Influence of extractives on wood gluing and finishing—a review

Chung-Yun Hse
Mon-lin Kuo

Abstract

Migration of extractives to the wood surface alters the properties of wood as an adherent. Extractives change the wettability and the curing properties of adhesives. A desirable wettability-permeability relationship is sometimes affected by extractives, thus reducing the gluebond strength and performance. Past efforts to determine which of the components of extractives affect adhesion are reviewed. The most common deleterious effect of extractives on finishing is discoloration of coatings and paint films. Another adverse effect is that extractives retard the hardening of finishes. Not all the effects are unfavorable, however. Some extractives significantly improve the durability of the surface coating and contribute to paint holding. Methods of minimizing the effects of extractives are also reviewed. Their application depends on the wood species involved and on the relative value of the products. Economic principles dictate the feasibility of the methods used.

All woods contain extractives. These minor components can be readily extracted from wood with neutral organic solvents or water. Extraneous substances are extremely variable in composition and quantity both between and within (i.e., sapwood vs. heartwood) species. They may include hydrolyzable or condensed tannins, flavonoids, lignins, stilbenes, fatty acids, resin acids, other complex terpenoids, waxes, sterols, sugars, cyclitols, and starch. Although extractives occur as minor, nonstructural constituents in the cell walls and cell cavities, they often are of decisive importance in contributing to many of the characteristic properties and possible uses of wood, such as its odor, color, light stability, flammability, hygroscopicity, density, strength properties, decay and insect resistance, and permeability. Extractives often alter the surface properties of wood, which in turn affects adhesion properties and finishing characteristics.

The following review describes how wood extractives can influence adhesion and finishing and presents some methods of controlling or reducing the effect of these extractives.

Surface contamination

Extractives are common and important sources of surface contamination harmful to wood adhesion. Water-soluble extractives are transported to the wood surface along with water during the drying operation and are deposited as solids when the water evaporates. The quantity transported is dependent on temperature because of solubility effects, and the concentration gradient is dependent on the relative humidity conditions. Anderson et al. (7) found that the outer surface of kiln-dried redwood lumber had about five times the amount of water-soluble extractives as did the inner core, and that this outer layer accumulated over twice as much water-soluble extractives as compared with the corresponding region in the green lumber. Heavy deposits of extractives on white and red oak veneer surfaces after drying were also shown by SEM and light microscopic analysis (28). Vapor phase migration of water-insoluble extractives may also occur at high drying temperatures (41). Bonding strength of wood is adversely affected by contamination of wood surface. Contamination of the surface may reduce bond strength in a number of ways including:

1. Heavy deposits of extractives on the surface increases the possibility of contaminating and reducing the cohesive strength of the adhesive;

The authors are, respectively, Principal Wood Scientist, USDA Forest Serv., Southern Forest Expt. Sta., 2500 Shreveport Hwy., Pineville, LA 71360; and Associate Professor, Forestry Dept., Iowa State Univ., Ames, IA 50010. This paper was received for publication in October 1986.

Forest Prod. J. 38(1):52-56.

2. Extractives may block reaction sites on wood surfaces and prevent true wetting by the adhesive, thus decreasing the adhesion between adhesive and wood substrate;

3. Oxidation of extractives tends to increase the acidity of wood and promote degradation.

These three possibilities may act individually or, more often, act as combined effects. The quantity and composition of extractives, properties, and characteristics of adhesives, and the nature of wood surface are all believed to be involved in the relationship of extractives to wood gluing.

Attempts have been made to specify which of the different components of extractives affect adhesion. However, due to the chemical complexity of extractives and the many variables involved in the gluing process, it is difficult to define the compound or compounds that cause inactivation. Hancock (21) has shown that the reduced adhesion of ovendried Douglas-fir veneer is primarily the result of extractive migration to the surface. He also determined that acetone or a combination of acetone and methanol/benzene extractable fraction was involved. In fact, Hemingway (22) has shown that the reduced wettability was related to the oxidation of the linoleic acids and esters. There is also evidence that the water-soluble galactans in western larch prevent good adhesion (5,34). By dipping hoop pine (*Araucaria cunninghamii*) veneer into solutions of commercial tannins, crude wood extracts, and model compounds, Plomley et al. (36) found that contamination of the bonding interface with hydrolyzable tannins significantly reduced the bond quality of a phenol-formaldehyde resin adhesive. Removal of a large part of the ether and benzene-soluble portion of the wax present in a tropical wood, determa (*Ocotea rubra* Mez), caused a considerable increase in the gluebond quality obtained with a phenolic resin (42). The result indicated chemical incompatibility between the wax and the phenol-formaldehyde resin. This incompatibility may be due to a difference in polarity, which would result in the inability of the adhesive to wet the wood and to secure adequate penetration. Hillis (23) indicated that water-repellent extractives affect the surface tension of wood surfaces and the application and penetration of the adhesives, which subsequently affects bond strength. Chen (14) also reported that the bonding strength of many tropical woods was improved by surface treatments with sodium hydroxide solution, acetone, and alcohol-benzene. The gluebond quality of white and red oaks was increased significantly by soaking veneers in 1 percent sodium hydroxide solution (28). Wellons et al. (43) examined delaminated kapur (*Dryobalanops* spp.) and keruing (*Dipterocarpus* spp.) plywood panels under a scanning electron microscope and found that the gluelines were "unanchored." These gluelines failed to adhere to the cell walls and the adhesive penetrated very little into the fiber structures. They attributed the "unanchored" gluelines to both premature gelation of the phenolic resin and the physical blockage of extractives coated on the cell walls.

Change in polarity and wettability

Extractives may have an unfavorable effect on the polarity and wettability of wood. Chen (14) found that the removal of extractives from wood surfaces with various solvents improved the wettability of wood. When urea-formaldehyde resin adhesive was used, a positive linear relationship existed between bond strength and wettability. However, no such correlations existed between bond strength and wettability when resorcinol-formaldehyde resin was used. Jordan and Wellons (26) confirmed the expectation that nonpolar extractives reduced wettability. They also observed that there was no direct relationship between wettability and gluability using phenolic resins.

Swanson and Cordingly (41) showed that vapor migration of resinous materials in wood pulps changed the first layer of molecules on the fiber surface to a less polar and more hydrocarbon-like chemical composition. Redistribution of these nonpolar materials decreased surface free energy. Sinclair et al. (40) also showed that paper could be sized with fatty acids in vapor form. Since extractions with various organic solvents could not remove absorbed fatty acids, they suggested that the fatty acids were anchored on the fiber surfaces by forming ether bonds with the cellulose. Both these studies confirm the work of Hancock (21), in which he found that the removal of extractives in Douglas-fir veneer prior to drying increased the gluability and that extraction after drying did not improve gluebond quality.

It is clear that lowering the surface free energy of wood reduced wettability and produced slower penetration or loss of absorbency. As a consequence, the viscosity and flow properties of adhesives are altered and the wettability-permeability relationship of a particular adhesive is changed. Under these conditions, "undercure" and "casehardening" may occur. Furthermore, some volatile extractives (i.e., pitch) in hot-pressing will add to the vapor from the moisture and increase the chances of "blow" in the gluelines. There is evidence that extremely pitchy surfaces on southern pine veneer are not favorable for gluing for these reasons.

Prolonged curing and setting

The effect of extractives is generally considered relatively unimportant in obtaining a maximum gluebond strength with alkaline-catalyzed glues (35). However, the acidic extractives of oak (38) and kapur (1,25) were found to prolong curing of the resol type phenolic resin. The acidic extractives caused formation of dimethylene ether linkages, as seen by infrared spectroscopy and TG-DSC examination (1) and further confirmed by the potentiometric titration with pyridine-tetrabutylammonium (2).

Wellons et al. (43) have shown that a high concentration of extractives at the gluing surface may affect the curing and setting of phenolic resins in the following manner. The acidity of extractives may reduce glueline pH and this reduction in pH requires a significant increase in press time to obtain a proper cure of the resin. The reduction in glueline pH may also cause phenolic resin solids to precipitate, resulting in a less crosslinked adhesive at the wood-adhesive interface. Extractives at the gluing surface may reduce the gel time and this premature gelation of the adhesive would hinder penetration of the adhesive. Finally, extractives may increase the water solubility of the cured adhesive resulting in a less durable glueline.

For acid-catalyzed urea resin adhesives, extractives may inhibit or accelerate the curing rate, depending on the buffering capacity and reaction pH of the resin. The water extract of Kapur wood (3), teakwood (27), and red oak (4) retarded the gelation of urea and urea-melamine resins. Measurement of pH and determination of methylol-formaldehyde showed that the rate of the pH descent and the decrease of methylol formaldehyde content were also delayed by adding the extractives (3). On the other hand, Albritton and Short (4) reported that the ethanol-soluble extractives of white oak decreased the gel time of urea-formaldehyde resin as much as 41 percent.

Effect on finishing

The effects of extractives on wood finishing have drawn considerable attention. However, the effects of extractives are generally small in comparison with degradation caused by moisture changes and weathering. The most common deleterious effect of extractives is discoloration of finishes. The water-soluble extractives may migrate with moisture to the wood surface and discolor coatings (11,30). The colored substances in the resin of the heartwood (resolved in the oils and solvents used in coatings) also cause discoloration (30). Furthermore, several chemicals quickly become brown to nearly black by oxidation and degrade performance of surface coatings (24). Another adverse effect is that extractives retard the hardening of finishes. The water-soluble extractives of redwood and western redcedar, the essential oil of bald cypress, and the tannins in oaks, all retard paint hardening (12). Methanol- and acetone-soluble extractives in eastern redcedar also retarded the hardening of lacquer coatings (33). Ether-soluble extractives, particularly the phenolic fractions (25,29,39), strongly inhibited the curing of unsaturated polyester resins. Knots in pine exude resin that tends to impart a brittleness to the paint films, with subsequent cracking, checking, and peeling over the knot area (6). The composition and distribution of the resins in red and eastern white pine also affected discoloration, blistering, and lifting of paint (31).

Not all the effects are unfavorable, however. For example, although redwood and bald cypress extractives retard paint hardening, they appear to significantly improve the durability of the surface coating (12). Water-soluble extractives located in the cell walls reduce shrinking and swelling of the wood surface and thus contribute to paint holding. Some phenolic extractives in western redcedar act as a natural antioxidant on the wood surface and stabilize paint films (10).

Methods of minimizing the influence of extractives

Wood adhesion

The effects of extractives on wood adhesion can be minimized or reduced by mechanical or chemical means. A light sanding immediately before gluing is a rapid and economical method for removing almost all types of surface contamination. Planing is even more effective (18). A light planing removes surface contamination and at the same time also exposes the highly polar S2 layer of the cell walls to which adhesives bond most efficiently (13). A surface treatment with sodium hydroxide solution or neutral organic solvents to remove surface contaminants is also effective (14,18,28,43). The deleterious effect of low pH caused by extractives and other contaminants (e.g., preservatives or fire retardants) may be eliminated by applying a proper amount of sodium hydroxide to the wood surface (15,38).

Solvent seasoning is a possible method of drying wood and simultaneously removing a large proportion of extractives. Rather extensive work has been done on solvent seasoning of tanoak and redwood (8,9). Several cycles of acetone extraction may be required to reduce the moisture content of green wood to 10 to 15 percent (44). The cost of solvent seasoning has been estimated to be at least three times more expensive than conventional kiln-drying, thus limiting its economical application.

Wood finishing

The influence of extractives on wood finishing can be eliminated or reduced by removing extractives from the wood or chemically treating the wood to insolubilize the extractives. Extensive studies have been done on insolubilizing extractives.

Kiln-drying is probably the most practical way to remove some of the volatile portion of the extractives. After kiln-drying, some of the terpenes in the resins are removed, which immobilizes the pitch and minimizes bleeding. Removal of some of the volatile extractives may reduce the level of interactions between extractives and coating films (33). Solvent seasoning can be applied here, but its application is again limited for economic reasons.

Attempts have been made to modify the extractives near the wood surface by reacting them with chemicals. Resin acids are known to react with primary amines to form a precipitate of an amine salt. However, there was evidence that the amine not only combined with the extractives but also reacted with many types of paint. The volatile terpene fraction of red pine may be polymerized by catalysts to form a mixture of viscous and relatively immobile polymers. Several catalysts have been used including aluminum chloride (37) and boron trifluoride (32). The boron trifluoride treatment has so far been shown to be the most promising. Levitin (32) reported that α- and β-pinene could either be converted into other volatile products or into polymerized products depending mainly on the concentration of the alcoholic boron trifluoride solution. He showed that a 26 percent solution was the optimum concentration to produce a maximum amount of polymerized terpenes. A brush treatment of 26 percent boron trifluoride solution on resinous wood surfaces effectively reduced resin exudation. One drawback to this treatment is the poor penetration of the reagent.

Redwood exposed to various halogens, hydrogen halides, and nitrogen dioxide rendered many of the redwood extractives insoluble in water (16). Titanium esters have also been used to react with the redwood extractives to form water-insoluble compounds (17). However, both of these studies indicated that the water-insoluble compounds formed were unstable when exposed to ultraviolet light. The use of diazonium salts coupled with redwood phenolic extractives to form water-insoluble color dyes has been reported (16). The resistance of these products to the degrading action of sunlight and water has yet to be evaluated.

The durability of wood finishes exposed to outdoor conditions can be vastly improved by treating the wood surface with various inorganic compounds (11,16,17, 19,20). Chromium-containing chemicals and especially those containing hexavalent chromium are most effective. Wood treated with these chemicals showed a greatly enhanced resistance to the natural outdoor weathering process, and in turn increased paint durability. Water-soluble extractives in redwood and western redcedar were insolubilized or fixed, preventing them from staining or bleeding through finishing coatings.

Summary and conclusions

Difficulties may arise in gluing wood species with high extractive contents. This is especially true in gluing tropical hardwoods. Such gluing difficulties have been attributed to extractive contamination resulting from the migration of extractives to the wood surface during drying. Extractive-contaminated wood surfaces often result in low strength and less durable gluebonds. Extractives may cause gluing difficulties in the following ways:

1. Heavy deposits of extractives on the gluing surface block the reaction sites, thus preventing the anchoring of adhesives;

2. Chemical incompatibility between the extractives and adhesives results in inferior gluebonds;

3. Extractives influence the wettability and polarity of the wood surface so that the wettability-permeability relationship of a particular adhesive is changed;

4. Extractives affect the curing and setting characteristics of adhesives.

These gluing interference mechanisms may act individually or they may act as combined effects.

A light planing is probably the most effective method of removing the deleterious effect of extractive contamination. Planing not only removes extractives contaminating the wood surface, it also exposes a fresh and highly polar surface to which adhesives bond most efficiently. In some applications, it is also feasible to use a simple chemical surface treatment (e.g., a dilute sodium hydroxide solution) to improve the bonding of the extractive-contaminated wood surface.

Some extractives discolor and retard the hardening of finish coatings. Others may cause cracking, checking, and peeling of paint films. These problems can be minimized by kiln-drying to remove some of the volatile extractives, followed by chemical treatments to insolubilize the remaining portion of the extractives. A surface treatment with chromium-containing chemicals increases the resistance to the weathering process of wood and simultaneously fixes the water-soluble extractives, which vastly improves the durability of finishes.

Literature cited

1. Abe, I. and N. Akimoto. 1976. The inhibitory effect of kapur wood extractives on the curing reaction of the resol. J. Japan Wood Res. Soc. 22(3):191-196.
2. ________ and K. Ono. 1980. Effect of the acidity of some tropical wood extractives on the curing of resol. J. Japan Wood Res. Soc. 26(10):686-692.
3. Akaike, Y., T. Nakagami, and T. Yokota. 1974. The inhibitory effect of kapur wood extracts on the gelation of the urea resin adhesive. J. Japan Wood Res. Soc. 20(5):224-229.
4. Albritton, R.O. and P.H. Short. 1979. Effect of extractives from pressure-refined hardwood fiber on the gel time of urea-formaldehyde resin. Forest Prod. J. 29(2):40-41.
5. American Plywood Association. 1960. Exterior gluing of western larch. Lab. Rept. No. 83. Douglas-fir Plywood Assoc. Tech. Dept.
6. Anderson, A.B. 1950. Chemistry of western pines. Pine knots and paint durability. Ind. Eng. Chem. 42(3):565-569.
7. ________, E.L. Ellwood, E. Zavarin, and R.W. Erickson. 1960. Influence of extractives on seasoning stain of redwood lumber. Forest Prod. J. 10(4):212-218.
8. ________ and W.B. Fearing. 1960. Solvent seasoning of tanoak. Forest Prod. J. 10(5):234-238.
9. ________ and ________. 1961. Distribution of extractives in solvent seasoned redwood lumber. Forest Prod. J. 11(5):240-242.
10. Barton, G.M. and B.F. MacDonald. 1971. The chemistry and utilization of western red cedar. Dept. of Fisheries and Forestry. Canadian Forestry Serv. Publ. No. 1023. 31 pp.
11. Black, J.M. and E.A. Mraz. 1974. Inorganic surface treatments for weather-resistant natural finishes. Res. Paper FPL 232. USDA Forest Serv., Forest Prod. Lab., Madison, Wis. 40 pp.
12. Browne, F.L. 1958. Wood properties that affect paint performance. Rept. No. 1053. USDA Forest Serv., Forest Prod. Lab., Madison, Wis.
13. Bryant, B.S. 1968. Studies in wood adhesion—Interaction of wood surface and adhesive variables. Forest Prod. J. 18(6):57-62.
14. Chen, C.M. 1970. Effect of extractive removal on adhesion and wettability of some tropical woods. Forest Prod. J. 20(1):36-41.
15. ________. 1975. Gluing study of pyresote-treated, fire retardant plywood. Part I. Forest Prod. J. 25(2):33-37.
16. Dost, W.A. 1959. Attempts to modify the weathering of redwood. Forest Prod. J. 9(3):18A-20A.
17. ________. 1959. Exterior finish study summary. Final Rept. Res. Proj. No. 5.10121. California Redwood Assoc.
18. Dougal, E.F., R.L. Krahmer, J.D. Wellons, and P. Kanarek. 1980. Glueline characteristics and bond durability of Southeast Asian species after solvent extraction and planing of veneers. Forest Prod. J. 30(7):48-53.
19. Feist, W.C. 1977. Wood surface treatments to prevent extractive staining of paints. Forest Prod. J. 27(5):50-54.
20. ________. 1979. Protection of wood surface with chromium trioxide. Res. Pap. FPL 339. USDA Forest Serv., Forest Prod. Lab., Madison, Wis.
21. Hancock, W.V. 1963. Effect of heat treatment on the surface of Douglas-fir veneer. Forest Prod. J. 13(2):81-88.
22. Hemingway, R.W. 1969. Thermal instability of fats relative to surface wettability of yellow birchwood (*Betula lutea*). Tappi 52(11):2149-2155.
23. Hillis, W.E. 1986. Forever Amber: A story of the secondary wood components. Wood Sci. Technol. 20:203-227.
24. Huff, R.H. 1974. Chemistry of painting surfaces from earliest time to unfathomable future—with hints of prophecy. J. Paint Technol. 46(588):62-73.
25. Imamura, H., T. Takahashi, M. Yasue, M. Yagishita, and J. Kawamura. 1970. Effect of wood extractives on gluing and coating of kapur wood. Bull. Govt. Forest Expt. Sta. No. 232: 65-96. Tokyo, Japan.
26. Jordan, D.L. and J.D. Wellons. 1977. Wettability of Dipterocarp veneer. Wood Sci. 10(1): 22-27.

27. Kanazawa, H., T. Nakagami, K. Nobashi, and T. Yokota. 1978. Studies on the gluing of wood articles. XI. The effect of teakwood extractives on the curing reaction and the hydrolysis rate of the urea resin adhesive. J. Japan Wood Res. Soc. 24(1):55-59.
28. Kuo, M-L, D. Dicarlo, and C.-Y. Hse. 1984. Influence of extractives on bonding properties of white and southern red oak. J. Adhesion 16:257-278.
29. Lee, C.-L., Y. Hirose, and T. Nakatsuka. 1974. The inhibitory effect of Taiwan *Cryptomerioides* heartwood extractives on the curing of the unsaturated polyester resin. J. Japan Wood Res. Soc. 20(11):558-563.
30. Laughnan, D.F. 1959. Effect of wood on durability of finishes. Forest Prod. J. 11(2):194-214.
31. Levitin, N. 1962. Extractives of red and white pine and their effect on painted lumber. Timber of Canada. June, 66-71.
32. _________. 1965. Ether extractives of red pine and possible means of reducing resin exudation. Forest Prod. J. 15(5):215-218.
33. McGinnes, E.A., Jr. and T.W. Dingeldein. 1971. Effect of light, extraction and storage on color and tackiness of clear-finished eastern red cedar. Forest Prod. J. 21(1): 53-60.
34. McNamara, W.W. 1964. Wettability of western larch veneer as affected by drying schedules and some extraction treatments. M.S. thesis, Univ. of Idaho.
35. Narayanamurti, D., R.C. Gupta, and G.M. Verma. 1962. Influence of extractives on the setting of adhesives. Holzforschung and Holzverwertung 14:85-88.
36. Plomley, K.F., W.E. Hillis, and K. Hirst. 1976. The influence of wood extractives on the glue-wood bond. 1. The effect of kind and amount of commercial tannins and crude wood extracts on phenolic bonding. Holzforschung 30(1):14-19.
37. Roberts, W.J. and A.R. Day. 1950. A study of the polymerization of *a*- and *b*-pinene with Fridel-Crafts type catalysts. J. Am. Chem. Soc. 72:1226-1230
38. Roffael, V.E. and W. Rauch. 1974. Extractives of oak and their influence on the gluing with alkaline phenol-formaldehyde resins. Holz Roh-Werkstoff 32(5):182-187.
39. Sandermann, W. and W. Schwarz. 1956. Effect of wood extractives on the resistance of weathering and the drying of oil and polyester varnishes. Farbe and Lack 62(4):134-144.
40. Sinclair, G.D., R.S. Evans, and H.R. Sallans. 1960. New methods for sizing fibrous products. Pulp and Paper Mag. of Canada 62(1):T23-T27.
41. Swanson, J.W. and S. Cordingly. 1959. Surface chemical studies on pitch. 11. The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps. Tappi 42(10):812-819.
42. Thomas, R.J. 1959. Gluing characteristics on determa. Forest Prod. J. 9(8):266-271.
43. Wellons, J.D., R.L. Krahmer, R. Raymond, and G. Sleet. 1977. Durability of exterior siding plywood with Southeast Asian hardwood veneers. Forest Prod. J. 27(2): 38-44.
44. Western Pine Association. 1960. Solvent seasoning. Res. Note No.4:312.