grams/liter) sodium hydroxide before bonding. The alkali may be spread anywhere from a few minutes to 24 hours before applying adhesive, although best strength and durability seem to develop after 1 hour of drying.

Table 2.--Significance of main effects and their interaction on shear strength and wood failure of dry and wet specimens and on resistance to delamination, Experiment II

Source of variation	Degrees of freedom	Dry specimens		Wet specimens		Delamination
		Shear strength	Wood failure	Shear strength	Wood failure	
Concentration	1	.007 ¹	.0001 ¹	.015 ¹	.0002 ¹	.0001 ¹
Drying time	4	.025 ¹	.163	.552	.020 ¹	.027 ¹
ConcxTime	4	.921	.078	.233	.056	.008 ¹
Error	570					
Total	579					

¹Significant at or above the 0.05 level of probability.

Table 3.--Effects of sodium hydroxide surface treatment on shear strength and wood failure of dry and wet specimens and resistance to delamination of specimens made from unplaned, CCA-treated wood, Experiment II

Chemical concentration	Drying time of surface	Dry specimens		Wet specimens		Delamination
		Shear strength	Wood failure	Shear strength	Wood failure	
Normality	Hr	Lb/in ²	Percent	Lb/in ²	-----Percent-----	
1N (NaOH)	0	779 ¹ / ₁	78 ¹ / ₁	451 ₁	82 ¹ / ₁	15.2 ₁
	1	822 ¹ / ₁	91 ¹ / ₁	474 ¹ / ₁	85 ¹ / ₁	10.3 ¹ / ₁
	4	802 ¹ / ₁	81 ¹ / ₁	470 ¹ / ₁	80 ¹ / ₁	9.5 ¹ / ₁
	8	792 ¹ / ₁	84 ¹ / ₁	464	84 ¹ / ₁	12.3
3N (NaOH)	24	801 ¹ / ₁	78 ¹ / ₁	445	94 ¹ / ₁	22.7
	0	788 ¹ / ₁	90 ¹ / ₁	443	85 ¹ / ₁	10.6 ₁
	1	859 ¹ / ₁	89 ¹ / ₁	447	93 ¹ / ₁	6.9 ¹ / ₁
	4	834 ¹ / ₁	90 ¹ / ₁	437	93 ¹ / ₁	8.0 ¹ / ₁
Control	8	829 ¹ / ₁	91 ¹ / ₁	452	97 ¹ / ₁	8.4 ¹ / ₁
	24	834 ¹ / ₁	91 ¹ / ₁	453	92 ¹ / ₁	5.8 ¹ / ₁
Control	-	689	58	436	64	18.8

¹Noted shear strength, wood failure, and delamination means are significantly different from the respective control means. Means are considered significantly different at or above the 0.05 level of probability.

Note. Sodium hydroxide attacks hemicellulose and lignin of wood, as well as resorcinolic adhesives. Two experiments were designed to determine if the 3N sodium hydroxide brush treatment could have any long-term deteriorating effects on the integrity of these bonds. The first test measured deterioration by continuous boiling of specimens for periods up to 600 hours. The second was a continuous exposure of specimens to a constant high humidity of 90-95 percent over a 3-year period. Deterioration was measured by periodically comparing wet shear strength and wood failure from specimens that were prepared with and without sodium hydroxide surface treatments. Continuous boiling up to 600 hours showed that sodium hydroxide did not cause any unusual rate of deterioration of adhesive bonds, either on untreated or CCA-treated wood. The high-humidity exposure test has not been completed, but after 1 year no unusual deterioration has occurred.

EXPERIMENT III--ADHESIVE-BONDED SHEAR WALLS

Design

This experiment was designed primarily to show the effectiveness of the gap-filling adhesive, and the alkali surface treatment, as a means of significantly increasing the racking resistance of foundation walls, without depending on mechanical fasteners for strength. Several methods of adhesive-bonding walls were tested, and for comparative purposes, walls constructed

by conventional nailing were included. The racking resistance of 27 wall panels were measured in terms of load deformation and ultimate load. These measurements were made while panels were in a dry condition, and also in a wet condition after being water soaked, dried, and soaked again. Three panels were tested for each method of construction, and each moisture condition, i.e., dry or water soaked. These methods of construction, as well as conditions at test, are listed in table 4 alongside respective test results.

Note in table 4 that two series of wall panels were prepared. The first series was fabricated with 5/8-inch-thick plywood and Type C preservative. In the second series, Type A preservative and 1/2-inch-thick plywood were used. The latter preservative was expected to interfere more with bond development because the wood was heavily coated with salt deposits. Also, the 1/2-inch plywood was not expected to be as stiff, and its thinner face veneer might contribute to lower rolling-shear strength.

Procedures

Racking tests were conducted on standard 8- by 8-foot wall panels similar to that specified in ASTM Method E-72 (ASTM 1974), with two exceptions. The studs were 2 by 6 inches in cross-section, and only one stud was used at each side of a panel. Studs were spaced 16 inches on-center. In tests of nailed construction,

2- by 4-inch lumber blocking was nailed between studs at mid-height to support adjacent edges of two plywood sheets. In tests of adhesive-bonded walls, no lumber blocking was nailed between studs.

As is common practice in constructing all-weather wood foundations, plywood sheathing was attached to framing with the face-grain of the plywood perpendicular to the length of the studs (horizontal application). The sheathing was attached by several techniques. For adhesive-bonded panels, plywood was nailed to studs with 8d double-headed nails, 16 inches on-center. The nails were pulled before the panel was tested. In tests where adhesive was not used, sheathing was fastened with 8d hot-dipped zinc-coated nails. These nails were spaced 6 inches on-center along all plywood edges and 12 inches on-center in the field.

The following routine was used when bonding wall sections. After a wall frame was assembled, 120 grams/liter of aqueous solution of sodium hydroxide was brushed on the edges of the lumber frame and plywood where the adhesive would be applied. The surfaces dried about 1 hour at room conditions. After drying, adhesive was extruded in a 3/8-inch-diameter bead onto the frame with quart-size caulking gun. Plywood panels were immediately placed on the frame, then nailed. When both panels were nailed in place, two parallel beads of adhesive were extruded along the two edges of a 4-inch-wide by 8-foot-long splice plate. This plate was nailed over the joint between the two plywood sheets to effectively make the two function as one sheet. When finished, the wall panels were stacked to cure for 7 days before testing.

Racking loads were applied to wall panels with apparatus similar to that described in ASTM Method E-72 (ASTM 1974). However, the panels were positioned horizontal to the floor. Loading apparatus, reactions and hold-downs were fixed to the floor. Roller bearings were placed beneath the loading beam and hold-downs to permit free movement of panels in the plane of load application. Four dial gauges, mounted on floor stands, were used to measure displacement and deformation of the panels under load. Loading was applied uniformly at 400 pounds per minute, while deflections were measured at 200-pound intervals until failure.

Results and Conclusions

The results of racking tests on 27 wall panels are summarized in table 4. The alkali surface treatment effectively increased the racking strength of panels, as well as minimized the variability in strength. The adhesive-bonded panels where alkali was applied to

bondlines (Group 4) were twice as strong panels without alkali treatment (Group 3). Without alkali, the adhesive didn't add much more strength to panels than nailing them (compare Group 3 with 1). The alkali treatment also effectively reduced variability in strengths, as indicated by the 2,300-pound range in Group 4, and 8,490-pound range in Group 3. Note that panels with effective adhesive bonding (Group 4) were twice as strong as the nailed panels (Group 1). They were also much stiffer.

The cyclic soak-dry-soak treatment, specifically designed for this experiment, was by far more rigorous than the cyclic water-spray treatment required in ASTM Method E-72 (ASTM 1974). A more severe test of resistance to water and dimensional change was needed because it is conceivable that foundation walls could be thoroughly soaked from ground water, and at the same time be required to withstand high racking loads from the pressure of water-soaked, fluid soils combined with wind. This cyclic test consisted of 3 weeks of underwater soaking, with an intermediate week of drying, and final loading to failure while panels were soaked (about 70 percent moisture content). The test caused an average 19 percent decrease in strength, and a 41 percent increase in deflection (compare Group 5 with 4). A similar 20 percent drop in strength occurred among the nailed panels and average deflection increased 39 percent (compare Group 2 with 1).

One of the more surprising and favorable findings in this experiment was that the perimeter-bonded panels (Group 6) actually averaged 3,230 pounds higher in ultimate load than panels that were bonded overall (Group 4). Average deflection was about the same. Bonding the panels around their perimeters required only one-half as much adhesive as when bonded overall.

Nine more wall panels were constructed to further investigate the perimeter-bonding technique, this time using thinner plywood and Type A preservative. The racking strength of Group 7 panels averaged 3,850 pounds less than the strength of Group 6 perimeter-bonded panels. The strength difference cannot be clearly tied to the influence of either one of these factors. However, less wood failure was observed in bondlines of the Group 7 panels where plywood and lumber surfaces were coated with salts.

The purpose of testing the Group 8 panels was to see if leaving nails in the perimeters would add to ultimate strength. Apparently the nails can be of some benefit (compare Group 8 with 7). The nails appeared to momentarily stop peeling action of the plywood at each nail near panel corners as the failure process began.

Table 4.--Performance of gap-filling adhesive with alkali brush treatments in wall panels under racking loads, Experiment III

Group	Fastening method	Area fastened	Condition at test	Average ultimate load	Ultimate load high-low	Average deflection at failure
<u>No</u>			<u>Dry-soaked</u>	-----Lb-----		<u>In</u>
<u>5/8-INCH PLYWOOD - TYPE C PRESERVATIVE</u>						
1	Nailed	6 & 12 In OC	Dry	8,750	9,350-8,000	1.814
2	Nailed	6 & 12 In OC	Soaked	7,020	7,650-5,950	2.497
3	Adhesive-No Alkali	Overall	Dry	9,140	13,050-4,860	0.240
4	Adhesive-Alkali	Overall	Dry	18,770	20,000-17,700	0.537
5	Adhesive-Alkali	Overall	Soaked	15,220	15,450-14,950	0.762
6	Adhesive-Alkali	Perimeter	Dry	22,000	24,650-20,550	0.563
<u>1/2-INCH PLYWOOD - TYPE A PRESERVATIVE</u>						
7	Adhesive-Alkali	Perimeter	Dry	18,150	20,550-14,600 ¹	0.485
8	Adhesive-Alkali-Nailed	Perimeter	Dry	19,067	23,900-14,300 ¹	0.569
9	Adhesive-Alkali	Perimeter	Soaked	13,000	17,150-10,200	0.522

¹Ultimate loads of wall panels with loose-face veneer of plywood in bond to lumber.

Perimeter-bonded panels tested while water soaked (Group 9) lost almost 30 percent in strength from Group 7. Here again, the salt-covered surfaces seemed to interfere with bonding in two out of the three panels in Group 9. In spite of very poor bonding surfaces, the strength of these panels still was remarkably high after the severe water-soaking treatments.

This experiment indicates that a gap-filling phenol-resorcinol adhesive, when used in conjunction with alkali surface treatments, can effectively bond unplanned CCA-treated plywood and lumber into foundation shear walls capable of withstanding the highest of racking loads without reliance on mechanical fasteners for strength or stiffness.

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AD P 002433

DETERMINATION OF WORKING STRESSES FOR STRUCTURAL ADHESIVES¹

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ABSTRACT

Structural adhesive applications are as sophisticated as those for any other structural material. The engineering design data for adhesives which is available to structural engineers, generally is insufficient and this problem is addressed in this report. Application examples are described and a methodology is presented for development of sufficient design data to handle these structural bonding problems.

INTRODUCTION

Structural adhesives are finding increasingly more sophisticated uses in structural engineering applications and correspondingly, the needs for engineering design property data are more important now than at any time in the past. These needs have been defined in a general way over the last twenty years, but to date, supplier and user groups have not responded in a way that adequately serves the needs of structural engineers.

In the past few years, some significant advances have been made in the determination of engineering design data in response to the specific needs of some structural engineering projects. These application projects have had a significant influence on several interested adhesive suppliers and these suppliers have now undertaken test programs which will yield engineering design data in a systematic manner.

In this report, several real applications will be discussed. In the course of the presentation, the commonality of these problems with some traditional bonding problems will be illustrated and the required engineering design data will be defined. Finally, a systematic approach for obtaining the design data will be outlined.

¹Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

STRUCTURAL ADHESIVE APPLICATIONS

The Institute of Wood Research at Michigan Technological University has been involved for a number of years in several projects which require the design and development of composite wood structures for the electric power utility industry. Both the composite wood crossarm project and the composite wood utility pole project require interface adhesive designs that are challenging and demanding of the adhesives.

Both structures are subjected to conventional static and dynamic loads as well as thermal and hygroscopic loads which result from severe environmental exposures.

The crossarm is essentially made of a box section with four longitudinal adhesive joints. The adhesives are subjected to an in plane shear stress as a result of conductor loads and an in plane shear stress and tension normal to the adhesive plane as a result of hygroscopic loads.

The composite wood utility pole has an octagonal, hollow cross section. There are eight longitudinal adhesive joints which are subjected to flexural shear stresses as well as shear stress and tension normal to the adhesive plane from hygroscopic loads.

In each of these applications, a parameter study was undertaken utilizing a finite element analysis of the cross section. The parameters which were varied were the adhesive shear modulus, the hygroscopic loading and the adhesive thickness. Reducing the shear modulus, of course reduces the biaxial

stress intensity. The objective of such a study is to be able to select the optimum adhesive which will reduce the stresses to a reasonable level, yet provide adequate long term adhesive and cohesive strength.

Some of the more traditional structural engineering applications are adhesive bonded gusset plates, shear walls and diaphragms and tensile lap joints. In the cases of gusset plates and shear walls, the stress conditions are usually inplane shear with minimal tension normal to the bond line. In the case of the simple lap joint, the stress condition is a high intensity tension normal to the adhesive plane along with shear in the plane of the adhesive. Stress concentration factors as well as relative values of shear and tension may be obtained from data presented by Wooley and Carver. (Journal of Aircraft, Vol. 8, No. 10, October, 1971, pp. 817-820) These factors are a function of adherend and adhesive stiffness ratios, thickness ratios and lap length.

ENGINEERING DESIGN DATA

The engineering designer of these and other structural applications is concerned with two concepts, safety and durability. A safe design is a design for which there is not unreasonable risk of death or injury to the user or to the public. The durability definition can be taken from the ASTM document E632-78. (Standard Recommended Practice for Developing Short-Term Accelerated Tests for Prediction of the Service Life of Building Components and Materials) "3.9 DURABILITY-the capability of maintaining the serviceability of a product, component, assembly, or construction over a specified time. 3.16 SERVICE-ABILITY-the capability of a building product, component, assembly, or construction to perform the function(s) for which it is designed and constructed."

The engineering design data must then be sufficient for the designer to satisfactorily insure the safety and durability of the structure.

In the case of wood bonding, the engineer can take one of two possible approaches in the design of an adhesive joint. In the first case, the adhesive can be assumed to be stronger and more durable than the adherends under all load and end use conditions for a specified time of service. The designer can then feel secure in designing the adherends by a working stress (allowable stress) method as used in wood design, steel design or masonry design. In most cases, however, the designer does not have this information and

in fact the basic assumption may very well be incorrect.

In the second case, the designer may attempt to generate the necessary information and in so doing, in fact produce sufficient data for a general design methodology for the adhesive in question. The information which is required for determining the working stresses for adhesives is much like that required for any other material.

A basic strength value is required for shear and tension normal to the adhesive plane for an extended period of time and under normal aging conditions. This value should be reduced to a statistically safe lower bound to account for variability and engineering judgment. In addition, provisions should be made for short term strength degradation factors as defined in ASTM E632-78. "Any of the group of external factors that adversely affect the performance of building components and materials, including weathering, biological, stress, incompatibility and use factors".

Finally, the designer must know how the material behaves under combined stress conditions such as tension plus shear which forms the biaxial stress state in most adhesive joints. The advantage of this approach is that the adhesive may very well be weaker than the adherend and still be quite serviceable for many applications.

In the event that it is desirable to vary the stiffness of an adhesive in order to optimize a joint design from the standpoint of stress distribution or stress intensity, clearly the shear stiffness and creep behavior must be known as minimum information.

ADHESIVE WORKING STRESS EQUATIONS

A paper titled "Evaluating Adhesives for Building Construction" (U.S.D.A. Forest Service, Research Paper, FPL 172, 1972) contains a suggestion for a working stress formula for adhesives and a suggested formula for stiffness. This paper provided much of the impetus for the development of the methodology which is presented here along with the fact that design stresses are not uncommon to structural engineers. Elastic design is permitted in building codes for all structural materials which are in common use today.

Since wood is an often used adherend, the method for determining working stresses for wood were examined in depth. It was concluded that the ASTM procedures for determining working stresses for wood could form a

satisfactory basis for the adhesive working stress procedure. The specific ASTM documents which were consulted were ASTM D245-74 (Establishing Structural Grades and Related Allowable Properties for Visually Graded Lumber), ASTM D2555-78 (Establishing Clear Wood Strength Values) and ASTM D2915-74 (Evaluating Allowable Properties for Grades of Structural Lumber).

Based on the considerations in these ASTM standards and the information in FPL 172, the following equations are recommended for strength and stiffness.

Shear strength (Fv) or Tensile strength (Ft) = (5% exclusion limit for strength) x (creep rupture factor) x (aging factor) x (degradation factors) x (factor of safety)

Shear modulus (g) = (mean modulus value) x (aging factor) x (degradation factors) x (creep factor).

DETERMINATION OF WORKING STRESS VALUES

A series of demonstration tests have been run and these tests can provide working stress values for any structural adhesive. It should be noted that the same test information is required to support the conclusion that adhesives are stronger and more durable than the adherends for utilization of an exclusively adherend dependent design method.

Some of the tests are standard ASTM tests which are identified by number and some are new tests that are best suited to shear modulus measurements, combined stress evaluation and creep rupture testing.

The degradation factors are divided into three groups: environmental, load related and parasitic. The environmental factors include extreme temperature conditions, water soaking and chemical soaking conditions. The load related factors include dead load or low level stresses, fatigue and cross grain effects. The parasitic factors include: mold, micro-biological, fire, insect and rodent effects. The following tables include all of the test recommendations with anticipated results.

SUMMARY

The determination and utilization of working stresses for adhesive design is a rational approach which is familiar to structural engineers. The advantage of the method is that adhesives are regarded as unique, designable materials and they may be used to

their full potential, but need not be grossly oversized. Interestingly, much of the design information already exists, and simply needs to be cast into an engineering format for design use.

Table 1.--Summary of Basic Tests

Identif-ication	Stress Type	Exposure Conditions	Adherend Type
ASTM D 905	Shear In-Plane	23°C-50%RH	Maple
ASTM D 897-72	Tension Normal to Plane	23°C-50%RH	Maple
Modified Rail	Combined Shear & Tension		Maple
Modified Rail Load Duration	Shear In-Plane	23°C-50%RH	Maple
ASTM D 897-72	Tension Normal to Load Plane	23°C-50%RH	Maple
ASTM D905	Shear In-Plane	150°C Dry 130°C Dry 110°C Dry	Maple Maple Maple
Continuous Rate-Process Aging		100°C Dry 90°C Dry 80°C Dry	Maple Maple Maple
Identif-ication	Number of Specimens	Results	
ASTM D 905	60	5% exclusion value on failure stress. % wood failure	
ASTM D 897-72	60	5% exclusion value on failure stress. % wood failure	
Modified Rail	60 total (20 each at 3 tension stress levels)	5% exclusion value on failure criteria. % wood failure	
Modified Rail Load Duration	3 Replications at 5 or 6 load rates (18 tot.) maximum	Stress vs rate of stress graph which yields endurance limit	
ASTM D 897-72	3 Replications at 5 or 6 load rates (18 tot.) maximum	Endurance limit in tension perpendicular to the adhesive plane	
ASTM D905	15	Remaining useful stress at 30 years	
Continuous Rate-Process Aging	15	yields a strength reduction factor for aging dry	
	15		

Table 1 (continued)

Environmental Durability Factors

● Short term exposure to high temperature. This test utilizes the ASTM D 905 shear block to determine the strength reduction when tested hot at 150°F. The exposure should be of sufficient length to bring the glue line to 150°F. Ten replications are tested hot at 150°F and the results are compared to a control value for calculation of a strength reduction value.

● Short term exposure to high moisture. In the event that an adhesive is specified for dry use, but short duration soaking might occur, this factor is applicable. The general procedure of ASTM D1151-72 "Test for the Effect of Moisture and Temperature on Adhesive Bonds" should be used with the ASTM D 905 Shear Block. Conditioning is at 23°C 50%RH prior to exposure. Blocks are soaked in cold water at 23°C and tested wet at intervals of time of approximately 1 day, 5 days, 10 days, 20 days with 5 specimens each. Twenty specimens of each of the adhesives are to be tested.

● Cold Temperature Exposure. Generally the procedure of ASTM D 1151-72 and ASTM D 2557-72 should be followed. Exposure temperatures of -50°F and -25°F are used. The ASTM D 905 shear block specimens are to be used with each of the adhesives. Ten replications are tested cold at each temperature and the results are compared to a control value for calculation of a strength reduction factor.

● Chemical Reagent Exposure. The test ASTM D 896-66 (72) for resistance to chemical reagents should be used with the shear block from ASTM D 905. The reagents which are recommended are oil, gasoline and salt solution. Ten replications for each of the adhesives are used. The exposed specimens are tested wet and the strengths are compared to control values for calculation of a reduction factor.

Parasitic Durability Factors

● Fire resistance. The test procedure E 286-69 (75) Test for Surface Flammability of Building Materials is recommended to assess a fire resistance factor which is determined by comparison with the standard red oak. A 2-foot tunnel is used to evaluate each of the adhesives. The specimen consists of a cast film on a non-combustible carrier and there are three replications of each test. A supplemental test consists of a small wall section subjected to increased temperatures and a fixed dead load. The time and temperature to failure is used to classify the adhesive.

● Microbiological Attack. The test ASTM D 1174-55 (76) for the effect of bacterial contamination is used initially with the lap shear specimen from ASTM D 2339. Three organisms in the test are used with 10 replications of each at each of 5 exposures. The adhesives are tested and the strength reduction factor is either one or zero. An alternate film test used by Abbott Laboratories is acceptable.

● Mold Exposure. The test ASTM D1286-57 (72) for mold contamination is used initially with the tension shear specimen from ASTM D 2339. Three mold cultures are specified and 10 replications of each are subjected to 5 exposures. The adhesives are tested and the reduction factor is one or zero. An alternate film test used by Abbott Laboratories is acceptable.

● Insect Attack. The test ASTM D 1382-64 (76) for attack by roaches is used with dry film specimens. The adhesives are tested and the reduction factor is either one or zero.

● Rodent Attack. The test ASTM D 1383-64 (76) for rodent attack is used with dry film specimens. The adhesives are tested and the reduction factor is one or zero.

Load Related Durability Factors

● Cyclic Loading or Fatigue. Theoretically, the adhesive can be stressed any number of times below the endurance limit and therefore low frequency cyclic loading should not cause an additional strength reduction. In order to check the rate of stressing and indirectly check the endurance limit, a high frequency cyclic fatigue test should be run on each of the adhesives for 1×10^6 cycles at 500 cycles/min. The test method is ASTM D 3166/73 and the single lap specimen of ASTM D 2339-70 (76) is recommended. A strength reduction factor may result which is less than the endurance limit, however, these effects are not cumulative.

● Cross Grain Swelling and Shrinking. In order to establish a baseline value, the maple shear block of ASTM D 905 can be laminated with cross grain instead of parallel grain. Ten replications of each adhesive should be subjected to the boil-dry cycle of ASTM D 3434-75. The average shear values of the exposed specimens can be compared to control specimens for calculation of the reduction factor.

● Low Level Stress Interaction with Normal Aging. There is some experimental evidence that low level stresses will accelerate aging

effects. For this test, a spring loaded jig was devised which utilizes the single lap tension specimen of ASTM D 2339-70 (76). This specimen along with a zero-stress control can be subjected to the aging exposures of the continuous rate process. A strength reduction factor can be determined which can be superimposed on to the aging effects.

Table 2.--Summary of Shear Modulus Tests

Identification	Stress Type	Exposure	Number of Specimens
Modified Rail	Shear	23°C-50%RH	10
Modified Rail	Shear	23°C-50%RH	Variable
Modified Rail	Shear	150°F	5
Modified Rail	Shear	0° -25° -50°	5
Modified Rail	Shear	23°C-Soaked	10
Modified Rail	Shear	Rate Process Aging	75

Identification	Adherend Type	Results
Modified Rail	Maple	Mean Modulus Value
Modified Rail	Maple	Modulus vs Rate of Load
Modified Rail	Maple	Mean Modulus Value
Modified Rail	Maple	Mean Modulus Value
Modified Rail	Maple	Mean Modulus Value
Modified Rail	Maple	Modulus vs Aging

Table 3.--Screening Test Summary

Major Test Description	Required for Screening		Modifications
	Complete	Modified	
Basic Shear 5% Exclusion		Yes	Reduced no. of specimens
Basic Tension 5% Exclusion Combined Stress	No	No	
Endurance - Shear		Yes	Reduced no. of specimens. Use fast rates only.
Endurance - Tension	No	No	
Dry Aging - Shear		Yes	Reduced no. of specimens. Use higher temperatures only.
High Temperature - Shear	Yes		
Cold Temperature - Shear	Yes		
Water Soaked - Shear	Yes		
Chemical Soaked-Shear	No	No	
Fire - Tunnel	No	No	
Fire - Creep	No	No	
Microbiological	No	No	
Mold	No	No	
Insects	No	No	
Rodents	No	No	
Fatigue	No	No	
Cross Grain	No	No	
Low Level Stress	No	No	
Mean Modulus Effective Modulus	No	Yes	
High temp.- Modulus		Yes	Reduced no. of specimens
Low Temp.- Modulus	No	No	
Water Soaked - Modulus	No	No	
Aging - Modulus	No	No	



AD P 002434

ADHESIVES FOR MOBILE HOMES--

RESPONSE FROM THE PRIVATE SECTOR

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ABSTRACT

The development of ASTM Standard D-3930, [†]Standard specification for woodbased materials for construction of mobile homes,[†] represents two significant issues. First, it represents the development of a consensus standard specifying end-use requirements for adhesives in the mobile home industry. Second, it represents a response from the Private to the Public sector resulting from a mandate by the Public sector.

There are two main points to be made. The first is that this standard represents a significant new type of adhesives-related standard. This is not simply a Commodity or Performance Specification standard, but something more. This standard describes the fashion that adhesives, any adhesives, be they phenol-based or elastomer-based, must perform in an end-use that may include not just one type of wood-based product but many types. That end-use is the manufacture of mobile homes. The significance of this is that previously excluded elastomer-based adhesives are not only allowed but are assigned allowable working stress values. This genera of adhesives, while proven valuable for construction purposes in the past, has been excluded from consideration in mobile homes due to restrictive commodity standards.

The second point is a personal one. I'm a firm believer in the responsibility and right of the Private sector to govern and regulate itself. I believe that the Private sector not only should but can do a better job of this regulation. ASTM Standard D-3930 represents one example of this belief.

The title of my talk embodies the two issues I will talk to today. I'm going to talk about the development of a consensus standard specifying end-use requirements for adhesives used in mobile home industry. And I'm going to talk about the response from the Private sector, to the Public sector, that the Standard's development represented.

There are two points I want to make today. The first is that ASTM Standard D3930 represents a new type of adhesives-related standard. It's not a commodity standard that describes how a particular genera of adhesives should perform. It's not a performance specification describing how a particular product

should perform in service. It's more than both of these. ASTM D3930 is a standard that describes in general the fashion that adhesives, any adhesives, be they phenol-based or elastomer-based, must perform in an end-use that may include having them bond a wide variety of wood-based products. That end-use is the manufacture of mobile homes. The significance of this is that previously excluded elastomer-based adhesives are now not only allowed for use in a structural fashion but are assigned allowable stress values. This genera of adhesive, while proven valuable for

[†]Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

construction purposes in the past, had been excluded from use by restrictive commodity standards.

The second point is a personal one. I'm a firm believer in the responsibility and right of the Private business sector to govern itself. I believe that the Private sector not only should but can do a better job of this regulation. ASTM D3930 represents one example of this belief in action.

Before expanding on the first point, I'd like to make a couple of broad generalizations that will help set the stage. The fact that so many representatives of the wood adhesives research and industrial community are here attests to the fact that the industry is experiencing problems. Increasing shortages and much higher costs of traditional adhesives' raw materials have forced the industry to look to new sources and new technologies. One characteristic of the Standard I will describe is that it incorporates both new sources and technologies.

During this meeting we will learn about new adhesives and technologies from different raw materials. Adhesives from agricultural residues and pulp mill effluents are promising examples. We will learn more of the fact that many of the new technologies, no matter how promising, create problems that preclude their use in certain situations. The formaldehyde emissions problem from certain adhesives is an example.

One type of adhesive that is becoming more widely recognized is the elastomer-based. This genera may be put into the class of Construction or Structural adhesives. While Dr. Hoyle spoke about the properties of elastomer-based construction adhesives at the start of this session his work with this type of adhesive began many years ago. He first published some of his findings in 1976 and 1977 in the Forest Products Journal and Wood Science. Those findings have served as the basis for the development and philosophy of ASTM D3930.

With regard to the mobile home industry, the significance of his work and elastomer-based adhesives is based on the fact that while those adhesives could not develop the high stresses more rigid adhesives could, elastomer-based adhesives had other properties valuable from a mobile home construction standpoint. Let me explain.

As we all know, constructions using wood-based materials may suffer a number of maldies because wood expands and contracts with changes in temperature and relative humidity. These changes cause stress buildups in parts of the structure that must find relief in another part of the structure in order that the whole system perform satisfactorily. Not

only is all this true for mobile home structure but mobile homes suffer from another factory in one place, put on wheels and transported over bumpy roads and around corners to another place. Transportation can cause problems with rigid structural and semi-structural adhesives as they may fracture extensively if the roads are bad. Fracturing causes drastic reductions in the strength developing nature of the adhesives. With this fracturing the structure loses some of its structural integrity and will not serve as well in the long run.

Elastomer-based adhesives have proved to be useful in situations where fracturing may be a problem. Early on Dr. Hoyle showed that these adhesives are just flexible enough to allow for some shock absorbing. In addition elastomer-based adhesives may develop up to 80% of the strength of more rigid adhesives in structural and semi-structural applications such as glue-nailed wall and floor panels. Other favorable properties include the ability to lessen stress concentrations at corners in panelized systems, dampen impact loads, and reduce the construction's sensitivity to assembly pressure, mating-surface quality, temperature and moisture content.

Elastomer-based adhesives suffered in only one area: they could not pass all the restrictive requirements specified in the Commodity standards. As a result these adhesives could not be assigned allowable stress values. Because of that they were not allowed in mobile home construction. With the consensus acceptance of this standard, however, that situation has changed. Now, not only will elastomer-based adhesives be acceptable but they will have allowable stress values assigned to them. This is a major breakthrough for the mobile home industry.

Perhaps a few words about the general types of standards will make this point a bit clearer. Most of you are familiar with adhesive Commodity standards. These standards specify the manner in which adhesive products can be made. Such standards typically define the minimum qualities an adhesive should have. For example, an adhesive type may be described by its permissible reactions to extremes of temperature and relative humidity, its maximum permissible deformation, i.e., stiffness or rigidity, under a given load, its aging characteristics, etc. Elastomer-based adhesives cannot develop stresses rigid adhesives can, thus they cannot be assigned allowable stress values. Without these values engineers cannot design structures using these adhesives.

More recent Performance Specifications on the other hand, specify how products must perform in a given situation and not how the products must be made. Standards specify in-service performance criteria and test methods by which to evaluate those criteria. For example, a Performance Specification for a type of plywood might state the maximum adverse conditions under which that type of plywood would be expected to perform. A set of testing criteria would then be given by which the manufacturer could test the product. This is a more flexible approach in that it allows different products to be fabricated for different situations and it assigns them realistic performance requirements. Before ASTM D3930 there were no Performance Specifications for adhesives.

This standard resolved the shortcomings of both Commodity Standards and Performance Specifications. D3930 got around the restrictive, unrealistic characteristics of the Commodity Standards and it created the Performance Specifications and test methods needed by the mobile home industry.

As part of my explanation of why I feel that it is important that the Private sector regulate itself I would like to describe when, why and how D3930 came into being.

Before 1976 the mobile home and motor coach construction industry was regulated by state regulations. There were no requirements describing the types of adhesives that could or could not be used. In the early 70's the Department of Housing and Urban Development had purchased a number of mobile homes as a part of a disaster relief program. Either due to faulty construction techniques or the adverse conditions in which they were used, or both, some of the mobile homes did not perform as they should have. Soon after HUD promulgated the Federal Mobile Home Construction and Safety Standards designed to regulate the industry. From my point of view this was an unnecessary and unfortunate act based on an unfortunate happening.

It was pointed out shortly after, that this standard was missing the part that specified what adhesives could be used and how. This was a major shortcoming since adhesives could be used in structural and semi-structural fashions and were an important element in such engineered structures. What should be done? was the question.

In 1976, at a meeting on adhesives here at the Forest Products Lab, a number of designers, engineers, manufacturers and researchers discussed this problem. Robert Hoyle had reported on some significant findings from his research on elastomer-based adhesives. While these types of adhesives, as I have mentioned, were mandated against by the strict requirements of the Commodity

Standards, the adhesives did appear to perform well in structural and semi-structural situations. These would be the types of situations found in mobile homes.

Engineers noted that because elastomer-based adhesives were slightly pliable, it was not possible for them to develop the high stresses of rigid adhesives. Also, because elastomer-based adhesives could not be tested by existing standards there could not be developed allowable stress values with which engineers could design using them. Elastomer-based adhesives did have a number of characteristics that would make them useful in mobile home constructions.

It was decided that the Private sector would respond to this need of an adhesives standard by creating a standard. It was further decided that this standard would be a consensus standard and that it would, if possible, allow the use of elastomer-based adhesives in structural and semi-structural ways.

Specifically the goal of the effort was to develop a standard that would provide: 1) an engineering tool to mobile home design engineers; 2) allowable stress values on adhesive formulations and not simply maximum stress values; 3) sufficient tests for adhesive manufacturers to evaluate their products and such that adhesives bearing numbers related to these tests could be identified as to the environmental conditions they could be expected to perform in.

I've just made two points I consider significant and I want to reemphasize them. The first was that it was decided that the adhesive standard would conform to the real-world needs of the design engineer and manufacturer and not to requirements found only in a laboratory. All parties agreed that it was important only that the adhesives perform well in service. Tests could be designed that would be sufficiently severe to test any adhesive under the worst possible conditions likely to be encountered. Also, it was understood that other parts of a mobile home, such as gypsum board, would develop far less strength than the elastomer-based adhesives, but that all the elements working together would form a structurally sound system. These were real world users designing for real world conditions.

The second point is that ASTM D3930 is a consensus standard. The HUD standard was a Public mandate. D3930 was made possible only by a consensus of opinion from all sectors of the user community. Users included well known experts from the mobile home industry, the adhesives industry, the engineering community and a representative from HUD. By this progress the committee was assured that the final product would serve everyone equitably.

I volunteered to work on the project for two reasons. First, I believe strongly that the Private sector has the responsibility and right to govern itself. Second, as an engineer I knew how important it was that the standard would be a working and useful one.

In developing the standard the first step involved 6 drafts that circulated only within PFS Corporation here in Madison. After we felt we had a good version it was submitted to individuals outside our corporation including persons from HUD. At about that time HUD contracted with an engineer from Boeing to consult with them about the adhesive specifications. That engineer felt there should be very strict Commodity standard-like specifications for the adhesives. To the relief of the standard's committee, HUD personnel had to admit there was no data indicating such a need. It was decided that the standard should be developed along the lines already set down in the early drafts.

At that time it was decided that further standard development should be turned over to an ASTM Task Force even though this would increase the time for the standard's final approval. This would, however, assure the development of consensus among all potentially affected groups thereby assuring a more durable end product. HUD personnel were urging us all at that time to proceed as rapidly as possible.

After several more years work, 7 more drafts, and several ballots in ASTM, the standard was finally accepted by full Society ballot this past summer as ASTM Standard D3930.

In summary: In 1976 it was pointed out that the new Federally mandated standard regulating the mobile home industry in the United States lacked specifications governing the types of adhesives that would be acceptable. The private sector took it upon itself to demonstrate that it was capable of creating a consensus standard to regulate itself. Experts from all segments of the industry, including a representative from the public sector were involved. The consensus standard was developed and has been accepted.

In ending, I am happy to be able to report of some recent achievements related to ASTM D3930. Gordon Krueger has just reported on his research, sponsored by HUD, regarding the determination of working stresses in structural adhesives. This work could be very important with regard to D3930 and I trust that the results will be used by the ASTM Task Force responsible for upgrading the Standard. This is significant for me in that it shows that even though the initial effort by HUD was lacking in one area they are very interested in sponsoring the research necessary to upgrade that part of their standard.

Another event of significance to D3930 will be described by Robert Gillespie later this afternoon. His work in developing a "rate process" for measuring some aspects of durability should also prove to be an important addition.

AD P 002435

METHODOLOGY FOR DETERMINING THE
DURABILITY OF SEALANTS

By

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ABSTRACT

This paper presents the framework for a methodology for insuring the durability of construction sealants. The basic approach involves determination of an allowable design strain from the product of the ultimate strain capacity of the sealant and various empirical reduction factors reflecting expected service conditions.

INTRODUCTION

The objective of this paper is to present the basis for a rational engineering approach to the use of sealants and, by extension, to suggest a procedure for the engineered design of sealant joints. Although many questions are yet to be answered, the general framework of this approach will allow new knowledge to be incorporated as it becomes available.

There are similarities between sealants, wood and adhesives. For each there exists a bewildering variety of material choices with a wide range of properties. Sealants, like wood and adhesives, are subject to various types of degradation. And they are often taken for granted during design and construction.

Sealants differ from wood and adhesives in one very important respect. Except for some glazing applications, sealants are not relied upon to carry load. Rather, they are expected to seal out the weather in joints which may be subjected to movements from various sources. Thus it is strain capacity rather than stress resistance which determines the performance capability of a sealant.

Within reason, there is no such thing as a bad sealant. But there is frequently misapplication of a given sealant. It is just as inappropriate to make a temporary, non-

critical seal with an expensive elastomeric sealant as it is to seal a monumental high rise with an unidentified compound whose only known virtue is low price. The best sealant is the one which will minimize total cost over the useful life of the structure. The challenge lies in predicting long term performance so that an intelligent selection of sealant and joint design can be made. Panek (1976) and Skeist (1977) provide an extensive listing of sealant specifications, both domestic and foreign. In the main, these specifications establish qualitative standards which are somewhat arbitrary and do not provide the data necessary to actually design a sealed joint.

The American Society for Testing and Materials (1980) lists 35 tests for evaluating building sealants, caulks, and gaskets. In addition, there are a number of related tests dealing with water and air transmission in windows, doors, and curtain walls. Many of the sealant tests are concerned with installation characteristics and appearance and, therefore, are not directly applicable to the durability question.

Several problems become evident when the ASTM tests are considered for possible use in a comprehensive test program. First, there is little consistency in specimen configuration or conditioning in the ASTM tests. Second, most of the tests are relatively short term and appear to be aimed at providing quality

control/quality assurance data rather than design information. Finally, the tests for accelerated aging, in many cases, include a number of aging variables, making it difficult to identify relative sensitivity to the individual variables.

METHODOLOGY

The most important measure of sealant durability is strain capacity. Even in so-called non-moving joints, the sealant must withstand some movement due to thermal or moisture induced expansion and contraction. Also, sealant shrinkage and hardening with age can result in strains similar to those caused by actual joint movement. Under adverse environmental conditions, a sealant must be able to withstand movements for the life of the structure or for some acceptable period prior to replacement.

The determination of an allowable strain for a sealant joint can be treated in a manner similar to that proposed by Krueger (1980) for establishing allowable stresses in adhesives. This method, in turn, is based upon an approach that has been in use for many years in the engineering design of structures and components from wood and other materials. As applied to sealants, the method involves reducing the basic ultimate strain capacity of a sealant by appropriate factors to arrive at an allowable design strain. This allowable design strain can be expressed as:

$$e_a = \pm (5\% \text{ exclusion limit for basic strain}) \times (\text{durability factors}) \times (\text{state of strain factor}) \times (\text{geometric shape factor}) \times (\text{substrate factor}) \times (\text{safety factor}).$$

The basic strain value can be determined from short term tests on either shear or tension specimens. Fryer (1966) defines the 5 percent exclusion limit as a value expected, with a selected degree of confidence, to be exceeded by 95 percent of all future values (3). The durability factors account for the effects of exposure to water, heat, cold, chemicals, ultraviolet radiation, fatigue, and displacement set. These factors can be obtained from accelerated or long term tests. While long term tests may be more accurate, they have obvious disadvantages. The state of strain factor accounts for differences in sealant joint behavior under axial and shear strain conditions. The geometric shape factor corrects for variations in strain capability that occur when the sealant is used in joint designs with width-thickness ratios or

configurations that are different from that used for the basic displacement and aging tests. Finally, the factor of safety accounts for uncertainties regarding actual behavior, installation, and service conditions, as well as reflecting a judgement on how critical the integrity of the joint is.

TEST PROGRAM

A testing program was developed to facilitate the determination of allowable strains for several typical sealant types. The tests used were similar in many respects to standard ASTM tests. However, specimen geometry and curing procedures were standardized so that all the specimens for a given sealant used in the various tests began with similar material properties. The specimens used are shown in Figures 1 and 2.

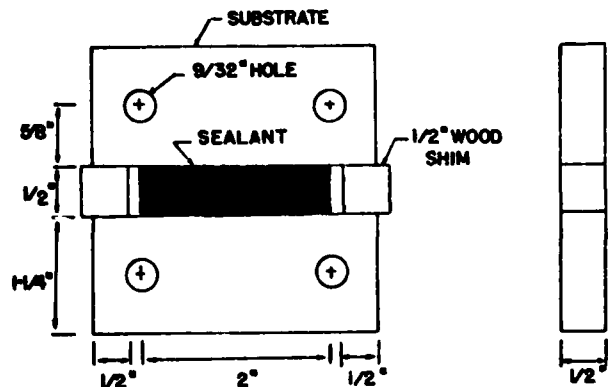


Figure 1.--Dimensions of Gunned Sealant Tension Specimen

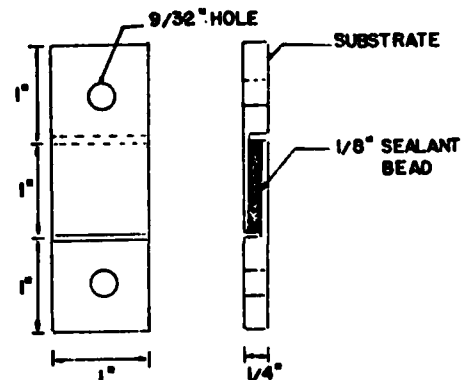


Figure 2.--Dimensions of Gunned Sealant Shear Specimen

All specimens were cured one week at 23°C (71°F) and 50 percent RH followed by another week at 40°C (104°F). All testing except for low temperature testing, was done at 23°C and 50 percent RH. The various tests used to develop the data for allowable strain determination are summarized below:

1. Basic Displacement Test-Tension.-- Specimens, as shown in figure 1, are elongated and the ultimate strain is recorded. From these results, an estimate of the 5 percent exclusion value for ultimate tension strain is calculated.

2. Basic Displacement Test-Shear.-- Lap specimens (fig. 2) are pulled in shear to obtain a 5 percent exclusion value for ultimate shear strain.

3. Fatigue.--Tension specimens are cycled in fatigue at various peak strain levels. The tests are run at 500 cycles per minute. The data, number of cycles to failure versus peak strain, are fit with a hyperbolic function to estimate a strain endurance limit.

4. Water Resistance.--Tension specimens are immersed in 23°C water. At various time intervals, up to 90 days, specimens are removed and tested wet to determine ultimate strain.

5. Heat Resistance.--Tension specimens are placed in a 70°C (160°F) ventilated oven. At various times, up to 90 days, specimens are removed and tested at room temperature to determine the effects of heat aging.

6. Low Temperature Flexibility.--Tension specimens are chilled in a freezer for one week and then tested cold in an insulated, cooled test chamber. The temperatures used are 0°C, -15°C, -30°C, and -45°C.

7. Chemical Resistance.--This test is the same as the water resistance test except the water is maintained at a pH of approximately 3.0 by the periodic addition of sulfuric acid.

8. Ultraviolet Exposure.--Tension specimens are placed in a Q-panel exposure unit. For times ranging up to 1200 hours. After exposure the specimens are tested to failure.

9. Compression and Tension Set.--This test measures the recovery ability of a sealant after the specimens are held in a displaced position for various time intervals. Tests are run at -30°C, 23°C, and 70°C.

10. Substrate Compatibility.--The adhesion of the sealant to various substrates

which might be encountered are evaluated in this test. The tension specimen of figure 1 is used.

11. Joint Design Sensitivity-Tension.-- This test measures the effects of different width-thickness ratios on tensile strain capacity. It is used to develop the geometric shape factor.

12. Joint Design Sensitivity-Shear.-- This test is similar to the one above, except it covers shear joints.

13. Joint Design Sensitivity-Special Configurations.--For joint geometries other than a butt tension joint or a lap shear joint, special tests must be run to determine the geometric shape factor. Fillet joints, for example, may require this additional test.

TEST RESULTS

To illustrate the application of the test data to determination of allowable strains, consider a solvent acrylic sealant on wood and aluminum substrates. The results from the basic tension and shear tests are shown in table 1. The strains are very large, particularly those for shear. As such, they are really nominal strains. The tension strains were obtained by dividing failure displacement by specimen width while the shear strains were calculated as failure displacement divided by specimen thickness, consistent with the usual engineering definition of shear strain. The significantly larger strain capacity in shear was expected (Cook, 1970). The state of strain factor for tension is 1.00 because all of the durability factors are derived from tension data.

The fatigue data for the acrylic is shown in figure 3. The test was run at 500 cycles per minute and was a non-reversing (tension only) cycle from zero displacement to some peak displacement. A reversing cycle may be more appropriate in general, but was not used because of the particular application that was considered in the study. All of the acrylic specimens failed cohesively. A hyperbolic equation was fit to the data and the results are shown in table 2.

The 2500 cycle limit is intended to account for thermal expansion cycling. Assuming three months of severe winter exposure per year results in 2500 of these cycles (at near peak amplitude) over a 30 year life. Other numbers of cycles could be used depending on the desired life and on availability of data for actual joint movements in buildings.

Table 1.--Basic tension and shear

Strain/ Substrate	Mean Strain %	Std. Dev. Strain %	5% Excl. Strain %	State of Strain Factor
Tension/W	205	49	117	1.00
Tension/Al	220	24	176	1.00
Shear/W	837	100	655	5.60
Shear/Al	880	43	803	4.56

W = Maple substrate Al = Aluminum substrate

Table 2.--Fatigue results for acrylic

Substrate	Equation	Std. Dev. (in)	2500 Cycle Factor	1 Million Cycle Factor
Wood	$Y = 386/x + .0326$.0072	.172	.0329
Aluminum	$Y = 823/x + .0202$.0097	.316	.0210

Y = Peak displacement (inch) x = Number of cycles to failure

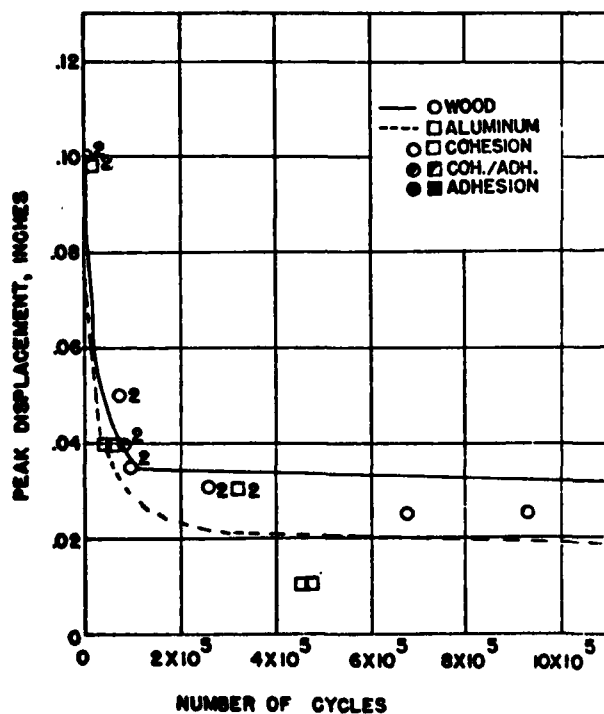


Figure 3.--Fatigue Test Data, Acrylic Sealant

The one million cycle limit is suggested for cases, such as mobile homes, where the structure will be subjected to transportation induced dynamic loadings.

To obtain the durability factors for fatigue, the 2500 cycle and one million cycle limits were divided by the appropriate mean strain from the basic tension test. The results are shown in table 2.

Since the tests for water, heat, and chemical resistance were conducted in much the same fashion, they can be discussed together. The data is shown respectively in figures 4, 5 and 6. Exponential decay curves were fitted to these points, but only a few of the curves were statistically significant. To obtain some estimate of the degradation, the data for 50, 70, and 90 days of exposure were averaged for each exposure type and divided by the mean strain from the basic tension test. The resulting durability factors are given in table 3.

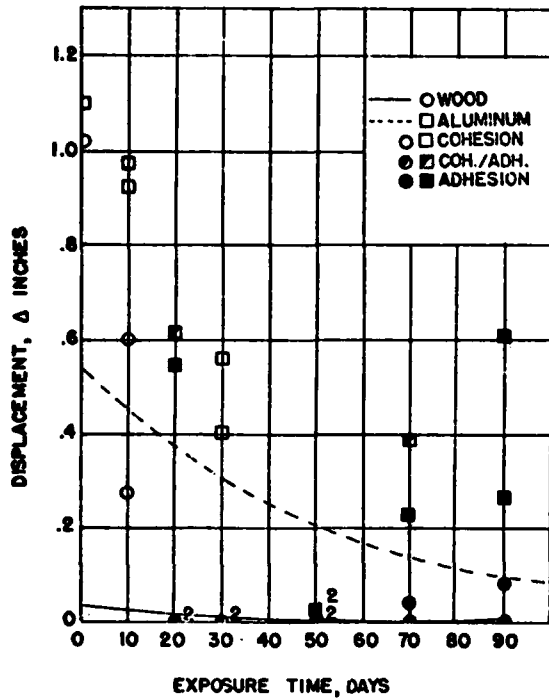


Figure 4.--Water Immersion Test Data, Acrylic Sealant

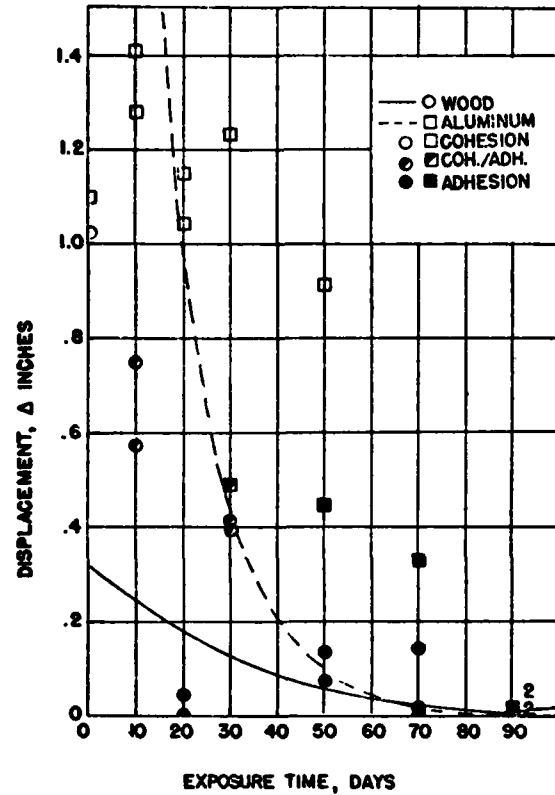


Figure 6.--Chemical Resistance Test Data, Acrylic Sealant

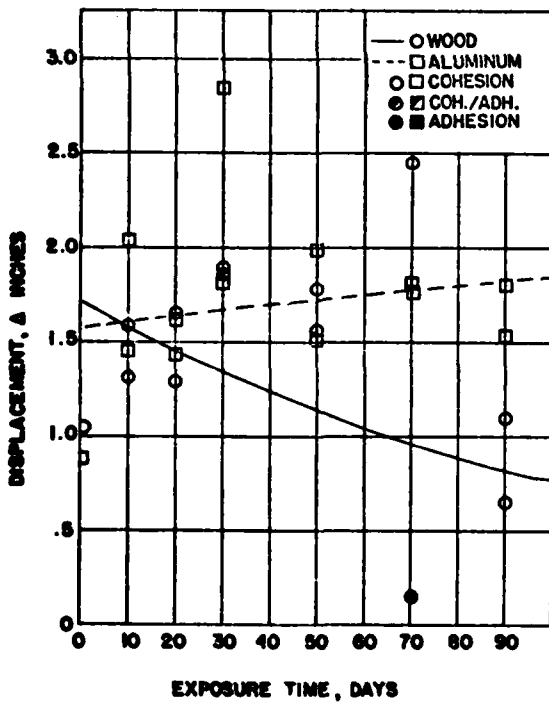


Figure 5.--Heat Resistance Test Data, Acrylic Sealant

Table 3.--Water heat and chemical factors

Substrate	Water	Heat	Chemical
Wood	0.02	1.00	0.07
Aluminum	0.22	1.00	0.26

The results of the cold temperature flexibility test are shown in Figure 7. A near total loss of displacement capacity occurred at -45°C . Calculation of a durability factor for cold must reflect actual expected conditions. For illustration, the data at -30°C was averaged and divided by the mean tension strain to get the factors given in Table 4.

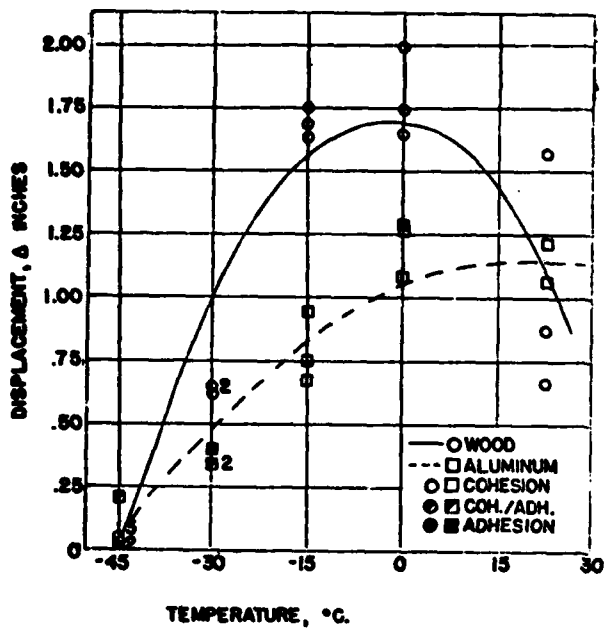


Figure 7.--Cold Temperature Flexibility Test Data, Acrylic Sealant

Table 4.--Low temperature factors, -30°C

Substrate	Factor
Wood	0.63
Aluminum	0.32

Results for the ultraviolet resistance test are given for the acrylic in figure 8. Note that displacement capacity actually increased with exposure. This was probably due to the effect on curing from the gentle heat (45°C) associated with the test. Ultraviolet light had little effect on any of the sealants tested, but it must be emphasized that these were opaque sealant and substrates. In situations where light can reach the sealant-substrate interface the results would probably be very different. For this test the durability factors for the acrylic were set at 1.00

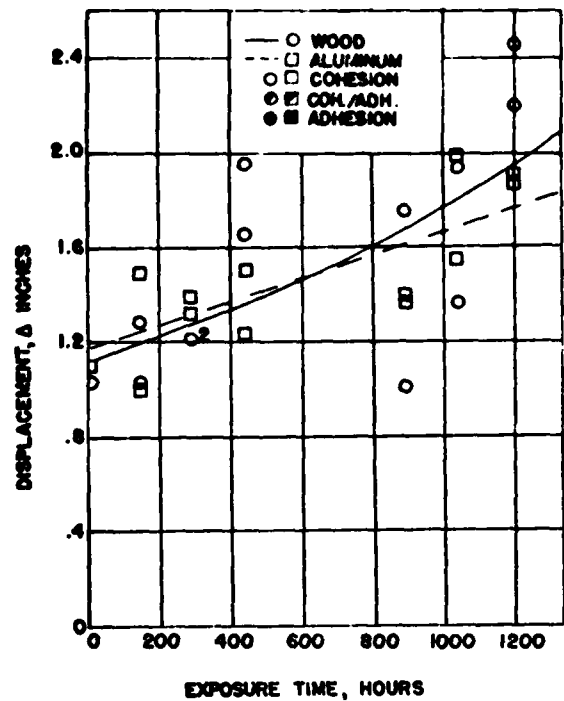


Figure 8.--Ultraviolet Exposure Test Data, Acrylic Sealant

The results for the compression and extension set tests for the acrylic are shown in figures 9 and 10. The initial strain was 15 percent. The most important data is that at 70°C since compression of a sealant joint is most likely to occur from expansion of adjacent substrates at high temperature. At the same time, irrecoverable creep deformations are most likely to occur at higher temperatures. Since the greatest movements generally would occur from daily thermal cycles, the six to twelve hour recovery, approximately 5 percent, was used to calculate the compression set factor. Compression set has the effect of increasing the total strain during subsequent extension. To account for this, the compression set factor is taken to be

$$C_{cs} = R/200 + 0.5$$

where R is the recovery in percent. Note that a perfectly elastic sealant has a compression set factor of 1.00 while a sealant with no recovery has a factor of 0.50. For this latter case, the sealant is assumed to go into tension as soon as movement reverses from compression to extension. Thus for movement

about the mean daily joint width, usable tensile strain capacity is one-half of the total capacity. For the acrylic sealant, C_{CS} equals 0.52.

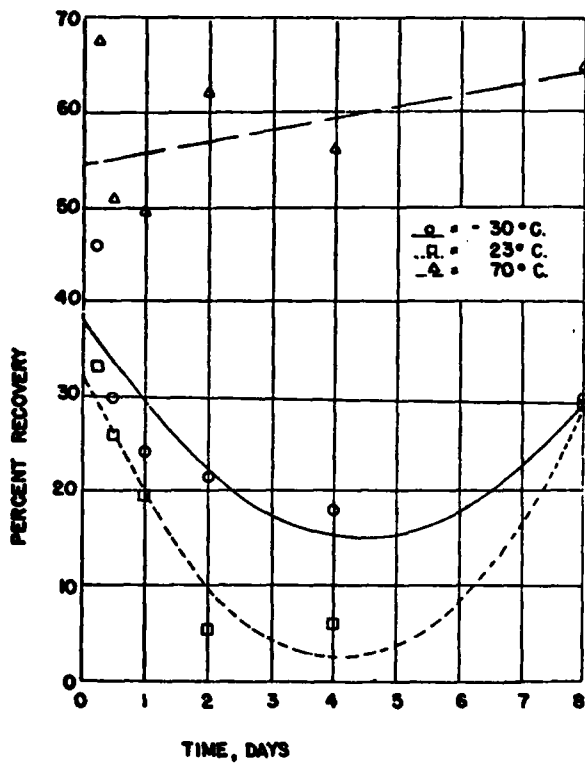


Figure 9.--Extension Set Test Data, Acrylic Sealant

The test for the effect of width-thickness ratio on tensile strain capacity was conducted with specimens with widths and thicknesses of 0.25 x 0.50, 0.375 x 0.50, 0.125 x 0.50, 0.50 x 0.375, and 0.50 x 0.25 inch. The resulting data is shown in figure 11. Neither a first order (shown) or second order polynomial fitted to the acrylic data proved statistically significant. Therefore, the geometric shape factor was taken as 1.00. Other sealants did show significant effects.

The width-thickness results for shear, shown in figure 12, show a definite second order relation between ultimate strain and width-thickness ratio. The widths used were 1/16, 1/8, 3/16, 1/4, and 5/16 inch, with the corresponding shape factors given in table 5.

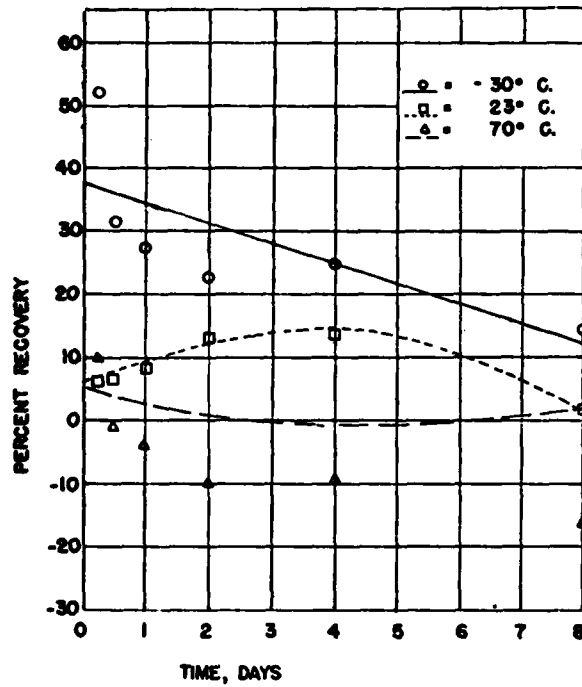


Figure 10.--Compression Set Test Data, Acrylic Sealant

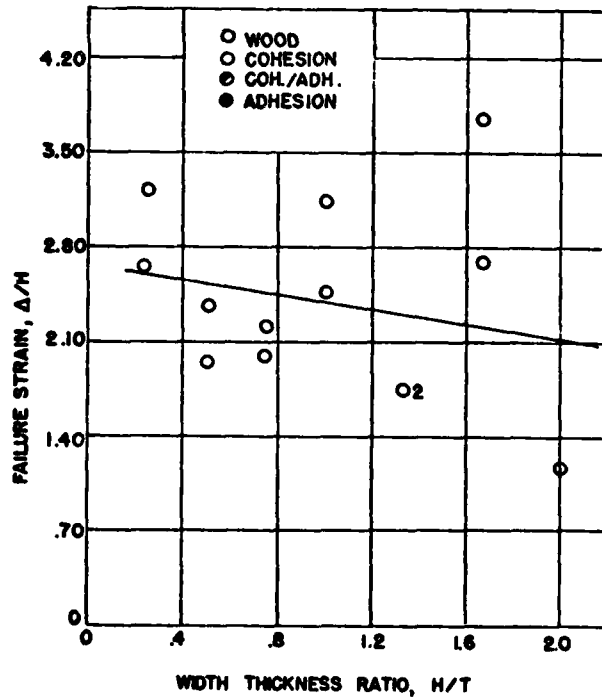


Figure 11.--Width-Thickness in Tension Test Data, Acrylic Sealant

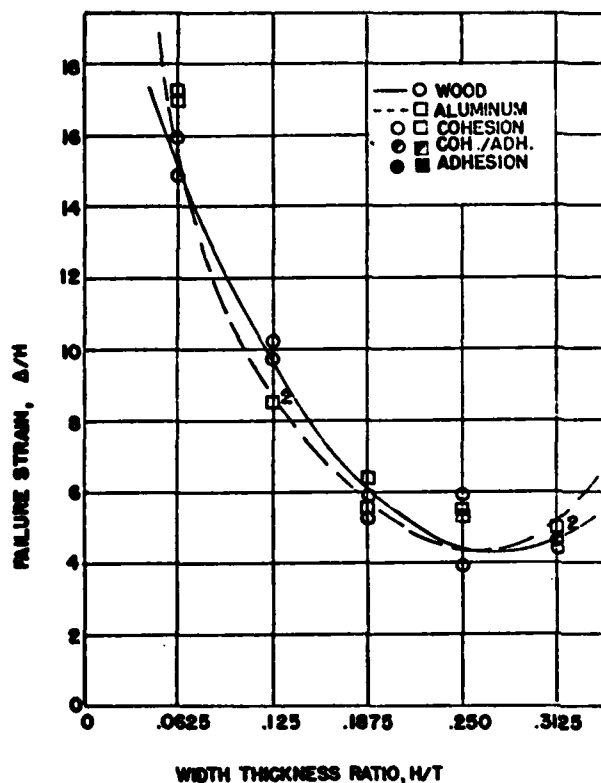


Figure 12.--Width-Thickness in Shear Test Data, Acrylic Sealant

Table 5.--Acrylic geometric shape factor - shear

Substrate	Width-thickness ratio				
	0.6	.13	.19	.25	3.1
Wood	1.59	1.00	.62	.44	.48
Aluminum	1.66	1.00	.59	.44	.54

Geometric shape factors may also be derived for other joint geometries, such as for the fillet joint specimen shown in figure 13. Here, the parts of the joint which are parallel to the displacement are primarily in shear and the part perpendicular to the displacement is under tension along with some shear. Failure occurred in the latter part of the joint for all sealant types.

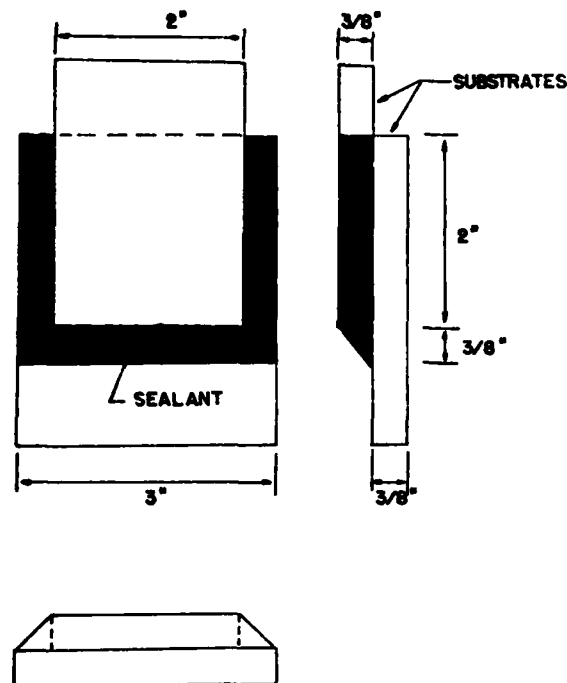


Figure 13.--Dimensions of Fillet Joint

The nominal strain in the critical area was calculated as simply the failure displacement divided by the leg size of the fillet (3/8 inch). The resulting mean strain divided by the mean basic tension strain yields the special geometric shape factor shown in table 6.

Table 6.--Fillet joint data

Mean Failure Strain (%)	Std. Dev. (%)	Geometric Shape Factor
168	6	0.82

Substrate compatibility requires very careful consideration. Obviously, the ideal approach would be to run a full battery of tests on each sealant-substrate combination that might be used. This would be prohibitive in cost. To explore a compromise approach,

the following procedure was adopted. First, all tests of a sealant were run with two substrates, wood and aluminum. These represent porous and nonporous materials, respectively, in terms of volatile release and soaking of the sealant substrate interface. To evaluate the effects of substrate on strain capacity, the following common construction materials were used: ABS plastic, galvanized steel, particleboard, polyester enamel coated steel, and PVC. None of these were primed, only carefully cleaned before sealant application. The specimens were given the standard cure and no other form of aging exposure. The one porous substrate, particleboard, was compared to wood, while the others were compared to aluminum to obtain substrate factors shown in table 7. The acrylic sealant used for illustration is of a type which is well known for its excellent adhesion characteristics (Cook, 1970). Some of the other sealants showed more significant adhesion dependence on substrate type.

Any attempt to simplify the problem of sealant-substrate interactions, including this one, must be approached with caution. Heat aging might have a significant impact on bonds to some plastics. Water will certainly affect bonds to various porous substrates in different ways. And high modulus elastomeric sealants may produce failure of an aged substrate. Thus, judgement is required, with selected aging tests being employed where the need may exist.

The final term in the allowable sealant strain equation is a safety factor, representing a reduction in strain from a level at or near ultimate to a level that will provide consistently acceptable performance in service. Several things influence the selection of the safety factor. First, there is the nature of the application. The considerations here include consequences of failure and cost of replacement. Second, there is the degree of uncertainty involved in the design. Thermal movements in buildings are not always easily predicted. The procedures for establishing allowable strains in the sealant and then allowable joint displacements are certainly approximations. And installation conditions may be less than ideal. Finally, the safety factor must be based on past experience with the sealant, where data is available. If the calculated allowable strain for a given sealant proves to be over or under conservative in light of field experiences, the safety factor provides a convenient means of adjustment. This may not be entirely satisfactory from a purely scientific viewpoint, but such adjustments to reality are not uncommon and merely recognize the limitations of applying simplified analytical or empirical models to extremely complex phenomena.

Table 7.--Effect of substrate

Substrate	5% Excl. Value % Strain	% Adhesion Failure	Substrate Factor
Wood	117	0	1.00
Particle board	139	0	1.00
Aluminum	176	0	1.00
A. B. S.	139	0	0.79
Galvanized steel	179	0	1.00
Polyester enamel	61	5	0.35
PVC	138	0	0.78

APPLICATION OF THE ALLOWABLE STRAIN EQUATION

A good deal of engineering judgement is required to apply the procedure for calculating an allowable sealant strain. Not all modification factors should be included in every case. In the case of an acrylic tension joint on aluminum in a building wall for example:

basic tension strain = 176%
state of strain factor = 1.00
2500 cycle fatigue factor - .32
water immersion = N/A*
heat aging = 1.00
chemical aging = N/A*
cold flexibility (-30°C) = .49
ultraviolet = 1.00
compression set = 0.52
shape factor (W/T = 1.00) = 1.00
safety factor = .67
allowable strain = \pm 6.3%

*These immersion factors are not considered necessary unless there is the possibility of prolonged immersion or soaking.

This is in close agreement with the recommended values for solvent based acrylics (Panek, 1976 and Skeist, 1977).

CONCLUSIONS

It is possible to treat sealants as full fledged engineering materials. The general methodology for this has been presented. While there are a number of refinements which are needed to effectively implement the procedure, it is a flexible procedure which can readily accommodate improvements as they become available.

A major need exists for reliable accelerated aging techniques which allow prediction of long term strain capacities with satisfactory confidence. Two approaches to this problem should be explored. First, the continuous rate process method may be adaptable to predicting sealant aging characteristics on an accelerated basis. This method has been applied to adhesives in the past, (Millett, 1976, Gillespie, 1976, and Krueger, 1980), and has potential for providing a rational measure of the long term effects of heat, water, chemicals, and ultraviolet light from accelerated laboratory tests. Second, correlations between field performance and allowable strains predicted in the laboratory are vitally important. This is undoubtedly the surest means of calibrating the proposed procedure for determining allowable strains.

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AD P 002436

EVALUATING DURABILITY OF ADHESIVE-BONDED WOOD JOINTS¹

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ABSTRACT

A wood joint properly bonded with a phenolic adhesive is said to be stronger and more durable than wood itself. But what happens to both wood and adhesive during natural aging, and how long might both materials last? The literature reveals that wood, when subjected to only the chemical effects of aging, can last for up to thousands of years with remarkably small changes in mechanical properties, chemical composition, and morphology. Durability of adhesives can be compared with that of wood by rate process methods of analysis under conditions that accelerate the chemical reactions occurring during natural aging. Results demonstrated that moisture plays a predominant role in determining the durability of both adhesives and wood and that all degrading reactions are highly dependent on temperature. A procedure is proposed for comparing the durability of any new adhesive with that of wood, based on the time each requires to lose 25 percent of its original shear strength under prescribed conditions of exposure. This procedure requires a small number of test specimens and a short time for evaluation. Results are of high precision which can be related to centuries of use in natural aging and directly compare performance of phenolic and melamine adhesives as commonly recognized benchmarks for two levels of durability in service.

INTRODUCTION

People involved in adhesives research often say that a wood joint properly bonded with a phenolic adhesive is stronger and more durable than the wood itself. Well-bonded joints made with phenolic adhesives have survived all accelerated-aging tests and weathering exposures with high wood failure resulting when tested for strength. However, the statement that phenolic bonds are stronger and more durable than wood can take on meaning only when a reasonably satisfactory answer is found for the question "How durable is wood?"

Durability of wood, of course, depends upon such factors as species differences and how they respond to the degrading influences in service environments. These influences may include heat, microorganisms, insects, fire,

and chemicals. Most of our wood is used in situations that minimize the opportunity for microorganism attack, for involvement in fires, or for insect attack. Special preventive measures can be taken for these effects. But in the absence of fire, insects, and microorganisms, with only the influences of heat and chemicals prevailing, wood can last for centuries. But this statement, too, is imprecise and requires documentation and explanation. We must understand the life expectancy of wood if we are to compare the durability of adhesives and bonded products to wood.

But how can we tell the age of old wood? The most common way is to search back in history and calculate from some data such as the year in which a structure was built. This gives only a rough approximation, but satisfactory in many cases. However, wood substance can occasionally be dated precisely with respect to the year in which each annual ring was formed by dendrochronology, the science of tree ring dating. The age of wood

¹ Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

artifacts, however, is usually measured by carbon-14 analysis since tree ring chronology for particular species and growth locations has not been developed in most cases.

WOOD DURABILITY

Age of Wood Structures

The oldest surviving wood frame house in New England, and possibly in the United States today, is the Fairbanks House in Dedham, Mass., which was built in 1637 (4).² This structure has survived 343 years of what is often called "the rugged New England climate." But in Norway, people still live in houses several centuries old and hold church services in wood structures built almost a thousand years ago (2).

An old wood structure in continual use is Horyuji Temple near Nara, Japan. This temple was founded in 607 A.D. and the middle gate to this complex of buildings is the only remaining structure of the original buildings. It is also said to be the oldest example of wood architecture in the world (18). The statues of the temple door guardians were carved from massive logs in 711 A.D. Here, wood has survived after installation for over 1,300 years in the Japanese climate.

Much of the wood we use today is older than any of us even before it is installed in a structure. I have a section of a Douglas-fir 2 by 10 cut as an edge-grain board for such uses as stadium seats. A tree-ring count reveals that the wood substance on one edge was formed 130 years before that on the opposite edge. This is just one board removed from some unknown location in a log which undoubtedly grew for a much longer period of time.

A cross section of such an old-growth Douglas-fir, which was harvested many years ago, is now a tabletop in a reception area of the Forest Products Laboratory. A tree-ring count shows the tree grew for over 250 years before felling. An even more impressive specimen used for display is a cross section of redwood. The tree was cut in 1932 with a ring-count age of 864 years. So some of the wood substance close to the pith is over 900 years old today.

If one applies this concept of age to the wood carvings flanking the entrance to the Horyuji Temple, some of the wood substance was formed 200 to 300 years before the gateway was built, which would be 1,500 to 1,600 years ago.

² Underlined numbers in parentheses refer to literature cited at end of this report.

Age of Wood Substance

The scientific study of tree rings provides a wealth of information about the age of wood substance and about past climates. This information is of great value to historians, geologists, climatologists, anthropologists, archeologists, and others. Dendrochronology or dendroclimatology has developed as a well-recognized scientific discipline only during the present century. The development of this discipline, the techniques employed, and the fascinating conclusions that can be reached are described in a recent book by H. C. Fritts (8). He credits Andrew E. Douglass to be the acknowledged father of dendrochronology.

Douglass' original interests were in weather-sunspot relationships; but on a trip through a forest in northern Arizona at the turn of the century, he noted the variation in width of tree rings in a freshly cut log. These variations in tree-ring width suggested to him that trees automatically stored a record of weather conditions each year they grew. Douglass collected borings from living trees, from wood beams in structures, and from wood artifacts; after innumerable careful observations and analysis, he established a tree ring dating system. This system depended upon finding specimens where distinct growth patterns could be identified, matched, and overlapped between specimens.

The southwest United States with its unique arid climate was the ideal laboratory for developing this scientific discipline because it preserved a large number and variety of wood artifacts for such a study back into time. Douglass' work led to the establishment in 1937 of the Laboratory of Tree Ring Research at the University of Arizona in Tucson. The accumulated work of this laboratory and by others has led to an archaeological chronology extending back to 322 B.C. in the Southwest, with more than 20,000 dates established for specific events from nearly 1,000 separate sites (5). This is a continuous tree-ring record of over 2,300 years in the United States. This dating system has been extended to many other regions of the world, including nonarid sites, and involving many species. It has also been applied to many different kinds of phenomena.

Some of the oldest known wood substance found in the United States exists in living trees, the ancient bristlecone pine, Pinus longaeva. This species grows at high elevations in various locations in the mountains of California, in Nevada, Utah, Colorado, Arizona, and New Mexico. An illustrated book describing these areas and the information obtained by extensive study has been compiled

by Meunch and Lambert (16). A living bristlecone pine over 4,500 years old was discovered by Schulman (19). By overlapping growth patterns between specimens of bristlecone artifacts, the chronology has been extended back over 7,000 years; it is felt that this calendar has the potential for extension to 15,000 or possibly 20,000 years (6).

The age of artifacts is usually measured by Carbon-14 analysis, but Carbon-14 dating has proved unprecise in comparison with tree ring dating. Bristlecone pine pieces which were dated at 4,500 B.C. by Carbon-14 analyses were shown to be actually 1,000 years older by tree ring dating--5,500 B.C. (16).

Wood survives well in either the dry state or when totally submerged or buried underground. Specimens have been found in dry caves and rock shelters, in massive open structures, and dry burial tombs. In most of these cases, the moisture content of the wood has been well below the fiber saturation point. But wood has also been found in bogs, lakes, in sunken ships, in old corduroy roads, and in underground burial places where the lack of oxygen discouraged microorganism attack (5). Here the wood is often completely saturated, and there is greater opportunity for hydrolytic reactions. Evidence indicates that bacteria and certain soft-rot fungi can attack submerged wood, but the resulting deterioration is very slow (20). Because of this extremely slow degradation, it has been possible to salvage and use lumber cargos from ships sunk many years ago in the Great Lakes. Logs have also been "mined" from cedar swamps on the East Coast where hurricanes felled the trees decades ago.

Charring wood also preserves the ring structure. Charcoal, which is impervious to decay, is the most common form of wood found in open sites, and it is perfectly suitable for tree ring analysis.

Natural Aging of Wood

Lyman Wood (23) evaluated numerous specimens of old lumber and concluded that wood did not change significantly in strength and stiffness after use of 100 years or more, and recommended reuse in structural applications.

A number of reports in the literature concern wood of much greater age and describe the changes that had taken place in their mechanical properties, chemical constituents, and morphology during the time span of their existence. Age was determined in most cases by the archeological history of the surrounding area in which found, or by Carbon-14 dating. Borgin (2) studied wood which had been unearthed from a Viking burial at Oseburg, Norway, after about 1,100 years.

Van Zyl et al. (21) evaluated the mechanical properties and chemical constitution of wood varying in age from about 200 to 4,300 years, which involved species of oak, pine, juniper, and acacia from Norway, from Egyptian pyramids, and Cape Town, South Africa. The morphological changes that took place during the aging of this wood were evaluated by Borgin et al. (3) using the same materials studied by Van Zyl et al. (21). Bednar and Fengal (1) studied the physical and chemical structure of various oak specimens that varied in age from 600 to 8,500 years.

Extensive studies have been carried out in Japan with a summary reported by Kohara and Okamoto (14). Both hardwoods and softwoods were evaluated for mechanical, physical, and chemical properties after removal from various buildings ranging in age from 240 to 1,300 years, the oldest timber being from Horyuji Temple. Kohara (13) also reported an extensive investigation on a number of specimens of cypress wood removed from structures ranging in age up to 1,300 years. However, extremely old samples of wood have been found in the rubble of iron mines where burial took place by some earth upheaval in past geological time. A white pine specimen 10 million years old, and a specimen probably of redwood 100 million years old, retained sufficient structure to allow morphological and chemical constitution evaluation (22).

Changes in Mechanical Properties and Chemical Composition During Natural Aging

This accumulated information about wood of various ages reveals that changes in mechanical properties and chemical composition take place remarkably slowly in the absence of decay. Impact strength was the property with the most pronounced loss. For example, the impact strength of cypress was reduced to one-half over a period of 1,300 years (13). Shear strength, the property normally measured in adhesive testing, was reported only for cypress (13). In this case, there was no significant shear strength loss for as long as 900 years, and only a 7 to 13 percent loss at 1,200 to 1,300 years.

In the wood evaluated by Bednar et al. (1), losses were found in the hemicellulosic or cellulosic constituents indicating a relatively low degree of chemical degradation. A similar reduction in cellulosic content with aging was reported by Kohara et al. (14) with a more rapid loss in hardwoods than in softwoods. Kohara suggested that changes of chemical composition and mechanical properties similar to those found in natural aging could

be produced by dry oven aging at 100° to 130° C in the laboratory.

Van Zyl et al. (21) also reported a gradual cellulose loss in wood from underground burial and sunken ships. From this, they speculated that the ultimate destiny of extremely old wood was its gradual conversion into coal which is believed to be derived from wood lignin. But they found wood samples from Egyptian tombs which seemed to be changing in a different manner, because analysis yielded higher cellulose and lower lignin values than was obtained for new wood.

ADHESIVE DURABILITY

When evaluating materials expected to last as long as wood is serviceable, accelerated aging is essential. The long-range nature of this service requires that the results from the accelerating conditions used for testing be extrapolated to those expected in service. Such extrapolations are always viewed with suspicion and doubts about the accuracy of the predictions made outside the experimental range. But for adhesives and wood products, there appears to be no better alternative at the present time.

The fact that strength losses are associated with chemical changes resulting from aging led to the development of the rate process method of analysis (9-12). This work involved evaluation of adhesives in plywood constructions wherein the rates of loss of shear strength were determined under continuous exposure to dry heat or water soaking at several elevated temperatures. As a matter of convenience, the time required to lose half the original strength under each exposure situation was arbitrarily selected for comparison purposes.

When the log values for the required time to lose half of the original strength were plotted against the reciprocal of the absolute temperature according to the Arrhenius temperature-dependent relationship, a straight line was obtained. This linear temperature dependence could then be extrapolated to temperatures normally found in service environments to yield values that appeared to be reasonable from the standpoint of wood's historical performance.

The next step in the rate process method of analysis development consisted of experiments designed to evaluate the precision of the method (15). In these experiments, solid lumber was laminated with grain directions parallel; and shear strength was determined after dry-heat and water-soaking exposures involving larger numbers of specimens and exposure temperatures than used previously. Sugar maple and white pine were evaluated as

solid wood, and when bonded by phenolic- or melamine-type adhesives.

In the analysis, the rate data were fitted in most cases with an exponential equation using regression analysis. From these equations, the times required to lose 25 percent of the original strength, as well as the 50 percent loss used previously, were computed. These data were regressed as the Arrhenius temperature-dependence relationship and extrapolated to room temperature (20° C). The upper and lower 95 percent confidence limits were also calculated as an attempt to express how the average specimen response at each temperature varied from the regression line.

In general, a significantly higher level of precision with respect to durability projections could be attained by carrying the deterioration to the 25 percent level of strength loss rather than the 50 percent level. Results appeared more in line with the low strength losses that occur during natural aging as previously described. An additional bonus is the greatly reduced aging time requirements for only a 25 percent strength loss.

Also, the experimental results demonstrated the dominant influence of temperature on life expectancy. As an example, table 1 shows the effect of temperature on the time required for a 25 percent strength loss in white pine as solid wood and phenolic-bonded wood under dry-heat and water-soaking conditions. Under dry heat, the time is reduced from 1 million years at 20° C to only 5 years at 100° C, with a further reduction to only 0.1 day with an increase in temperature to 200° C. The temperature ranges used for data collection are shown in table 1, but it is interesting to note the great differences in times that take place within the temperature range in which we normally live, 20° to 40° C (68° to 104° F). Under dry heat, the time for a 25 percent strength loss is reduced from 1 million years to only 27,000 years as temperature increases within this range.

Table 1 also demonstrates the tremendous decrease in the time required for 25 percent strength loss when the opportunity for hydrolysis is maximized. For example, at 60° C the time of 1,100 years under dry heat is reduced to 1.1 years during water soaking. Although white pine might lose 25 percent strength in 400 years at 20° C under water, this is reduced to only 4 days when the water is boiling. It is very difficult to appreciate the extent of temperature and moisture influences on durability without such a demonstration.

The dry-heat and water-soaking exposures represent extremes in moisture content rather than any simulation of conditions encountered in natural aging. Wood under natural aging is

Table 1.--Time for 25 percent shear strength loss in white pine

Aging temperature	Dry heat	Water soaked
200° C	0.1 days	
180	0.7	
Experimental range, dry	160 140 120	3.6 24 190
Experimental range, wet	100 90 80 70 60	5.0 years 17 64 250 1,100
	50	4.0 days 12 35 110 1.1 years
Human habitation range	40 30 20	5,200 27,000 160,000 1,000,000
		4 18 80 400

usually at a moisture content somewhere below 20 percent where microorganism influence is minimal, but the moisture content is never completely zero even in such dry situations as in the Egyptian tombs. Consequently, the times required to lose 25 percent strength, shown in table 1, establish the boundaries within which wood performs in natural aging.

Water-Soaking Effects

On the other hand, the water-soaking predictions might relate to those artifacts found as sunken or buried ships such as the Cape Town ship and the Viking ship described by Van Zyl et al. (21), the Vasa from the Harbor of Stockholm, Sweden (7), and others where the wood is still intact but requires polyethylene glycol treatment to prevent collapse upon drying. In these cases, the water-soaking exposure represents a degradation due mainly to hydrolysis reactions. These artifacts ranged in age from about 200 to 900 years. The time to lose 25 percent strength in hard maple, the only hardwood evaluated in the rate process study, was found to be about 800 years under hydrolysis at 20° C. These projections are remarkably consistent in light of the many unknown influences--the species differences, the temperature differences, and the low-level microorganism attack that could be involved.

Dry-Heat Effects

The dry-heat aging conditions provide opportunities for much more complex reactions to take place than occur under water-soaking conditions. These reactions involve chain scissions, dehydration, hydrolysis, oxidation, as well as others. The oxidation can take place because the heating is done in the presence of air. However, this effect appears to be very slight considering the long time required for significant strength losses. Hydrolysis reactions do occur even though the temperatures of exposure are above the boiling point of water. This was noted in the early rate process investigations (11) where the effects of acid catalysts in the adhesives caused an initial rapid loss of strength during dry-heat aging.

It is known that the last vestiges of moisture are extremely difficult to remove even under heating in a vacuum. This residual moisture could provide the water needed for hydrolysis while additional water could become available by thermal dehydration of labile constituents.

The fact that the acid-catalyzed hydrolysis reactions appeared to terminate after a certain period of time remains a puzzle. Possibly the residual water and that from dehydration reactions is soon used up, or only the most readily accessible regions in the cellulose structure are attacked in the exposure

conditions used. There is probably minimal opportunity for catalysts or reactants to move into positions for reaction in the dry state; any tendency to do so should decrease as the heating period progresses after the more heat-sensitive components have already reacted.

Evidence indicates that the reactions do change during dry-heat exposures as degradation proceeds. The reactions that take place during the first 25 percent strength loss depend more on temperature than when the strength loss extends to 50 percent with both hard maple and white pine. In other words, the slopes of the Arrhenius temperature-dependence plots of 25 and 50 percent strength loss differ and the projections cross (fig. 1). The projections to 20° C room temperature suggest that it takes longer for a 25 percent strength loss (1 million years) than for a 50 percent loss (72,000 years) which, of course, cannot be true. As degradation proceeds, it requires less energy to cause further degradation by the different reactions involved. This should not be unexpected in view of the many reactions that can be taking place simultaneously and sequentially, with some being catalyzed by acidic components or metallic ions. Furthermore, this suggests differences would result upon exposing other species to dry-heat aging or for wood substance grown on different soils and having variations in ash content.

The difference in temperature dependence for a 25 percent versus a 50 percent strength loss does not explain why hydrolysis reactions terminate after a certain time. The cause might be the decreased mobility or accessibility of the reactants. Also, a variety of new kinds of reactions, possibly involving products of early reactions, may take place with different energy requirements as degradation proceeds.

Acid Catalyst Effects

In the earlier work, the effects of acids as catalysts for hydrolysis were not detected during water soaking (9,11). This was interpreted as resulting from dilution and migration of acid constituents away from the bondline before detectable degradation could be realized.

Because the effect of acid catalysts shows up during dry-heat aging, and not during water soaking, it would appear that their full effect is not being measured, because the aging conditions limit the amount of water available for the hydrolysis reaction. This has led to a consideration of aging conditions that provides additional moisture, but not in sufficient quantities to allow water to be present and enhance diffusion and migration of acid from bondline.

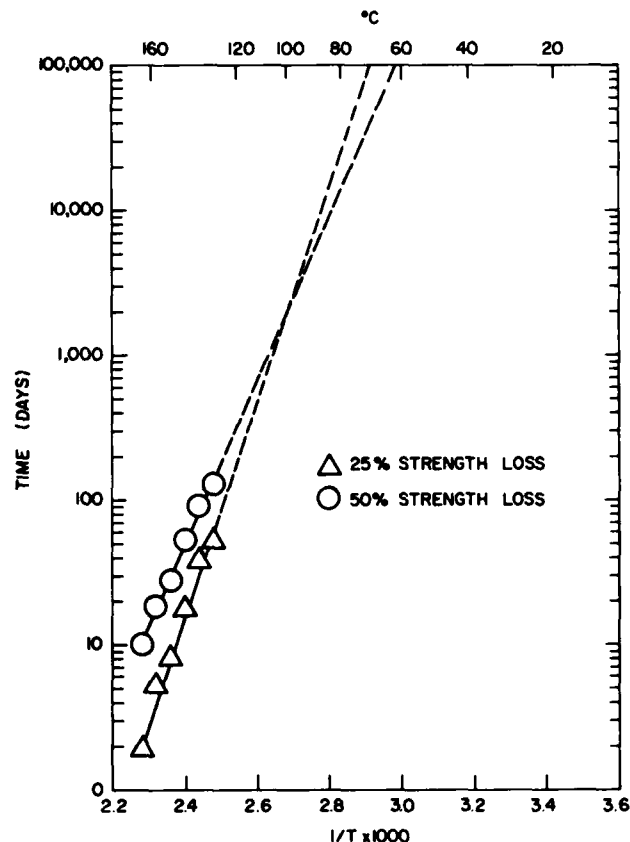
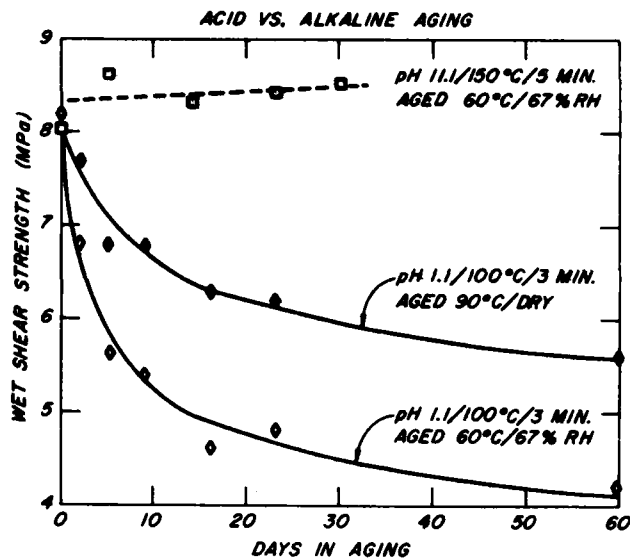


Figure 1.--Dry-heat aging of white pine and bonded white pine--temperature dependence of 25 percent strength loss.

Figure 2 (17) shows strength losses for joints formed from both alkaline- and acid-catalyzed phenolic adhesives. The pH of the adhesive mix along with the temperature and time used for bond formation are shown for each condition evaluated. The alkaline-catalyzed adhesive showed essentially no strength loss during aging at 60° C and 67 percent relative humidity, while the phenolic bonds catalyzed at a pH of 1.1 showed a rapid loss initially, with a moderation in rate in the latter stages up to 60 days aging. This was in contrast to dry-heat aging at a higher temperature (90° C) which showed the same shape of the curve but substantially less strength loss. This supports the idea that hydrolysis during dry-heat aging is limited by the amount of moisture available. The fact that the hydrolysis appears to terminate after a period of aging, even when moisture is continuously supplied, suggests that the accessibility of linkages susceptible to hydrolysis declines as aging progresses or the acid catalyst loses its effectiveness for some reason.



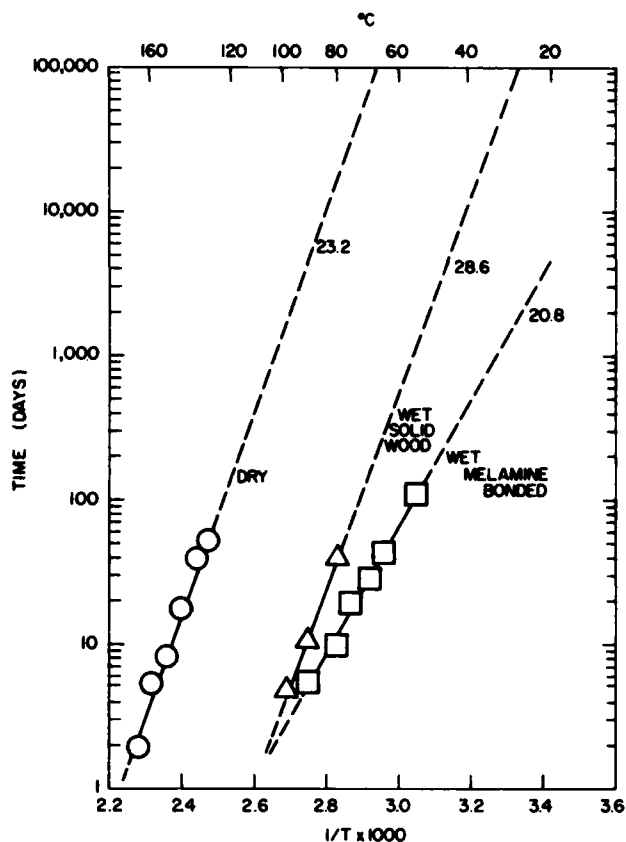
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Figure 2.--Effect of adhesive pH on strength loss during moist-heat accelerated aging.

Melamine-Formaldehyde Bonds

In the study on the precision of the rate process method of analysis (15), melamine-formaldehyde bonded joints were evaluated. The melamine was selected because of its high level of durability, although melamine bonds have not proved as durable in service as phenolic bonds. Figure 3 illustrates the results as the Arrhenius temperature-dependence plots for dry-heat aging and water soaking and compare the 25 percent strength loss results of bonded joints with that of solid wood--white pine in this case. The hydrolysis of the melamine bonds takes place more rapidly and with a different temperature dependence; the higher the temperature used to accelerate hydrolysis, the lower the ability to detect differences in strength loss.

Table 2 includes data for both sugar maple and white pine for times required to lose 25 percent strength in water soaking at 20° C, an intermediate accelerating temperature of 80° C, and a rapid acceleration in boiling water at 100° C. These data show that it takes at least twice as long for white pine specimens to lose 25 percent shear strength as it does for hard maple. Such species effects should be taken into consideration in accelerated aging evaluation of adhesive durability. In addition, the data in table 2 show that the time required for solid pine to lose 25 percent shear strength is 30 times longer than that for melamine-bonded pine at 20° C, but this difference decreases to a factor of only



M 149 282

Figure 3.--Accelerated aging of white pine and melamine-bonded white pine--temperature dependence at 25 percent strength loss.

1.6 at 100° C. Similarly, for hard maple the differences vary from a factor of 19 times at 20° C to only 2.7 times at 100° C.

It is interesting to note that a 25 percent loss of shear strength for melamine-bonded white pine represents a loss of only 190 lb/in.² as compared with 420 lb/in.² for melamine-bonded maple because of the difference in initial wet strength. At 80° C water soaking, this loss takes place at an average rate of only 17 lb/in.² per day for the melamine-bonded pine and 130 lb/in.² per day for melamine-bonded maple.

The activation energies calculated from the Arrhenius temperature-dependence regression lines show that the hydrolysis of melamine-bonded specimens takes place as a single rate controlling reaction. An activation energy of 21 kcal mole⁻¹ (88 kJ · mole⁻¹) as shown in table 3 was obtained at both the

Table 2.--Time to lose 25 percent wet shear strength during water soaking

Material and bond	Temperature		
	20° C	80° C	100° C
	----- Days -----		
Solid pine and phenolic-bonded pine	146,000	35	4.0
Melamine-bonded pine	4,700	11	2.5
Difference factor	30X	3X	1.6X
Solid maple and phenolic-bonded maple	29,000	13	1.8
Melamine-bonded maple	1,550	3.2	0.65
Difference factor	19X	4X	2.7X

Table 3.--Activation energy

Material and bond	Exposure condition	Shear strength loss	
		25 Percent	50 Percent
		----- kcal · mole ⁻¹ (kJ · mole ⁻¹) -----	
Solid maple, phenolic- and melamine-bonded maple	Dry	34.8 (145)	28.9 (121)
Solid pine, phenolic- and melamine-bonded pine	Dry	33.2 (139)	25.8 (108)
Solid maple, phenolic-bonded maple	Wet	26.3 (110)	27.7 (116)
Melamine-bonded maple	Wet	21.1 (88)	21.1 (88)
Solid pine, phenolic-bonded pine	Wet	28.6 (129)	24.0 (100)
Melamine-bonded pine	Wet	20.8 (88)	20.9 (88)

25 and 50 percent strength loss levels, and on either bonded maple or pine. In contrast, the complex reactions that take place in solid or phenolic-bonded wood result in differences in activation energy depending upon species and extent of reaction. Included in this table are the data for dry-heat aging where there is a marked difference between activation energies for a 25 percent strength loss compared with a 50 percent loss. This difference also seems to carry over for water-soak aging

in the case of white pine but not for hard maple.

Determination of 25 Percent Strength Loss of Bonded Joints

When comparing the durability of a bonded joint with that of the wood itself, it is necessary to determine the time required for

some specific strength loss--25 percent being suggested here. If, for example, the point in question is the hydrolysis resistance of a new adhesive, this can be determined on a comparative basis by water soaking under conditions selected from the background information presented previously. As an illustration, the data in table 2 show that white pine loses 25 percent shear strength in 35 days of water soaking at 80° C. White pine specimens bonded with the new adhesive could be prepared for exposure under the same conditions. The initial shear strength would be determined in the wet condition after a vacuum-pressure-soak using 20 specimens as recommended for determining a good estimate of the mean (15). Other sets of 20 specimens for each exposure period could be water-soaked at 80° C for periods of time up to 35 days.

The only remaining problem is the selection of appropriate intermediate exposure times before removing specimens for test. One approach to this problem is to run an exploratory set of specimens for the time required to lose 25 percent strength for melamine-bonded white pine--11 days in this case. A second set of 20 specimens could then be exposed for either a shorter or longer time, so that the time required for a 25 percent strength loss would occur between the two selected testing times, using a linear relationship to connect data points. A second approach would be to expose 3 sets each of 20 specimens, with a set removed for test after 5, 15, and 35 days. Again the time required for a 25 percent strength loss would be determined by the linear regression line connecting the two data points between which the 25 percent level was found. Such an evaluation should be supplemented with a moist-heat exposure in a similar manner to determine if water-soluble material is present to catalyze hydrolytic reactions.

This method provides information of only a comparative nature. For instance, is the hydrolysis resistance of the new adhesive equivalent to that of solid wood and phenolic-bonded wood, or is it better or worse than a melamine type? Such a comparison relates hydrolysis resistance to that of benchmarks with which most people are familiar.

Data obtained by this suggested method should be reported as having been obtained at the aging temperature used. For example, the time for melamine-bonded white pine to lose 25 percent strength at 80° C during water soaking is one-third the time required for solid pine or phenolic-bonded time. As the method does not determine the temperature dependence of the hydrolysis reaction of the new adhesive, an extrapolation of these data to room temperature cannot be made. However, in the case of the melamine adhesive, where

this temperature dependence has been determined, such an extension can be estimated. It can be stated that at room temperature (20° C) melamine-bonded white pine will lose 25 percent strength under conditions most conducive to hydrolysis in only 3 percent of the time required for solid or phenolic-bonded pine. But that still represents a long time--about 13 years.

SUMMARY AND CONCLUSIONS

1. Wood, in the absence of degradation by fire, insects, and microorganisms, will last for centuries with only minor changes in mechanical properties, chemical composition, and morphology.

2. The changes in mechanical properties during natural aging are brought about by chemical reactions such as hydrolysis, oxidation, molecular rearrangements, chain cleavage, etc., which are all highly temperature dependent.

3. A loss of shear strength of 25 percent in wood represents a change which would require several centuries of natural aging in the absence of degradation by fire, insects, and microorganisms.

4. The evaluation of adhesive durability by accelerated aging can be carried out in such a way that direct comparisons can be made with wood's ability to resist the same degrading influences while losing the 25 percent shear strength representing centuries of natural aging.

5. Three different accelerated-aging conditions should be used to evaluate the different degrading influences of importance to natural aging--dry heat, moist heat, and water soaking.

6. Dry-heat and water-soak aging represent the extreme range of degrading influences, with the exception of acid catalysis effects on hydrolysis which require separate evaluation by moist-heat exposure.

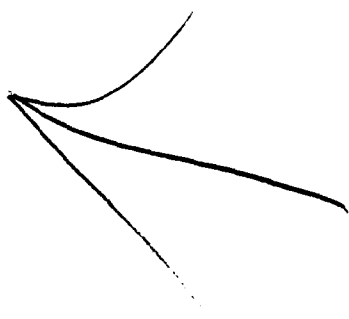
7. Measurements of strength loss on bonded joints for comparison with wood depend on species and should be determined with the species of interest.

8. The durability of a new adhesive can be compared with that of solid wood, and of phenolic-bonded wood or melamine-bonded wood under dry heat or water soaking, without excessive material or testing time requirements.

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AD P 002437

CORRELATION BETWEEN EXTERIOR EXPOSURE AND

AUTOMATIC BOIL TEST RESULTS¹

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ABSTRACT

ASTM D 3434 (The Automatic Boil Test) exposes specimens to 20 cycles boil/dry per day for 40 days. The evaluation of various adhesives by this system are compared to 11 years exterior exposure and several actual failure related applications. The ABT is shown to be a good method for evaluating adhesives and predicting durability. The exact relation between ABT cycles and exterior exposure varies somewhat depending on adhesive type; but (41+6) cycles = 1 year is a good approximation for better wood adhesives.

INTRODUCTION

Many new adhesive formulations and types are being considered for use by the wood industry. Large numbers of wood adhesives and new uses envisioned require an accelerated method predicting exterior durability of the bond. This method must not only work but be acceptable to federal and local regulatory and code agencies.

To date, no entirely satisfactory method exists for correlating accelerated test data with actual long-term exterior exposure data. The desired technique would enable us to use an accelerated test method to predict actual exterior exposure performance.

Several organizations are proposing different types of accelerated aging test methods as being the most suitable; some of these are being discussed at this symposium. This discussion presents a proposed model for using Automatic Boil Test data to compare with experience and exterior exposure data.

In most cases I will not go into detail by including the detailed test data but rely instead on comparing averages.

41+02-6 AUTOMATIC BOIL TEST

The Automatic Boil Test is an approved ASTM procedure; ASTM D 3434, Standard Recommended Practice for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet-Use Wood Adhesives.

The test specimens are glued with the recommended processing conditions and the wood species desired, tested for 40 days in the Automatic Boil Test and then based on performance and correlation equations, a prediction is made on long-term durability. To develop this technique and the required equations, data from the accelerated aging test method must be correlated with exterior exposure data for identical specimens. The relationship between the accelerated aging data and the exterior exposure data can then be developed. When a new adhesive is developed, it is only necessary to conduct the accelerated aging portion of this study and then predict the exterior durability.

In the mid 1960s, SCATA (the Steering Committee for Accelerated Testing of Adhesives) evaluated several accelerated

¹Paper presented at the "Wood Adhesives - Research, Application and Needs" Symposium, Madison, Wisc., Sept. 23-25, 1980.

multiple-cycle testing methods (Northcott - 1966). This was primarily done with the cooperation of the Canadian Forest Products Laboratory, Oregon State University and the Weyerhaeuser Company. The test which later became the Automatic Boil Test most nearly ranked the ten adhesive types evaluated as would be expected for long-term durability. The Automatic Boil Test consists of the following cycles:

Cycle 1: Ten minutes in boiling water.

Cycle 2 and beyond:

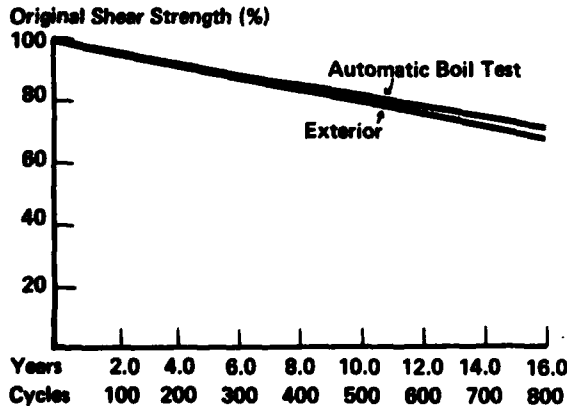
- a. Four minutes exposed to forced-circulation room temperature air;
- b. Fifty-seven minutes exposed to forced-circulation 106°C air; and
- c. Ten minutes in boiling water.

The above cyclic procedure gives 20 cycles per day. Tests are carried out through 40 days giving a total of 800 cycles. Samples are pulled at periodic intervals so a rate of performance change curve can be drawn. This curve can then be used to compare performance with other adhesives and with solid wood. The specimens are soaked, prior to testing, from one hour to three days in room temperature water and tested wet, except the 0 value which is tested dry.

TEST SPECIMENS

Specimen design plays an important part in testing glue line durability.

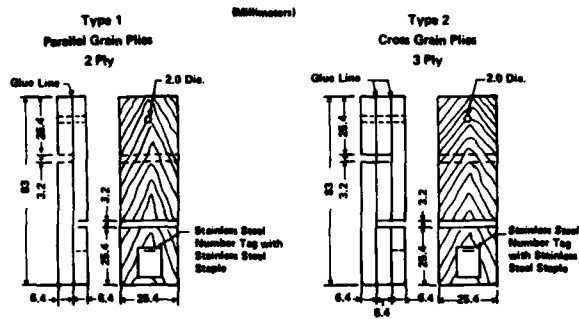
Figure 1
LOSS OF WOOD STRENGTH DURING ACCELERATED AGING AND EXTERIOR EXPOSURE - DOUGLAS FIR



Ideally, the wood itself should show no signs of strength loss enabling all of the reduction in performance to be attributed to reduction in glue line durability. It is impossible to design a specimen which does not experience loss of wood strength during accelerated testing. There is also some loss of wood performance in actual real world exposure of glue line and wood combinations (see fig. 1).

Work done by M. D. Strickler of Washington State University (Strickler - 1968) and ourselves has developed what we feel is the best specimen design. Figure 2 shows the selected thin specimens with 25.4 x 25.4 mm test glue line area.

Figure 2
TEST SPECIMENS



Note: All Laminations Made with 6.4 mm Lumber Thickness

It is felt that this type of specimen using lumber rather than veneer, as would normally be expected with this specimen configuration, gives a specimen which shows the optimum stress changes between boiling and drying and yet produces very little checking in the wood.

EXTERIOR EXPOSURE SITES

Since the behavior of the adhesive is somewhat dependent on the climatic conditions at the use locations, the test method must include this variable for exterior exposure. Such things as radiation, heat, cold, moisture from both rain and humidity and microorganisms should be considered. Difficulty occurs in trying to conduct exposure tests for all of the possible combinations. The following four sites were selected as including the most aspects of climate.

Site	Comment	
	Winter	Summer
Electric Mills, MS	mild,rain	hot,humid
Modesto, CA	warm,dry	hot,dry
Seattle, WA	mild,wet	mild,wet
Albert Lea, MN	cold,snow	mild,humid

The test racks used to hold the specimens are shown in figure 3.

Figure 3



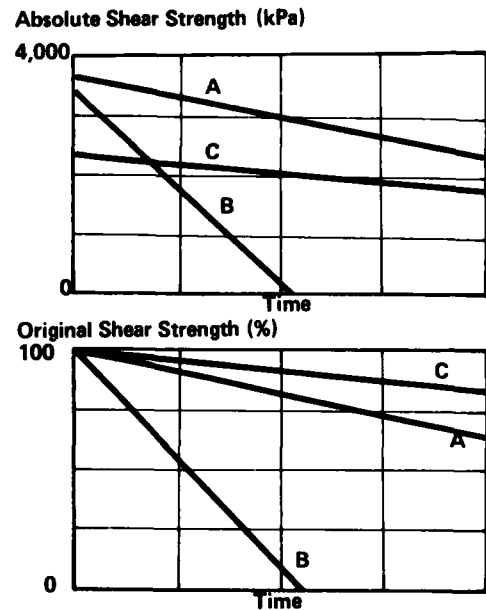
Because the data for Albert Lea is limited, all comments for exterior exposure are based on Electric Mills, Modesto and Seattle data unless otherwise noted.

EQUATION COMMENTS

One of the first steps in correlating the data is determining the equation (or equations) that best fit the data. Changes in shear strength for both Automatic Boil Test and exterior exposure are much greater and more statistically significant than those for wood failure. Most of the discussion to follow is aimed at shear strength.

I don't really have room in this paper to discuss the mathematics used in developing the reasons for selecting the final equations other than to say that data from about 30 adhesives for 800 Automatic Boil Test cycles and eleven-year exterior exposure were used. Also, in order to compare the adhesives, it is easier if they all start with the same initial strength. This is done by converting all shear strengths to percent of original shear strength. The starting point for each shear strength is then 100. All changes for each adhesive can be compared with this one point (see fig. 4).

Figure 4
CONVERTING DATA TO PERCENT OF ORIGINAL



This, of course, means I am comparing rate of change and not absolute strength. Table 1 provides a statistical way of comparing equation reliability.

Table 1.--Index of Determination for Several Equations

Equation	Index of Determination ¹	
	ABT Data	Exterior Exposure Data
$y = A+Bx$	0.8185 _{+0.0928}	0.7216 _{+0.2117}
$y = Ae^{B/x}$	0.3278	
$y = Ae^{Bx}$	0.9352 _{+0.0537}	0.7670 _{+0.2203}
$y = Ax^B$	0.6580	-
$y = A+B/x$	0.4023	-
$y = 1/(A+Bx)$	0.8973 _{+0.0771}	0.7787 _{+0.2053}
$y = x/(A+Bx)$	0.2670	-
$y = A+B\sqrt{x}$	0.7808	-
$y = AB^x$	0.8000	-

¹ (the higher the value the better the curve fit)

Normally, we have found two equations are required for the Automatic Boil Test data.

1. $y=C+Dx$: $0 < x < 20$, x is in cycles, y is in percent of original shear strength.
2. $y=Ae^{Bx}$, $x > 20$. The two equation approach is referred to as the EMP method.

For exterior data, one equation can be used for all data, $Y=Ae^{Bx}$; x is in years exposure.

For simplifying the discussion to follow, I have often used the $y=Ae^{Bx}$ equation for all Automatic Boil Test data (MJP method). When talking in generalities, this is accurate enough but for more detailed work, the EMP two equation method should be used. For ranking of adhesives and relative durability comments, the MJP method ease of use is worth the slight loss in accuracy.

ADHESIVES SELECTED FOR USE

The following ten adhesive types are being evaluated in this study. They will hereafter be referred to by the type code reference.

Type Code	Type	Com-ponents examined	Total No. of this type ¹	Total No. of this type Reported here ²
PRF	Phenol resorcinol formaldehyde	2	13	3
PF	Phenol formaldehyde-heat cured	1	1	1
MF	Melamine formaldehyde	2	2	1
MUF	Melamine urea formaldehyde 60/40	2	2	1
C	Casein	2	2	1
UF	Urea formaldehyde	2	2	1
SCE	Slow Cure Epoxy (1 hr.)	2	2	1
FCE	Fast Cure Epoxy (5 min.)	2	2	1
U1	Urethane	1	2	1
U2	Urethane	2	2	2
SW	Solid Wood	-	-	-

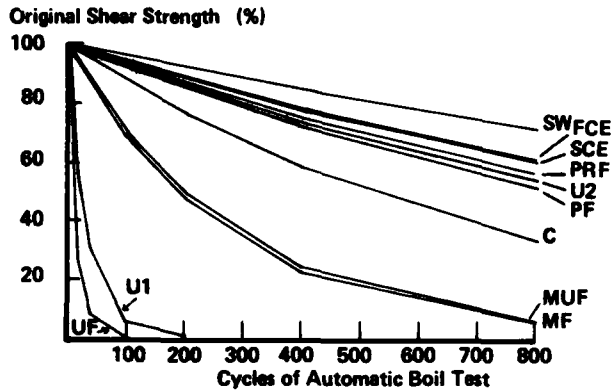
¹All are standard "good" adhesives used for various wood laminating applications.

²Reason for not using all available data is that adhesives reported have same amount of ABT and exterior exposure data. Those not used have some data missing, but appear to have similar performance.

AUTOMATIC BOIL TEST DATA

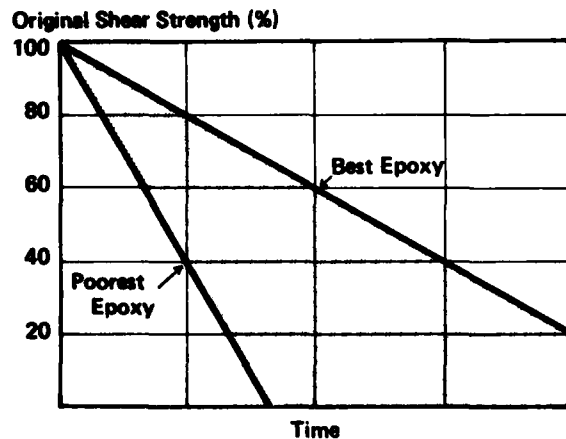
The Automatic Boil Test data tends to break the adhesive types down as shown in figure 5.

Figure 5
TEN ADHESIVE TYPE COMPARISON, ABT



When placing several tested adhesives into one type, the average may or may not be representative of the class. For example, there are several epoxies which could give a range as shown in figure 6 from the best to the poorest.

Figure 6
PERFORMANCE OF DIFFERENT EPOXIES



In the adhesives placed on the test fences, I have, therefore, tried to use only those recommended as exterior wood adhesives by the manufacturer. Since some prescreening

was done, what I have shown represents optimum performance for adhesive types when used on wood. The epoxies selected for evaluation turned out to be excellent but there are epoxies not designed for wood gluing which would have a poor performance in our test program.

As shown in figure 1, solid wood will show a loss of strength through the 800 cycles. It is assumed that for an adhesive to have full exterior durability with no failure, it should come quite close in performance to the wood curve. PRF, PF, U2, SCE and FCE are the only ones which approach this. Many adhesives which are being used for exterior applications fall in ranges considerably below this line so this assumption that adhesives should be at the level of the wood curve is somewhat arbitrary. But, since we do have adhesives that approach the wood curve, I am saying this should be our goal. This will be discussed again later when ABT data is compared with exterior exposure data.

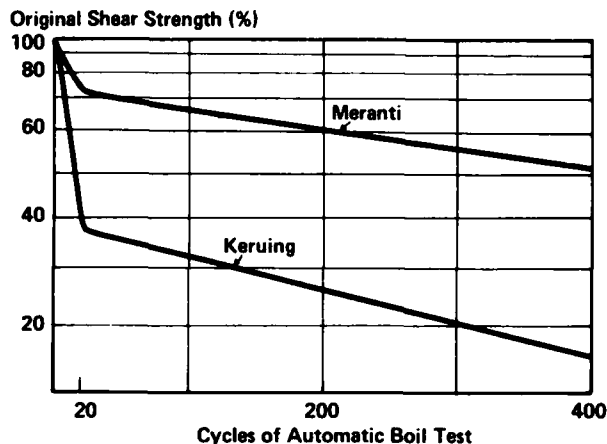
Without talking about how this data correlates with exterior exposure, knowledge of adhesives used in the wood industry would tend to show that these ratings are what would basically be expected. We can, therefore, start using some of this data to evaluate processes and products being made today. The 75% of original shear strength solid wood figure after 800 cycles can be used as a guideline to compare some data.

Many products have been made which pass standard production quality control tests but then fail quite rapidly in service. Five examples will be discussed briefly. Since only a few curves are needed on each graph, I have used the EMP method.

1. Keruing and meranti veneer are being used by one manufacturer to make exterior grades of plywood siding. The examples we tested used PF. Both materials after production turned out equally satisfactory in vacuum soak and APA cyclic boil tests.

The keruing plywood begins to delaminate after several years of exterior exposure. The meranti does not. We submitted specimens to the Automatic Boil Test and obtained the results shown in figure 7.

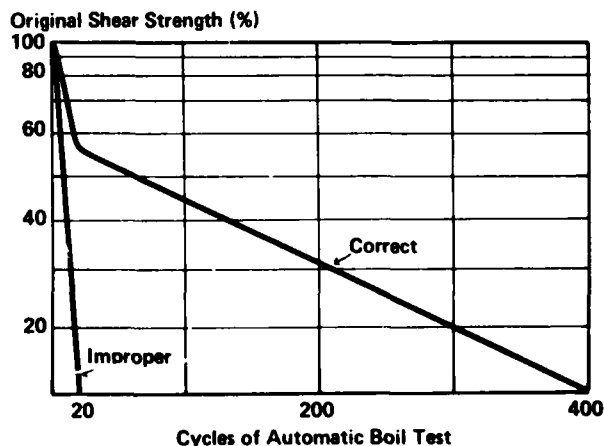
Figure 7
ABT DATA FOR KERUING AND MERANTI PLYWOOD



As can be seen from the figure, the keruing failed very rapidly in the Automatic Boil Test while the meranti performed at an acceptable level.

2. Another manufacturer had a beam problem, which involved the use of an improper gluing and process combination, which passed the quality control requirements in the product standard. The adhesive in this application was casein. Again, in service, the beams begin to delaminate after three to five years. Controls were tested against the bad gluelines (fig. 8).

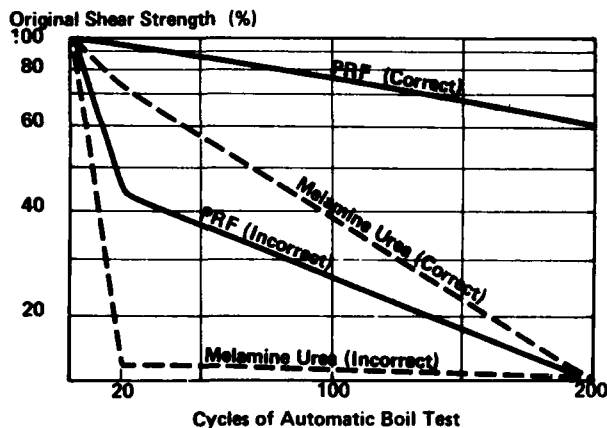
Figure 8
ABT DATA FOR CASEIN GLUED BEAMS



In this case, even the control casein would not meet full exterior durability requirements (match solid wood).

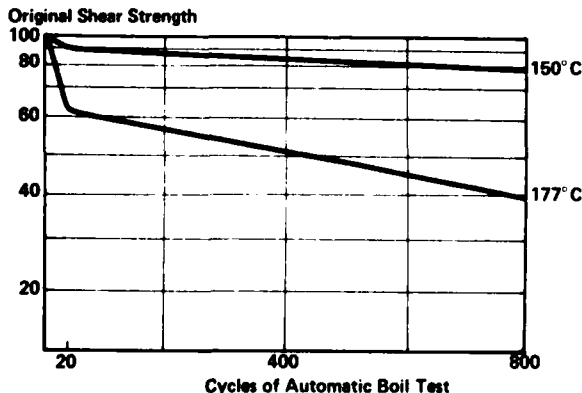
3. Another manufacturer's beam problem also involved the use of the wrong process. Both PRF and MUF glues were involved. Again the gluelines were tested after production with the required quality control methods. The results were satisfactory. These beams failed almost immediately in service, some during erection. Controls were tested against the poor gluelines with the results shown in figure 9.

Figure 9
ABT DATA FOR INCORRECT BEAM GLUING PROCESS



4. As part of determining the optimum processing conditions on a preheat line using a PRF adhesive, samples from different trials were tested with the Automatic Boil Test method. Figure 10 shows an example of durability performance with two different preheat temperatures. The 150°C process temperature appears to provide better durability.

Figure 10
ABT DATA FOR PROCESS OPTIMIZATION

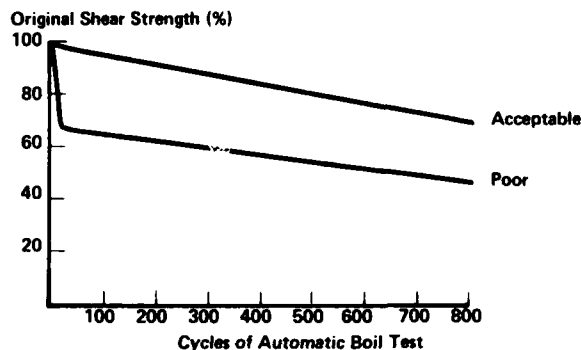


5. An obvious use of the ABT is to screen new adhesives developed in the laboratory.

Adhesive	Dry Shear		AITC	Strength
	SS	WF	110 Delam %	After 800 Cycles ABT % of Orig.
A	7790 kPa	91	1.3	73
B	8120 kPa	93	1.8	53

Figure 11 shows that the two PRF adhesives which passed dry shear and AITC delam tests gave different ABT results. Based on this, we would not consider adhesive B.

Figure 11
LABORATORY SCREENING OF PRF ADHESIVES USING ABT



These five examples show that the Automatic Boil Test is quite a good indicator for evaluating adhesives, predicting improper processing or evaluating other problems which might not show up in standard quality control procedures.

EXTERIOR EXPOSURE DATA

The exterior exposure portion of this work started in 1969. The latest data was obtained in 1980, which means we have data for up to 11 years. The original adhesive exposure involved only ten adhesive systems; about 40 others have been added at periodic intervals since. This means that less data is available for some adhesives than others. For the exterior data, I have shown plots to 16 years, but remember, all data past 11 years is extrapolated.

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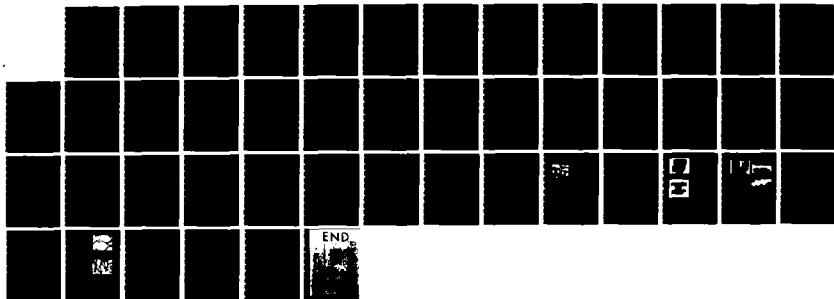
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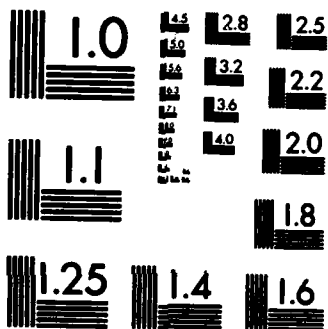
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Unless otherwise noted, all exterior data is the average of data obtained from Electric Mills, MS, Modesto, CA, and Seattle, WA.

DOUGLAS-FIR VERSUS SOUTHERN PINE

Using the six adhesive types (PRF, SCE, FCE, U1, U2, MUF) for which we have the most exterior data available on both Douglas-fir and southern pine and averaging the results, the following comparison was made for specimens made on Douglas-fir and southern pine.

Table 2.--Douglas-fir Versus Southern Pine

Adhesive	Exterior Exposure (11-Year Value)					
	SS			WF		
	DF	SP	SP/DF	DF	SP	SP/DF
Avg. of 6	64*	34*	0.53	89*	78*	0.88
Solid Wood	89*	40*	0.45	100*	100*	--
Ratio Avg. of 6/Solid Wood	0.72	0.85	--	--	--	--
Adhesive	ABT (800 Cycle Value)					
	SS			WF		
	DF	SP	SP/DF	DF	SP	SP/DF
Avg. of 6	43*	28*	0.65	73*	46*	0.63
Solid Wood	70*	49*	0.70	100*	100*	--
Ratio Avg. of 6/Solid Wood	0.61	0.57	--	--	--	--
Adhesive	Total Average (Ext. and ABT)					
	DF	SP	SP/DF			
	Avg. of 6	67*	47*	0.70		
Solid Wood	80*	45*	0.56			

*Data percent of original value

In all cases, the southern pine values are lower than the Douglas-fir.

The ABT SS data shows (approximately) that the adhesives when used on DF or SP would be ranked the same (based on ratio of the average of the six adhesives to solid wood). Unfortunately, the exterior comparison does not. This could be expected since the glueline durability depends upon the substrate and adhesive/substrate interface as well as the adhesive composition. The rest of the data in this paper deal only with Douglas-fir.

THREE-PLY VERSUS TWO-PLY

We also have data which compares the two-ply parallel grain layups with the three-ply cross grain layups for exterior exposure and Automatic Boil Test.

Table 3.--Three Ply Versus Two Ply

Adhesive	Exterior Exposure (11-Year Value)			
	SS		WF	
	2 Ply	3 Ply	2 Ply	3 Ply
Avg. of 6	62*	37*	88*	78*
Ratio $\frac{3 \text{ ply}}{2 \text{ ply}}$	0.60		0.89	
Adhesive	ABT (800 Cycle Value)			
	SS		WF	
	2 Ply	3 Ply	2 Ply	3 Ply
Avg. of 6	45*	34*	57*	48*
Ratio $\frac{3 \text{ ply}}{2 \text{ ply}}$	0.76		0.84	
Adhesive	Total Average			
	2 Ply	3 Ply		
	Avg. of 6	63*	49*	
Ratio $\frac{3 \text{ ply}}{2 \text{ ply}}$	0.78			

*Figures percent of original value.

Table 3 shows three-ply to be about 20-40% lower in performance level. Probably the same ranking of adhesives would occur with 2-ply or 3-ply specimens. All the following analysis deals only with the 2-ply parallel grain specimens.

GRAIN EFFECT

We also made layups with vertical/vertical grain, flat/vertical grain and flat/flat grain combinations. This is summarized below.

Table 4.—Vertical Versus Flat Grain (DF)
(Adhesives Types Used: PRF, U1, U2, SCE, FCE, C)

Adhesive	Exterior Exposure (11-Year Value)					
	SS			WF		
	VV	VF	FF	VV	VF	FF
Avg. of 6	66*	57	67	78	89	93

Adhesive	ABT (800 Cycle Value)					
	SS			WF		
	VV	VF	FF	VV	VF	FF
Avg. of 6	45	50	45	58	62	52

Adhesive	Total Average		
	VV	VF	FF
Avg. of 6	62	79	78

*All figures percent of original value.

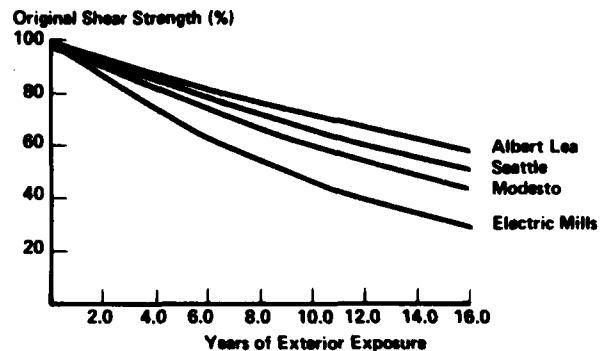
These data show that a similar rate of change occurs for vertical, flat or vertical-flat grain layups, even though absolute value may show different results. Based on this opinion, all further analysis is based on using VV, VF and FF data interchangeably after conversion to percent of original. Later additions to this study were made with only the FF layup.

EXTERIOR EXPOSURE

Figure 12 shows the difference in performance using the PRF-type adhesive for the four sites which have samples.

The Albert Lea data are for eight years only, so the graph beyond that point is extrapolated; the other sites are extrapolated beyond 11 years. The ranking shows that Albert Lea samples are retaining their performance the best; Seattle next; Modesto next, with Electric Mills showing the greatest deterioration. Electric Mills has shown the greatest deterioration right from the start. This was expected due to the hot, humid climate. When I analyzed the data five years ago at the six-year time point, Modesto had shown up as having the least loss in performance. I was surprised this hot, dry climate condition is no longer showing the least deterioration after 11 years.

Figure 12
PRF FOUR SITE COMPARISON, EXTERIOR

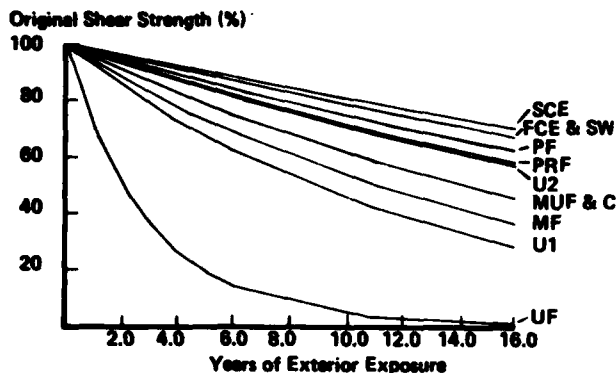


As mentioned previously, not only is the Albert Lea data based on fewer years but not as many adhesive systems are being tested. For this reason the following comments on exterior exposure do not use Albert Lea data; all are based on the three-site average of Seattle, Modesto and Electric Mills. Assuming all adhesive types follow the same pattern as the PRF data in figure 12, then Seattle and Modesto are performing slightly above average and Electric Mills considerably below.

Since my test specimens are small and exposed directly to the weather, the strength loss reported is much greater than would be experienced by an actual laminated beam.

Figure 13 shows how the 10 adhesive types are performing in exterior exposure conditions for the three-site average. (For fig. 13, only the three PRF's mentioned on Page 4, Footnote 2 are used while for fig. 12, nine systems which have data available were used.)

Figure 13
TEN ADHESIVE TYPE COMPARISON, EXTERIOR



Since we now have curves for both ABT and exterior exposure, we can compare rankings. Also, I asked six Weyerhaeuser Company "experts" in wood gluing to rank the 10 adhesive types based on their experience.

The following results were obtained:

RANKING OF ADHESIVE DURABILITY
(1 best - 10 poorest)

Adhesive Type	By Weyerhaeuser Company Experience		By Exterior Exposure Test
	By ABT	By ABT	By ABT
PRF	1	3	4
PF	2	5	3
SCE	3	2	1
MF	4	8	8
U2	5	4	5
MUF	6	7	6
FCE	7	1	2
U1	8	9	9
C	9	6	7
UF	10	10	10

You can see that some of the curves are very close together and the exact order might not be reproducible. Appendix A shows statistical accuracy of data used.

A surprise is how well the carefully selected epoxies have performed. These do represent epoxies which were formulated for exterior wood gluing, but still I had not expected them to beat out PF and PRF in both exterior exposure and ABT.

Figures 5 and 13 (actually the data from which they were derived) provides us with a way of comparing ABT with exterior exposure.

Table 5 answers a question I have been asked several times: How many ABT cycles are equivalent to one year's exterior exposure?

Table 5.--Comparing ABT/Exterior Exposure

ABT Ranking	Adhesive Type	ABT Cycles/ Years Exposure
1	FCE	38.3
2	SCE	36.0
3	PRF	44.6
4	U2	49.3
5	PF	36.5
6	C	46.3
7	MUF	14.1
8	MF	17.1
9	U1	2.7
10	UF	5.1
	SW	57.8

For adhesive types 1-5, considered to be acceptable exterior wood adhesives, the cycles/year value is 40.9 ± 5.8 cycles/year. This is not saying that running 41 cycles in the ABT will predict the first year's durability. It only represents an average if the test is carried through 800 cycles. Since not all adhesive types do give this value, care must be used in interpretation. Solid wood has the highest value of all which means the ABT cycles do less damage to wood when compared to the adhesives than exterior exposure. The poorer adhesives MUF, MF, U1 and UF show a relatively rapid failure in ABT when compared to exterior exposure.

As mentioned during the previous discussion, much more data is available than has been analyzed, and I have relied on averages more than possibly I should. As time permits, I will refine the interpretations and work the data up to rank the adhesives on southern pine and rank them based on wood failure.

SUMMARY

In summary, I would again emphasize that the ABT is the best accelerated aging method for predicting long term durability of wood adhesives. For good exterior adhesives 40.9 ± 5.8 cycles in the ABT is equivalent to one year (average for three sites) exterior exposure. Poorer adhesives require fewer ABT cycles to equal one year exterior exposure.

The adhesives divide into three groups for both ABT and exterior exposure. The best group comprises SCE, FCE, PRF, PF and U2. A middle performance group is MUF, MF and C. The U1 and the UF are in the poor performing group. The "best" adhesives in each of these types would be expected to always fall in this three level grouping. The exact order i.e., SCE, FCE, PRF, U2 and PF could probably not be reproduced.

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Northcott, P. L. and Hancock, W. V., "Accelerated Tests for Deterioration of Adhesive Bonds in Plywood", Durability of Adhesive Joints, ASTM STP 401, Am. Soc. Testing Mats, 1966, p. 62.

Strickler, M. D., "Specimen Designs for Accelerated Tests" - FPJ Sept. 68, p. 84.

Appendix A.--Statistical Reliability of Data Used in Figures 5 and 13.

Adhesive Type	Index of Determination for ABT Data (Fig. 5)	Index of Determination for Exterior Exposure Data (Fig. 13)
PRF	0.930	0.980
SCE	0.975	0.902
FCE	0.980	0.734
U2	0.850	0.919
U1	0.998	0.920
PF	0.925	0.514
MUF	0.841	0.620
MF	0.974	0.860
UF	0.955	0.984
C	0.969	0.716
SW	0.889	0.287

RECENT RESULTS ON FRACTURE TOUGHNESS OF BONDED WOOD¹

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INTRODUCTION

The measurement of fracture toughness in bonded wood specimens has been shown to be sensitive to various bonding variables in the preparation of adhesive joints (4,5,8,9).² The results are similar to those obtained involving metal and glass adherends (1,2,6,7). The behavior with wood adherends is more complex due to the orthotropic nature of wood. This complexity has especially been shown in grain angle studies both with phenol-resorcinol and epoxy adhesives.

Recently, fracture toughness measurements have been used to characterize adhesive properties in a large variety of systems involving ceramic, metal, and wood adherends. These measurements require well-controlled specimens so that only one major flaw is propagated. This has advantages in reducing scatter of data which can be considerable for wood adherends using other destructive test methods. Extrapolation of this type of data for long term durability properties then becomes possible. Also the evaluation of a variety of adhesives can be more accurately measured.

By designing the specimens properly, the stored energy of a loaded specimen needed to propagate a large crack can be directly obtained from simple load-displacement measurements. The stored energy needed to initiate the crack propagation is usually referred to as the fracture toughness, strain energy release rate, or simply the fracture energy for crack initiation. The larger this value the more difficult it is to propagate a crack and hence the specimen is "tougher."

¹Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

²Underlined numbers in parentheses refer to Literature Cited at end of this paper.

A variety of specimen geometries can be employed to measure fracture toughness. This study reports results on height tapered double cantilever beam specimens (HTDCB) or width tapered double cantilever beam specimens (WTDCB) involving maple and birch adherends using phenolic-resorcinol and epoxy adhesives. The measurement of crack length is not necessary for these two types of specimen geometries which considerably simplifies the data measurement as mentioned before. Also these specimens model cleavage fracture processes, often referred to as mode I failures, which are largely observed in practice for structural adhesives.

This paper summarizes the influence of the following bonding variables on fracture toughness:

1. Bondline thickness,
2. Wood grain angle with respect to the plane of the bondline,
3. Wood surface roughness,
4. Wood moisture content,
5. Aging of wood surface,
6. Adhesive cure time,
7. Initial adhesive viscosity, and
8. Effect of adhesive fillers.

Most of the data is from HTDCB studies, but some recent WTDCB results (which are more applicable specimens for laminate studies) are also reported.

SPECIMEN PREPARATION

The details of specimen preparation has been published for the HTDCB (4,5,9), and details for the WTDCB are also available (8). In order to correlate the fracture toughness accurately with all the variables of bonding, strict control of the bonding procedures and wood adherends is absolutely necessary. Although specimen preparation may be more difficult, the rewards in reducing data scatter more than offset any problems of specimen preparation.

WIDTH TAPERED DOUBLE
CANTILEVER BEAM SPECIMENS

HEIGHT TAPERED DOUBLE
CANTILEVER BEAM SPECIMENS

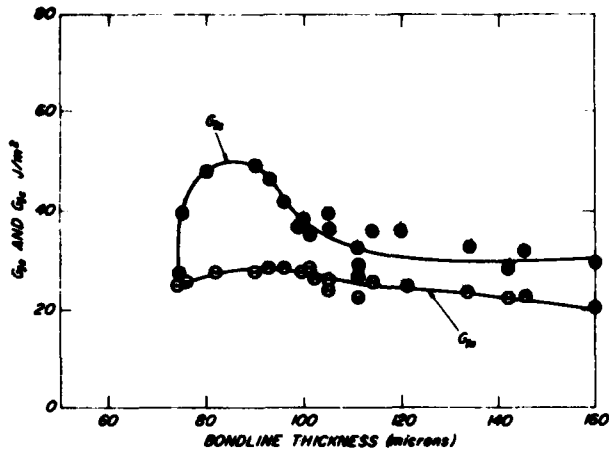


Figure 1.--Fracture toughness, G_{Ic} , of specimens at different bondline thickness. (Phenol-resorcinol adhesive with maple adherends at 20° grain angle.)

(M 146 817)

BONDLINE THICKNESS (BLT) EFFECTS

It was quickly found that bondline thickness influences fracture toughness particularly at small thicknesses. An example of this is shown in figure 1. Note the maximum near 80 microns and the nearly constant value beyond 100 microns. This behavior has been reported for other adhesive systems and is thought to be influenced by the "plastic zone" size of the propagating crack (2). It is important to note that all other bonding variables were fixed. For other bonding variable changes, the BLT was kept greater than 100 microns to insure this effect was minimized. The value of G_{Ia} is the maximum stored energy

in the specimen which arrests a propagating crack. The behavior of G_{Ia} is less under-

stood and is sensitive not only to bonding variables and specimen but also to the inertia of the testing machine and fixtures. However, the difference of $G_{Ic} - G_{Ia} = \Delta G_I$ is a measure

of the "brittleness" of the adhesive system (4) and can be used to correlate with adhesive cure state which will be mentioned later. A small ΔG_I indicates a stable, tearing crack propagation while a large ΔG_I indicates an unstable crack-jump and arrest phenomena.

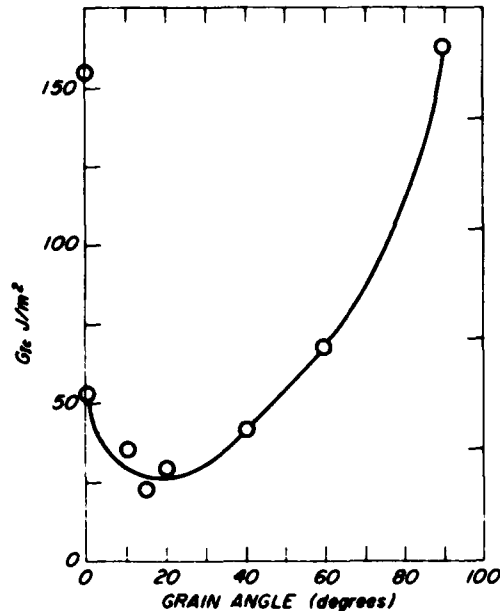


Figure 2.--Grain angle influence on fracture toughness. High values at 90° indicate crack blunting. The curious high values observed for 0° indicate crack propagation into the wood beams rather than crack propagation in the bondline region. Hence laminates (0° bonding) could give erratic results depending on the crack location.

(M 146 807)

GRAIN ANGLE AND SURFACE ROUGHNESS EFFECTS

These two bonding variables are considered together since both can affect the blunting of the crack. Figures 2 and 3 show these effects (4,9). Grain angles of 90° (end grain gluing) and large roughnesses involving back and forth reciprocating hand sanding, give large values of G_{Ic} . It is thought that both proce-

dures achieve the greatest possibility to blunt the propagating cracks and hence increase G_{Ic}

by producing weak planes oriented perpendicular to the bondline. As the crack proceeds it causes these weak planes (either grain boundaries or prefailed interfaces) to separate, thus blunting the crack front, as shown in figure 4. This phenomena has recently been observed with bonded specimens whose surfaces were slotted perpendicular to the bondline

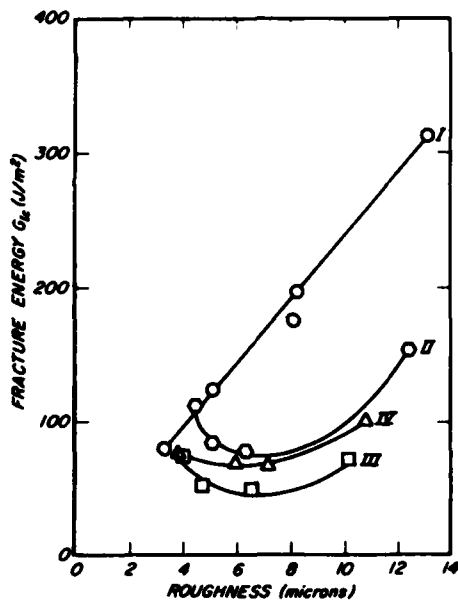


Figure 3.--Increasing wood surface roughness increases G_{Ic} . Hand-sanded surfaces, I, give highest values due to prefailed interfaces. II-IV are machine belt sanding data. Perpendicular abraded to crack propagation direction surfaces, II; parallel abraded surfaces, III; and aged parallel abraded surfaces, IV.

(M 146 813)

prior to bonding and filled with Teflon to prevent glue penetration.³

MOISTURE CONTENT OF WOOD AND WOOD AGING

The fracture toughness is quite sensitive to the wood surface chemistry. This is evident in moisture effects (fig. 5). Large amounts of moisture inhibit cure or give bubbles, thus decreasing G_{Ic} . It must be noted

that modulus changes in the wood have been taken into account for the G_{Ic} calculations.

³B. H. River, USDA Forest Products Laboratory, Madison, Wis., (private communication, 1980).

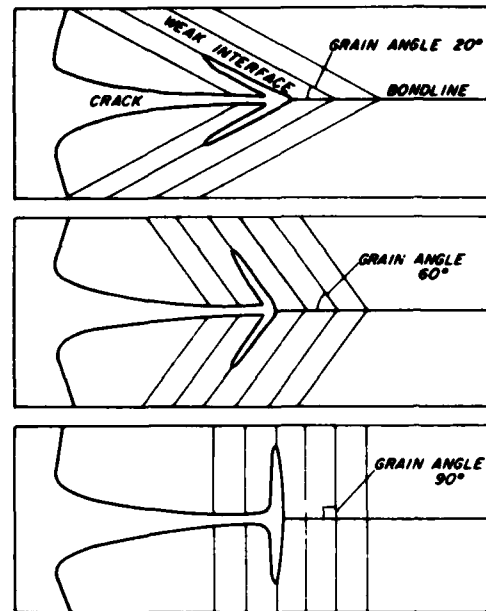


Figure 4.--Geometry of crack blunting for different grain angles of bonding. The 90° grain angle gives the greatest blunting of the propagating crack. Sanding will also prefail interfaces perpendicular to crack propagation and enhance G_{Ic} .

(M 148 126)

The interesting effect of aged wood surfaces is shown in figure 6. For aged surfaces the G_{Ic} is lower than freshly prepared jointed surfaces. This effect can also be seen in oven-treated samples at high temperatures. It is thought surface inactivation and non-wettability play a role in influencing the G_{Ic} (3).

ADHESIVE CURE TIME AND VISCOSITY

The behavior of G_{Ic} and G_{Ia} with cure time for adhesive bonded wood (maple) parallels that of other substrates and indicates the degree of cure of the system. Figure 7 shows the effect of cure time for maple adherends bonded with phenol-resorcinol adhesive at 85° C. Note the increase of ΔG_{Ic} to a constant value with a simultaneous maximum of G_{Ic} and G_{Ia} . These data show the importance

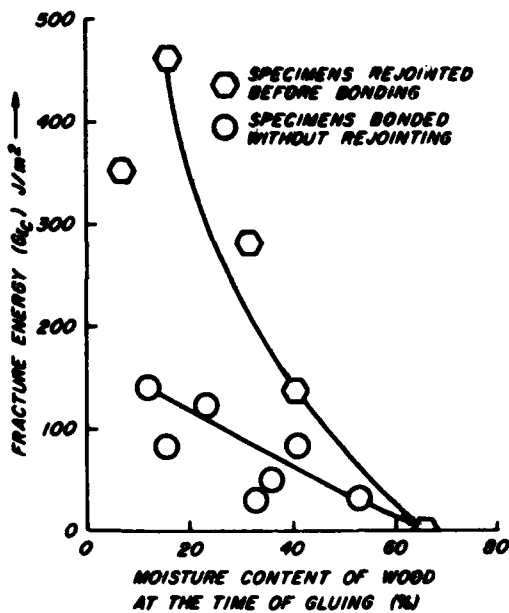


Figure 5.-- G_{Ic} of phenol-resorcinol-bonded maple beams at different initial moisture contents. Specimens were glued at the elevated temperature (80°C) for one-half hour and equilibrated to room temperature and humidity (40 pct).

(M 149 457)

of kinetics on adhesive properties and gives important information for durability testing. This will be covered later.

The initial viscosity of the adhesive can play a major role on fracture toughness. Low initial viscosities can give a glue starved bondline, while high initial viscosities do not give enough glue penetration. The result is that a maximum G_{Ic} is observed with initial

adhesive viscosity (3). This corresponds to what is observed by other test methods.

EFFECT OF ADHESIVE FILLER

The influence of fillers on adhesive performance is complex but can be evaluated using fracture toughness methods. As would be expected, those fillers whose surfaces strongly

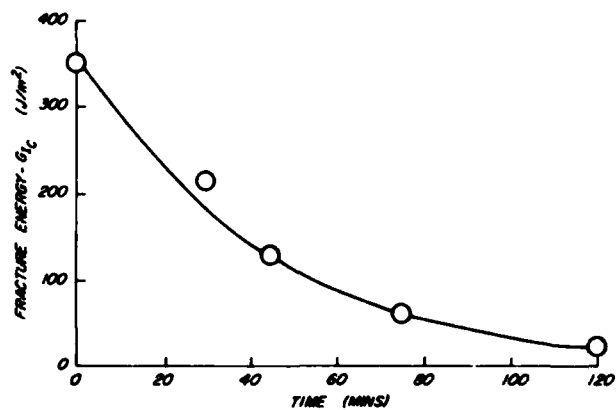


Figure 6.--The effects of drying at 250°C on G_{Ic} . The decrease is due to surface inactivation.

(M 149 456)

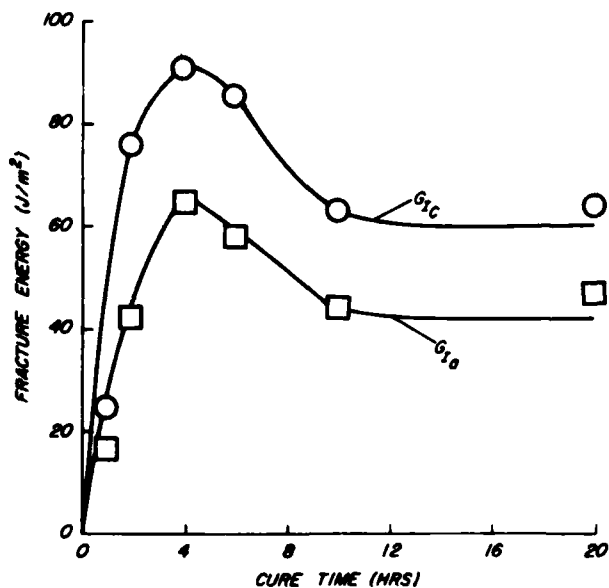


Figure 7.--Cure time (at 85°C) effects on G_{Ic} . Note maximum of G_{Ic} and G_{Ia} coincide.

This behavior is similar to bulk resin fracture toughness properties.

(M 146 908)

interact with the adhesive (viz. phenol-resorcinol with wood flour or walnut shell flour) give high G_{Ic} values. Those substrates

which do not chemically bond well give lower G_{Ic} values (viz. mica and phenol-formaldehyde)

(3). It must be emphasized, however, that filler particle size and geometry have a large influence on G_{I_c} . Also preferential migration

of the filler in the bondline can considerably influence the crack direction and therefore G_{I_c} .

(3). Much more research is needed to establish the effects of fillers on fracture toughness of adhesively bonded structures in order to predict behavior.

FRACTURE TOUGHNESS FOR WTDCB BEAMS

All the data presented have been for HTDCB specimens. It was thought that for ease of bonding and for modeling laminates that WTDCB geometries would be desirable. Similar theoretical criteria are involved, and investigations with maple and birch beams have been initiated. Details of specimen geometry and bonding can be found elsewhere (8).

The most startling data found with the WTDCB are the height effects of the beams. If beams of small height are used, very large values of G_{I_c} are observed while large height specimens give small values of G_{I_c} (fig. 8).

What is important to note is that at large heights G_{I_c} values are consistent with G_{I_c} values of WTDCB specimens. These data indicate that small height specimens (i.e., thin laminates) have considerable plastic flow at the crack tip due to very large stress gradients at the crack tip (8). This necessitates

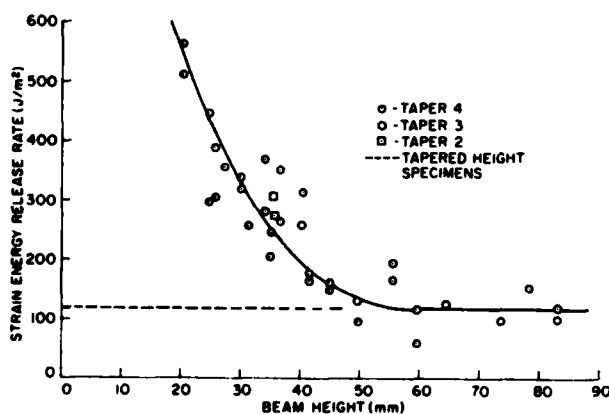


Figure 8.--The influence of specimen height on G_{I_c} for WTDCB specimens. Note the constant value of G_{I_c} at large heights corresponds with HTDCB values.

(M 148 510)

that if adhesives are to be evaluated, then large height beams must be used since in small height beams the dominant energy dissipation is wood plastic flow.

FRACTURE TOUGHNESS AND DURABILITY MEASUREMENTS

As was mentioned before, kinetics of cure have an important influence on G_{I_c} and G_{I_a} .

Figure 9 shows data on a wood-filled phenol-resorcinol adhesive and maple beam adherends. If the temperature of cure was lowered, the maximum of G_{I_c} and G_{I_a} would be delayed to longer times.

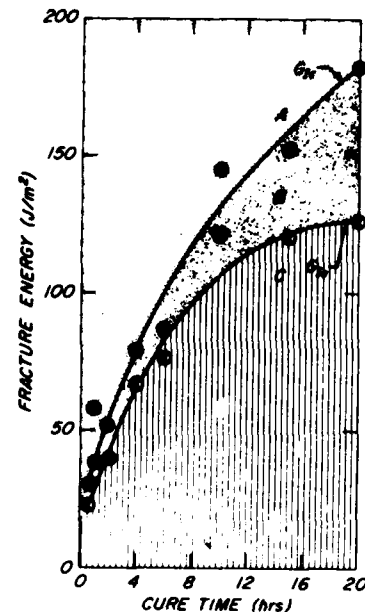


Figure 9.--The cure time fracture characteristics of a walnut shell flour filled phenol-resorcinol adhesive with maple beams. Behavior is similar to figure 7 except cure temperature is 70° C and maximum in G_{I_c} has not been reached even after 20 hours of cure.

(M 146 810)

Let us suppose a specimen is dead loaded so the stored energy can be controlled to whatever we wish. If we dead load it with a very large load, we might be in region A. Catastrophic failure would ensue. If lower loads were used, we might be in region B, an unstable region, where external environmental variations such as moisture changes, wind

loads, shock loads, etc., might propagate cracks. If, however, we load to region C, the specimen would be stable and no cracks would grow. Hence the structure would still remain intact.

Recent dead-load experiments on epoxy bonded specimens show this behavior and give promise for accurate durability assessment using a fracture toughness approach. Of course one must remember that the maximum in G_{Ic} and G_{Ia} are time-temperature dependent.

For instance, undercured specimens might cure slowly, achieving greater strength but at very long times and could become weaker and more brittle. Therefore, the kinetics of cure are essential for proper adhesive durability evaluation.

CONCLUSION

Fracture toughness methods have been shown to be sensitive to a wide variety of bonding variables. Also, these methods can be used for more accurate durability prediction and adhesive formulation. Much more work needs to be done to understand the interrelationships of G_{Ic} and adhesive formulation,

such as fillers, adhesive chemistry, and wood species.

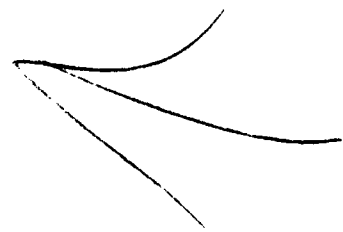
ACKNOWLEDGMENTS

I wish to thank the Forest Products Laboratory and the Weyerhaeuser Corporation for their generous support for this work. Special thanks must go to Drs. Robert Gillespie, George Myers, Roland Kreibich, Joseph Murphy, Lidijs Murmanis, Irving Sachs, and John Barrett for their comments and support throughout this research.

Of course my students, Marc Luce, Dr. Jovan Mijovic, and Dr. Robert Ebevele and coworker, Brian River of the Forest Products Laboratory, must be given most credit for this research. It was a very great pleasure to work with this very capable group.

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AD P 002439

BONDING BY SURFACE REACTION¹

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ABSTRACT

This paper reports on the continuing research in the area of the chemical bonding of wood. Chemical bonding is a technique which actively attempts to chemically involve the surface of wood in the joint formation process. In previous work, nitric acid at either 50 or 72 weight percent was applied to very dry (>2% MC) flakes and given a period of reaction time before the application of the interphase, an aqueous mixture of ammonium lignosulfonate, furfuryl alcohol and maleic acid. This was followed with typical panel hot pressing. The relative importance of acid assembly time, interphase pot life and total assembly time have been previously reported.

In the research being reported here, an attempt has been made to improve overall board properties while, at the same time, making the whole process more practical from a large scale application point of view. Accordingly, a 50% solution of nitric acid was applied to green Douglas-fir ring-cut flakes and, after some period of time, dried in a laboratory drier. The variables considered in this research included acid assembly time before drying, time between drying and application of the (same) interphase mixture, and total assembly time. Board properties determined include internal bond (IB), modulus of rupture (MOR), modulus of elasticity (MOE), and wet MOR.

Results show that there is a substantial improvement in the board properties when compared to boards made with the initially reported technique. Boards made with drying after acid treatment, when compared to control values, showed a 55% improvement in IB, 8% improvement in MOE, 10% improvement in wet MOR, and a 10% improvement in dynamic MOE, with no change in MOR. The effects of the various assembly times, as well as the statistical implications of this research, are discussed.

INTRODUCTION

The chemical bonding of wood is an interesting and potentially valuable nonpetrochemical alternative to the conventional bonding of wood using familiar adhesives such as phenol-

or urea-formaldehyde resins. Chemical bonding refers to a technique which strives to chemically involve the wood components on the surface of wood in the bonding reaction. Thus, the goal of chemical bonding is to use covalent bonds from adherent to adherent for the total span of the joint. Chemical bonding is typically achieved by treating wood surfaces with a material which predisposes the wood surface to further reaction either with wood

¹Paper presented at the Wood Adhesives--Research, Application, and Needs Symposium, Madison, Wisconsin, Sept. 23-25, 1980.

or with an interphase (gap-filling) material. Typically, the surface treatments are of an oxidizing nature with materials such as nitric acid or hydrogen peroxide most commonly used. The work being reported here will review some of the past history of chemical bonding of wood and discuss recent observations regarding the effects of heat and assembly times on bonding efficiency.

REVIEW OF LITERATURE

The chemical bonding of wood is not new. Reports of various researchers going back to 1945 have been noted (Linsell 1945). Reviews on the topic are available (Johns, et al 1978; Stofko 1974). One approach not covered in the previously mentioned reviews is that of Emerson (1963). This work involved the treatment of wood with a strong mineral acid such as nitric or hydrochloric acid followed by the application of a mixture of lignosulfonate, urea and furfuraldehyde. This technique for wood bonding, known as the Emerite process for the production of "cultured wood", was developed enough that a plant was built to produce panels for the furniture industry (Ward 1960). This process is very interesting because it is surprisingly similar, in philosophy and materials, to the research being reported here. The research in this report was developed to its current status without prior knowledge of the Emerite process.

PROBLEM DEVELOPMENT

In a previously reported study (Johns, et al 1978), it has been shown that flakeboard panels can be made by first treating wood with 40% nitric acid and then applying an aqueous mixture of 4.2% ammonium lignosulfonate, 1.8% furfuryl alcohol and 1.0% maleic anhydride (all values based on the O.D. wood weight). In this same study, the importance of acid assembly time, pot life of the crosslinking mixture, and the total assembly time were discussed. Acid assembly time is defined as the time between the spraying of acid onto dry wood, and the application of the interphase mixture. Pot life is defined as the time between the addition of a maleic anhydride-water mixture to lignosulfonate-furfuryl alcohol-water mixture, and the application of this mixture to the acid-sprayed wood. Total assembly time is defined as the time from the spraying of the gap-filling mixture to hot pressing of the flakes into panels. The approach taken in this earlier work was to use a fairly strong acid (40% by weight) and very dry wood (less than 2% MC). This was desirable because in a direct comparison between 25% acid and 40% acid, the 40% acid yielded boards

with better properties. The assumption was made that the stronger the acid concentration on the wood surface, the more effective the wood bond. Consistent with this assumption was the fact that very dry wood was used since wood at moisture contents greater than 2% would add substantial water to dilute the acid applied to the wood surface. Further, with the application of acid and the aqueous gap-filling mixture, the moisture contents of the mat going into the press made it difficult to process boards without encountering a large number of blows if the initial wood MC was in excess of 2%. This approach to the manufacture of chemical bonding yields boards of good strength and stability; however, it has some problems. First, it is necessary to dry the wood to a very low moisture content. Also, once acid is initially sprayed onto dry wood, that wood is committed to being pressed in a fixed length of time. In earlier work (Johns, et al 1978) that time period is an average of 4 hours for the manufacture of boards from white fir.

A new approach was thought desirable, because it would lead to the development of good bonding and be more conducive to large scale manufacturing techniques. The approach taken was to apply nitric acid to wood at high moisture contents, typically in the range of green wood, and then to dry the wood in a normal manner. Accordingly, the experiment evolved as follows. Dry Douglas-fir Pallmann flakes with an average thickness of 0.015 inch were blended with water to yield a moisture content of 50%, bagged in polyethylene for approximately 3 hours, and then sprayed with a 50% solution of nitric acid at a standard of 1.5% nitric acid, O.D. wood basis. This wood was then dried after 0, 2, or 24 hours in a small laboratory drum drier at 175°F to 5% MC; this time period was the "wet assembly time". After drying, the wood was then sprayed with a gap-filling material, the same as used previously which is mixed 2 hours before application, after periods of 0, 24, or 72 hours. The non-volatile component of the gap-filler was 7% O.D. wood basis. This time period is defined as the "dry assembly time". Finally, the boards were pressed after 0, 2, or 24 hours of "total assembly time". Boards with a target density of 0.75 g/cc were pressed to 1/2-inch thickness in a 350°F press. The pressing schedule included time-to-stops, which was one minute, with a total press time of 7 minutes. Two types of control boards were prepared. The first control type was based on the application of nitric acid to dry wood in the manner previously reported (Johns, et al 1978) with a two-hour acid assembly time, a two-hour pot life, and a two-hour total assembly time. The second set of control boards were prepared with 6% (based on O.D.

TABLE 1

Experimental Design and Results of Physical Tests of Chemically Bonded Boards

WET Assembly Time	DRY Assembly Time	Total Assembly Time	MOR psi	MOE psi x 10 ⁶	IB psi	WET MOR psi
0	0	0	1677	0.483	64	232
		2	1690	0.471	95	247
		24	1671	0.482	79	251
	24	0	1425	0.417	63	224
		2	1714	0.559	75	217
		24	1740	0.510	88	208
	72	0	1678	0.494	93	294
		2	1666	0.513	75	185
		24	1625	0.522	66	134
2	0	0	1567	0.460	79	306
		2	1715	0.504	76	189
		24	1778	0.535	64	117
	24	0	1625	0.506	81	174
		2	1718	0.539	73	164
		24	1666	0.536	69	133
	72	0	1646	0.497	76	193
		2	1680	0.516	81	148
		24	1734	0.505	80	152
24	0	0	1551	0.476	65	241
		2	1456	0.476	55	184
		24	1804	0.556	71	180
	24	0	1544	0.462	67	261
		2	1585	0.481	64	142
		24	1758	0.541	78	238
	72	0	1713	0.501	89	140
		2	1816	0.520	78	133
		24	1623	0.525	63	104
0	72	0*	2029	0.523	62	321
0	72	0**	1508	0.427	86	102
Control Nitric Acid			1665	0.457	60	268
Control Phenol-Formaldehyde			3511	0.431	154	1485

* Aspen dried at 175° F

** Douglas-fir dried at 120° F

wood) phenol-formaldehyde particleboard resin.

After the statistical analysis of this main body of experiments, two other sets of boards were made. The first set of boards, at the observed relative optimum of 0 hours wet assembly time, 72 hours dry assembly time, and 0 hours total assembly time, were made with acid-sprayed wood dried at 120°F instead of the 175°F used previously. Finally, the last set of boards were prepared using the same assembly time schedule as the above set, but made with aspen flakes and dried at 175°F. Four replications for each experimental variable or control factor were made--a total of 124 boards.

Testing consisted of the determination of internal bond (IB), modulus of elasticity (MOE), modulus of rupture (MOR) according to ASTM D-1037, and the determination of wet MOR, which is defined as the MOR after a 2-hour boil followed by a 1-hour cold soak with all calculations based on dry dimensions. Statistical analysis included analysis of variance, with the Duncan's new multiple range test to identify significant values, with 1% used as the minimum level of significance.

RESULTS AND DISCUSSION

The complete results of the experiment are reported in table 1.

One-Factor Interactions

There are three possible one-factor interactions with the experimental design. The effects of wet assembly time are shown in table 2.

Table 2.--One-Factor Interactions: Board Properties as a Function of Wet Assembly Time.

	Wet Assembly Time in Hours		
	0	2	24
MOE x 10 ⁶ psi	0.494	0.510*	0.502
Wet MOR psi	221*	175	180
IB psi	78*	75*	69*
MOR psi	1654	1681	1650

* Identifies which values are significantly different from other values of the same property @ 1% level.

Both internal bond and wet MOR decrease by increasing wet assembly time. Such parallel behavior does not occur with the dry assembly

time (table 3) because wet MOR decreases with increasing dry assembly time, and IB increases with dry assembly time. In this latter case, MOE parallels the behavior of wet MOR.

Table 3.--One-Factor Interactions: Board Properties as a Function of Dry Assembly Time.

	Dry Assembly Time in Hours		
	0	24	72
MOE x 10 ⁶ psi	0.510	0.505	0.492*
Wet MOR psi	217*	196*	165*
IB psi	72	73	78*
MOR psi	1656	1641	1687

* Identifies which values are significantly different from other values of the same property @ 1% level.

Table 4 shows the effect of total assembly time on board properties. Internal bond was not significantly influenced by the total assembly time. What is shown is interesting because both MOE and MOR decrease with increasing total assembly time, while wet MOR decreases with increasing total assembly time. The thickness swell of the specimens was not noted during wet testing, so the effect of specimen swell, which would tend to increase the bending resistance up to the point of specimen failure during testing, could not be determined but swelling could be related to the observations noted in tables 3 and 4.

Table 4.--One-Factor Interactions: Board Properties as a Function of Total Assembly Time.

	Total Assembly Time in Hours		
	0	2	24
MOE x 10 ⁶ psi	0.474*	0.508*	0.523*
Wet MOR psi	230*	179	168
IB psi	75	75	73
MOR psi	1603	1671	1711*

* Identifies which values are significantly different from other values of the same property @ 1% level.

Two-Factor Interactions

Figure 1 shows the dual effects of wet assembly time and dry assembly time on the wet and dry MOR. There are no significant interactions for the dry MOR while the wet MOR of the boards pressed after a dry assembly time of 72 hours and a wet assembly time of 24 hours had a significantly lower wet bending strength. Also of interest are the effects of wet and dry assembly time on IB as shown in figure 2. A dry assembly time of 72 hours can eliminate the effects of wet assembly time. This contrasts to wet MOR where an extended dry assembly time dramatically reduced wet bending strength for the 24-hour wet assembly time.

Total assembly time did not demonstrate any significant two-factor interactions.

Three-Factor Interactions

Every board property investigated showed significant three-factor interactions. The interpretation of these interactions will probably remain an unknown factor until the chemistry of this bonding system is better understood and the nature of each individual factor can be documented. Discussion of three-factor interactions must therefore be postponed until such time as it is possible to work from a position of greater knowledge.

Other Interactions

In reviewing the results shown in table 1, several combinations of assembly times identify a high level of bonding. One such combination includes a wet assembly time of 0 hours, dry assembly time up to 72 hours, and total assembly time of 0 hours. This particular combination was selected for two side tests.

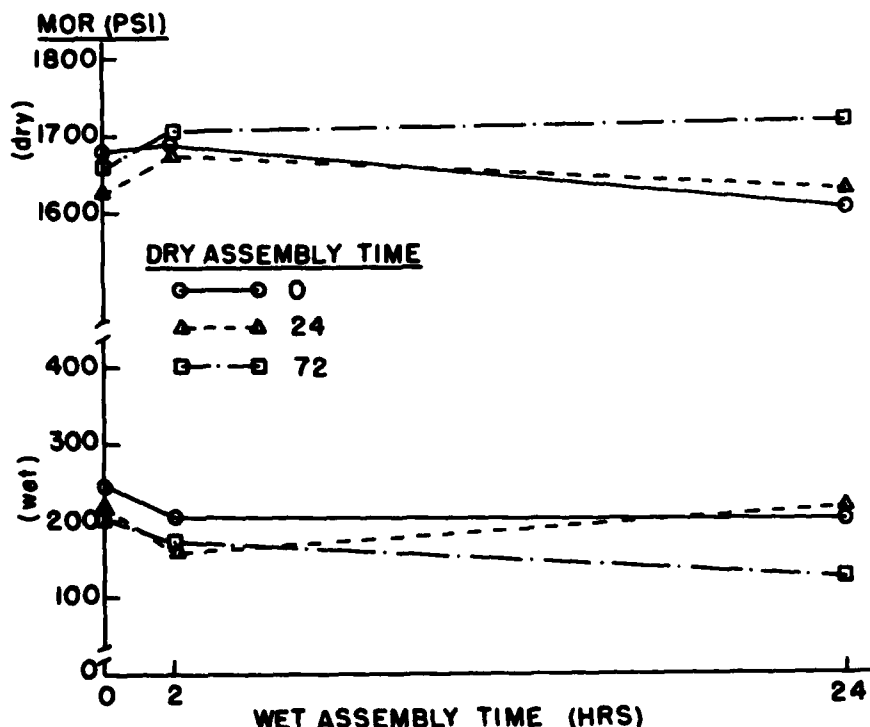


Figure 1.--Two-factor interaction showing relationship between dry and wet assembly time, and dry and wet MOR.

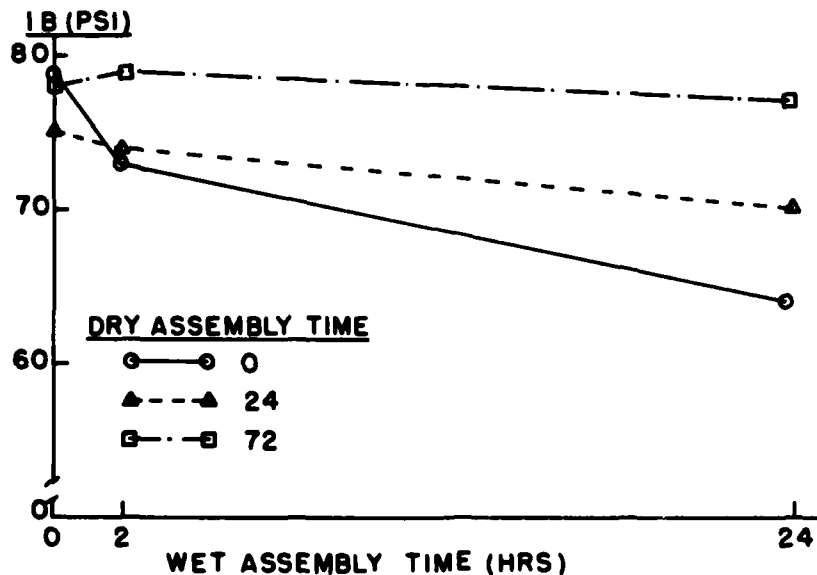


Figure 2.--Two-factor interaction showing relationship between internal bond and dry and wet assembly time.

The effect of a drying temperature of 120°F is shown in table 1. While board properties during dry tests were roughly parallel to boards processed from 175°F dried flakes, the wet properties dropped off to approximately 1/3 the value of the higher temperature treatment.

The use of aspen was included to see if a hardwood had the potential of bonding with surface reaction in a manner similar to softwoods. No attempt was made to optimize the stoichiometry or assembly time factors for the aspen furnish. While the aspen was flaked through the same Pallmann ring flaker, the material was not classified afterwards and had a higher percentage of fines than the Douglas-fir used for the main body of the experiment. As shown in table 1, the aspen did yield a board of broadly comparable properties. The only property which was lower was the IB. This suggests that the application of chemical bonding technique to other species may not involve any major changes in a technique that is comparable to the approach taken here.

The nature of the bonds which are formed is not known. This is a direct result of our lack of information about the chemical nature of the surface of wood and how this chemistry is influenced by the various treatments which are used to produce the bonding. However,

there is considerable information known about the oxidation of both the lignin and carbohydrate fractions of the wood. Excellent reviews are available for each (Sarkanen and Ludwig 1971; Stofko 1974; Jenkins 1976). The problem is in interpreting the cause and effect relationships between the bonding treatments, such as wet and dry assembly times, and the specific changes in components of the wood or on wood mechanical behavior. Until such time as the surface chemistry of wood can be quantified before and after various treatments, the problem of understanding the pathways to bond development will still exist. This does not imply that progress cannot be made. The data presented here show the results of direct effort to improve bonding, while at the same time to modify the techniques to more closely resemble an industrial approach to board manufacture. One of the key developments of this study involves the effective strength of the acid used to pre-treat the wood. In previous work (Brink, et al, in press) acid concentrations up to 72% were applied to dry wood. When the amount of water present in wood, even at low MC levels, is included in the calculations, the effective acid concentrations normally found are in the range of 35%. For the work reported here, the effective acid concentration present on the wood surface is 2.8%. These observations suggest that the history of the wood, with respect to moisture

content and heat exposure, is far more critical than the working concentration of the pre-treatment acid. To this end, future research should be directed to studying the effect which heat and moisture have on the effectiveness of any pre-treatment technique as a standard screening process.

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ADHESIVES FOR WOOD COMPOSITES¹

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ABSTRACT

In the production of composites from comminuted wood, the adhesive performs under conditions which appear to be different from conventional gluing procedures. Actually, the parameters are the same but in different, and sometimes extreme degree. The adhesive also responds in the same way but in an invisible manner, making causal observations difficult. A number of conditions and responses are examined and their implications to the efficiency of the process noted.

INTRODUCTION

Throughout all of this century, we have seen an ever increasing role of adhesives in the conversion of wood to useful products. In order to maintain a flow of wood products consistent with anticipated demand for the remainder of this century and into the next, our dependence upon adhesives must necessarily increase. This is mandated by the need to utilize more and more of the wood available in the forest but remains unutilized because of poor form, size or species, and because the cost of harvesting exceeds the value of conventional products to which it might be converted. Adhesives offer a way out.

Two deductions may be drawn from the reasons for non-use of low grade wood: one that harvesting methods are too costly; and two, that potential products are too low in value. Both are solvable; the first by engineering, the second by technology. In this paper, we are interested only in the latter on the hope that if high value products can be produced in an efficient manner, utilization of low grade wood would be assured independently of what improvement is achieved in harvesting methods.

At the present time, there are only three products that can sustain forestry and harvesting costs: lumber, veneer, and fiber. Of these, only fiber can feed off of residues; lumber and veneer require prime logs. However,

despite technical feasibility, there seem to be some constraints to the voluntary use of forest residues for pulp products, except when driven by scarcity. The conclusion seems inescapable that one of the more propitious ways of extending timber supplies is through the conversion of forest residues to products representing lumber and plywood values. Since we are dealing with wood of poor form and size, the options reduce to fiberboard and flakeboard both in random and in aligned formation. The conversion processes will involve reduction and reconstitution operations, the latter highly dominated by the adhesive, both in operational efficiency, and in cost and performance of the product. Operational efficiency, that is, the performance of the adhesive in consolidating comminuted wood, should in my opinion be a first order consideration. It is to this facet of the problem, I wish to direct a few thoughts with the view of encouraging departures from present practices which seem to me to constrain development of both new adhesives and new processes.

ADHESIVE FUNCTIONS

According to ASTM, an adhesive is defined as a substance capable of joining two materials by surface bonding. As noted earlier by George Marra, the bond can be represented by seven links, each of which calls

¹Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980.

for a specific action by the adhesive. Two actions, particularly, are basic to the process. One is the establishment of adhesion, i.e., anchorage to the wood surface; the other is the formation of a bridge across the gap between the two surfaces to be joined. Adhesion should readily occur to a freshly cut surface unless defeated by some form of surface inactivation or high viscosity. Two forms of inactivation may exist; one due to contaminants such as grease, oil, wax or gases; the other due to creation of a hydrophobic surface through the action of heat. Considerable defeating of adhesion action has a good chance of occurring in most reconstituted products since wood surfaces are subjected to high heat, both direct and indirect prior to application of adhesive. However, there are some contradictions.

The behavior of a drop of water placed on a wood surface should tell something about degree of inactivation. If the drop disappears rapidly into the wood, one can conclude no inactivation has occurred and maximum adhesion can be expected. On the other hand, if the drop remains in drop form for several minutes or until it evaporates, the wood surface would be assumed to be highly inactivated and unfit for adhesion. This can be misleading. Repeating the experiment with a drop of glue, one would be dismayed to observe the drop maintain the form characteristic of no adhesion even on relatively fresh surfaces. If the drop be allowed to cure, however, often it cannot be pried off without wood failure, even on surfaces considered to be inactivated. If actual bonds are made and tested, one can in some cases observe that surfaces exhibiting some inactivation will produce greater strength than fresh surfaces. This is particularly true of room-temperature, chemically-cured adhesives. The strength effects on solvent-loss or heat-cured adhesives could be the opposite. Thus, apparently the same surface condition can produce different effects in different adhesives.

There must, first of all, be different degrees of inactivation, beyond the ability of a drop of water to differentiate. A highly inactivated surface would certainly reject most adhesives. However, some adhesives can tolerate certain types and amounts of inactivation either by absorption of contaminants or by modification of the surface as, for example, by swelling.

In addition to inhibiting the adhesion action, this kind of surface can also affect other adhesive actions, particularly penetration and hardening. This it does by affecting the solvent-resin-catalyst balance needed to optimize these actions. For example a clean,

very dry surface that otherwise might be considered ideal for adhesion, could quickly destroy the solvent balance of a chemically cured adhesive, and thus interfere with the curing reaction by robbing it of its reaction medium prematurely. On the other hand, an adhesive that hardened by solvent loss would not suffer reduced hardening, but might suffer penetration loss on a similar surface if its solvent was removed too fast by the wood, and its viscosity raised too quickly. Both these adhesives, therefore, appear to profit by surface conditions that prolong an optimum fluid stage.

An adhesive that cures by action of heat responds in a different manner to the surface activity of the wood. These adhesives are often applied with an excess of solvent to improve application mechanics. It is expected that the wood will draw off some of this excess water before the heating step. Inactivated surfaces, however, reduce the rate of water sorption from the adhesive. Heat plus too much water then lowers the viscosity of the adhesive below that necessary to keep it on the surface, and over-penetration occurs. Formulating adhesives around this kind of surface variable is difficult, since correcting one extreme invites problems at the other.

On the matter of the adhesive forming a bridge between two pieces of wood, the need is predicated on the physical impossibility of bringing surfaces close enough together that molecular forces residing in the surface can create a bond. The adhesive is expected to fill the gap and make the connection. The adhesive thus functions volumetrically and the more volume there is to fill, the more adhesive is necessary, and the more cost will be incurred. There are two main ways of reducing the volume to be occupied by adhesive. One is to provide surfaces so smooth and true that they naturally lie close together. The other is to compress or otherwise flatten by means of pressure any unevenness that prevents surfaces from coming together. The former is preferred, but the latter is the common practice.

SPECIAL FACTORS IN COMPOSITES

Some idea of the magnitude of the volumes involved in glue bonds can be obtained by calculation. In face gluing Douglas fir lumber into beams, if the glue line averages 0.005 inch thick, and assuming a depth of penetration of about 0.001 inch on either side (wood specific gravity .45), the total volume to be filled with adhesive is about 0.53 cubic feet per thousand square feet of glue line. If the cured resin has a specific gravity of 1.2,

Table 1.--Comparison of adhesive usage in consolidating one cubic foot of various wood elements of Douglas fir, original density 28 lbs/cubic foot

Wood Element	Bond Area Sq. Ft.	Lbs Resin / MSGL	Lbs Resin / Cuft Wood	Lbs Resin / Lb Wood	Thickness Inches Glue Line
1" thick ¹ boards	11	39	0.43	0.015	0.005
0.1" thick ² veneer	119	7.5	0.89	0.032	0.0012, 0.0028 ⁵
0.050" thick ^{3,4} wafers	240	5.8	1.40	.050	0.0009
0.010" thick ^{3,4} flakes	1,200	1.2	1.40	.050	0.00019
0.001" thick ^{3,4} fibers	24,000	0.05	1.40	.050	0.000009

¹Lumber spread @ 60lb/MSG L, adhesive @ 65% resin solids.

²Veneer spread @ 30lb/MSG L, adhesive @ 25% resin solids.

³Wafers, flakes and fibers blended with 5% resin solids.

⁴Assuming no compaction.

⁵With 50% filler.

the amount of resin required would be 39 lbs. It is of interest to compare the adhesive usage in consolidating one cubic foot of various composite products. Table 1 gives the comparisons with respect to different parameters.

In the first column the surface area to be glued is seen to go from 11 square feet for one inch lumber to 24,000 square feet for one thousandth inch thick fibers, with veneer and flakes in between. Parenthetically, it should be noted that the laws of physics assure us that the energy required to produce each element is directly related to the area of the surfaces created. Thus the separation of wood into one thousandth inch thick fibers requires 2182 times more energy than that required to produce one inch lumber.

The second column displays the dramatic consequences in binder coverage of increasing surface area, going from 39 lbs per thousand square feet in the case of lumber to 1.2 lbs for thin flakes, and 0.06 lb for fiber; not very much resin to spare for penetration losses. To counter penetration losses one can increase the amount of resin applied, but only at a penalty in cost. The method used in practice is to distribute the resin not as a continuous film but as drops or particles. Hence at any one point, the hope is that there will be sufficient resin to carry out the necessary adhesive actions.

The matter of resin penetration, however, deserves a second thought or two. Very few wood surfaces are created under production conditions without subsurface damage, particularly comminuted wood. Since adhesive bonding is by surface attachment, if the surface is weak, the bond will be weak. Hence the adhesive must perform the extra function of repairing the damage incurred in preparation of the surface. This cannot be done without penetration to some degree. The very small amount of adhesive used per square foot of nominal surface makes it unlikely that much repairing can occur, and if it did, would be at the expense of the primary surface bond.

There is some reason to suspect that repairing subsurface damage may be difficult in any case, and may in fact represent the ultimate limiting factor in developing higher performance products. Studies of varying resin levels usually show increasing strength with increasing resin content, but level off at 10 to 15%. This suggests that interparticle bonding may be maximizing with increasing resin, but since the strength is below the potential of solid wood, it seems plausible that a strength reducing factor within the wood particle is persisting in the reconstituted product.

While acceptable strengths are possible despite such internal weaknesses, there may be critical side-effects affecting performance.

One of these is creep under long-time loading. It is conceivable that these minute fractures allow low stress deformations that accumulate over time. Another effect of internal particle fractures is the moisture absorption pathways they provide. Some means of dealing with this problem seems imperative; if not by binder action, then by some other treatment. In any case, research attention is needed on subsurface damage in order to promote reconstituted products into load bearing applications.

The last column in Table 1 is a calculation of the film thickness that the given amount of adhesive would achieve if spread uniformly at the rate indicated. Although uniformity of spread is never obtained, the figures promise that distances between surfaces greater than those shown will definitely not be bonded given that amount of adhesive. Except for lumber, these figures do not account for penetration, and except for lumber they do account for shrinkage of the adhesive in curing.

The thinness of these adhesive films is strongly mandated by costs. Columns three and four indicate that adhesive costs would increase with decreasing particle size if the same rate of coverage were maintained. It has proven to be cheaper to apply more pressure on an assembly to improve contact between surfaces than to apply more adhesive. The resulting higher density of the product is accepted as a technologic necessity. However, a number of other penalties are also incurred by high pressure which, although accepted by industry, should be the object of intensive research.

One of the main penalties of excessively high pressures is compression of the wood beyond its proportional limit, with buckling and rupture of cell walls. Such wood is not only weakened, but also is made more unstable to moisture than uncompressed wood. The result is further propensity to undergo creep behavior, but worse, the product also thus tends to acquire a mechanism for its own destruction, needing only moisture to trigger it. The problem is compounded by the relatively poor flow properties of a mat of particles undergoing compression. Areas containing a relatively higher concentration of particles will receive pressure higher than the average while areas of low concentration will be less compressed or not at all. This produces wedge effects by high compression points as they expand more during moisture uptake.

Another penalty of high pressure is the closing of the void structure in a mat. This prevents escape of moisture during pressing, and in turn mandates harsh drying procedures to reduce wood moisture content in preparation

of particles. Reduced moisture content is made more necessary by the need for high temperatures to cure the resins, which otherwise would cause steam pockets in the product.

DIRECTIONS FOR CHANGE

Thus the resin, in a very real sense, dictates both good and bad aspects of processing wood into reconstituted products. In general, it can be said that the resins used are capable of maintaining an achieved bond under anticipated conditions of use. Hence improvement in performance may appropriately include two other considerations: one, that there is insufficient bonding, and two, that the bonding process which the adhesive itself controls is at the same time disadvantageous to bond formation and performance. The major approaches to improved reconstituted products and processes thus seem to involve changes in the adhesive as well as in procedure.

The changes begin with the standard request for lower prices. This would lead to some immediate improvement if more would then enter the product. For enough more to enter the product, the price would have to be substantially lower; as a target perhaps in the order of two to four times the cost of wood per pound. If the additional resin (or additive) would induce some lubricity to the mat, more flow of particles would occur and this would help equalize point-to-point pressure and density variations.

Means for dealing with subsurface damage may have to be treated as a separate problem. Preferably, the damage should be avoided in the first place. Alternatively, since binders are ordinarily formulated to function at the surface for maximum efficiency, rather than penetrate and be lost to the primary bonding process, it would appear that a second adhesive component of greater penetrability could be included. The chief function of this component would be to repair ruptures within particles, both those preexisting and those formed during pressing. This would have important fringe benefits in promoting greater stability as well as strength. Perhaps, this is too large an order, but it needs to be included in development planning.

A final change in resin properties, which I feel would be particularly beneficial, is lower temperature curing, down to room temperature if possible. This would not only speed up the process, but would also simplify it and make it more tolerant of variables which otherwise require expensive controls.

In my own slow work, I have had the above

changes in mind. Some still look sufficiently plausible, despite cost obstacles, to warrant continued research. The use of foaming urethane resins, for example, removes the problems of heating, pressure, moisture content, springback, and curing speed. Although requiring a special particle which allows mat formation as a first operation, followed by dosing with resin and consolidating in seconds without heat, the resin itself is expensive. Hence, only high value products can be justified. However, since the mat is easily formable after resin addition, various kinds of molding processes can be fed with the same furnish. Also overlays can be consolidated to the mat during resin cure to produce sandwich panels at a high rate of speed. Needing no input of heat, panels of any thickness can be produced at the same speed.

In an effort to reduce costs of the binder, Portland cement was made more adhesionable to wood by addition of resins. This produced a fast-setting binder at room temperature, costing about 12 cents per pound. Its high specific gravity, however, means a considerable load of binder in order to obtain the necessary coverage. Foaming of these resinated cement mixtures allows reducing the binder load and bringing the product density down to more normal levels. Again, being room temperature setting, speed of production is independent of thickness of product, and molded shapes as well as panel products can be made.

In both the foamed urethane and resinated cement binders, one can perceive a sense of simplification in producing different types of products from the same furnish, with different size operations. Although the processes they make possible require further development to make feasible, they illustrate what might be done to change the way comminuted wood is converted to useful products.

A MEDIUM FOR CHANGE

The marvelously engineered products and processes of modern wood composites command the admiration of all who deal with materials. It seems almost a sacrilege to criticize them in any way. However those who can look dispassionately at the entire scene might see a complexity that to them appears unwarranted. Given a chance to design de novo, ignorant of the constraints imposed by the adhesive, one would come up with something entirely different, almost surely unworkable in the present context of men, materials, machines, markets, and money. If we can bring ourselves to avoid rejecting the unworkable, and begin working on the context, the chances of success

of innovations would be greatly improved. But first there must be a source of ideas. Where is this source?

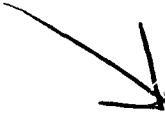
One source of ideas might be expected to spring from those who use adhesives and make composites. However they often are so concerned about everyday production problems, getting out orders, seeing to the flow of materials, attending to equipment, that they cannot be expected to be thinking of how to do anything differently. Aside from price, users are primarily interested in working properties of adhesives, spreadability, washability, viscosity, smell, curing speed. If a new adhesive is proposed, it must function exactly as the one currently being used, but at lower cost. This practically guarantees the status quo, and effectively closes the door to progress (although admittedly, a significant cost reduction could be the difference between success and failure of a reconstituted product).

Adhesive suppliers, being the servants of the users, are equally constrained since their main objective has to be to keep production people happy. Thus what should and can be the main sources of innovation are to some degree under a form of mutual constraint.

Which puts us back to the dispassionate observer. One who has no stake in the status quo, nor perhaps enough knowledge of it, but is otherwise smart, intelligent and responding to some sense of pressure to change things. What can he do at his own private bench, unencumbered by tradition? He will produce a lot of dead cats. Developments that involve drastic changes, and that is the essence of innovation, cannot be made in isolation. They must invoke all the other elements that form an interdependent, ecological type, network of factors in a total system. There must, in short, be close collaboration among people who have intimate knowledge of materials, machines, markets and money, as well as knowledge of other people, the environment, energy, and politics. Since any one of these can render an idea unworkable, they are as important as the idea itself. A successful idea is an alloy, a composite, engineered with many components, often synthesized in a pressure cooker, but better done at ambient in a think tank atmosphere.

Only a team effort, it seems to me, can develop the new compositizing systems that will be needed to satisfy future timber demands from declining resources.

AD P 002441



RECENT ADVANCES IN PLYWOOD TECHNOLOGY^{1/}

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Georgia-Pacific started its first plywood operation in the South 17 years ago at Fordyce, Arkansas initiating the southern plywood manufacturing revolution. At its inception there were many factors inhibiting the success of this venture, one being the difficulty of bonding the wood. This was a major technological hurdle to overcome and presented the neophyte industry a major challenge.

The gluing state of the art since the initial startup of the Southern Plywood Manufacturing industry has made significant strides to enhance the bond quality of its product and as a result more than 40% of total plywood production is southern pine.

Many factors affect glue-line quality as reflected by percentage of wood failure. To maximize wood failure eight variables must be scrutinized to assure maximum glue-line integrity. These variables are:

1. Wood specific gravity.
2. Rate of growth.
3. Tightness of peel.
4. Resin content of mix.
5. Extender type.
6. Glue spread.
7. Assembly time.
8. Veneer moisture content.

The above variables if properly controlled will provide the insurance of avoiding the intrusion of governmental regulation in plywood manufacturing and meet consumer increased quality demands on plywood. Let us look at how we are approaching the need to improve plywood adhesion since 95% of all our claims in the field are caused by delamination.

The eight plywood plants in the Crossett Division utilize glue spray application in laying up veneer. We have found spray systems

a definite improvement over spreaders and curtain coating systems which we have had experience with in the past. The systems give us layup flexibility, quality, glue savings, improves wood utilization and productivity. The sprayline is designed and manufactured by Georgia-Pacific.

The resin we use is a phenolic type termed a thermosetting resin; that is, the cure of the resin is established by the application of heat with a state of cure such that the cured resin is insoluble and infusible. It is from such a state that phenolic glue-line derives its exterior application.

The resin we use is of recent vintage with the development and pioneering occurring in the Crossett Division. We call it Georgia-Pacific Semi-Resi-Mix.

This adhesive gives the plywood producer an alternative to the conventional glue mix that is produced at the plywood mill. Resi-Mix is a glue supplied to the plywood mill ready to use. A drawback of resi-mix is that the ability of the mill to utilize its wash water is limited. A need for a simplified glue mix intermediate between Resi-Mix and conventional glue mixes was evident. Semi Resi-Mix was developed to satisfy that need. Utilizing high shear glue mixers (as opposed to the old paddle type) mixing time for semi Resi-Mix is reduced to 10-15 minutes as compared with 45-50 minutes for conventional mixes. This reduces the manpower required for glue mixing. Wash water is utilized in semi Resi-Mix as it is in conventional mixes. With the Semi Resi-Mix adhesive system, no caustic soda is required in the glue mix. This eliminates the handling of dangerous raw material in the glue loft and it eliminates the lengthy caustic digestion step used in conventional mixes. Semi Resi-Mix utilizes either the new Resi-Fil or superfine Furafile as primary extenders. Semi Resi-Mix has been in regular use in the Georgia-Pacific Crossett Division plywood mills for the last three years with excellent results.

^{1/}Paper presented at "Wood Adhesives--Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

Koch's studies established the important affect of extender on gluebond quality and the superiority of a good wheat flour as the secondary extender.

As stated earlier, glue extenders are an important variable in affecting glueline quality. In recent years the quality of the Furafile primary extender used in plywood glue mixes has become more and more variable. For example, the current ash content is 10% and current moisture content is 20%. Both these values are double what they were in earlier years. There have also been frequent changes in raw material sources. This causes gluing problems across the plywood industry whenever such a change is made. The higher ash content has caused more wear on panel saws, cutter-heads for T&G and siding panels.

Because of problems like these, G-P started looking for an alternative primary extender. Resi-Fil is a result of that search. Resi-Fil is the superfine (70% through 270 mesh) fraction of particleboard sander-dust and is used as a direct replacement for furafil. Resi-Fil gives improved pre-pressing and bond quality as compared with Furafile. Georgia-Pacific Resi-Fil wood flour has been thoroughly tested over a long period of time and is approved by A.P.A. for use in Region "D." and is being commercially produced at this time at the Crossett Extender Plant.

Now that we have a good resin and a compatible extender we must blend the ingredients which are present for definite reasons. The amount, order of addition and mix are critical in maintaining the correct adhesive characteristics such as viscosity, percent resin solids, level of alkalinity.

To do this all glue is mixed in Globe high shear mixers with 9,500 pounds individual mix capacity. By using large mixers we make fewer mixes per 24-hour schedule. All mixing is usually accomplished on two 8-hour shifts, with four hours between each shift.

Increased sophistication in making plywood dictates we maintain in close contact with our suppliers for adherence to our extender specifications of grind, moisture content, bag wt. and resin viscosity especially with a glue-spraying system.

After mixing, glue is pumped to G-P designed pumping station where glue is filtered through a 30 mesh vibrating Sweco screen, passes through a heat exchanger of our own design where glue is warmed to an even 105° temperature range. Low pressure pumps deliver glue to spraybooths at even pressure. Glue is atomized through a carbide tip manufactured

by Spraying Systems, Inc. We use tip number 1278-4 for summer gluing that delivers large droplets of glue on the veneer in a uniform pattern. During cooler weather we change to tip number 12728-2 which gives a finer glue pattern.

We utilize a newly developed glue saver which we call a glue trimmer mounted inside each spraybooth and adjusted hydraulically to cover 49 3/4-inch width veneer. Glue overspray is recycled to central pumping station, filtered and returned to heat exchanger. Glue spreads are monitored constantly with accurate weighing of desired spreads on Ohaus triple-beam balance scales. Glueline operators constantly check spread, veneer temperature, mill temperature and adjust spreads if conditions warrant. Glueroom supervisors work closely with the line operators in checking glue bonds behind presses and adjust spreads if necessary.

Effective October 1, 1980 all eight gluelines will be controlled electronically by a programmed logic control unit using Allen Bradley controls. The system was developed by the Crossett Division to automate package traffic flow up through the presses. The system eliminates human error, facilitates production monitoring and troubleshooting. It eliminates long assembly times, manpower, and provides future automation expansion. For example, comply production.

The controls I have described are super essential since glue costs make up 9% of total cost of sales.

There are three primary attributes of veneer which can profoundly affect the good adhesive bond. These are surface roughness and thickness variation, veneer moisture control and distribution of surface activation.

Drying of peeled veneer affects glueline quality in plywood. The Crossett Division maintains strict control of dried veneer moisture content. This has not always been the case. Previously veneer moisture content varied from shift to shift depending upon dryer tender or foreman at the time. Dried veneer would vary from overdried or "casehardened" condition to wet. Our Division goal is that 90% of all dried veneer is between 3% and 7% moisture. We are attaining this goal through computerized drying.

This development in electronic wizardry is the veneer dryer computer. All eight of our plywood mills have installed the Ward Systems Moisture-Logic, or 23% of all computers installed in the industry.

The computer is an integrated control and data collection system specifically designed to increase dryer production and operating efficiency. Input to the computer is from a Ward Systems segmented, self-balancing dry veneer moisture detector, an optical scanner, and dryer temperature sensor. To start a run the desired percent redry is entered by positioning a pair of digital thumbwheels under redry setting. Sheet length has a bearing on the programming as a "window" is provided by the computer for information from each dryer discharge. Full sheets cannot be divided if the two halves are of different moisture sorts; therefore, stock size must be included in setting up a run. There are two groups of three switches each, for length and width. Activating the proper switches is necessary for a correct program. Width settings are for full, one-half, and strip, or random.

When operating in the automatic mode, the 400 dryer computer will recognize and compensate for variations in moisture content, dryer temperature, stock flow, green-end mis-sorts, gaps and other veneer drying variables.

After each discharge of veneer stock has passed through the moisture detector and over-wet areas, if any, have been identified, this information is sent to the computer for evaluation; and a corrected speed of the dryer, if required, is initiated. Since speed changes are usually minute and often very frequent, the dryer motor must be capable of precisely following commands of the computer. A DC-SCR-type drive system is recommended. Selectivity of horsepower is critical, since higher speeds and greater speed ranges will be demanded with the use of the computerized control system.

The many advantages and subsequent areas of payout resulting from optimized drying schedules through computer control, are:

- 1) Increased production.
- 2) Reduced drying cost.
- 3) Higher average moisture content - 83% - 5-7%.
- 4) More uniform moisture content.
- 5) Less dry-out.
- 6) Improved glueline integrity.
- 7) Less veneer breakage.
- 8) Eliminates human error and releases dryer tender for other assignments.

All systems are designed around state-of-the-art integrated circuits, all components are mounted on easily replaceable plug-in circuit cards. There is complete self-test capability.

The surface texture or roughness of peeled veneer is an indication of the degree

of damage done to the wood structure. This damage is generally of two types: Lathe checks and compression tearing.

Recognizing the significance of this the Crossett Division has strived to better condition its peeler blocks.

Confirming our experience in December of 1979 a bulletin was printed entitled, "Heat conditioning of veneer blocks." Helmuth Resch and Robert Parker were the authors. They listed the following advantage of heat conditioning of blocks:

<u>ADVANTAGE</u>	<u>BECAUSE OF</u>
1. Reduced glue spread.	Smoother peel.
2. Tighter veneer with finer checks and reduced nosebar pressure, especially for thickness about 1/8 in.	Wood is more plastic and less resistant to fine checking, thus reducing deep splits.
3. Greater tensile strength of veneer perpendicular to the grain.	Tighter veneer and finer, shallower checks.
4. Reduced drying time.	Some heat is stored in wood, and steamed wood is more permeable.

Recognizing the need for good block conditioning Georgia-Pacific will, in a few weeks, implement a mini-computer based plywood block conditioning system at our Crossett plywood operation.

The ASI system 2000 operates as follows:

1. Logs from woodlands are scaled for length before bucking. The information is saved for management reports.
2. Conveyor chain control is used to ensure that enough space between blocks exists for stop operation at the vat infeed (about 4 feet).
3. Block diameters are measured and blocks are assigned to appropriate vats using sort break points (diameter range per vat) currently in effect. Diameter readings are taken every inch of block travel and smoothed so as to discard distorted readings. Volume is computed and saved for management reports.
4. Blocks are tracked to designated vats. The system then operates the stops and kickers so as to kick each block into the appropriate vat.

5. Blocks in a vat are grouped into "buckets" of about 20 blocks each and "tracked" through the vat by counting blocks going in and coming out. The dwell time of each "bucket" is controlled to ensure proper conditioning. The vat bottom chain is operated to convey the blocks toward the outfeed side of the vat.
6. Vat temperature and water level are monitored, and alarm indicators are lit if they fall below designated values.
7. At the outfeed side, the system operates a jackladder to pull blocks from the vats and routes them to the two lathe charging decks. The system will pull from as many vats as necessary to keep both lathe charging decks full. Those vats whose blocks are readiest are selected for pulling; ideally, "readiest" means fully conditioned, but if that is not possible (due to perhaps insufficient vat capacity) most fully conditioned blocks will be pulled. The lathes will not be starved.
8. Operators can at any time, cause infeed or outfeed operation to revert to manual mode by flipping a switch. Any vat or lathe charging deck can also be taken out of operation via a switch. For best conditioning, these controls should be only used to take care of some unusual condition (such as a broken jackladder). Sort break points (diameter range per vat) are computed by the system after every 100 blocks scaled at the infeed. They are also recomputed whenever a vat becomes full or becomes not full, and whenever the operator enables or disables a vat. In determining new break points, incoming block distribution by diameter, rate of pull from each vat, vat availability and space availability in each vat are taken into account.

The main benefit is, of course, increased profits due to higher yield, better quality veneer, cost savings and greater management control.

It is general consensus that hot water soak vats generally do a better job of conditioning blocks than steam vats provided water heat exchanger design is properly engineered. Recognizing this, G-P developed a product known as Resi-Vat for accelerating the block conditioning process.

Resi-Vat is a combination of alkaline chemicals used in conjunction with the hot water heating medium in the log soak vats. The heating plasticizes the wood so that the veneer peel is smoother and tighter, with fewer splits. The hot alkaline treatment further plasticizes the wood, providing better quality veneer and improved grade recovery.

Veneer peeled from blocks treated with Resi-Vat can actually be dried at a faster schedule in the veneer dryer.

Having put all the adhesive chemistry to work and seeing to it that equipment processes are properly functioning so veneer quality is at optimum gluability texture it then becomes a management function to control the gluing process.

A concept originating two years ago is worthy of mention relative to the in-plant control functions. A certified inspection program was originally launched at the Crossett Division and is an alternate to the random audit quality assurance method used for many years in APA member mills. The new program features a Certified Inspector on the payroll of participating mills, trained and certified by the APA staff functioning under surveillance of quality auditors on the APA staff. The program monitors all manufacturing processes by the Certified Inspectors. The concept has greatly improved quality, reduced consumer complaints and continues to be most effective. The outstanding reception given this program by our management was the key to its success.

Georgia-Pacific has steadily worked to reduce the number of customer complaints since it pioneered the southern pine plywood industry 17 years ago. The results of this work are clearly recorded. Customer complaints per thousand sq. ft. of plywood produced have steadily decreased. This is a result of advances in plywood process technology, resin technology, and a conscientious corporate approach to improved quality.

The following is an interesting blend of plywood process technology and plywood adhesive technology. In the early days of the southern pine plywood industry, it was commonplace to hot press five ply, 1/2-inch thick panels for 7 minutes at 270° F. The relatively low temperature was used to avoid blows. As the industry developed, it was learned that three ply, 1/2-inch panels could be substituted directly for five ply in most applications. Production efficiency is obviously much better with three ply than with five ply. Three ply, 1/2 inch inherently can be cured in the hot press faster than five ply. In addition, faster and faster curing resins have been developed over the years. At present, the usual hot press schedule for three ply, 1/2 inch is three minutes at 330°. So the production rate for half-inch plywood is double that of the early days of the industry.

The forest products industry must continue to modernize its plants and facilities to avoid the problems now facing America's steel and automobile industries. As I have pointed out we have been making progress but in my book the industry's rate of technological innovation has to be stepped up.

Along these lines I would like to share some of the areas we are exploring in resin development:

A. Energy Efficiency

In the future, resins for plywood will have to be increasingly "energy efficient." Energy is a cost to the plywood producer that can only increase, and it will have to be increasingly conserved. Resin development trends will include the following ideas:

1) Liquid resins with higher resin solids content

These will be reacted at a higher resin solids content, not distilled. Distillation is not energy-efficient. More usable pounds of resin solids per reactor hour can be produced and these resins can be transported more efficiently: more pounds of resin solids can be transported per trip. We anticipate this to become effective within six months or less.

2) Faster curing resins

Faster curing resins are more energy-efficient because plywood panels glued with these resins cure in the hot press in a shorter time. More plywood can be pressed per pound of steam. Georgia-Pacific is working to produce resins that cure faster than conventional adhesives. One of these phenolic resins includes a catalyst that reduces hot press times by 25%.

3) Moisture tolerant resins

Resins that tolerate higher than normal veneer moisture can be considered energy efficient. If the resin tolerates more veneer moisture, more veneer can be dried per pound of steam - faster drying schedules or lower temperatures. Georgia-Pacific is developing resins of this type and has some resins available now that can tolerate 20% moisture content (in spots) in the veneer. This project is being given strong impetus.

B. Non-Polluting

1) The trend in the future will be away from any polluting resin characteristics. Most resins in use today are mixed with plywood plant wash water in making the glue mix. In the early days of the southern pine plywood industry, fresh water was used to make the glue mix and the wash water was dumped into the creek. Our plants presently are maintaining a "0" discharge posture as to waste water.

2) On the West Coast some plywood mills are restricted by air quality regulations. One of these regulations restricts the sodium emissions in boiler smoke. The boiler is fired with plywood waste containing some plywood glue. Phenolic resins usually contain sodium hydroxide. Burning plywood waste containing conventional resins would exceed the sodium emission limit. Georgia-Pacific has developed low sodium resins which permit mills in sodium restricted areas to meet the air quality standards.

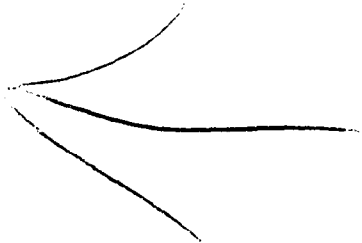
C. Less Dependent Upon Petrochemicals

Petrochemicals are likely to become scarcer and more expensive. The trend in plywood resin technology will be away from total dependency on petrochemicals for raw materials. In the past, there has been no substitute for petrochemical raw materials in plywood resins. One of the first possible substitute materials that comes to mind is sulfite process or kraft process lignins. There are quite a few reports in the literature that describe experimental substitution of lignin for petrochemical raw materials. At Georgia-Pacific one successful lab experiment has been the substitution of polyphenolic material from southern pine bark for part of the phenol requirement in plywood resin. This resin gave good performance in the lab study, with bond durability equivalent to conventional phenolic resins.

Two urea/formaldehyde resins, GP-1940 and GP-1949, represent the best technology currently available on the West Coast for gluing hardwood-faced plywood (interior and marine grades). The resins are classified as "low-fuming," most panel constructions bonded with these products emit formaldehyde odors at these products emit formaldehyde odors at levels far lower than emissions measured from panels bonded with older, more conventional resins. Both resins feature the ability to successfully bond relatively high moisture

content veneer (e.g. 10-20%) providing glue mix formulations are optimized to meet imported tropical hardwood core and face material (e.g. lauan mahogany). In addition, both resins feature excellent storage stability. The GP-1940 exhibits good to excellent assembly time tolerance with adequate pre-pressing properties; in contrast, the GP-1949 exhibits excellent pre-pressing properties with fair to good assembly time tolerance. Both resins are easier to manufacture and handle than are the aforementioned older, more conventional products.

These are exciting new developments and hopefully we can accelerate these processes since a definite need exists in the industry. Technology feeds on itself. Technology makes more technology possible, as we can see if we look for a moment at the process of innovation. Technological innovation is a self-reinforcing cycle. First, there is the creative feasible idea. Second, its practical application. Third, its infusion through the industry. Today there is evidence that the time between each of the steps in this cycle has been shortened. We are in an accelerating change in the forest products industry and may the business climate in Washington D.C. be such that we can nurture the momentum. It has been my pleasure to share some of this change with you.



AD P 002442

CURING UREA-FORMALDEHYDE ADHESIVES IN THICK PARTICLEBOARD MATS¹

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ABSTRACT

A review of literature regarding high frequency heating of composition board mats is presented.

Results of a study involving high frequency heating at the hot press, with high frequency heating begun after press closing, are also discussed. Uniform-density boards were obtained at lower platen temperatures. These boards had soft, rough surfaces and inferior bending properties. At 325 F (163 C) platen temperature high frequency heated boards had density distributions comparable to those of boards produced by straight-forward contact heating at equal platen temperature.

INTRODUCTION

This presentation is concerned with the heating of wood composition board mats in board production.

The most common method of raising mat temperature is with heated press platens. In this hot platen, or contact heating, the mat surfaces in contact with hot platens, are heated first, and the mat interior is subsequently heated primarily by convection of water turned to steam from the mat's surface towards its center (Strickler, 1959). In contact heating, temperature rise is not uniform through the mat thickness, and the heat transfer mechanism by which the mat center is heated depends upon the existence of a temperature gradient.

A heating method which can speed the heating of composition board mats, and the method emphasized in this presentation, is dielectric heating. This is the heating of materials which are electrical insulators to DC or low frequency AC voltages with high frequency electrical energy. In dielectric heating, also known as high frequency (h.f.) or radio frequency (RF) heating, electrical energy is dissipated within the volume of the material as heat, rather than heat being

transferred into the mass from its surfaces. For this reason, temperature rise can be uniform through the thickness of a composition board mat, and average, and especially core, temperature rise can be quicker than with contact heating.

Moslemi (1974) categorizes the ways in which high frequency heating is used in board manufacture as: (1) preheating of the mat prior to pressing in a conventional hot press or (2) application of RF energy at the hot press itself.

Preheating of the mat has received fairly recent attention from German researchers (Gefhart 1975, 1976, 1977, and Koschke 1975), and has been used for many years in a continuous board pressing system in Europe (Maloney 1977, Leppin *et al.* 1966, and Fraser 1975). The Japanese researchers Huang and Mori (1978) investigated prepressing of particleboard mats with simultaneous application of RF energy. This differs from simple preheating, as pressure is exerted on the mat during RF energy application.

Application of high frequency energy to the mat at the hot press is practiced in the United States for the manufacture of medium density fiberboard (MDF) (Raddin 1967, Keesey 1970, Hopkins 1970, and Gray 1974).

The use of h.f. heating in the production of composition boards, like everything else, has its advantages and disadvantages.

¹Paper presented at the "Wood Adhesives - Research, Application and Needs" Symposium, Madison, Wis., Sept. 23-25, 1980.

DISADVANTAGES OF HIGH FREQUENCY HEATING

Disadvantages of h.f. heating include: (1) expense of equipment, (2) expense of energy, (3) potential lack of heating uniformity, and (4) arcing.

High frequency heating requires expensive equipment, particularly when it is applied at the press itself (Maloney 1977, Moslemi 1974). The electrical energy consumed is a valuable form of energy, and RF generators are usually 60% or less efficient (Pound 1973, Raddin 1970).

At a given frequency of RF energy (and hence wavelength), electrode length is limited by voltage variation along the electrode from its feed point to its other end. This voltage variation results in variation in dielectric heating with position along the electrode (Pound 1973). This suggests that panel size is limited when h.f. heating is performed at the hot press. An 8- by 65-foot (2.4- by 19.8-meter) single opening RF hot press has been used for MDF manufacture in the United States (Maloney 1977). It is likely that heating uniformity is attained by multiple feed points on the energized platen.

Arcing between electrodes can be caused by tramp metal, resin balls, or a curled or bent caul plate which contacts both electrodes.

All of the disadvantages discussed here may affect commercial viability of the method, but they generally do not affect board properties of small laboratory manufactured boards, and therefore are infrequently addressed by researchers.

ADVANTAGES OF HIGH FREQUENCY HEATING

Advantages of h.f. heating in composition board production include: (1) shortened press times, (2) reduced (vertical) density variation through the board thickness (not necessarily an advantage), (3) reduced vertical moisture distribution, and (4) improved resin bond (in some instances).

Application of h.f. energy can markedly reduce hot press time, particularly where steam convection to the mat core is slow, as in thick mats. With caul-less systems in particular, platen temperature is limited by resin precure on the bottom surface. At lower platen temperatures, heating of thick mats, particularly of fiberboard, without RF energy application results in long press times.

Reduction in press time obviously depends on the rate of RF energy dissipation in the mat per unit mass (or per unit volume) of the mat. Rate of h.f. power dissipation in the mat is frequently limited by RF generator capacity, but may be limited for reasons other than equipment capacity, such as arcing.

Many researchers have reported press time reductions. Only Pungs and Lamberts (1962) and Leppin *et al.* (1966) report measured RF power dissipation. Researchers usually report nominal high frequency power dissipation stated in terms of generator capacity, or simply make no mention of rate of high frequency energy dissipation.

Neither RF power dissipation, nor temperature rise in a composition board mat placed in a h.f. field is easy to measure. A voltage is induced in thermocouple wires placed in an RF field due to motion of the field relative to the thermocouple conductors. Leppin *et al.* (1966) monitored mat temperature with thermocouple wires by use of an "external voltage division" while applying high frequency energy. Pungs and Lamberts (1962) reported (in German) a method enabling continuous measurement of h.f. power dissipation.

The density distribution of hot pressed composition boards is a result of temperature and moisture distribution through the board thickness, and the interaction of pressure on the mat with these distributions. Application of RF energy alters the temperature (and hence moisture) distribution in the mat and can thereby result in a board of more uniform density distribution. Suchsland and Woodson (1976) however, found that commercial MDF produced on an RF press possessed a marked vertical density gradient. Maloney (1977) indicates that in commercial MDF production (where RF energy is applied at the hot press), the h.f. power is not turned on until the mat has been compressed to the approximate final board thickness. Under these circumstances, the density distribution is probably altered little by application of RF energy.

The works of Stevens and Woodson (1977) and of Leppin *et al.* (1966) who investigated h.f. heating at the hot press (h.f. heating during press closing) and RF preheating, respectively, show that use of h.f. heating can, but will not necessarily, result in boards of more uniform vertical density distribution than does solely contact heating.

The temperature gradient inherent in contact heating, with the convection of steam towards the (comparatively) cooler board core usually results in a moisture distribution through the board thickness. Hopkins (1970) states that this can cause blistering and splitting (blowing) at the center plane of medium density fiberboards. Application of RF energy, because it yields a more uniform vertical distribution of temperature, yields a more uniform vertical distribution of moisture (Pungs and Lamberts, 1962). If, however, the mat is exposed to RF energy while its surfaces contact cold press platens, moisture can migrate to the surface, resulting in an

"inverted" moisture distribution. To avoid this inverted distribution, a lack of resin cure at board faces and platen rusting, the platens are always heated by conventional means (Maloney 1977).

Hafner (1964) and Maloney (1977) state that h.f. heating results in superior inter-particle bond quality due to wetting of particle surfaces which improves resin distribution. They hypothesize that heat generated inside each particle drives moisture to the particle surface thus wetting it.

Koschke (1975) and Leppin et al. (1966) suggest that plasticization of wood particles during preheating of mats improves bond quality. If the particles are plasticized by h.f. preheating, and the resin is not precured, the mechanical properties of the plasticized layers should be improved due to better inter-particle contact and reduced damage to the particles by crushing. Where h.f. heating is performed at the hot press, and h.f. power is not turned on until the press comes closed to stops, reduction in particle damage is not expected.

Stevens and Woodson (1977) applied RF energy at the hot press, activating the generator before closing to stops. High frequency heating permitted faster press closing and yielded superior internal bond strength than that of solely contact heated boards of equal core density.

EXPERIMENTAL WORK

The succeeding section of this paper concerns work involving RF heating at the hot press. The work was performed by the author at Washington State University while a student at the University of Idaho.

One-inch (25.4 mm) thick particleboards of Idaho white pine (*P. monticola*) planer shavings were produced by the five different heating methods shown in Table 1. For each heating method the press times as listed in Table 2 were examined. The press times listed in Table 2 include 45 seconds of press closing. The RF generator was turned on after press closing to insulating stops. Board production constants are listed in Table 3.

The press times examined resulted in boards of approximately equivalent internal bond strength² for the different heating methods (Fig. 1). The boards produced by combined RF-contact heating at 175° F (79.4° C)

²Internal bond and static bending tests were performed according to American Society for Testing and Materials (ASTM) Standard D-1037-72a.

Table 1.--Heating methods

1. Combined heating ¹	175° F platen
2. Combined heating	225° F platen
3. Combined heating	275° F platen
4. Combined heating	325° F platen
5. Contact heating	325° F platen

¹All combined heating treatments involved input of h.f. energy at the same h.f. generator setting.

Table 2.--Press times

Heating treatment	Press times		
	Min and sec		
Combined 175° F	6:45,	7:15,	7:45
Combined 225° F	5:15,	5:45,	6:15
Combined 275° F	4:15,	4:45,	5:15
Combined 325° F	3:15,	3:45,	4:15
Contact	8:00,	10:00,	12:00

Table 3.--Board production constants

Thickness	1.0 inch
Target density	0.72 gm/cc
Resin	Urea-formaldehyde @ 6%
Press closing	45 seconds
RF energy	After press closing (where RF used)

platen temperature had soft rough surfaces which failed in internal bond tests. With the exception of some specimens from combination heated boards at 325° F (163° C) platen temperature, all other internal bond specimens failed in the board center layers. A Duncan's multiple range test showed significant difference (0.05 level) in IB strengths between only two of the treatments (where a treatment is

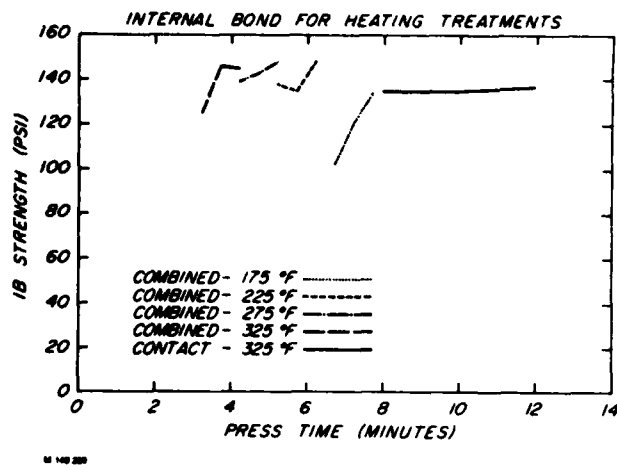


Figure 1.--Internal bond strength versus press time for five different heating methods.

defined as a press time nested within a heating method) in which IB failures occurred in board center layers. The treatments which showed significant difference in IB strength both involved RF heating. It should be noted that the Duncan's test involved no correction for density in the layer of failure. The center densities of h.f. heated boards were higher than those heated strictly by contact with hot platens (Table 4). This suggests that h.f. heating did not result in superior bonding at equal layer density as reported by Stevens and Woodson (1977). A possible explanation for this difference in results is that particle crushing was not avoided or mitigated in this study. Table 5 however, indicates that springback was greatest for boards heated with a combination of h.f. energy and hot platen contact, particularly at lower platen temperatures. If springback is a reliable indicator of degree of resin cure, even between boards of different vertical density distributions, then this suggests that the boards heated by combined means were not as completely cured as those heated solely by contact with hot platens at longer press times. In summary, the results lead to no reliable conclusion regarding comparison of specific IB strength between contact and combined h.f.-contact heating methods.

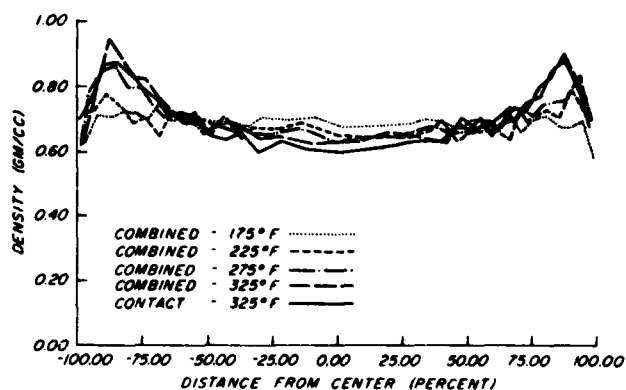
Density distributions of boards produced by the different heating treatments are shown in Figure 2. Lower platen temperatures and application of h.f. energy resulted in boards of more uniform vertical density distribution. The density distributions of h.f. heated boards became more peaked at the faces as platen temperature was raised. At 325° F (163° C) platen temperature the density distributions of h.f. heated boards were

Table 4.--Board center densities

Heating method	Center density gm/cc
Combined (175° F platen)	0.664
Combined (225° F platen)	0.656
Combined (275° F platen)	0.640
Combined (325° F platen)	0.624
Contact heating	0.619

Table 5.--Board thickness

Heating method	Thickness mm
Combined (175° F platen)	26.75
Combined (225° F platen)	26.47
Combined (275° F platen)	26.01
Combined (325° F platen)	25.50
Contact heating	25.32



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Figure 2.--Vertical density distributions for five different heating methods.

nearly identical to those of the solely contact heated boards. The bending properties (Figs. 3 and 4) are believed to largely reflect the boards' density distributions.

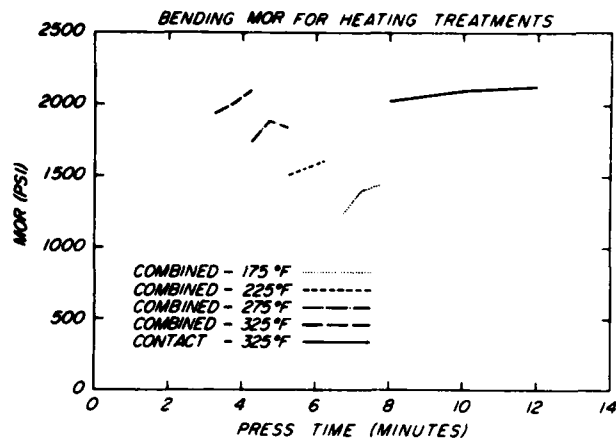


Figure 3.--Bending modulus of rupture versus press time for five different heating methods.

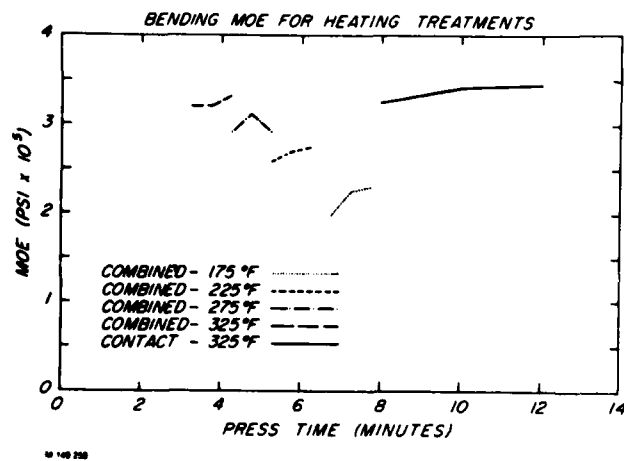


Figure 4.--Bending modulus of elasticity versus press time for five different heating methods.

CONCLUSIONS

Platen temperature had a marked effect on vertical density distribution of boards heated by a combination of high frequency energy and contact with hot platens.

ACKNOWLEDGEMENTS

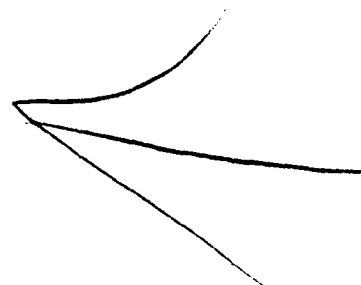
The author expresses his gratitude to the following individuals and organizations: Thomas Maloney, Martin Lentz, John Saunders, and E. Max Huffaker of Washington State University, Mr. George Hespelt of the

University of Idaho College of Engineering, Dr. James Evans, statistical mathematician, U.S. Forest Products Laboratory, Mr. T. A. Wilson of Louisville, Kentucky (formerly with Votator Division of Chemetron Corp.), Potlatch Corporation, and Borden Chemical.

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AD P 002443

EFFECT OF ABRASIVE PLANING STOCK REMOVAL RATE
ON ADHESIVE-BONDED JOINT PERFORMANCE^{1/}

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ABSTRACT

Abrasive planing has certain economic and technical advantages over knife planing of lumber. However, in many instances, the adhesive bonds in lumber products surfaced by abrasive planing before bonding have been found to be of poor quality. In this first of a series of studies on how abrasive planing affects bond quality, feed speed and depth of cut were investigated. Damage was found at every combination of these machining variables evaluated. The amount of damage in terms of bond strength reduction was not strongly or even consistently related to the machining variables. There was no significant difference in the bond strengths among the six combinations of feed speed and depth of cut. The ASTM D-905 block shear specimen when exposed to a soak-dry cycle before testing was far more sensitive to the machining damage than unexposed shear specimens or a tension test specimen, unexposed or exposed. Swelling and shrinking of the crushed cells by the soak-dry treatment in combination with the higher internal stress of the shear specimen account for this difference in sensitivity.

KEY WORDS: Abrasive planing, knife planing, surface quality, gluing, surfacing.

INTRODUCTION

Abrasive planing offers higher volume and higher grade recovery in surfacing lumber as

compared to knife planing (1). Consequently, many companies use abrasive planing to prepare high-grade material for high value bonded wood products. Evidence indicates that wood products companies are experiencing difficulty with bond quality when surfaces are prepared

¹Paper presented at "Wood Adhesives-- Research, Application, and Needs" Symposium held at Madison, Wis., Sept. 23-25, 1980

by abrasive planing. Quality is reduced sometimes from excessive damage to the cell structure of the wood surfaces during abrasive planing. A typical shallow wood failure due to surface damage caused by abrasive planing is shown in figure 1.

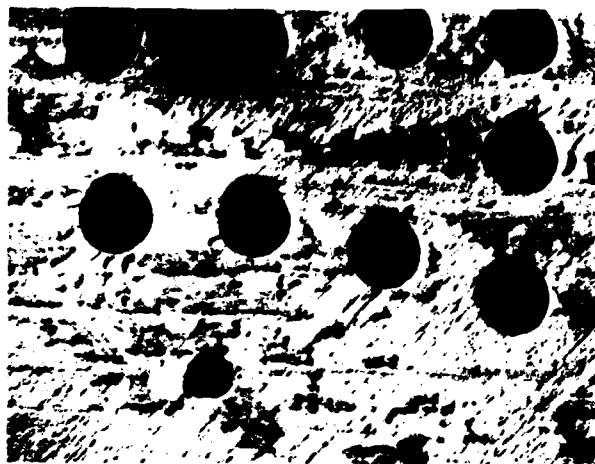


Figure 1.--Shallow wood failure in an industrial bonded hard maple laminate.

Some companies have reported that satisfactory, i.e., undamaged surfaces can be obtained by planing with successively finer grit sizes, finishing with around 100-120 grit size, but this information has not been published. However, Jokerst and Stewart (4) have reported severe damage and reduced bond quality in Douglas-fir and southern pine planed with grit numbers ranging from 36 to 80.

The present study is the first in a series planned to investigate the effects of certain machining parameters on the quality of bonded joints with the expectation that an optimum set of conditions exist where cell damage may be minimized to a satisfactory extent. Both belt loading and power consumption increase with rate of stock removal up to a point. Beyond this point belt loading decreases (6,7). Observations of surface appearance and the geometry of particles removed by the abrasive indicate that at high stock removal rates the abrasive is cutting more than ploughing and crushing. The implication would be that the surface created at a high stock removal rate might not be damaged as much as one created at a lower stock removal rate. To test this theory the effects upon adhesive joint strength of different levels of feed speed and depth of cut using 36-grit-size abrasive were compared with conventionally knife-planed stock.

EXPERIMENTAL

The materials and procedures are outlined in tables 1 to 8. Douglas-fir and yellow-poplar 2 x 4 lumber was cut into 18-inch-long billets free from knots, short grain, and other defects as outlined in ASTM D-905 (3). The billets were conditioned to the selected equilibrium moisture content before further machining. Only the effects of 36-grit abrasive were evaluated.

Table 1.--Materials

Douglas-fir/Phenol Resorcinol
Yellow-poplar/Urea

Table 2.--Machining parameters

Feed speed	
Abrasive planer	45 and 90 ft/min
Knife planer	30 ft/min
Depth of cut	0.010, 0.040, and 0.080 inch

Table 3.--Bonding and testing conditions

Douglas-fir--12% EMC	(27° C--65% RH)
Yellow-poplar--8% EMC	(23° C--44% RH)

Table 4.--Test specimens

Block shear (modified ASTM D-905)
Tension (ASTM D-143)

Table 5.--Bonding conditions

Adhesive spread rate	60#/1,000
Open assembly time	0-5 min
Closed assembly time	15 min
Temperature	73° F
Pressure	150 psi
Cure time under pressure	21 hours

Table 6.--Specimen distribution

	Shear block	Tension
No. Trees	?	?
No. Planks	?	?
No. Billets	56	96
No. Glued Blanks	28	48
Specimens/Blank	5	3
Total Specimens	140	140
No. Treatments x		
No. Exposures	14	14
Specimens/Treatment x		
Exposure	10	10

Table 7.--Exposure before test

- I None--Test at 8 or 12% EMC
- II Soak-dry--Test at 8 or 12% EMC
 - Submerge in water
 - Apply vacuum (30 min)
 - Release vacuum
 - Apply pressure (30 min)
 - Release pressure
 - Dry at 70° C 16 hr

Table 8.--Experimental design

Depth of cut	Exposure			
	None feed speed		Soak-dry feed speed	
	1	2	1	2
1	*			
2				
3				

* 10 replications per block

Two levels of feed speed, 45 and 90 ft/min, and three depths of cut, 0.010, 0.040, and 0.080 inch, were studied in Douglas-fir and yellow-poplar specimens in both the shear and tension loading modes. Knife planing for the control surfaces was at 1/16-inch depth of cut and 20 knife marks per inch.

Before the experimental machining of the surface to be glued, the billets were machined in three steps down to a thickness equal to

the desired finish thickness (1 in.), plus the depth of the experimental cut (i.e., 1.010, 1.040, or 1.080 in.) with a carefully sharpened and set knife planer. Abrasive planing variables of feed speed and depth of cut were randomized to reduce any effect belt wear might have on the wood surface quality. The actual order or sequence of machining was recorded and used in the analysis of the results. Immediately after machining, the billets were sealed in polyethylene bags and stored at -10° F until 4 hours before bonding.

Bonding environment was controlled at 23° C (73° F), 44% relative humidity (RH). Yellow poplar blanks were loaded with urea-formaldehyde resin adhesives and Douglas-fir blanks with phenol-resorcinol formaldehyde resin adhesive. The adhesives were mixed according to the manufacturers directions and applied with a conventional grooved rubber roll spreader. The spreader was set to apply nominally 60 pounds of adhesive per 1,000 square feet of glueline on the abrasive-planed billets. Spread was incidentally lower on the smooth knife jointed control billets than on the rough abrasive-planed surfaces. Spread rate also varied slightly with time due to the adhesive viscosity change over the approximately 1 hour required to bond a group of billets. After the open assembly period the billets were assembled and pressed in manual screw presses at 150 lb/in².

The bonded blanks were removed from the press after approximately 21 hours and allowed to further cure for 30 days at the appropriate conditions for each species (12% EMC--Douglas-fir or 8% EMC--yellow poplar). Block shear specimens (fig. 2) were cut from the cured blanks as prescribed in ASTM D-905. Tension specimens (fig. 3), as described in ASTM D-143 (2), were made by first drilling carefully spaced 1-inch diameter holes (using a jig) in each blank and then sawing individual specimens from the drilled blank. (Note: a great deal of difficulty was experienced because the drill center spur wanted to ride to one side of the bondline or the other, thus forcing the holes off center. A better technique has since been found to use a 1-inch outside diameter plug cutter instead of a drill.) The cut specimens were stored at the appropriate conditions until testing or exposure. Before testing, the specimens of each species-specimen type group were further subdivided into two subgroups; one subgroup to be tested as conditioned without further exposure, and the second subgroup to be subjected to 1 cycle of vacuum-pressure soak-dry. Specimens subjected to the vacuum-pressure soak-dry exposure were re-equilibrated at the appropriate conditions before testing.

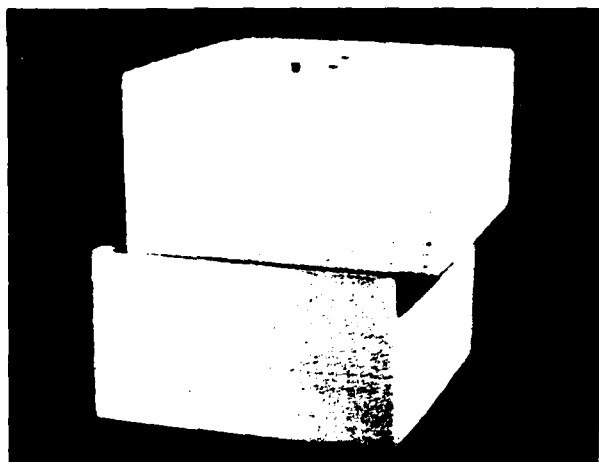


Figure 2.--Modified ASTM D-D905 shear specimen.

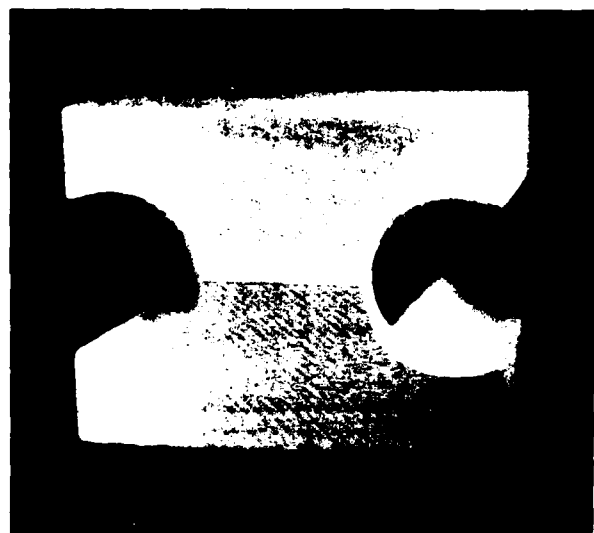


Figure 3.--ASTM D-143 tension perpendicular to the grain specimen adapted to bondline testing.

Bonded joints and the fracture surfaces after testing were examined by white light and fluorescence microscopy as well as scanning electron microscopy.

RESULTS AND DISCUSSION

The data were analyzed using the Statistical Analysis System (SAS) (5). The analysis included multiple-regression analysis of the model:

$$Y = a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5$$

where Y = joint strength

X_1 = machining sequence

X_2 = feed speed

X_3 = depth of cut

X_4 = specific gravity of the least dense adherend

X_5 = specific gravity of the more dense adherend

$a_1, a_2, a_3, a_4,$ and a_5 = fitted coefficients

The model was fitted to the 60 data points comprised of 10 values from each of the six abrasive-planing treatments. The knife-planed specimens were not included in the analysis. Each independent variable was tested for its contribution to the model, and in a second step the two-way and three-way interactions between the independent variables were tested.

Analysis of variance of the six abrasive-planing treatments was conducted and the differences among treatment mean strengths were compared by Duncan's Multiple Range Test.

Figure 4 shows typical deep wood failure in a shear specimen of Douglas-fir which had undamaged surfaces at bonding, and shallow wood failure in a specimen which had damaged surfaces at bonding. Figure 5 shows transverse sections through the bondlines between undamaged and damaged surfaces.

Shallow wood failure and damage, as shown in the figures, was caused by the 36-grit abrasive at all feed speeds and depths of cut used in this study. No strong or consistent relationship between the machining parameters and adhesive bond strength was found. Very few significant differences were found between the treatment mean bond strengths, and no differences due to abrasive treatment were found in four of the eight species-specimen-exposure groups.

Initial high-quality joints were formed in knife-planed yellow-poplar specimens bonded with urea-formaldehyde adhesive and in Douglas-fir specimens bonded with phenol-resorcinol adhesive. Dry unexposed specimens with the exception of Douglas-fir shear specimens equaled or exceeded the species shear value

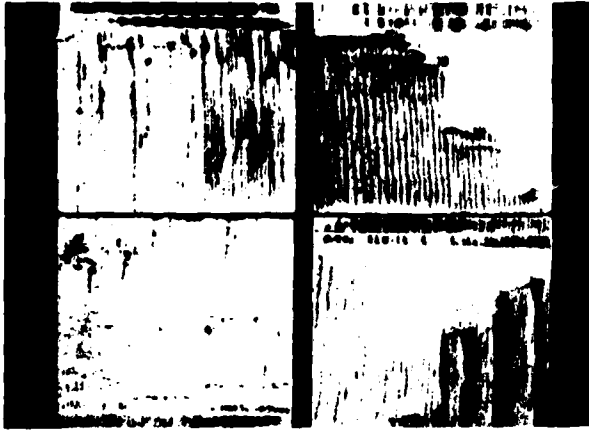


Figure 4.--Deep wood failure (left) in a specimen with a bond between undamaged surfaces and shallow wood failure (right) in a specimen with a bond between damaged surfaces (Douglas-fir).

for solid wood. Soaked and dried knife-planed specimens with the exception of yellow-poplar shear specimens all retained at least 70% of their respective solid-wood values as published in table 4-2 of the Wood Handbook (8). Figures 6 through 9 show the strength of the solid-wood, unexposed (dry), knife-planed specimens and exposed (soaked) knife-planed specimens. The large decrease in strength of yellow-poplar shear specimens after exposure is due to the effects of water and swelling and shrinkage stresses on the urea-formaldehyde adhesive.

The large stress gradient which occurs in the shear specimen during the soak-dry treatment may be significantly larger than occurs in the tension specimen which explains the difference in the performance of the two specimens.

Although the strengths of the unexposed (dry) shear specimens (figs. 10 and 11) varied somewhat by the abrasive treatment, they were generally comparable to the strengths of dry, knife-planed joints. The effects of abrasive planing were not apparent in this comparison. The effects were quite obvious, however, after the soak-dry exposure of the fir shear specimens (fig. 11). After this exposure, the

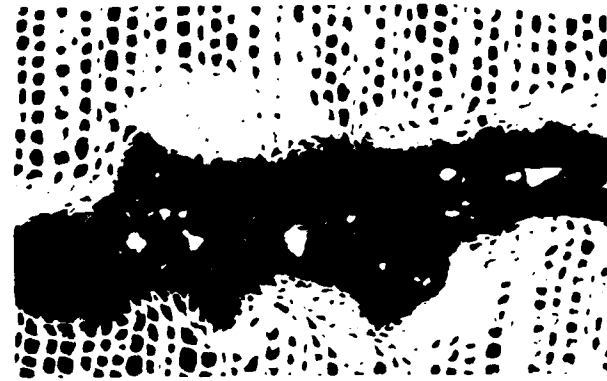
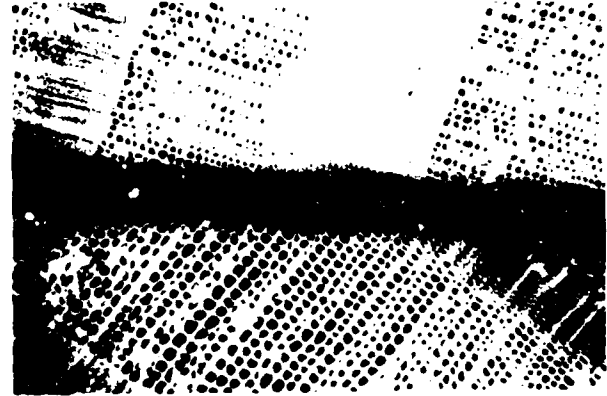
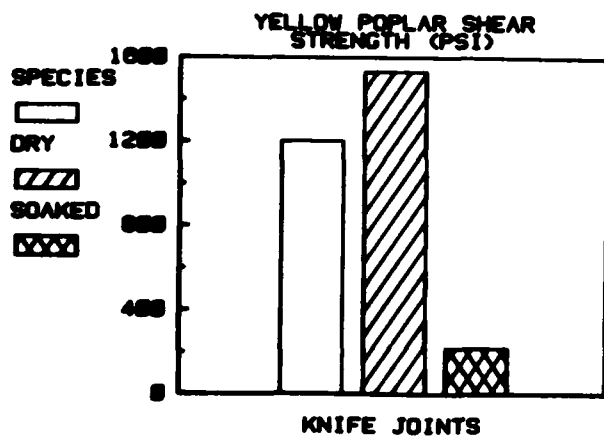


Figure 5.--Light micrographs of transverse sections through bondlines between sound surfaces (top) and damaged surfaces (bottom) (Douglas-fir). Note crushing of the cells in the bulge areas where abrasive particles have passed.

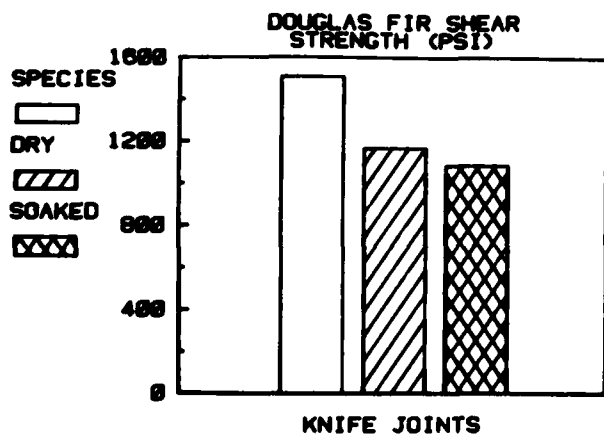
shear strength dropped to 8 to 80% (generally 30-50%) of the value for exposed knife-jointed specimens. This result agrees with Jokerst and Stewart's (4) findings that abrasive-planing damage was not evident in the shear strength of unexposed Douglas-fir and southern pine specimens, but was readily apparent in the percentage of delamination of knife-planed versus abrasive-planed specimens after soaking and drying. No conclusions about the effects of machining damage on yellow-poplar specimens after exposure could be drawn because of the deterioration of the adhesive itself during the soak-dry treatment.

Jokerst and Stewart's earlier results suggested that a cleavage or tension specimen simulating the stresses at the edge of a joint during swelling and shrinking might be more sensitive to machining damage than the shear test. Indeed, both dry and soaked tension specimens showed small to moderate reductions in bond strength (figs. 12 and 13), whereas only the soaked shear specimens showed the effect. However, none of the tension specimens showed the dramatic reduction that the soaked Douglas-fir shear specimens did.



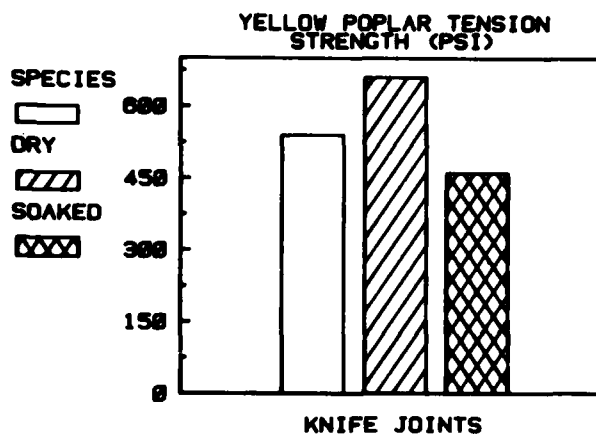
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Figure 6.--Comparison of the shear strengths solid yellow-poplar wood and of bonded knife-planed specimens without exposure and after exposure to a soak-dry cycle.



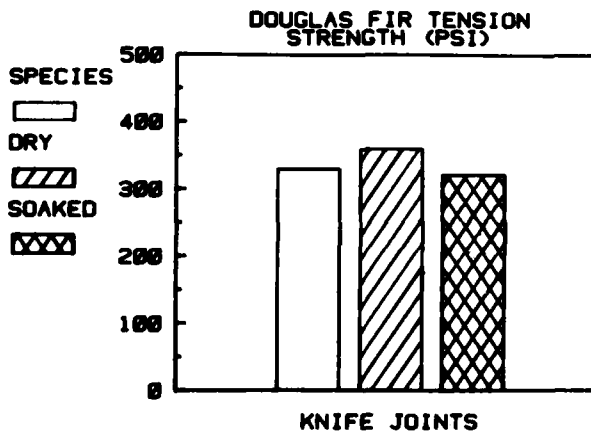
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Figure 7.--Comparison of the shear strengths solid Douglas-fir and of bonded knife-planed specimens without exposure and after exposure to a soak-dry cycle.



M 149 185

Figure 8.--Comparison of the tension strengths of solid yellow-poplar wood and of bonded knife-planed specimens without exposure and after exposure to a soak-dry cycle.



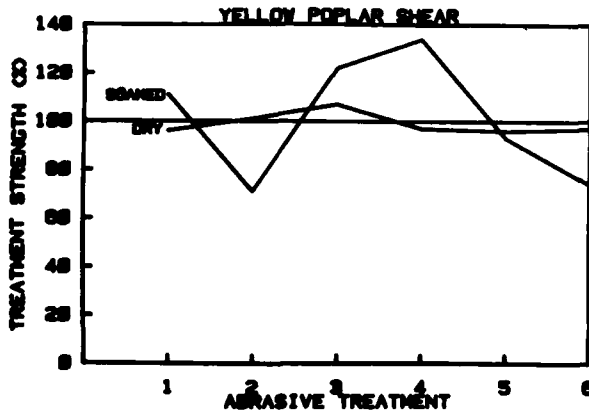
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Figure 9.--Comparison of the tension strengths of solid Douglas-fir and of bonded knife-planed specimens without exposure and after exposure to a soak-dry cycle.

Based on these observations, apparently two factors besides crushing of the wood surface cells are necessary for the strength of the bonded joints to be greatly reduced; swelling of the crushed cell walls and an internal shear or cleavage stress of a critical magnitude. Figure 14 shows a portion of bondline with undamaged (knife-planed) Douglas-fir earlywood. Figure 15 shows many ruptures of the cell walls. In particular it

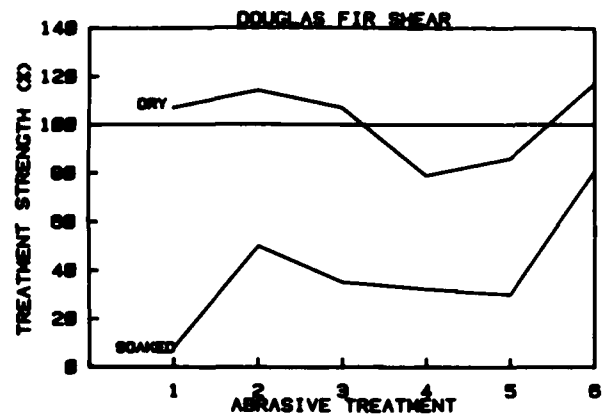
is evident that the S_1 layer has been ruptured along the cell radius. But, because the bulk of the cell wall is the S_2 layer, which is still intact, the cell still has a high strength. However, with the S_1 layer ruptured, restraint of the S_2 layer against swelling has been removed. Unrestrained swelling of the cell wall and the internal stress from the overall swelling break the S_2 layer and other layers apart.

Figures 16-19 show the coefficients of variation for shear strength of specimens from the four species-specimen groups. Treatment 7



M 148 177

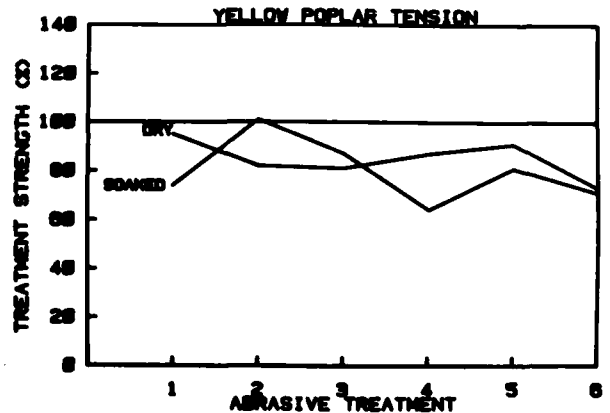
Figure 10.--The shear strength of bonded abrasively planed yellow poplar specimens as a percentage of the appropriate bonded knife-planed specimen strength. The abrasive treatments are as follows: (1) 45 fpm/0.010-inch depth of cut, (2) 45/0.040, (3) 45/0.080, (4) 90/0.010, (5) 90/0.040, (6) 90/0.080.



M 148 178

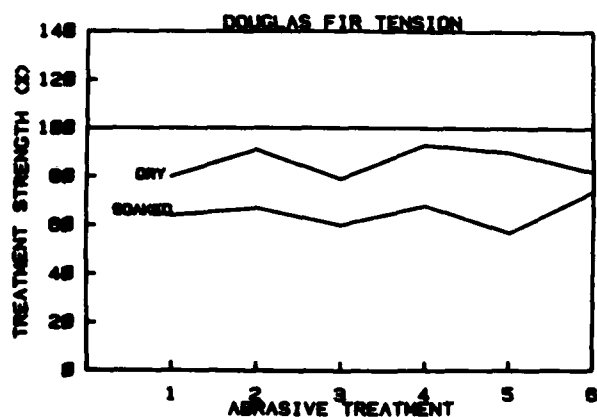
Figure 11.--The shear strength of bonded abrasively planed Douglas-fir specimens as a percentage of the appropriate bonded knife-planed specimen strength. Abrasive treatments are described in figure 9.

in the figures is the knife-planed specimen data. The coefficients for dry specimens generally ranged between 10-20% which was expected. Dry yellow-poplar shear specimens in figure 16 had the lowest and most uniform coefficients. Soaked yellow poplar shear specimens had the highest and least uniform coefficients due to the large number of failures (zero values) during soaking. Soaked and dried specimens in the other groups (figs. 17-19) were also considerably higher and less uniform than their unexposed counter-



M 148 178

Figure 12.--The tension strength of bonded abrasively planed yellow-poplar specimens as a percentage of the appropriate bonded knife-planed specimen strength. Abrasive treatments are described in figure 9.



M 149 178

Figure 13.--The tension strength of bonded abrasively planed Douglas-fir specimens as a percentage of the appropriate bonded knife-planed specimen strength. Abrasive treatments are described in figure 9.

parts. The variable effects of the swelling and shrinking stress may be related to specific gravity variation.

Multiple-regression analysis failed to show any straightforward or consistent relationship between the machining parameters and strength. R^2 , a measure of the adequacy to the model ranged from 0.02 to 0.43. (The R^2 value for a perfect model would be 1.00.) The inclusion of two- and three-way interactions (i.e., depth of cut x low specific gravity, etc.) increased the R^2 range to 0.15 to 0.67. Specific gravity of the lower density adherend was the best predictor of joint strength in many of the species-specimen-exposure groups.

Duncan's multiple-range test detected occasional differences between machining treatment in terms of bond strength means in three out of eight species-specimen-exposure groups. The difference between the lowest and highest rates of stock removal (0.09 in.³/in./sec in the 45/0.010 treatment versus 1.44 in.³/in./sec in the 90/0.080 treatment) was a factor of 16 times. However, no difference between machining treatment was detected in five out of eight species-specimen-exposure

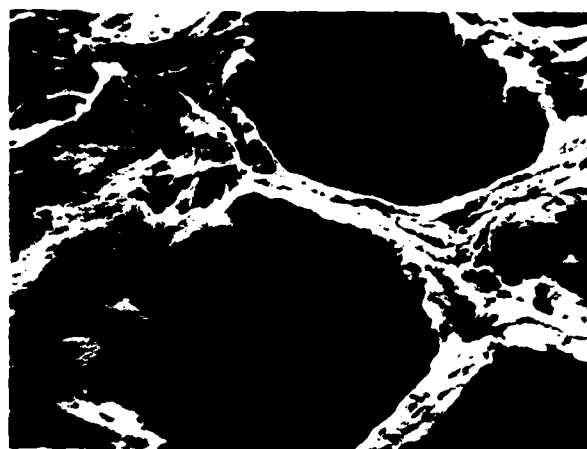


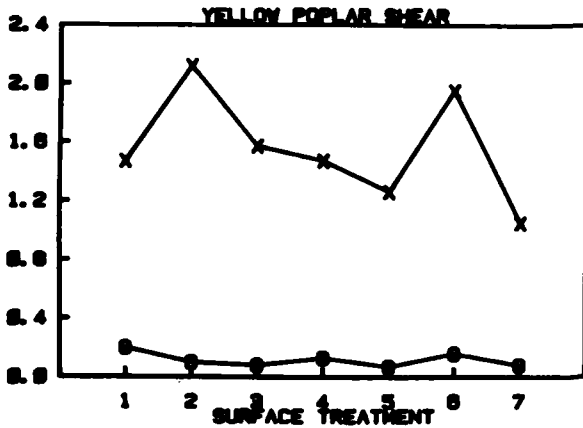
Figure 14.--Earlywood in knife-planed Douglas-fir adjoining the adhesive bond line. No damage is evident.



Figure 15.--Earlywood in abrasive-planed (36 grit, 90 fpm, 0.080-inch cut) Douglas-fir adjoining the adhesive bondline. Severe buckling and rupture of cell walls is evident.

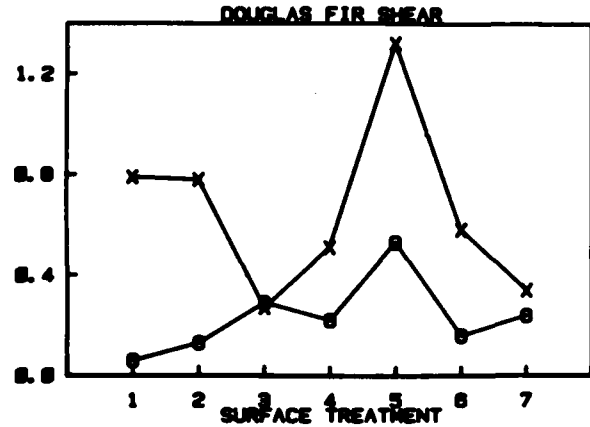
groups. Only in Douglas-fir shear specimens soaked and dried before testing was a pronounced difference noted among any of the treatment mean strength.

In this case, contrary to what might be expected, the highest rate of removal resulted in significantly higher strength than the lowest rate of removal and all the other rates as well. Grinding processes remove stock more or less by plowing or cutting. The plowing may be associated more with the low stock removal rates and cutting more with the high stock removal rates. The systematic differ-



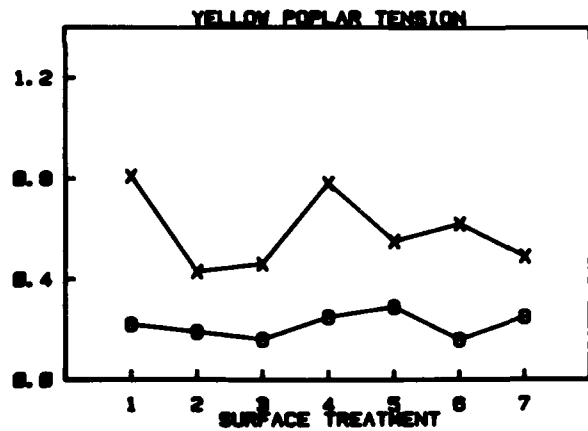
M 148 181

Figure 16.--Coefficients of variation of the six abrasive planing treatments and one knife planing treatment average strengths (yellow-poplar shear). Surface treatments 1-6 are abrasive, treatment 7 is knife planed. Treatments 1-6 are as follows: (1) 45 fpm/0.010-inch cut, (2) 45/0.040, (3) 45/0.080, (4) 90/0.010, (5) 90/0.040, (6) 90/0.080.



M 148 180

Figure 17.--Coefficients of variation of the six abrasive planing treatments and one knife planing treatment average strengths (Douglas-fir shear). Surface treatments 1-6 are abrasive, treatment 7 is knife planed. Treatments 1-6 are as follows: (1) 45 fpm/0.010-inch cut, (2) 45/0.040, (3) 45/0.080, (4) 90/0.010, (5) 90/0.040, (6) 90/0.080.



M 148 182

Figure 18.--Coefficients of variation of the six abrasive planing treatments and one knife planing treatment average strengths (yellow-poplar tension). Surface treatments 1-6 are abrasive, treatment 7 is knife planed. Treatments 1-6 are as follows: (1) 45 fpm/0.010-inch cut, (2) 45/0.040, (3) 45/0.080, (4) 90/0.010, (5) 90/0.040, (6) 90/0.080.



W 148 103

Figure 19.--Coefficients of variation of the six abrasive planing treatments and one knife planing treatment average strengths (Douglas-fir tension). Surface treatments 1-6 are abrasive, treatment 7 is knife planed. Treatments 1-6 are as follows: (1) 45 fpm/0.010-inch cut, (2) 45/0.040, (3) 45/0.080, (4) 90/0.010, (5) 90/0.040, (6) 90/0.080.

ences in bond quality which were expected due to the step-wise changes in the machining parameters tested were not evident in terms of bond strength.

SUMMARY AND CONCLUSIONS

Abrasive planing has attractive economic advantages over knife planing. However, some manufacturers of adhesive-bonded wood products have experienced delamination of joints between abrasive-planed materials. The cause of the delamination has been determined to be crushing damage of the surface cells by the abrasive. The objective of this study was to examine the effects of machine feed speed and depth of cut upon the surface damage and bond quality.

The abrasive-planed joints tested without a swell, shrink exposure showed little or no difference in strength from knife-planed joints, although the wood failure of the abrasive-planed joints was almost entirely shallow compared to the typical deep wood failure of a joint between undamaged surfaces. The strength of exposed abrasive-planed joints was considerably reduced. A need for improved glue joint testing apparently exists.

Multiple-regression analysis and tests for significant differences failed to reveal any consistent relationship between the bond performance and the abrasive-planing treatment of differences in bond performance due to the treatments tested.

The conclusions drawn from the results are:

1. Surface damage occurs in planing with 36-grit abrasive.
2. Damage occurs over a wide range of feed speeds and depths of cut.
3. There is no trend toward more or less damage as the feed speed or depth of cut is varied.
4. Machining damage is evident in the type of failure of dry, unexposed specimens but not in strength.
5. The effects of machining damage on the strength of abrasive-planed joints is only evident after a swelling and shrinking cycle.
6. The tension specimen is only slightly more sensitive to machining damage than the shear specimen in the dry test, and is distinctly less sensitive in the soak-dry test.

FUTURE PLANS

In the next study, grit-size effects and adhesive-penetration effects will be studied using both yellow-poplar and Douglas-fir shear specimens.

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