

HOW OVERDRYING WOOD REDUCES ITS BONDING TO PHENOL-FORMALDEHYDE ADHESIVES: A CRITICAL REVIEW OF THE LITERATURE. PART I. PHYSICAL RESPONSES

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(Received September 1989)

ABSTRACT

This review critically evaluates literature on the ways in which excessive drying (overdrying) inactivates wood surfaces to bonding, primarily for phenolic adhesives. In Part I of a two-part review, three inactivation mechanisms involving physical responses to overdrying are considered: (1) exudation of extractives to the surface, which lowers the wettability or hides the surface; (2) reorientation of wood surface molecules, which reduces wettability or places for bonding; and (3) irreversible closure of large micropores in cell walls. I believe that extensive evidence from wood bonding and paper sizing research supports the mechanism of extractives-induced low wettability as the cause for inactivation of Douglas-fir and southern pines. Molecular reorientation and irreversible micropore closure are proposed wood inactivation mechanisms that involve loss of wettability and bonding sites.

Keywords: Drying, inactivation, adhesive, bonding, review, extractives, mechanism, wettability.

After 50 years of production experience and investigations, bonding problems are frequently encountered with wood veneer that has been taken to complete dryness (overdried) at high temperatures. In 1987, production of structural panels was estimated (Anonymous 1988) to be greater than $24 \times 10^6 \text{ m}^3$ ($27 \times 10^9 \text{ ft}^3$, $3/8$ -in. basis), of which $20 \times 10^6 \text{ m}^3$ ($23 \times 10^9 \text{ ft}^3$) was plywood. If we consider only the several percent of plywood panels with bond deficiencies caused by overdrying [5–10 percent has been estimated by Lambuth (1987)], then at an average 1987 value of \$158/ m^3 (\$140/ 10^3 ft^3) (Spelter personal communication), this represents \$160 to \$320 million of panels that either must be sold by the manufacturer for lower value purposes than intended or that will require earlier replacement than the end user expected. Either alternative has a negative impact on the timber resource and increases costs to consumers. The introduction of high moisture content gluing processes and gentler redrying procedures has reduced the problem somewhat in recent years, but these innovations have not eliminated the problem. A flurry of work in the 1960s and 1970s sheds light on aspects of the problem, but no definitive solution to the problem or commonly accepted understanding of the cause or causes for inactivation was found.

An American Plywood Association publication (Erb 1975) states that overdried

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veneer can be caused by any of three problems in dryer operation: drying temperature too high, drying time too long, and dampers open too far (recycling less heated air). Low-moisture content veneer will result if unnecessarily long drying times are used, at any temperature. Very dry wood absorbs too much moisture from the adhesive, reducing resin flow during hot pressing. This may or may not be accompanied by surface inactivation. Surface inactivation is caused by high drying temperature and is aggravated by long drying times, low dryer humidity, and low veneer moisture content. As the moisture content of the wood falls below the fiber saturation point, the more strongly held bound water moves to the surface as a vapor. Upon leaving the surface, this vapor will not produce the cooling effect that the evaporation of free liquid water did. Thus, the veneer surface temperature begins to increase. If the surface temperature exceeds safe limits, surface inactivation will occur. For the most sensitive American coniferous species, this limit appears to be 160 C (Erb 1975). Hancock (1963) appears to have first used the term inactivation. Previously, Northcott et al. (1959) defined casehardening as "a change in surface condition of the wood, other than a coating from external source . . . , that is induced or intensified by the manufacturing process and that makes the surface difficult to bond." Northcott et al. (1962) indicated a number of conditions that add to the problem, most of these involving insufficient resin moisture penetration into the wood during the assembly period.

This is the first critical review of the literature dealing with the mechanisms by which overdrying inactivates wood surfaces to bonding. In reviewing the literature, I have come to some conclusions and insights that I hope will aid in understanding and eventually solving the inactivation problem. In Part I, inactivation mechanisms involving physical responses of wood to overdrying are examined. In Part II, to be published separately, mechanisms involving chemical reactions that may cause inactivation are examined.

Little of the literature on room temperature wetting phenomena of wood is discussed, except as that information appears to relate to high-temperature drying phenomena. I discuss related work on wettability of plastics and paper and pulp. The wettability of these materials has important implications for the mechanisms of wood inactivation. One conclusion I have come to is that extractives have a leading role in the inactivation of the two most important species groupings in the United States: Douglas-fir and southern pines. For more than a decade, this effect was overshadowed by the seeming weight of evidence in favor of oxidative and pyrolytic mechanisms of inactivation.

BACKGROUND

As early as 1950, researchers attempted to explain why a normally satisfactory bonding process occasionally produced an unusually large number of bonds with low wood failure values (Northcott et al. 1959). The problems were associated with dryers that were too hot or drying times that were too long. Northcott et al. (1959) were the first to suggest that inactivation occurred because the bonds were not adequately curing, or hardening. Water needs to be eliminated from the adhesive for fast cure. Some of the water usually diffuses into the wood during the assembly time, but for inactivated wood, too much water was being retained in the bondline. This excess water slowed the cure.

Inactivated wood is just not very dry. Wood dried slowly at low temperatures to a very low moisture content readily absorbs moisture from an adhesive (Wellons 1980). An inactivated surface will not let the moisture or resin easily penetrate the surface layers. Erb (1965) notes that a phenolic adhesive applied to a good veneer surface will not transfer to an inactivated veneer surface, but an adhesive will transfer from an inactivated veneer to another veneer if that second one is properly dried.

The problem became very important economically on the West Coast of North America in the 1950s, and that is where the majority of studies have occurred. Several of the western softwoods were found to be susceptible to inactivation. When the plywood industry started to develop in the southern United States in the 1960s, southern pines were also found to be susceptible to inactivation. The symptoms of the problem are more difficult to recognize for particle- and flake-based products, because of the multitude of interconnected variables; consequently, less research has focused on these furnishes.

Inactivation has been noted for several resins, all of which need to dissipate water during their cure. Of those resins, only phenol-formaldehyde resin has been widely investigated, and for that reason this review focuses on research involving that adhesive. However, some work has been published on each of the following resins: urea-formaldehyde (Chow 1975; Kaufert 1943; Northcott 1957; Tsutsu-moto and Sato 1965); phenol-resorcinol-formaldehyde (PRF) (Isaacs and Choong 1969; Bohlen 1972); casein (Kaufert 1943; Northcott et al. 1959); hot-press protein (Erb 1965); cold-set soybean (Sisterhenm 1961); and poly(vinyl acetate) with lumber joints (Eckelman et al. 1986). Discussion of several general areas of production and research experience will set the stage for discussion of the mechanisms of inactivation.

Species effects

Inactivation is more prevalent in some wood species than in others (Erb 1965, 1975). Erb (1975) notes that the maximum safe drying temperatures for avoiding inactivation in several softwoods varies with species. Southern pines are the most susceptible to inactivation, followed by ponderosa pine; then a group consisting of inland Douglas-fir, western white pine, and larch; and finally coastal Douglas-fir. Hemlock and white fir are not considered to be severely damaged by normal drying temperatures, though extremely high temperatures can cause surface inactivation. Canadian researchers (Northcott et al. 1959; Chow 1971; Troughton and Chow 1971) have studied inactivation in spruces. Spruce heartwood is more easily overdried than other types of wood because it is quite low in moisture content, compared to the sapwood. When Engelmann spruce heartwood and sapwood, which are difficult to separate visually (Erb 1965), are sent through a dryer together, the dryer will be set to fully dry the sapwood, which is wetter. Consequently, the heartwood will be overdried. Difference in species is one of the factors that weighs against a simple degradative mechanism, such as oxidation, which should affect most softwood species in much the same way. Unfortunately, few publications on high-temperature inactivation have compared species based on bonding results. Hardwoods have not been ranked according to their relative susceptibility to inactivation.

Effect of high temperature

As noted earlier, inactivation is promoted by long heating times at high temperatures, starting at 160 C in some species. Inactivation seems to occur after the wood surface has essentially lost its last moisture. At this point, the diffusion rate of moisture up to the surface is slower than the evaporation rate of water away from the surface (Atherton and Welty 1972). Evaporative cooling can no longer keep the surface temperature from climbing to temperatures near that of the air in the dryer.

The problem is aggravated because the raw material on or coming onto the production line is not extensively sorted for its initial dryness or likely drying speed before it is dried (e.g., separating heartwood from sapwood where that is possible, wetter logs from drier logs, and one species from another). Unfortunately, the needs of maximum acceptable production rates with the fewest necessary personnel do not allow detailed sorting. The lack of sorting can also occur in a particleboard plant running on various residues.

Inactivation of plywood veneer has been a major problem for 30 years, but mills can alleviate this problem by not drying large portions of veneer to near the oven-dry state on the first pass. The small quantity of veneer that is above moisture limits can later be redried. Most mills will set aside veneer that is above moisture specifications and dry that batch separately at milder conditions. The redry rate now quoted by conventional plywood plants not using radio-frequency redryers is generally in the 8 to 12% range, but some of the redried material and some of the originally dried material can be overdried. It has been estimated that in 1987, 5 to 10% of plywood was produced from overdried veneers (Lambuth personal communication).

A number of researchers have shown that high drying temperatures affect the bond strength of plywood. De Bruyne (1939) appears to be the first to have suggested that poor bondability of plywood surfaces might be due to overheating. Currier (1958) showed poor bondability between plies for Douglas-fir veneer dried in several types of dryers. He concluded that Douglas-fir heartwood dried at temperatures above 205 C suffered a loss in breaking strength in 2-cycle boil tests when compared to veneer dried at 177 C or below. Full-immersion water adsorption tests showed decreased water absorption capacity with either increased dryer temperature or increased drying time.

Northcott et al. (1959) wrote that the hygroscopicity and wettability of wood are reduced by drying wood at high temperatures (or by seasoning it at lower temperatures for longer times). Because the water cannot be adsorbed into the wood during the assembly period, water is retained within the bondline. Northcott et al. thought this could have two effects. First, at the start of hot pressing, the water and high temperature can excessively fluidize the resin, too much of which penetrates the wood. Second, the excess water necessitates a longer than usual time to cure the adhesive. Northcott et al. found that bonding at 3% moisture content, rather than at 6% or higher, gave the best bond quality for four species investigated: Englemann spruce, Douglas-fir (coastal and inland), a true fir, and black cottonwood. Sanding, increasing the closed assembly time, and increasing the press time improved the bond quality for these species, apparently by letting more water penetrate the wood before or during the hot-pressing operation. Undercured plywood bonds increased in strength while sitting at normal temperatures

(some for 2 years) or while exposed to accelerated aging conditions. The authors also noted that earlywood-to-earlywood bonds were more resistant to inactivation than latewood-to-latewood bonds as drying temperatures rose. Northcott et al. (1962) confirmed that inactivation induced by heat treatment resulted in a decrease of the absorptivity of the wood. The effect occurs much more quickly at higher temperatures.

Inactivation can be alleviated by removing the surface layer, for example, by sanding, to reveal a fresher surface (Kaufert 1943; Hancock 1963, 1964; Northcott et al. 1959; Walters 1973); however, some reports suggest that inactivation can affect layers below the surface (Walters 1973). Unfortunately, removal of inactivated surfaces is uneconomic for full-size veneers and would be impossible for flake furnishes.

Effect of jet drying

In jet dryers, the high air velocity allows for faster water and heat transport across the air-wood interface. The increased surface drying rates may increase the chances for surface inactivation before the veneer is completely dried. Veneers exposed up to 427 C initial drying temperatures for only limited times, before a lower temperature dryer section was used to complete drying, showed little effect of initial jet dryer temperatures on the bond strength of heartwood and southern pine sapwood (Kozlik 1974). However, as veneers were taken to lower final moisture contents (at 316 C or 427 C, but not at 177 C), or as the velocity of the drying medium was increased from 450 to 1,800 m/min (1,500 to 6,000 ft/min), the wood discolored more, a likely sign of inactivation. At higher temperature and air velocity combinations, discoloration started to occur when the average moisture content of the piece was not yet below the fiber saturation point (Laity 1970; Kozlik 1974). Superheated steam lowered the final moisture content more quickly than air at 316 C and higher (Laity 1970; Kozlik 1974). Kozlik concluded that the drying medium had no effect on wood failure for either species, but drying with steam allowed a slightly higher value for shear strength in the southern pine plywood. For low temperatures and low air velocities, steam helped protect wood against charring better than did air (Laity 1970). In another study, Walters (1973) showed that, for two fixed-time jet dryer schedules on southern pines, veneer with higher initial moisture content had better surface wettability after drying and produced plywood with higher wood failure values. Milligan and Davies (1963) jet-dried western softwoods (including fir, spruce, hemlock, and Douglas-fir) down to 3 to 5% moisture content. Veneer surface temperatures, measured by radiation pyrometer, remained substantially below the dryer temperatures as long as the veneers still contained some moisture that could be evaporated. This cooling effect continued down to overall veneer moisture contents as low as 3%, while the high velocity dryer gases were at temperatures well above those ordinarily considered safe.

POSTULATED PHYSICAL MECHANISMS

Three inactivation mechanisms involving physical phenomena are discussed in this section: extractives-related nonwetting, surface molecular reorientation, and micropore closure. A fourth possible mechanism, contamination by soot or

other airborne deposits, is seldom a problem. Wire brushing sooty surfaces to improve their bondability (Currier 1958) removes not only such deposits but also the outer layer of wood. This top layer of wood was the actual locale of inactivated material (Lambuth personal communication).

Effect of extractives on wettability

Time-dependent changes of wood wettability at room temperature have often been attributed to migration of extractives to the surface. The most extensive wettability study is that of Gray (1962). He measured advancing and receding contact angles for 19 wood species, and he measured the changes of contact angles with time. Sanding the surfaces of "contaminated" specimens produced lower contact angles in subsequent wetting tests, the amount of the effect varying by species. Gray attributed surface contamination to low molecular weight fatty acids, high extractives content, and high resin content. From wetting and adhesion theory, he reasoned that wetting involved an interaction of the wood surface energy with the surface tension of adhesives and finishes.

The increase of contact angles with time for extracted and unextracted Douglas-fir and redwood was studied by Nguyen and Johns (1979). Douglas-fir was more wettable after extraction with benzene-alcohol, both initially and after 84 h, whereas redwood showed a slight decrease of wettability after extraction. Nguyen and Johns felt that environmental factors influenced the equilibrium values, because the ratio of dispersion forces to polar forces came to about the same equilibrium value in each case, regardless of the total surface energy.

A lack of wettability of very dry veneer at room temperature is not sufficient to predict its bondability. Wellons (1980) dried and conditioned Douglas-fir sapwood to moisture contents between 3 and 18% at temperatures of 21 C to 32 C. Contact angles for aqueous sodium hydroxide droplets on these dried surfaces were initially high, and the angles decreased with time. The driest sample had the highest initial contact angle and showed the smallest absolute or relative change of contact angle with time, decreasing from 117° to about 102° in 4 min. The sample having 18% moisture content had an initial contact angle near 74°, which decreased to about 22° in 4 min. In bonding experiments with high-temperature inactivated wood, one expects bonds to fail because too much retained moisture inhibits cure. The bonds between very dry wood in Wellons' experiments failed, but for just the opposite reason. The adhesive lost too much moisture to the wood, leaving the adhesive incapable of flowing over the surface or penetrating the wood properly.

A recent, short paper (Hse and Kuo 1988) reviews evidence for influences of extractives on wood bonding and finishing. That review includes some references to both phenolics and other wood adhesives.

Temperature effects

Conventional high-temperature drying and fatty acids.—Hancock (1963) explored the effects of extractives on the bonding of Douglas-fir. He showed that extracting inland Douglas-fir heartwood with acetone left veneers that could resist inactivation at 171 C, unlike unextracted veneer. However, his attempts to reimpregnate extracted veneers with extractives did not result in lower bond quality. Subsequently, Hancock (1964) found a correlation between the percentage of fatty

acids containing 20 or more carbons and the susceptibility of various Douglas-fir specimens (heartwood and sapwood, coastal and inland types) to inactivation at 185 C. Furthermore, after applying 1% by weight of distinct species of fatty acids to veneer surfaces, he found that wood failure values for plywood shear tests decreased as the fatty acid chain lengths increased from 12 to 22 carbons. There was also a dramatic decrease in wood failure upon increasing the drying temperature from 150 C to 185 C. In addition, bond quality results indicated that the causal agent could be removed, either before or after drying, with *n*-hexane or petroleum ether. Boiling or soaking in water did not reverse inactivated surfaces.

In seeming contradiction to Hancock's work (1963, 1964), Troughton and Chow (1971) found that the amount of fatty acids collected at the surfaces of white spruce did not correlate with plywood bond quality. Silicic acid powder (100 μ) was spread on undried veneer surfaces to absorb fatty acids coming to the surface during drying. Only 0.1 to 0.2% by weight of total fatty acids collected on the silicic acid after heating at 150 C for 20 to 80 min. The amount collected did not vary greatly with heating time. Of that small amount of fatty acids collected, the fraction having acids with chain length greater than 20 carbons was so small that it was felt those longer-chain acids were not worth including with the tabular data on the 16- to 20-carbon fatty acids. However, the data show that the small amount of the 18- and 20-carbon saturated fatty acids in both heartwood and sapwood did increase gradually by a factor of 2 to 3 over that period.

Panels made from veneers dried for those same times showed a substantial decrease in wood failure and a reduction in strength, for both heartwood and sapwood veneers. Troughton and Chow (1971) tried to correlate the amount of total fatty acids detected on the surfaces with strength and wood failure, but did not find a correlation, either for increasing times at 150 C or for two widely different times at each of four other temperatures. Troughton and Chow felt this lack of correlation between analyzed fatty acid concentration and measured bond quality, combined with Chow's (1971) oxidation studies, relegated the role of fatty acids to a catalytic role in the inactivation process. The analysis with silicic acid presumes that the fatty acid moves onto the silicic acid almost as an extension of the same environment as in wood. Movement of fatty acids to the silicic acid particles may not be this simple, and airborne movement of the acids is possible, as will be mentioned in later work on paper sizing. With airborne movement, vapor pressure differences between species of fatty acids could skew the molecular weight distribution of fatty acids arriving on the silicic acid particles.

Hemingway (1969) found that high temperatures drastically changed the wettability (measured by water drop penetration) of yellow birch surfaces, but had less effect when the surfaces were previously extracted in acetone. He concluded that acetone-soluble components are responsible for the changes in wettability. Sanding a heated surface restored the wettability. Hemingway extensively analyzed the fatty acid and ester contents after several heating times at three temperatures. He used 10-h acetone extractions of ground wood to obtain the samples. Calculations based on estimated wood surface areas indicated that it would be necessary for the fatty acid concentration to be about 130 parts per million (ppm) to begin to influence the surface wettability and about 400 ppm to provide a monomolecular layer on the wood surface. Saturated fatty acids in the free state (not tied up in esters) in fresh wood amounted to only 20 to 40 ppm of the oven-dry wood weight.

The amounts of free, saturated fatty acids did increase with time at high temperatures (105 C, 160 C, and 220 C), presumably by hydrolysis of the respective esters. The measured amount of saturated fatty acid esters (fats), originally present at ten times the concentration of the corresponding free fatty acids, tended to decrease with heating time at these temperatures. Unsaturated fatty acids and esters were initially present at six times the concentration of the saturated types.

Because of their general structural similarity to saturated fatty acids, unsaturated fatty acids and esters also repel water. However, the predominant di- and tri-unsaturated 18-carbon fatty acids (linoleic and linolenic) and their esters decreased by over 50% during 20 min heating at 220 C. The decrease of these species was attributed to their oxidation to other products. Hemingway wondered whether "the reduced wettability [of birch surfaces] might be related to the oxidation of the linoleic acids and their esters" (1969).

Postdrying extraction trials (not detailed) in a variety of different organic solvents (including acetone, petroleum ether, and benzene-ethanol) reportedly did not increase the wettability of high-temperature-dried veneer (Northcott et al. 1962). However, extractions in mild solutions of sodium hydroxide did increase wettability. Solutions of sodium hydroxide or sodium carbonate, sprayed on wood to retentions of 5 to 10% of dry wood weight, helped restore wood surface bondability, especially at longer closed assembly times. The drying temperature of the Douglas-fir heartwood was not mentioned by Northcott et al. (1962). Hancock (1964) had used 185 C for most experiments. That temperature is at the threshold for inactivating inland Douglas-fir over very long drying times but below the threshold for coastal Douglas-fir (Erb 1975).

Sizing of paper and pulp. – At this point, it is important to introduce literature on the self-sizing of paper (i.e., decreased wettability of cellulosic fiber materials without intentional additives) and on related work. Paper stored on a shelf or in a warehouse for weeks or months will often become much less absorbent, and in some cases, highly resistant to penetration of aqueous fluids. The chemical composition of the paper will not have changed to any discernible extent. Swanson and Cordingley (1959) reasoned that the change of wettability must be due to surface changes that produce a surface less polar and more hydrocarbonlike. That could be accomplished either by movement of some extractives or by a chemical reaction making the surface molecules more like hydrocarbons. Stearic acid was chosen as a typical fatty acid found in paper extractives. In a closed chamber, stearic acid vapors were able to diffuse through the air to previously extracted paper handsheets, even at room temperature. The rate at which paper absorbed stearic acid increased with temperature, the rate roughly doubling every 10 C between 25 C and 105 C. The degree of sizing increased quickly at first but then leveled off. Aluminum and calcium ions from the pulping process promoted quicker sizing development, although the absorption rates for stearic acid did not increase. Paper exposed to methyl esters of fatty acids at 105 C did not develop sizing even after many hours; this behavior indicates the importance of carboxyl groups, presumably in anchoring the sizing molecules to the surface.

Another fatty acid extractive that will cause sizing in paper is oleic acid. Many wood species contain larger quantities of oleic acid than of stearic acid. Oleic acid has a higher vapor pressure than stearic acid, but Swanson and Cordingley (1959)

found that oleic acid develops sizing more slowly. They also found that resin acids and unsaponifiable fractions of pitch will produce sizing of paper.

Sinclair et al. (1960) found that even straw pulp, which contained none of the rosin chemicals used for artificial sizing, became quite water resistant when pulped. The presence of metal ions (Pb, Cu, Fe, Cr, Al, Zn) could promote sizing, but the pH range of sizing effectiveness was dependent on the type of ion (usually acidic conditions were more favorable). Several types of wood pulps also contained substances to make them water resistant; again, the effect varied with the pH of the pulping process. From preliminary, undescribed tests, Sinclair et al. (1960) concluded that lignin, phenols, flavones, and fatty acids were the sizing substances, and that the metal ions formed water repellent metal derivatives with these compounds. Fiberboards of straw pulp were exposed to vapors of fatty acids containing 10 to 16 carbons at 125 C for up to 8 h. Fiberboards treated this way absorbed 90% less water; for caproic acid (10 carbons), this required 1 h of treatment; for myristic acid (14 carbons), 4.5 h were needed. At 140 C, palmitic acid (16 carbons) required 3 h; with shorter fatty acids, this level of sizing was reached in less than an hour. The sizing effect was not lost if the treated boards were subsequently heated in a vacuum (100 C at 660 mm Hg) for 8 h, in an attempt to evaporate the molecules causing the sizing. Neither could the sizing effect be removed by thorough extraction with either diethyl ether, ethyl alcohol, or a petroleum naphtha solvent. It was assumed that an ester bond had been formed between the fatty acid and the cellulose. A cellulose powder exposed to hot lauric acid (12-carbon) vapors gained 0.5 to 0.6% in weight, by crude weighing. This treated cellulose powder would float on top of water, whereas the untreated cellulose readily wet and sank in water. Subsequently, the treated powder was mixed with hot alcoholic sodium hydroxide to saponify the esters and release the acid as its salt. The quantity of lauric acid later recovered, 0.35% by weight, roughly agreed with the original amount of lauric acid.

A monolayer of fatty acids deposited on metal substrates show increased wettability to water droplets over time as the fatty acid molecules reorient to the water environment, unless the monolayer of molecules is firmly attached to the surface (Yiannos 1960). Elevated temperatures, which provide moderate mobility for sizing molecules to flow and spread, may encourage stronger bonding between the sizing molecules and cellulose and, most important, encourage polar groups to reorient inward away from the air-particle interface, thereby creating a strongly hydrophobic surface (Davison 1975). Swanson et al. (1971) reported that paper fibers could be rendered water repellent by stearic acid (18 carbons) absorbed from either the vapor state or benzene solution, provided the paper was subsequently heated for a long time (conditions not described). After attempting to remove the stearic acid with benzene, Swanson et al. found that a small proportion could not be removed. This small amount of stearic acid was thought to have esterified with the cellulose, producing an extremely water-repellent paper. The amount remaining on the fibers was determined to be 0.012% (120 ppm), based on dry fiber weight; reportedly, this is equivalent to 6% of a continuous monolayer film on the fibers.

Swanson (1978) found that stearic acid and behenic acid (22-carbon) easily chemisorbed onto cellulose film, the rates and the maximum concentrations being

about 2.5 times greater at 105 C than at 85 C. The layers of chemisorbed fatty acids could not be extracted with benzene, water, or weak hydrochloric acid, but the fatty acids could be removed with sodium hydroxide or 0.01 M sodium methoxide-methanol. Evidence from infrared spectra showed that an ester bond had formed between the fatty acids and cellulose. During the first few percentage increases of monolayer absorption, the contact angle of water on the surfaces rises disproportionately fast, indicating that the molecules are masking an area far greater than their own cross-sectional area. From an analysis of the relative efficiencies of surface coverage by the fatty acids and from theoretical models for packing in fatty acid monolayers, Swanson showed his data are consistent with a model of molecules being oriented at an acute angle inclined to the surface, while the molecules have sufficient kinetic energy for the hydrocarbon tail to flail about the surface. This model would allow the molecule to cover over 10 times as much surface area as when they lie down flat and 60 times as much as when they stand straight up, packed tight. As chemisorption continues, the molecules appear to orient perpendicular to the surface.

Other work confirms the helpful effects of sodium hydroxide on paper wettability. Takeyama and Gray (1982), using electron spectroscopy for chemical analysis (ESCA), also came to the conclusion that stearic acid was chemically bonded to paper treated with stearic acid and vapor. This was based on the characteristic energy states of the carbon and oxygen atoms in the atomic layers nearest the surface. Neither acetone nor ethanol-benzene extraction was able to remove the stearic acid. A drop of water put on the treated paper showed no tendency to spread, even after several hours of contact time. However, after that paper was treated with 0.01 M sodium methoxide-methanol, water blotted into the paper as readily as into fresh filter paper.

If fatty acids are responsible for inactivation, then converting those acids to salts, by means of free alkali, might retard or prevent the process. Higgins and McKenzie (1963) found some evidence that pulps maintained their strength better in the presence of alkaline salt solutions than without the alkali. Horn (1975) found that soaking sized, recycled paper in 0.5% NaOH restored the bonding strength to levels found with unsized pulp.

In normal drying, one can visualize that the surface and area beneath it are at or near 100 C for quite some time. Water at this temperature is probably hydrolyzing fats and providing a liquid surface on which the fatty acids can spread. Directly at the surface the water turns to steam, at which point the more volatile fatty acids will steam distill from the surface. Singleton (1960), citing Gensecke, displayed a graph showing the steam distillation pressures of the fatty acids. At 205 C, 10-carbon capric acid in steam will boil at 100 mmHg pressure. This is a fairly high vapor pressure, considering that 100 mmHg is also the vapor pressure of methanol evaporating at 21 C. The less volatile (higher molecular weight) fatty acids will be deposited at the surface. Water being continually driven off at the wood surface should enhance an esterification reaction between fatty acids and wood hydroxyl groups, thus bonding the less volatile fatty acids at the surface, as in chemisorption.

Conventional high-temperature drying and other extractives. —Migration of wood resins to the surface of veneer was mentioned as a possible cause of poor wetting

(Sellers 1977). Pitch-soaked southern pine veneer has lower wood failure values than normal veneer (Koch 1964; Haskell et al. 1966). A complicating factor for interpretations is that veneer from pitch-soaked areas, usually in heartwood, is often brittle and has a rougher surface (Haskell et al. 1966), which would result in poorer bonding strength or wood failure. Temperatures higher than 190 C cause excessive flow of pitch and glazed surfaces, which impair bondline quality (Haskell, in Koch 1972). Pitch deposits, containing excess resin, occur most likely in conifers normally having resin canals: pines, Douglas-fir, spruces, and larches. However, Hancock (1964) did not find a correlation between the amounts of resin acids or volatile extractives from Douglas-fir and the susceptibility of Douglas-fir to inactivation. Moreover, abietic acid, a common resin acid, was added to veneer at the same 1% levels as for the fatty acid tests (see earlier section, Conventional High-Temperature Drying and Fatty Acids). The abietic acid did not appreciably inactivate the surfaces even after heating at 185 C.

Suchsland and Stevens (1968) found that extracting southern pine sapwood with acetone, before drying, improved final plywood strength when the veneer was dried to surface temperatures of 260 C. For unextracted veneer, there appeared to be no degradation of bond quality when the surface temperature of unextracted veneer reached just 218 C. When surface temperatures reached 260 C, plywood made from the unextracted veneer had only 77% wood failure and its strength was 15% lower than the average of all veneers heated to lower temperatures. However, when extracted veneer was used and the surface temperatures reached 260 C, the bond quality of extracted veneer was little affected, even though the surfaces had a “scorched, brittle appearance.” The wood failure of these darkened, extracted veneers was 87%, and the average plywood shear strengths declined only 5% relative to all veneer heated at lower temperatures.

Lambuth (1980) mentions natural latex, oleoresins, phenolic substances, and polysaccharides as materials that may concentrate on the surfaces of hardwood veneers by drying, thereby presenting barriers to bonding.

A polysaccharide exudate from larchwood can inhibit good bond formation. The Douglas Fir Plywood Association (1960) reported that galactan (arabinogalactan hemicellulose) can exude out of western larch heartwood in substantial quantities, particularly from the outer heartwood during high-temperature drying. Adhesive bond quality decreases as the amount of galactan on the surface increases. The galactan is soluble in water; thus, increasing the assembly time apparently benefits bond quality.

Hot-press drying. – Another drying process to transfer heat quickly to wood is hot press, or platen, drying. A light pressure ensures contact of a hot platen against the wood surface, and a grooved caul plate allows the moisture to escape from the wood surface. Kadlec (1980) and Sandoe (1980) both used one source of platen-dried veneer to study the effects of this drying method on wettability and on bondability, respectively, of Douglas-fir at four veneer thicknesses (from 2.5 to 10.1 mm). The range of platen temperatures used was from 163 C to 238 C. In both studies, the pressing times at platen temperature were varied to get the desired final moisture contents (1, 5, and 9%). There was no attempt to cause severe overdrying. In Kadlec’s study (1980), the wettability, measured by contact angle or by liquid drop penetration time, generally decreased with increased platen

temperature; however, the trend was not strong or consistent, and the wettability measures did not correlate well with platen temperature. Sanding improved the wettability, but allowing surfaces to sit for 30 days decreased the wettability.

Sandoe found that wood failure of his parallel-laminated specimens was consistently high for all conditions and tests (Sandoe 1980; Sandoe et al. 1983). There was no consistent trend of bond shear strength with platen temperature. The shear strength values for the platen-dried material were scattered among those for control specimens oven-dried at 218 C to the same moisture contents. There was only a 5% decrease of average shear strength as final out-of-dryer moisture content changed from 9 to 1%. A piece of solid wood of the same total thickness had a shear strength comparable to that of laminated platen-dried veneers. It appears the platen-dried surfaces were not inactivated, possibly because they were not strongly overdried.

The presence of the platen at the surface may also influence the hot-press drying results. The aluminum platen provides an aluminum oxide surface. Bogue et al. (1986) credit an aluminum surface with an orienting force similar to, though weaker than, polar liquids like water. A platen also excludes oxygen over much of the surface. Moreover, the wood surface in contact with the hot platen is, almost from contact, above the boiling point of water, in contrast to normal steam-heated air-drying or direct-fired gas drying. Kadlec (1980) mentions that the water probably leaves through the lathe checks that run across the caul grooves. Within the lathe checks, the temperature may be closer to the boiling point of water. It is possible that the chemical potential gradient is such that fatty acids will not be moved to the platen surface but will distribute themselves in some unknown way, influenced by lathe checks. In addition, if much of the fatty acids are generated by hydrolysis from fatty acid esters in the presence of water, the quick drying out of the surface layer would quickly slow the hydrolysis there, although the process would continue unabated further into the wood bulk. The decrease of wettability Kadlec saw over the 30-day storage period may be due to migration to the surface of the fatty acids generated at deeper levels.

Not all press drying trials have been so benign. Northcott's (1957) initial hot-press drying trials showed an inactivation effect. However, his veneers were dried at very high temperatures (to 284 C) with intermittent steam release every 10 sec. Koch (1964) dried 11.1-mm ($\frac{7}{16}$ -in.) southern pine veneer between screens and ventilated cauls at platen temperatures at 149 C for 23 min. He found severe resin exudation and substandard wood failure results.

Bohlen (1972) preheated two 50-mm-thick billets of Douglas-fir for 1 min against a heated platen, spread a PRF resin on the first of the two, assembled the two billets, and pressed them together for another minute, using their residual heat to cure the resin. The platen temperatures were varied between 171 C and 260 C. The proprietary, commercial method Bohlen used with the high-temperature PRF adhesive required pretreating the wood with a 50% aqueous resorcinol solution before heating. For controls, Bohlen used billets that had been heated at those same temperatures and some that had not been heated. The control billets were bonded at room temperature using a standard PRF adhesive. Bonded test samples and controls showed bond strength losses as the platen temperatures used for heating the billets were increased to 260 C. The test samples bonded with the resorcinol treatment and residual heat showed greater strengths and higher wood

failure than the controls. Bohlen noted that all billets heated at 260 C and some heated at 238 C showed charring of the wood surface. No clear conclusion can be drawn as to any inactivation effect on the high-temperature bonding in these tests because of the uncontrolled and changing wood surface temperatures, the obvious wood degradation (charring) at higher temperatures, and the likely effects the different high temperatures of billets had on the viscosity of the PRF resin during final assembly. However, the room temperature bonded controls showed a continuous decrease of ultimate shear strength and of wood failure as pretreatment platen temperatures rose from 193 C to 260 C. This behavior is likely due to an unspecified inactivation effect.

Measures to counteract nonwetting

The wettability of wood surfaces by adhesive resins might be increased by several means. First, wetting agents can be included in the adhesive formulation (Sellers 1985; Casilla et al. 1984). Second, a nonaqueous solvent, such as methanol, can be incorporated in the formulation to carry resin components into the wood where water cannot penetrate (Sellers 1985). Third, higher levels of sodium hydroxide can enhance wettability in several ways. Sodium hydroxide helps wet the surface (Kadlec 1980; Casilla et al. 1981) and swells the wood structure. By hydrolyzing ester bonds between fatty acids and cellulose, sodium hydroxide can break down a chemisorbed nonwetting layer, and the resulting sodium salt of the carboxylic acid should be more soluble in the resin. Fourth, higher humidity levels can be used within the dryer. This assumes that water is maintained at the wood-air interface, retarding formation of strong fatty acid-wood ester bonds at the surface.

Treatments of the wood may also produce the desired wettability improvements. A patented chemical treatment to produce better adhesion from overdried veneers uses the reaction product of ethylene oxide with a multifunctional active hydrogen compound from groups such as alcohols, amines, amides, fatty acids, or mercaptans (Huff 1973). A preferred class of such compounds includes the polyhydric alcohols or long chain fatty acid mono esters of these compounds. Huff noted that the products generally could be classed as nonionic surface active agents.

The compound highlighted in the patent examples was tris (polyoxyethylene) sorbitan monooleate. Applied typically as a 2% aqueous solution to green veneer at retention levels of 0.26 kg/m² (0.5 lb/1,000 ft²), this compound improved the bond strength of Douglas-fir dried at 177 C for 26.5 min or severely overdried at 199 C for 45 min. The oleate chain should make the compound more compatible with hydrophobic surfaces, and the polyoxyethylene chains branching off the sorbitan ring provide a somewhat more polar substrate for polar adhesives to wet. Treatment of wood surfaces after drying was not effective. Because several chemical reactions are needed to produce this chemical, the resultant cost might limit its use in normal production.

Early Forest Products Laboratory results (U.S. Department of Agriculture 1953) on lumber joints of several species indicated beneficial effects from the application of a 10% sodium hydroxide solution to wood surfaces for 10 min, after which the excess was wiped away and the wood was bonded with casein adhesives. The treatment was deleterious to white oak, but did help six other species. Similarly,

calcium hydroxide solution treatment also gave improved bond strength for some species.

In the early days of direct oil-fired burners for drying plywood, insufficiently burned oily contaminants sometimes deposited on veneer. Removing the darkened surface layer of Douglas-fir with wire brushes significantly improved the durability of adhesive bonds (Currier 1958). However, industrial tests (Lambuth personal communication) found that the cause of poor bonding was not soot but inactivation of the wood surface. With the recent increased use of wood-fired heaters, which use bark, board trim, wood shavings, and other waste wood, there can still be problems from carryover materials if surface deposits are very heavy or interfere with the resin curing process. In these cases, prevention is the best measure.

Molecular reorientation at surfaces

Evidence from nonwood polymers

It is known that synthetic polymers molecules on the surface can reorient to present a low energy (hydrophobic) surface to air. For polyethylene that was plasma-treated to introduce nitrogen-containing groups onto the surface (Everhart and Reilley 1981), subsequent reorientation resulted in fewer reactive groups remaining on the surface for chemical reaction. Reorientation was aided by solvents that break up hydrogen bonding at the surface. In some cases, solvent vapor may just as effectively hasten reorientation as does a liquid solvent, whereas dry aging may induce the change only over much longer times (Everhart and Reilley 1981). Briggs et al. (1980) speculate that during aging of corona discharge treated poly(ethylene terephthalate), the less mobile chains slowly reorient so that the newly created phenolic hydroxyl groups form internal hydrogen bonds. That would result in fewer polar sites for bonding one surface to a like surface. This aging effect is accelerated at higher temperatures.

In some cases polymer reorientation is reversible. Gagnon and McCarthy (1984) showed that the contact angles of oxygen-modified polyethylenes could be varied between 70 C and 95 C by alternate exposures to alkaline solution and to hot air. A fluorinated plastic, made wettable by surface modification and then made hydrophobic by heating in air, did not exhibit lower contact angles again when exposed to alkaline conditions. Conditioning styrene-butyl acrylate films against water or against air produced peel strengths that differed by a factor of two (Bogue et al. 1986), reflecting changes in wettability, based on contact angles.

Water placed on the surface of polyethylene grafted with acrylic acid side chains similarly shows alterable wetting behavior (Lavielle and Schultz 1985). A wide range of surface-sensitive techniques gave evidence that a surface that initially starts out as hydrophobic can reorient within days, at room temperature, to show a very hydrophilic surface capable of reacting with polar molecules. The acrylic acid groups were initially more than 4 nm below the surface, judging by photoelectron spectroscopic evidence. Sorption of water into the plastic, though much faster than the reorientation, may have helped plasticize the reorienting movements of the polymer chains. Heating the acrylic acid-grafted polyethylene above its melting point leads to the original hydrophobic surface.

Of interest in regard to press (platen) drying of wood, and the lack of inactivation seen in those experiments, is the demonstration by Mazeau (cited in Lavielle and

Schultz 1985) that when acrylic acid-modified polyethylene bonds to aluminum, a reorientation effect occurs such that a chemical reaction can take place at the interface between the oriented acrylic (carboxylic) acid groups and the aluminol functional groups on the aluminum oxide surface. It would be interesting to determine if the good bonding results of Sandoe (1980) for platen-dried veneer, mentioned earlier, had anything to do with the polar aluminum surface. Masking the platen surface with a thin coating of a fluoroplastic would lower the surface energy and should affect the bonding, if aluminum does affect surface energy.

Yasuda et al. (1981) showed that even quite hydrophilic molecules can display hydrophobicity at air interfaces. Water contact angles were measured on a hydrogel that had been cast from a hot solution of gelatin. That gelatin, containing 97.5% water showed advancing contact angles in the range of 90° to 120°, but the difference between advancing and receding angles was more than 90°. On a much longer time scale, contact angle hysteresis was observed for polypropylene that had been plasma-treated to introduce more polar (oxygen) functionality onto the surface. Large changes in the initial contact angle occurred over the first 8 days after the plasma treatment, but the advancing and receding angles were quite different at any stage. In both systems, the phenomena are attributed to molecular mobility under the influence of a driving force. When the polypropylene is strongly crosslinked, the rate of contact angle decrease for surfaces in contact with water is slowed down, because chain mobility is reduced.

Implications for wood behavior

Reorientation should be a significant factor in loss of wettability of wood, which has both very polar parts and hydrophobic parts. Indeed, this may be part of the aging process in which surfaces become less wettable as they are stored (Stumbo 1964). For the cut-through cell walls, perhaps the molecules reorient to present the least hydrophilic surface possible. To differentiate hydrophobicity caused by reorientation from hydrophobicity caused by extractives migrating to the surface, one could extract those migrating substances out of the wood before testing and aging. Indeed, for cellulose Swanson and Cordingly (1959) found benzene-alcohol extracted pulp handsheets did not develop sizing (water-repellency) after 3 days heating at 105 C. At high drying temperatures, reorientation and other molecular movements will be speeded up, allowing a hydrophobic surface to be formed in less time. This would be particularly true when the temperature and moisture content are such that lignin and hemicellulose are above their glass transition temperatures, which is likely even for dry surfaces, at temperatures above 200 C (Kelley et al. 1987). If there is a substantial amount of steam in the drying atmosphere, this may reduce the driving force for a hydrophobic adjustment, which in turn would slow down the development of surface inactivation.

Micropore closure

The behavior of cellulosic cell walls changes upon exposure to high temperatures or upon drying out. There may be clues to the inactivation of wood in the behavior of cellulose. Never-dried cellulose is much more reactive than air-dried or heat-dried cellulose (Fahmy and Mobarak 1972). The sorption and diffusion properties change irrecoverably once the first drying has occurred (Ingram et al. 1974).

Stone and Scallan (1965) presented a lamellar model of the cell wall in which

flat micropores weave between the lamellae, with spacings from 2 to 30 nm. The data indicate that during a first-ever drying, the large micropores are lost first, and these are not fully recoverable during a subsequent soaking. A low degree of this effect can be produced by room temperature drying over phosphorous pentoxide. If the drying is done at 105 C, more porosity is lost, and drying at 150 C causes the loss of yet more porosity (Stone and Scallen 1966).

Hatakeyama et al. (1976) showed that heating amorphous cellulose to progressively higher temperatures seemingly induces reorganization to a slightly more crystalline form. In a cell wall, drying perhaps creates new, more perfectly aligned hydrogen bonds between parts of lamellae pressing together. These more perfectly formed bonds, as in crystalline cellulose, may no longer be separable by intrusion of water.

Micropore closure on drying has implications for wetting; for example, Wellons (1980) has shown that it is harder to wet wood that is at a lower moisture content. And, if anchoring of resins is important, as Nearn (1974) has stated for phenolic adhesives, the closure of larger micropores should limit penetration by larger resin molecules and lessen the bond strength and wood failure.

CONCLUDING REMARKS

Part I of the review has considered four types of inactivation mechanisms: airborne contamination from the dryer, extractives-related nonwetting, reorientation of molecules at the surface, and irreversible closure of larger micropores in cell walls. I believe that inactivation is not one phenomenon, but several. The evidence is strong that migration of extractives that are not wettable by water and their chemisorption at the surface is the likely mechanism for high-temperature inactivation of Douglas-fir and southern pines. The exudation of galactan hemicellulose, which can hide much of the surface area, is apparently responsible for the inactivation of western larch.

Part II of this review (a separate publication) will discuss the effects that chemical reactions can have on inactivation phenomena and summarize my interpretation of the literature regarding the phenomena known collectively as surface inactivation.

ACKNOWLEDGMENTS

The author thanks Dr. Alan Lambuth for initial encouragement to do this review and for discussions of industrial experience with wood inactivation.

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