



Chemical and Mechanistic Aspects of Wood Finishing: A Review Encompassing Paints and Clear Coats

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This review article considers the formulation of a broad range of coatings designed for the protection and changing the appearance of wood surfaces. Findings from the literature are considered from the standpoint of the main chemical components, how they can be formulated into a spreadable product, the events leading to curing, and factors affecting the performance of the resulting coating layers on wood surfaces. A series of hypotheses are considered, relating to the mechanisms underlying wood coating products and their usage. Special attention is paid to the topics of adhesion at the coating-wood interface, the development of film strength and hardness, and challenges related to the past and continuing development of waterborne coating formulations. The modern technologist seeking to coat wood has many options to choose from, and there has been a need to make current knowledge related to the field more available to the wider scientific community.

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INTRODUCTION

The painting of wood can appear to be simple (Flexner 1994). Stir the paint, dip the brush, apply the paint, and wait for it to dry. The goal of this review article is to examine some of the underlying details. Though the application of a wood coating may seem easy to implement, the successful finishing of wood has required a great deal of innovation and optimization, which continues up to the present. This article attempts to answer questions such as, “How do these systems work?” Published literature is reviewed as a way to answer this and related questions.

Motivations to Apply Coatings to Wood

In a broad sense, a primary purpose of a layer of finish on a wood surface is to protect the wood (Williams *et al.* 1996; Allen 1984; Flexner 2005). This role is highlighted in Fig. 1, along with an additional role of affecting the visible appearance of the surface. Wood is an exemplary sustainable material, but without a protective finish or “coating,” it can suffer from early degradation. Factors responsible for such degradation have been reviewed (Feist 1982; Cogulet *et al.* 2018; Kropat *et al.* 2020). Modes of degradation of wood can be categorized as weathering (Grüll *et al.* 2014; Kropat *et al.* 2020), decay or rot (Clausen 1996; Goodell 2003; Brischke *et al.* 2006), insect damage (Stirling and Temiz

2014), surface damage, distortion of the shape (Flexner 1994), and mechanical breakage (Smith *et al.* 2007).

With the exception of the last listed category, all of these undesired degradation effects can be slowed down by application of a finish, which typically includes some form of polymeric resin, a liquid vehicle to either solubilize the resin or disperse emulsion droplets of the resin, and some other optional materials. These can include ultraviolet (UV) light-absorbing materials and various colorants. The finish is generally applied to wood as a liquid, after which it dries or cures to form either a stain effect or a solid film. The goal of this article is to explore published literature that explains the mechanisms by which wood coatings function.

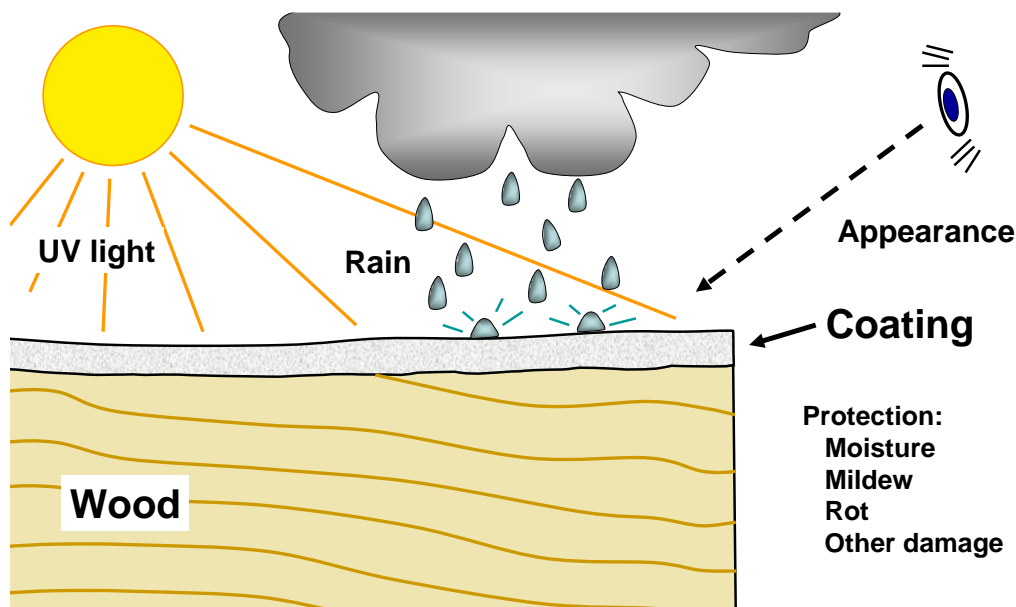


Fig. 1. Figure highlighting some of the main functions of a coating layer on wood

Some further reasons to apply coatings to wood fall under the broad category of appearance (Marschner *et al.* 2005). Among the most basic of these is that finished wood can be a lot easier to clean (Flexner 2005). A wood surface lacking a finish layer will be susceptible to dirt, grime, and stains that can be difficult to remove. Categories of appearance to be considered later in this review include color, gloss, and the extent to which the finish has been designed to hide the appearance of what is below it.

Hypotheses

To help guide the discussion in this article, some general hypotheses can be offered, as listed below.

1. Understanding wood's degradation and the factors that affect it can provide a foundation for understanding the role of protective finishes.
2. By blocking all or most rainwater from wetting the wood itself, a finish is able to decrease the swings of cyclical changes in moisture content that would have been experienced by unprotected wood exposed to outdoor weather.

3. Due to its ability to absorb incident ultraviolet (UV) light, a suitably formulated finish can avoid or slow down the photodegradation of lignin near the surface of the wood, thus helping to maintain the integrity of the wood surface.
4. By presenting a suitably hard and contiguous film at the wood surface, the finish can protect the wood from scratching and abrasion.
5. By drying and curing in a way that develops smoothness, the finish can contribute to a glossy appearance, and the level of gloss can be adjusted by formulation of the finish mixture.
6. Surface preparation steps and many other details are foundational to achieving film and reliable adhesion of the finish to the wood to achieve an expected service life of multiple years or even decades in some cases.
7. To perform its various functions, an effective layer of finish will need to have undergone a curing process, which can involve evaporation of one or more carrier fluids (drying), oxidation and other chemical changes, and even covalent crosslinking in some cases.
8. To be able to spread effectively onto either wood or a previous layer of finish, each successive layer of coating to be spread needs to be formulated with a suitable surface tension, as well as having resins able to spread and interact with the functional groups facing the surface.
9. A final hypothesis to be considered in this article can be attributed to Flexner (1994, 2005). The background for this hypothesis involves the design of water-borne wood finishes. The general expectation of a water-borne finish is that it ought to perform its various roles equally well in comparison to traditional oil-borne formulations. The hypothesis states that a well-performing water-borne finish formulation will contain not only water, but also a minor amount of a slower-to-evaporate vehicle, which in addition needs to be a good solvent for the polymeric binder in the finish. Such a system can be expected to permit intermixing among polymer segments of adjacent macromolecules, thus resulting in a contiguous film.

Formulation principles can account for finish performance

As an approach to addressing the various hypotheses given above, it will be assumed that the ingredients and composition of a coating formulation can account for how well it performs. One of the most consequential changes in formulation, when comparing typical modern finishes with those used a century ago, has been the emergence of waterborne finishes (Flexner 1994, 2005; Cox 2003; Landry and Blanchet 2012; Poussard *et al.* 2016; Shukla *et al.* 2019). In comparison to the traditional finishes, all of which have been formulated with more non-polar fluids, the waterborne formulations of finishes have a reputation of being more challenging to use, especially when facing issues related to the surface to be covered, weather conditions, and some aspects related to performance (Flexner 1994, 2005; Cox 2003). Despite such concerns, the late 1990s began a strong and continuing trend toward waterborne formulation of many finish products, and the main driver has been to reduce the emission of volatile organic solvents (Williams and Feist 1999). Since that time, waterborne formulations have undergone a maturation process, and users have gained experience in using such products.

Published Reviews Related to Wood Finishing

Some topics related to the chemical and mechanistic wood finishing already have been covered in review articles and books. Some notable examples are listed in Table 1.

Table 1. Review Articles and Books Covering Some Chemical or Mechanistic Aspects of Wood Finishing

Topic Area	Citation
Textbook emphasizing interior applications, clear coats	Waring 1963
Textbook on wood finishing practices and technology	Scharff 1974
Water repellent and preserving finishes for exterior use	Feist & Mraz 1978
Handbook with emphasis on skilled workmanship	Allen 1984
Textbook (2 editions) emphasizing chemistry & methods	Flexner 1994, 2005
Durability of external waterborne wood coatings	de Meijer 2001
Textbook with broad coverage of wood coatings	Bulian & Graystone 2009
Durability of clear coatings for external usage	Evans <i>et al.</i> 2015
Clear coatings for external usage	Cogulet <i>et al.</i> 2018
Waterborne polyurethane coatings	Agnol <i>et al.</i> 2021
Antimicrobial finishes formulated with nanomaterials	Ganguli & Chaudhuri 2021
Non-isocyanate polyurethane adhesives & coatings	Gomez-Lopez <i>et al.</i> 2021
Natural-sourced formulation for wood finishes	Teaca <i>et al.</i> 2019
Finish types, their chemistry, & effects of wood anatomy	Mali <i>et al.</i> 2021
Epoxidized vegetable oil finishes for UV protection	Varganici <i>et al.</i> 2021
Electrostatic powder coatings for furniture	Ayrilmis 2022
Self-healing coatings formulated with microcapsules	Chang <i>et al.</i> 2023
Sustainable and functional wood coatings	Landry <i>et al.</i> 2023
Multifunctional polymer coatings with nanocellulose	Wang <i>et al.</i> 2023
Fire-resistant coatings involving nanocellulose	Turku <i>et al.</i> 2024

CHEMICAL ASPECTS OF WOOD FINISH TYPES

A wide variety of chemical ingredients are used in coating formulations for wood, and the commercial products can be categorized in different ways. For instance, one can differentiate between the major classes of oil-based finishes, waterborne finishes, reactive coatings, and powder coatings. Alternatively, one can focus on the intended end-usage, such as interior finish products and exterior finish products. Another option would be to differentiate between clear coatings, stained or wash coatings, *vs.* opaque finishes. In this section, the main focus will be placed on the chemical composition of the resin, *i.e.* the ingredient that will be providing the main adhesion within the coating layer.

Types of Finish, with Emphasis on the Binder Component

Because of this article's focus on chemical and mechanistic aspects, the cited examples are not limited to commercially available products. For example, the history of shellac finish goes back about 5000 years (Ahuja 2024), and shellac continues to be used in antique restoration and in specialized applications (Waring 1963; Williams *et al.* 1996; Flexner 2005). However, shellac has largely been displaced in the market by products that offer greater water-resistance and other advantages. At the other end of the spectrum, recent university research often focusses on concepts and formulations that lie beyond what is presently commercially available. Though the results of such studies have potential to contribute to a better understanding of how coating formulations and applied coatings

behave, it is important to keep in mind that many of the systems described in scientific articles will not ever become available for purchase. Reasons can include high costs of materials, inherent difficulties of displacing mature technologies that already are on the market, and practical disadvantages not yet revealed by the initial research.

Table 2 highlights key attributes of some of the major types of finish uses for a variety of applications. For readers who need even more details, perhaps when paying attention to narrowing down the best selection for a specific application, more extensive tables are provided by Flexner (2005).

Table 2. Finish Formulation Options, with Emphasis on the Binder

Type of Finish (main resin)	Citations
<p>Shellac (lac bug deposit) The lac bug, <i>Tachardia lacca</i>, deposits this resin on tree bark, from which it is scraped. It is scraped from the trees, and the flakes are dissolved in alcohols (especially ethyl alcohol). It hardens by evaporation. The formulation has a short shelf life. The finish is not very water-resistant, so it is exclusively for indoor usage. In use it can last a long time. Shellac was used for a lot of antique furniture. The USA FDA calls it “generally recognized as safe”. A content of 10% lac resin gives good binding.</p>	Waring 1963; Gupta <i>et al.</i> 1983; Allen 1984; Flexner 1994, 2005; Williams <i>et al.</i> 1996; Remadevi <i>et al.</i> 2015; Weththimuni <i>et al.</i> 2021
<p>Lacquer (nitrocellulose) Professionals prefer this type of finish and apply it by spray to achieve durable, hard, colorless coatings, especially on furniture. A plasticizer such as cellulose acetate butyrate (CAB) needs to be used to decrease the brittleness of the nitrocellulose. The finish can be redissolved and reworked. High amounts of volatile organic carbons (VOCs) are released during application. The “diluting solvents” evaporate quickly, and active solvents render the resins sticky as the film cures.</p>	Allen 1984; Flexner 1994; Sarma <i>et al.</i> 2001; Cox 2003; Krystofiak <i>et al.</i> 2016; Shukla <i>et al.</i> 2019
<p>Lacquer (cellulose acetate butyrate/acrylic/vinyl) These types of lacquer are also cured by evaporation. They give intermediate quality (not as hard as nitrocellulose).</p>	Flexner 1994; Cox 2003;
<p>Lacquer (polyurethane) This version has been commonly used in India. The conventional lacquer gave a higher coating thickness than its waterborne version formulated by the cited authors.</p>	Shukla <i>et al.</i> 2019
<p>Alkyds (polyester) The name comes from a combination of “alcohol” and “acid”, which literally means an ester. These finishes have good application characteristics. But they are sensitive to weather during application, and also they are hard to repair and do not resist outdoor weather well. Addition of alkyds to polyurethane may optimize properties.</p>	Flexner 1994; Cox 2003; Lu <i>et al.</i> 2004; Lu & Lin. 2008; Steiner <i>et al.</i> 2020; Patil and Jagtap 2021; Yaremchuk <i>et al.</i> 2023
<p>Varnish (polyurethane) In these formulations the polyurethane is suspended in a drying oil such as linseed oil, safflower oil, or soybean oil. Apply by brush. The coatings have high durability and relatively low cost. The drying/curing time is relatively long. High oil content (long-oil varnish) gives a tough finish that is more weather resistant (spar varnish). Low oil content (short-oil varnish) gives a harder surface that is suitable for</p>	Allen 1984; Flexner 1994, 2005; Cox 2003

furniture. Metallic driers (Co, Mn, Zn, Zr) accelerate the curing.	
<p>Varnish (conversion)</p> <p>These varnishes are formulated with driers (catalysts) for more rapid curing. Alkyd resins are a popular option. The finishes are classed as thermosetting, meaning that they cannot be redissolved after the curing. Solvents can include methyl ethyl ketone, various alcohols, toluene, ethylbenzene, and xylene. Emissions also may include formaldehyde, depending on the type of resin. Skill is needed for defect-free coatings, usually applied by spray.</p>	Allen 1984; Howard <i>et al.</i> 1998; McCrillis <i>et al.</i> 1999; Flexner 1994; Cox 2003; Rawat <i>et al.</i> 2019
<p>Drying Oils</p> <p>Tung oil, linseed oil, safflower oil, castor oil, and soybean oil share that they are all plant-based oils having sufficient unsaturation so that they are susceptible to oxidative curing. One of their main applications is in varnish formulations. The Italian violin-maker Stradivari used linseed oil and colophony (pine rosin) as main ingredients in the finish.</p>	Allen 1984; Chang & Lu 2012; Weththimuni <i>et al.</i> 2016; Lu & Chang 2020; Chang <i>et al.</i> 2023
<p>Two-part coatings (epoxy)</p> <p>Epoxy resins need to have two liquids freshly combined in the right proportion and promptly applied (often by pouring). Often the goal is to build a relatively thick layer, for instance for bar tops and tabletops. Waterborne versions (emulsified components) have been developed. Since adhesion to the wood can be a problem, it is recommended to use a relatively coarse sanding before application of the finish.</p>	Allen 1984; Flexner 2005; Eyann <i>et al.</i> 2023
<p>Waterborne coatings (latex)</p> <p>These finishes, which have become highly popular due to their greatly reduced volatile organic carbons (VOCs) level and easy cleanup with water, can be regarded as emulsions of oil-based finish ingredients in water. The term latex refers to bead-like clusters of polymerized acrylics or other polymers that have been stabilized in the aqueous medium by surfactants or minor substituents on the polymer. The nonpolar solvents are still there, but in relatively low quantities. The nonpolar solvents (<i>e.g.</i> glycol ethers) are selected such that they evaporate more slowly than the water, hanging around long enough to render the resins tacky and self-adhering. Non-ideal weather conditions during outdoor application can lead to bad results. Waterborne finishes tend to raise the grain of wood, due to its swelling in water, leading to increased roughness. In general, the dried finishes are flexible but allowing the passage of water vapor to a much greater degree than other kinds of finishes.</p>	Allen 1984; Flexner 1994, 2005; Ekstedt 2003; Dvorchak 1997; Darmawan <i>et al.</i> 2018; Kristyna <i>et al.</i> 2020; Steiner <i>et al.</i> 2020; Eyann <i>et al.</i> 2023; Alves <i>et al.</i> 2023; Kelkar <i>et al.</i> 2023
<p>UV-curing finishes</p> <p>Such coatings are formulated with unsaturated compounds (-C=C-), such that irradiation with ultraviolet light, in the presence of a suitable photoinitiator, can induce enough crosslinking to cure the coating. Often the resins are acrylate oligomers, which may be replaced by epoxy, polyurethane, and polyesters components. Advantages of the UV curing can include development of greater hardness, chemical resistance, resistance to staining, and thermal tolerance. The formulations often contain less</p>	Allen 1996; Decker 2005; Jung <i>et al.</i> 1998; Landry <i>et al.</i> 2000a,b; Hwang <i>et al.</i> 2009; Irmouli <i>et al.</i> 2012; Sabani <i>et al.</i> 2012; Salleh <i>et al.</i> 2013; Kardar <i>et al.</i> 2014; Herrera <i>et al.</i> 2015; Tathe & Jagtap 2015; Lokhande <i>et al.</i> 2017; Montazeri & Eckelman 2018; Rawat <i>et al.</i> 2019; Wang <i>et al.</i> 2019; Ibrahim

volatile organic compounds (VOCs) than other kinds of coating.	<i>et al.</i> 2020; Su <i>et al.</i> 2020; Agnol <i>et al.</i> 2021; Hermann <i>et al.</i> 2021, 2023; Li <i>et al.</i> 2021; Karbalaei <i>et al.</i> 2022; Huang <i>et al.</i> 2022, 2023; Mahajan <i>et al.</i> 2023; Zhang <i>et al.</i> 2024
<p>Film-forming coatings</p> <p>This is a general term referring to finish formulations having a relatively high ratio of resin to solvent or oil, such that a layer enriched in resin ends up as a continuous layer on the surface.</p>	Feist and Mraz 1980
<p>Penetrating coatings</p> <p>This is a general term referring to finish formulations having a relatively low ratio of resin to solvent or oil, such that most of the coating formulation will be absorbed into pores, such as fiber lumens and vessels. Products labeled as “tung oil,” whether or not they actually contain tung oil, generally fall within this category.</p>	Feist and Mraz 1980
<p>Primer coatings</p> <p>The term primer is used to denote a coating formulation that is intended to penetrate well (as in the case of the preceding item) and also to provide strong anchoring to the wood material, as well as excellent bonding to subsequent film-forming layers (see above). By having a high oil content, the formulation more easily permeates into the pores of the wood, thus achieving good adhesion, which is one of its main functions. Oil-based primers develop a moderate barrier to vapor and oil permeation, whereas waterborne primers do not. In either case, as long as the final coat is applied within a few hours or days from when the primer layer is applied, the adhesion between such layers of coating is seldom a problem.</p>	Allen 1984
<p>Stains</p> <p>A stain can be defined as a non-pigmented formulation having a high oil content (to favor penetration) and a selected colorant. An advantage of such finishing treatments is that they don’t ever peel or blister. They perform well regardless of the roughness of surfaces. They don’t trap moisture. Also, one is free to repeat the staining treatment, as long as no subsequent finish has been applied on top. As an alternative, clear-coat products, such as varnishes, can be premixed with colorant. Commonly used colorants include tannic acid, ammonia to render the tannic acid brown, potassium permanganate, and iron compounds. Alcohols are often used as the solvent, rather than water, in order to avoid the raising of the grain pattern, due to swelling of the wood.</p>	Feist and Mraz 1980; Waring 1963; Allen 1984; Flexner 1994, 2005; Cox 2003; Landry <i>et al.</i> 2013
<p>Powder coatings</p> <p>In principle, such coatings avoid the release of volatile organic compounds (VOCs). The powder (various thermoplastics) is heat-cured, such that it hardens upon cooling. The coatings generally are not tolerant of deformation of the substrate.</p>	Wenning 2002; Köhler <i>et al.</i> 2017; Akkus <i>et al.</i> 2019, 2022; Hazir & Koc 2019

General Formulation Principles

This section considers some basic requirements of coating formulations, which can be expected to be valid regardless of their contents and fluid medium. This includes such issues as initial uniformity, continuing uniformity over time, and whether some of the components are dissolved or dispersed as colloidal particles.

Uniformity of the mixture

The human eye is very good at finding imperfections, especially when viewing surfaces that are intended all to have the same color or gloss. Any clumping of the formulation can be expected to show up as tell-tale bumps in the coating, which will be regarded by viewers as evidence of poor workmanship. The first step in achieving an even mixture is likely to involve some form of milling or stirring. For instance, Landry *et al.* (2008b, 2010) compared high-speed mixing vs. several kinds of milling relative to the even dispersal of a nano-sized clay component. A strong correlation was found between the quality of dispersion of the particles in the formulation and the resulting optical and mechanical properties of the coatings. In follow-up work, the same research team found that sub-optimal coating results were obtained in a case where nano-sized solid particles had formed agglomerates in a UV-curable waterborne formulation (Sow *et al.* 2011). The findings of that study suggest that some of the problems were due to incompatibility of overly hydrophobic (silane-treated) mineral surfaces when attempting to prepare a waterborne formulation. More promising results were obtained by Vardanyan *et al.* (2014), who were using cellulose nanocrystals (CNC) as a reinforcing agent in another UV-curing waterborne formulation. The authors noted increases in hardness and scratch resistance, while not seeing any deterioration in appearance, all of which provide evidence that the starting formulation must have had a uniform distribution.

As illustrated in Fig. 2, the mixing of solids particles, especially the resins and any pigments, into the coating formulation typically involves impeller stirring. The hydrodynamic shear forces are expected to help break apart connections between individual particles such as to achieve a uniform dispersion, which can be regarded as a necessary condition in order to achieve uniformity in the coated layer.

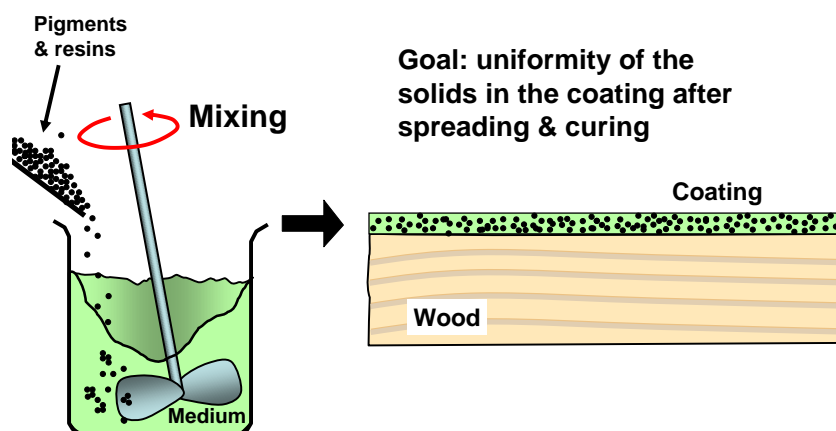


Fig. 2. The essential role of impeller stirring in the preparation of typical wood finish formulations

Colloidal stability

Effective mixing, usually brought about by application of hydrodynamic shear, is not the only issue faced by formulators aiming to achieve a uniform suspension, especially in cases where the formulation needs to contain emulsion droplets or solid particles. In order for the formulation to remain stable over the expected length of time (*e.g.*, the listed shelf life), there will need to be something to prevent the particles from coming together and forming agglomerates. In other words, there need to be colloidal-range repulsive forces between the particles or droplets in the mixture.

Colloidal instability problems often can be overcome by adding a small amount of a well-chosen surface-active agent (Baumstark and Tiarks 2002; Godnjavec *et al.* 2012; Acarali and Demir 2021; Bansal *et al.* 2022; Pan and Yan 2023). The idea is that one end of the surfactant is attracted to the surface of the entity to be dispersed, and the other is compatible with the suspending medium. In the formulations of wood finishes, such agents are typically nonionic.

Another possibility is to employ particles as emulsion stabilizers, *i.e.* the formation of Pickering emulsions (Chevalier and Bolzinger 2013). A recent trend has been to study the use of nanocellulose particles for formation of wood finishes. Thus, Grüneberger *et al.* (2015) found that addition of nanofibrillated cellulose (NFC) aided in the stabilization of UV-absorbing ZnO nanoparticles in a waterborne finish. The approach worked well in formulations containing acrylic resin, but aggregation phenomena could not be overcome in formulations containing alkyd resins (Grüneberger *et al.* 2014). Mikkonen *et al.* (2019) found that hemicelluloses from wood could be used as an effective stabilizer for alkyd resins.

Since hemicelluloses are hydrophilic, their adsorption onto the alkyd resins would be expected to provide a steric stabilization effect (Napper 1977) that can be helpful in formulating a waterborne emulsion. The concept is that the hydrophilic material at the surfaces prevents their close approach, thus tending to maintain colloidal stability. Poaty *et al.* (2014) employed a contrasting approach for preparing a waterborne finish formulation. Their first step was to treat the surface of cellulose nanocrystals with acryloyl chloride or alkyl quaternary ammonium bromides, thus making the surfaces hydrophobic. The acrylic resins, after stabilization by the hydrophobized nanocellulose, showed good stability in the aqueous system, but the main benefit was improved scratch resistance of the resulting finish. The effects were attributed to better compatibility between the coated nanocellulose and the resin. Related work was reported by Veigel *et al.* (2017). A linseed oil-based coating was improved by adding NFC that had been derivatized with alkyl groups, to render it hydrophobic. Yoo and Youngblood (2017) surface-modified cellulose nanocrystals so that they could be more compatible with a tung oil finish system. The distribution of the CNC was improved, as was the scratch resistance of the coatings. Salleh *et al.* (2013) noted a positive effect of modifying a silica pigment with a hydrophobic silane additive before its usage in a finish formulation with a radiation curable acrylate resin. Related work was reported by Sow *et al.* (2011). Zhu *et al.* (2016) showed that it is possible to reduce the volatile organic carbon (VOC) content of a finish formulation by the usage of nanoparticles acting as a stabilizer of waterborne polyurethane varnish.

Solubility principles

Highly noticeable blemishes in coatings, known as fisheyes, appear to be associated with phase separation phenomena (Allen 1984). A frequent cause of such blemishes is the movement of wood resins into the wet layer of the finish. But because of differences in the

solubility behavior between the resins and the fluid medium, the phases remain separate. Similar effects may be seen when highly hydrophobic silicon oils or waxes, possibly coming from a previous layer of finish, fail to be well mixed in the next finish formulation (Cox 2003; Flexner 2005; Huang *et al.* 2023). Such problems often can be predicted and addressed by the application of solubility principles (Hansen 2007). As illustrated in Fig. 3, the Hansen system is based on determination of three characteristic properties for each component in the formulation, namely the Hildebrand parameter (related to the cohesive energy density), the hydrogen bonding ability, and the polarity. Because the two materials represented in Fig. 3 show an overlap of the solubility regions (represented as spherical regions), one predicts that a uniformity mixture can be achieved. Though it will not be possible to avoid incompatibilities between ingredients of a coating formulation and various contaminants, the solubility calculations can be helpful for identifying additives that can serve as compatibilizers between components having contrasting solubility.

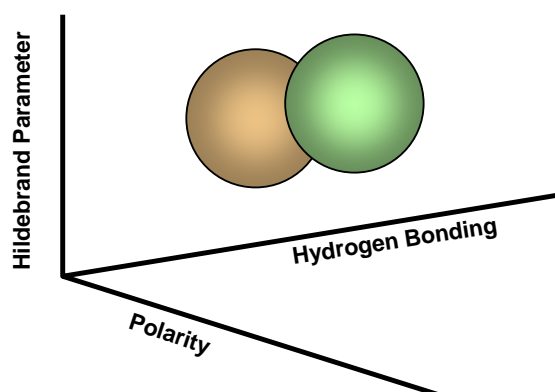


Fig. 3. Representation of the three main parameters considered in the Hansen system to predict phased compatibility of mixtures

Pigments or Filler Particles

This section considers some different ways in which solid particles present within a coating formulation can affect not only the final properties of the coating, but also how it behaves during its application to the wood. They can scatter light, thus contributing to hiding power. In addition, they can provide reinforcement of the film layer, they can affect the permeability of a coating layer, and they can affect the flow characteristics.

To avoid confusion, it is important to note that the word “filler” can mean two different things in the context of coatings for wood. A “paste filler” is a viscous mixture that can be used to fill large pores in wood surfaces, as in the end grain of oak (Allen 1984; Flexner 2005). This section will consider a different optional meaning of the term, referring to solid particles and their effects on appearance and mechanical properties.

Hiding power

Solid particles, especially titanium dioxide, are widely used in finish formulations when the goal is to achieve opacity. Additional reasons to add particles include absorption of UV light (to protect the wood), and to act as a reinforcing agent. Thus, one can envision a pigmented coating for wood as a kind of composite, in which the particles can play a reinforcing role, and the resin may be envisioned as playing the role of the matrix material.

The ability of white particles, added to a paint formulation, to prevent light from passing through the coating depends on the random scattering of the light. Each time the light encounters a localized abrupt change in refractive index, the light energy changes its direction. A contrasting effect happens in cases where the surface is smooth, at the scale of the light waves; in such cases there will be some mirror-like reflection (gloss), which will be discussed later. Effects of light scattering, resulting from particles or bubbles within a dense layer can be estimated by applying equations developed for that purpose by Kubelka and Munk (1931), whose results have been subsequently made more precise (Yang and Kruse 2004). Kubelka and Munk derived relationships that envision the one-directional progress of a single beam, being subject to both scattering (random change in direction) and absorption (gradual decrease in intensity) during its progress. The superior performance of titanium dioxide, and to a lesser extent ZnO and PbO, can be attributed to their much higher index of refraction than a typical resin, making up most of the remaining content of the coating. A higher contrast in refractive index gives rise to a greater light scattering effect, and hence greater hiding power.

Some key aspects associated with light interactions, including the Kubelka-Munk analysis, are illustrated in Fig. 4. Notice that the incident light is envisioned as coming from the upper level. To the extent that the surface is smooth enough, within a length scale associated with the wavelengths of light, some of the light may be reflected in mirror-like fashion. But more likely, the rough nature of a realistic coating layer will mean that much of the light is diffusely reflected as it encounters a change in refractive index as it passes from the air into the coating material. Further scattering of light, leading to more diffuse reflection, can be expected when the light encounters particles, especially if they have contrasting values of refractive index. The transmitted light beam is depicted as becoming gradually thinner as it passes through the coating layer. This is due to an expectation that some of the light energy will become absorbed by chromophores in the coating.

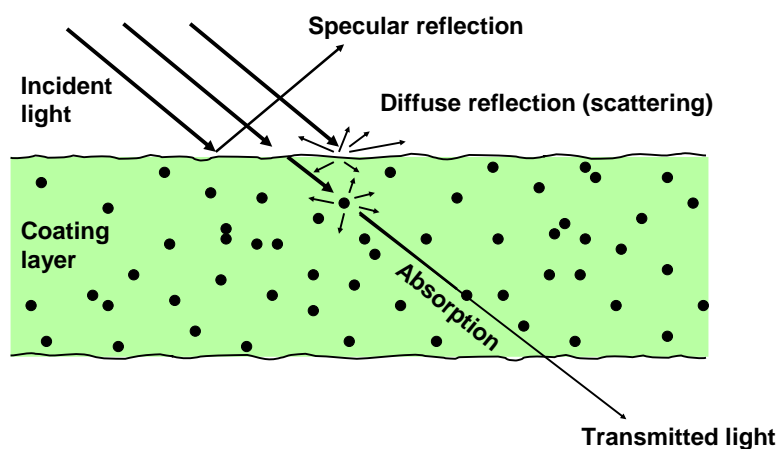


Fig. 4. Some ways in which light can interact with a coating layer

Reinforcement effects

It is well known that the incorporation of solid particles, especially if they have a high aspect ratio and strong interfacial adhesion with the matrix material, will give rise to an increased elastic modulus of the material (Hubbe and Grigsby 2020). Such a system is illustrated schematically in Fig. 5.

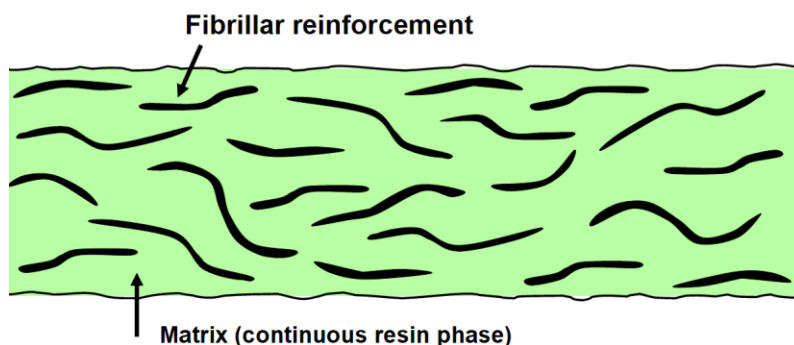


Fig. 5. Representation of a coating film that has been reinforced by elongated articles, such as fibers

As shown by Huang *et al.* (2022), particles present in a wood coating can provide additional benefits, such as scratch resistance. Increased hardness was observed when lignin-containing nanofibrillated cellulose was added to the formulation for a waterborne coating (Huang *et al.* 2019). However, all of the potential benefits just mentioned can be achieved only if there is molecular contact over at least a large proportion of the interfacial area. Poor compatibility between the matrix and reinforcing particles can be expected to result in strength properties similar to or lower than that of the matrix by itself (Hubbe and Grigsby 2020).

Studies have shown that in addition to increasing the Young's modulus of a formulated system, the presence of stiff reinforcing particles generally will decrease the elongation ability before breakage (Hubbe and Grigsby 2020). This effect is illustrated in Fig. 6.

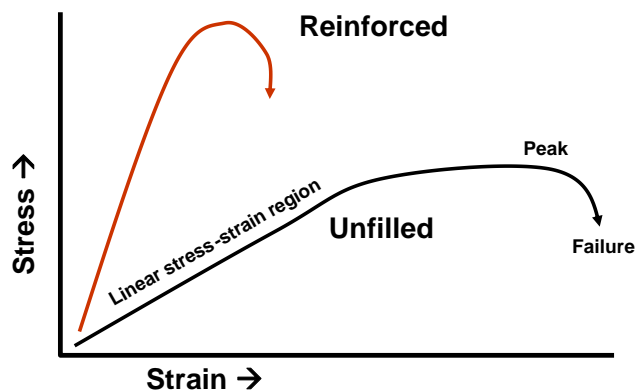


Fig. 6. Expected effect of elongated reinforcing particles on the elastic modulus and elongation to breakage of a plastic material

A further, sometimes unrecognized effect of small solid particles present in the formulation of a wood coating may involve the nucleation of interactions occurring at the interface between polymer components of the mixture. Thus, Fallah *et al.* (2017) attributed an observed increase in the glass transition temperature, Young's modulus, and hardness of a coating to the repression of polymer segment movements by the added nano-silica particles.

Permeability effects

Though crystalline mineral particles can be regarded as being totally impermeable to the passage of gaseous or liquid molecules, such permeants still will be able to diffuse around the outsides of such particles. The term “tortuosity” is used to quantify the average increase in diffusion path length when a coating contains impervious particles having various shapes (Wolf and Strieder 1990; Ghanbarian *et al.* 2013; Simões da Silva *et al.* 2022). In principle, the greatest contribution to tortuosity will be observed for thin, platy particles. Such a system is illustrated in Fig. 7. Wolf and Strieder (1990) compared the calculated tortuosity values obtained from a large number of empirical studies. Only in the case of platy particles, such as clays, mica, *etc.*, were the benefits in terms of slowing diffusion clearly evident, relative to other potential effects, such as the possible creating of air gaps by the incorporation of particles in a film. Another potentially confusing effect has been demonstrated for a case in which an interfacial layer surrounding a mineral particle (glass beads in the cited work) may provide enhanced permeation, compared to diffusion through the matrix phase (Donkers *et al.* 2013). In light of the relatively low cost of platy mineral particles, together with the importance of being able to control the rate of water vapor permeation, it would make sense to use such an approach to control water vapor permeation in future formulations of wood coatings. There appears to be a need for research focused on this topic. However, depending on the details of the situation, an excessive barrier against vapor permeation may trap moisture on the inside of the coating, thus promoting rot formation (van Meel *et al.* 2011).

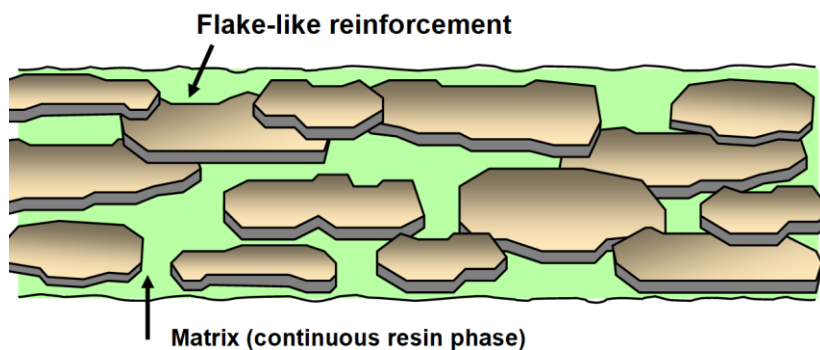


Fig. 7. Representation of highly platy and somewhat aligned particles in a coating layer, giving rise to enhanced resistance to diffusion of molecules through the layer

Rheological effects

The flow characteristics of a coating formulation are expected to be important, especially during storage, application, and drying or curing phases. During storage, it may be advantageous for the mixture to adopt a transient “house of cards” type of structuring, thereby hindering any tendency for settling of dense particles to the bottoms of containers. Upon mixing, it can be advantageous in some cases for there to be a shear-thinning effect, thus favoring spreading of the mixture as a thin film. In general, the rheological behavior of wood coating formulations can be described as viscoelastic (Mihaila *et al.* 2022). A higher viscosity also has been shown to slow the permeation of the coating formulation into the pores of wood (Nussbaum *et al.* 1998; de Meijer *et al.* 2001a,b; Van den Bulcke *et al.* 2008; Nejad and Cooper 2010, 2011; Tamantini *et al.* 2023). When high-aspect particles, such as nanofibrillated cellulose, are used in formulations, one can expect a large

contribution to viscosity coefficients, in addition to strong shear-thinning behavior (Hubbe *et al.* 2017; Song *et al.* 2023).

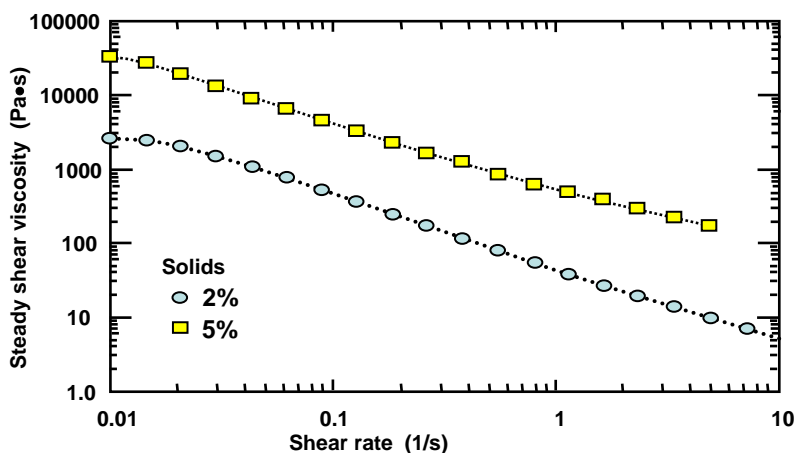


Fig. 8. Example of a shear-thinning effect attributable to the progressive alignment of elongated particles in suspension with increasing shear rate (selected data replotted from Nazari *et al.* (2016)).

As illustrated in Fig. 8, the coefficient of viscosity in a suspension of particles tends to decrease as a function of increasing shear rate. The data represented in Fig. 8 are replotted from Nazari *et al.* (2016), who studied suspensions of nanofibrillated cellulose particles, which have a very high aspect ratio. The downward slope represented by the data indicates a strong shear-thinning effect, which can be attributed to a progressive alignment of the particles with increasing shear rate.

Spreading and Immobilization

The next logical step after preparing the components of the formulation and mixing them together is applying them to the wood (or previous coating layer) surface. Two aspects of this process will be considered here, the wetting of the surface and the flow phenomena. The most common modes of application are by brush, roller, spray, and dipping (Williams *et al.* 1996). A typical paint brush incorporates some features intended to facilitate holding a large amount of the coating formulation, as well as the accurate placement onto the surface. The ends of the individual bristles of a paint brush are typically flagged (separated into narrower filaments) as the end of the brush is approached, thus providing more surface to accommodate the wet material (Flexner 1994, 2005). In addition, the tip is often cut as a chisel shape. When large amounts of finish need to be transferred, as in the case of some stain applications, a foam pad is recommended (Allen 1984).

Regardless of how the finish is applied, it can be a challenge to evaluate the thickness and other aspects of coating topography. Kibleur *et al.* (2022) describe a dual-energy computed tomography method, which is based on X-ray imaging. This approach made it possible to differentiate between the coating and the underlying wood fiber material, for the creation of 3D images representing the coating.

Wetting

The contact angle of a droplet of coating formulation on the surface that needs to be covered provides key evidence regarding whether or not adequate spreading of the

formulation will occur, resulting in molecular contact between the two phases (Hubbe *et al.* 2015a). Phenomena such as rough “alligator” surfaces can result when at least some parts of the substrate give rise to contact angles that are near to 90 degrees or higher, thus representing nonwettable parts of the surface. The relatively high interfacial tension of pure water implies that more difficult wetting may be expected with waterborne coating formulations onto certain wood surfaces. Addition of small amounts of surfactant to such formulations will help to overcome such effects (Flexner 1994). A particular challenge is faced when attempting to apply waterborne coatings to surfaces that are both hydrophobic and covered with large pores. In such cases, the finish may fail to penetrate into the pores, as can be predicted by the equation derived by Cassie and Baxter (1944).

Rheological factors and immobilization

The shear-thinning behavior mentioned earlier can become important when the formulation is being applied, especially in the case of spray applications, which can involve relatively high levels of hydrodynamic shear. Once the wet coating formulation has been applied to a surface, its viscosity will affect the degree to which it penetrates into pores in the wood, including fiber lumens and vessel openings. When there is an intention to limit the amount of penetration, it may be favorable if the stationary material gradually develops a higher viscosity, possibly as a means to control or limit the degree of penetration into a porous wood surface. Corcione and Frigione (2012) showed evidence confirming the increased viscosity and shear-thinning behavior of a UV-curable waterborne coating formulation, upon the addition of platy boemite nanoparticles. Likewise, de Meijer *et al.* (2001b) found that increasing the solids content in a wood coating formulation tended to increase the observed coefficient of viscosity. The coefficient of viscosity can be expected to rise rapidly during the drying and curing of a coating (Fumero and García 2005). Factors that are expected to contribute to an increase of viscosity with the passage of time can include the randomizing of alignment of particles within the formulation, the establishment of structures among polymers or particles (Kulichikhin and Malkin 2022), any crosslinking reactions or effects (Romani *et al.* 2002), and the evaporation of solvent (Caicedo-Casso *et al.* 2019).

The formation of a “skin” at the outer surface of a freshly applied coating on wood can be regarded as a specific aspect of immobilization of the coating (Fumero and García 2005). The immediate cause of the phenomena is likely to be the evaporation of the most volatile component(s) in the formulation. The positive aspect of skin formation is that it may shorten the time that has to pass before the object can be touched gently without damaging it. A potential negative aspect is that after skin formation, any moisture that has been trapped under the coating may promote blister formation, especially if heat is being applied (Williams *et al.* 1996).

Curing Issues

Different coating formulations can cure by different mechanisms, sometimes with more than one process happening at once. The term curing will be used here to denote the transformation from a fresh, wet layer to a layer that is not only dry but approaching its ultimate strength. As noted by Carera *et al.* (2022), it is generally desirable that a coating should dry relatively quickly under a broad range of environmental conditions. For instance, the coating should be able to withstand a rain event that occurs sooner than expected after its application. On the other hand, it ought not to set so quickly as to make the application difficult or lead to defects. In addition, it has been proposed that the rate of

curing of a wood coating needs to be fast enough to prevent excessive penetration into the wood (Rawat *et al.* 2019). There is a critical need to evaluate the required curing time in the case of systems that are cured by the application of ultraviolet light (Wenning 2002; Karder *et al.* 2014; Hermann *et al.* 2021).

It can be argued that the actual curing of a finish must involve interactions among the resin component elements, which may be dissolved polymers or latex particles, *etc.* Thus, it has been stated that some penetrating finishes, containing only oils, can be regarded as non-curing (Flexner 1994). Such a characterization can be disputed, however, since (as will be discussed below), drying oils such as tung oil and linseed oil are expected to gradually cure by oxidation. According to Flexner (1994), the main curing mechanisms involves with various kinds of coatings are evaporation, reaction, and coalescence.

As suggested by Fig. 9, curing can involve at least three different zones of activity, starting with the evaporation of water, organic solvents, or both. In addition, the initial immobilization of the coating onto the surface can be assisted by capillary wicking and or diffusion of the vehicle into the porous structure of the wood. Certain kinds of coating are able to undergo a chemical reaction (see later section on epoxy resins, for instance). The scheme for the oxidation reaction, which pertains to an alkyd varnish system, is based on work by Miccichè *et al.* (2006). This is an example showing how oxidation of a highly unsaturated fatty acid species resulted in dimerization. Note that the “R” group shown in the figure represents another similar monomer that also has at least two unsaturated groups along its alkyl chain. By the same mechanism, or by other reaction paths, such oxidation reactions and their subsequent reactions contribute to insolubilization of the coating.

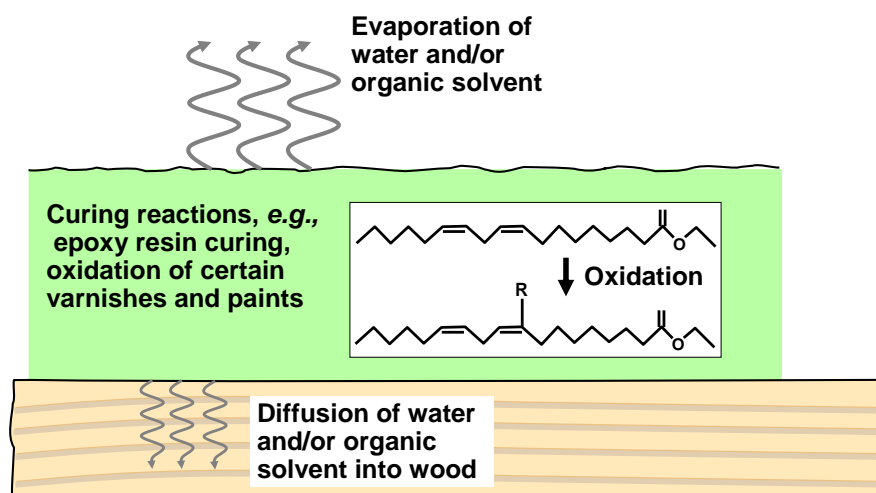


Fig. 9. Three important locations affecting the curing of various wood coatings, namely the adjacent air (evaporation of vehicle), the coating itself (optional curing reactions), and the underlying wood (absorption of vehicle)

Evaporation

Especially in the case of shellac and lacquer finishes (Waring 1963), it is clear that evaporation is the main mechanism by which drying occurs. Mihaila *et al.* (2019a,b) used a thermogravimetric analysis (TGA) device to track the drying of various commercial varnish films applied to fir wood as a function of time. Models of the drying process, fitted to the data, were judged to be consistent with a diffusion-limited process of drying. Two periods of drying were shown, a rapid drying period (about ten minutes) followed by a

decreasing speed of drying period. Song *et al.* (2023), who used hot-air drying of a waterborne formulation, showed that the drying rate was affected by both the temperature and the humidity.

Figure 10 shows both the lac bug, which produces the crude lacquer compound, and its chemical structure (Ahuja 2024). Using the resins of a host tree, for instance the kusum tree (genus *Schleichera*), the bug excretes a material that is readily soluble in ethyl alcohol and thus cures by solvent evaporation.

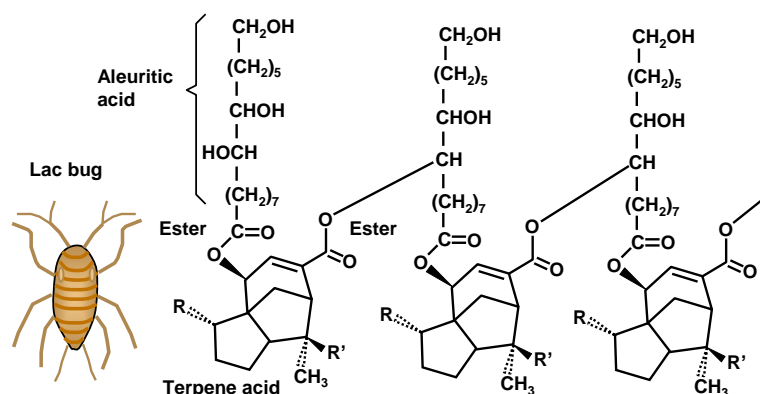


Fig. 10. Lac bug and its excreted product, lacquer, a traditional wood finish that is soluble in ethyl alcohol

Oxidation

Varnishes, which generally are formulated as resins dissolved or colloiddally suspended in drying oils, are well known to be slow-curing (Flexner 1994, 2005). A possible explanation is that such coatings require substantial time to complete a chemical reaction. The reaction, involving oxidation, appears to bring about polymerization of the chemically unsaturated oils (Stenberg *et al.* 2005; Arminger *et al.* 2020). Stenberg *et al.* (2005) showed that the results of such curing depended on the detailed structures of the unsaturated oils that were used. Metal salt additives, known as dryers, are often added as a way to accelerate the curing (Flexner 1994; Arminger *et al.* 2020). Flexner (2005) lists the salts of calcium, manganese, and zinc as some of the most common dryers.

Figure 11 shows a representative structure for linseed oil (Orlova *et al.* 2021), which is one of the most widely used drying oils for preparation of varnishes. Linseed oil stands out from other vegetable oils has having an especially high level of the most highly unsaturated component, the linolenic acid. This high degree of unsaturation renders it susceptible to a series of curing reactions, which include oxidation. As was shown already in Fig. 10, oxidation can be followed by additional reactions, further oxidation, and radical combination, which contribute to curing of resins that contain linseed oil. Another reaction path starts with hydroperoxide formation (Orlova *et al.* 2021).

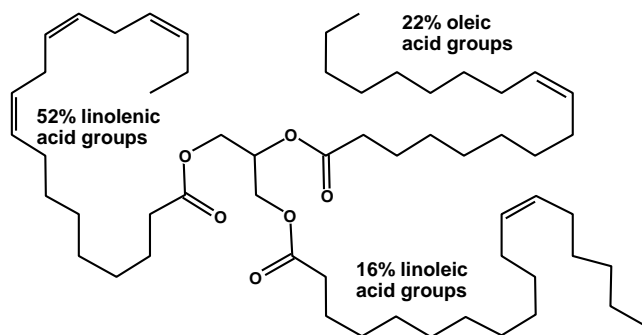


Fig. 11. Representative structure for linseed oil, showing the relative frequencies of three of the major components of the natural product (figure redrawn from an original by Orlova *et al.* 2021).

Interdiffusion

Cabrera *et al.* (2022) envision a basic four-step process by which a conventional waterborne latex coating formulation will cure. Initially the wet form on the wood surface will contain a continuous water phase, within which the latex particles are still separate from each other. In the next stage, sufficient evaporation will have taken place so that the latex particles come into contact. Further evaporation causes the initially spherical latex particles to adopt deformed shapes, resembling polygons, in order to fit more closely together. In the last stage, diffusion occurs among polymer segments at the latex particle surfaces, thereby creating a strongly bonded condition.

Another aspect that may hold the key to effective formulation and curing of latex paints and clear finishes is the presence of various slow-to-evaporate solvents, in addition to water. As mentioned earlier, once a substantial amount of water has evaporated, solvents such as glycol ethers or propylene glycol ethers will become enriched in the mixture. The changed solutions conditions can be fine-tuned in a formulation so as to achieve greater solubilization, or at least tackiness of latex (Flexner 1994, 2005). In principle, this mechanism would be expected to facilitate polymer segment interactions among adjacent latex particles, bringing about an interdiffusion of chain segments. This type of process is shown schematically in Fig. 12.

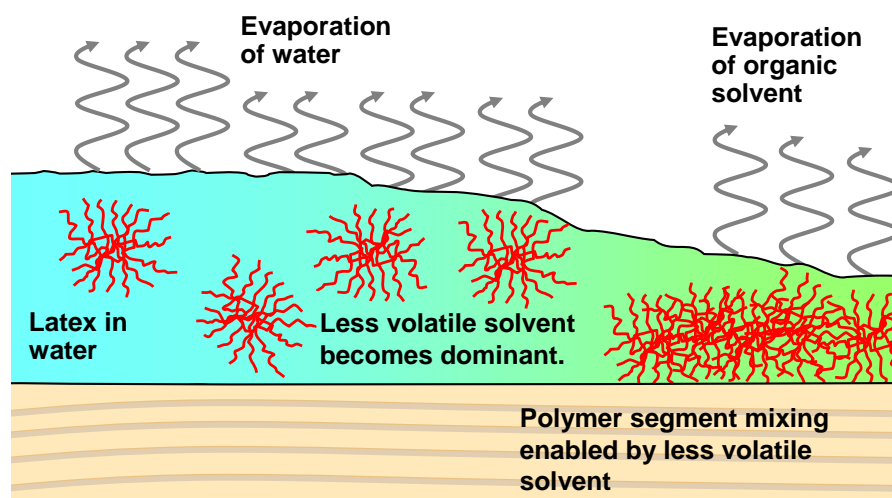


Fig. 12. Schematic diagram of a proposed mechanism of curing of a waterborne latex coating formulation

Time to cure

Cabrera *et al.* (2022) presented evidence suggesting that colloidal destabilization plays a key role in coating formulations having a quick-drying capability. These formulations were found to rely upon rapid formation of a surface film as a main mechanism. Such a mechanism was found not to require major evaporation of the formulation's fluid phase. One can envision a process by which relatively rapid evaporation of some of the local solvent (which may be water), leads to coalescence of resin entities present near to the air interface. A question that does not seem to have been considered is whether resin particles, which would tend to be more hydrophobic than the water medium, might be enriched at those surfaces even before evaporation of a freshly applied waterborne coating on wood.

Reactive Curing Systems

A contrasting group of curing mechanisms to be considered here is specific to certain pairs of chemical compounds that are able to react and form covalent bonds with each other in the course of drying of a coating layer. The prime example is epoxy resins. The UV-curing systems also fall into this category, as well are some coating formulations that include cross-linking agents.

Epoxy resins

Epoxy resins are favored for applications in which the coating needs to be able to resist intensive usage, as in the case of a bar surface or tabletop (Allen 1984). As illustrated in Fig. 13, a typical epoxy resin is prepared by first reacting bis-phenol A with epichlorohydrin to form bisphenol A diglycidyl ether (BADGE). The next step is to react the BADGE with a selected multifunctional amine, which undergoes an addition reaction and results in polymerization. Conditions need to be optimized to achieve a prepolymer molecular mass that is still low enough to allow easy pouring and a suitable shelf-life, but high enough so that the addition of a hardener will be able to bring about suitably rapid crosslinking. Hardeners can include phenalkamines, polythiophenes, and other multifunctional amines. The amine groups react with available epoxy rings on the resin. In addition, there can be further reaction between epoxy groups and hydroxyl groups. This chemistry is illustrated in Fig. 13.

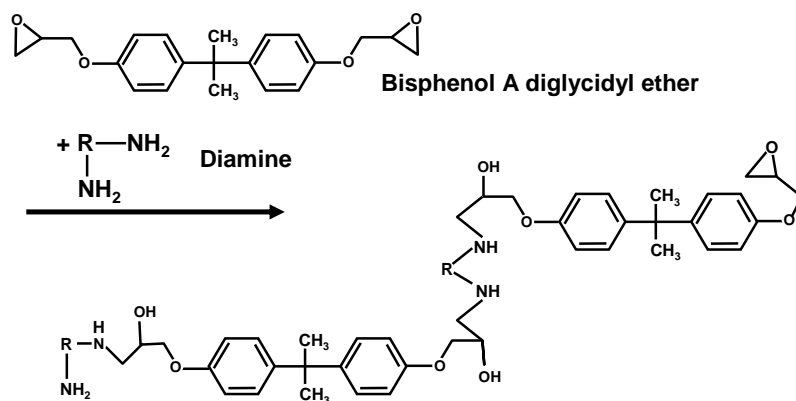


Fig. 13. Reaction of bisphenol A diglycidyl ether with a diamine to achieve curing of an epoxy resin

The chemistry of a typical epoxy system is based on combining two liquids, each of which has the potential to be prepared “solvent-free” or mostly just active ingredients. An inherent advantage is that low levels of volatile organic solvent (VOC) emissions can be achieved (Dvorchak 1997; Fortmann *et al.* 1998; de Meijer 2001). Though epoxy systems can achieve very high film strength and hardness (Motawie and Sadek 1999), they sometimes provide insufficient adhesion at the wood interface. Flexner (2005) recommends using a relatively coarse sanding pretreatment to overcome such deficiencies.

It is also possible to formulate an epoxy system by preparing emulsions, allowing for application in a manner resembling a waterborne latex system (Eyann *et al.* 2023). The cited article pertains to a mixed system with acrylate chemistry in addition to the epoxy system.

UV-cured finishes

Based on the number of recent publications, there is intense interest in UV-curable formulations. The explanation may lie in some practical advantages. Unlike the epoxy systems, the whole formulation can be prepared as a single batch, and the batch has a relatively long shelf life. In addition, by being less dependent on evaporation to cure the coating, formulators have been able to reduce organic solvents (Agnol *et al.* 2021; Gustafsson and Börjesson 2007). Landry *et al.* (2015) demonstrated that the UV light can be applied by means of light-emitting diodes. The function of the UV light, in typical cases, is to catalyze the addition polymerization of an acrylic-type prepolymer or an epoxy acrylate oligomer (Ali *et al.* 1997). Photoinitiators are used to convert the UV light to odd-electron species, *i.e.* free radicals (Allen 1996). An example is shown in Fig. 14 (Dossin *et al.* 2022). The resulting coatings can be optimized to develop moderate durability relative to weathering in varnish formulations (Ayata 2019; Cavus 2021; Gurleyen 2021). Dixit (2021) showed that a successful coating formulation of this type can be prepared with bio-based citric acid, together with other ingredients. Zhang *et al.* (2022) tested a variety of treatments with silane coupling agents and showed that they generally improved the adhesion performance of waterborne paint. Zhang *et al.* (2023) found that increasing levels of sol-gel treatment tended to decrease the level of cracks in layer of waterborne polyurethane-modified acrylic acid varnish.

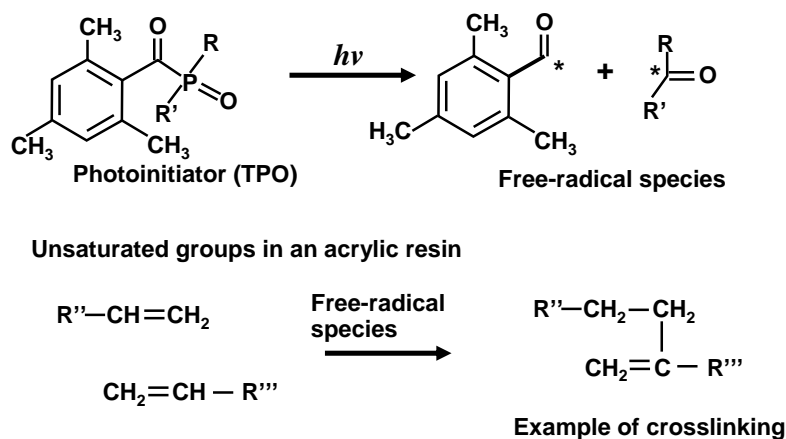


Fig. 14. Example of a photoinitiator, the generation of free-radical species, and the establishment of crosslinking within an acrylic-type resin

Sol-gel systems for wood coatings

The curing process for a typical sol-gel-type coating formulation involves a reaction between a trialkoxysilane reagent and water, followed by further reaction with the -OH groups at a wood surface. Figure 15 provides a general scheme for this kind of reaction system (Hubbe *et al.* 2015b). At the upper left of the figure, the starting material is assumed to be various alkyl-triethoxysilanes or alkyl-trimethoxysilanes, which are commonly available reagents falling into the category of alkyl-trialkoxysilanes. As a first step, these are added to water, rendering unstable intermediate species. The lower part of the figure indicates successive condensation reactions in which water is lost, leading eventually to three-dimensional cross-linked clusters of increasing size.

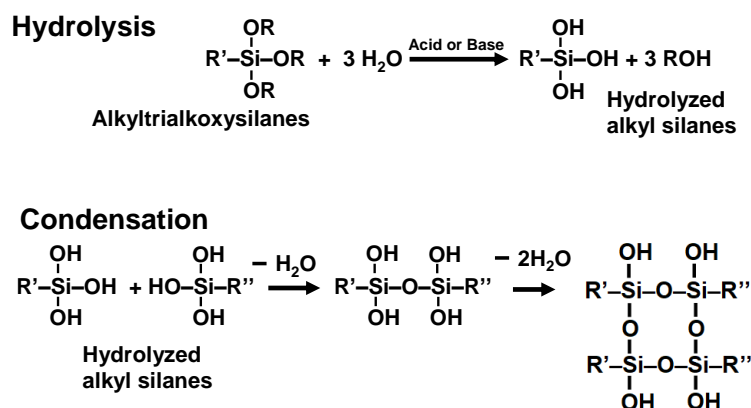


Fig. 15. Schematic diagram of a sol-gel condensation of silica species. Figure adapted from Hubbe *et al.* 2015b, copyright owner

Gholamiyan *et al.* (2016) studied the feasibility of carrying out such a process as a pre-coat, with the aim of establishing a better adhesive foothold on the wood surface. Indeed, better adhesion was achieved with the subsequent coating layer, compared to its direct application to the wood. Yona *et al.* (2021a) achieved mixed results, finding better effects of the sol-gel treatment when the surface already had been treated with mineral. Further work (Yona *et al.* 2021b) showed better performance when using a hydrophobically substituted silane reagent.

Zheng *et al.* (2015) reported the preparation of tough, abrasion-resistant coatings containing titanium dioxide pigment along with an alkoxy silane to develop a sol-gel curing system. The cross-link density was improved and excellent adhesion to the wood was observed. However, the coating was found to gradually lose its hydrophobic character over time. Members of the same research group (Zheng *et al.* 2020) showed that a silane coupling agent could be added along with the application of waterborne acrylic resin. That approach was reported to improve both the strength of the coating and its bonding to the surface.

ADHESION TO THE WOOD

The purpose of this section is to look more closely at the topic of adhesion, taking advantage of some of the sub-processes and mechanisms already considered in this review. It can be hypothesized that successful adhesion – especially the adhesion of a coating to

the wood, will depend on such factors as the chemistry of the resin, effects due to drying oils, uniformity and colloidal stability issues, wettability issues, as well as the state of curing. As shown in Fig. 16, some of the key contributions to adhesion, at the molecular level, can include covalent bonding, hydrogen bonding, London dispersion forces, and mechanical interlocking between the coating structure and the pores of the wood material. Inadequate adhesion of finish to wood can have serious consequences, including premature peeling and cracking, as well as failure to protect the wood. Before considering several kinds of factors that may contribute to better adhesion of coatings layers, some methods of testing the adhesion will be reviewed.

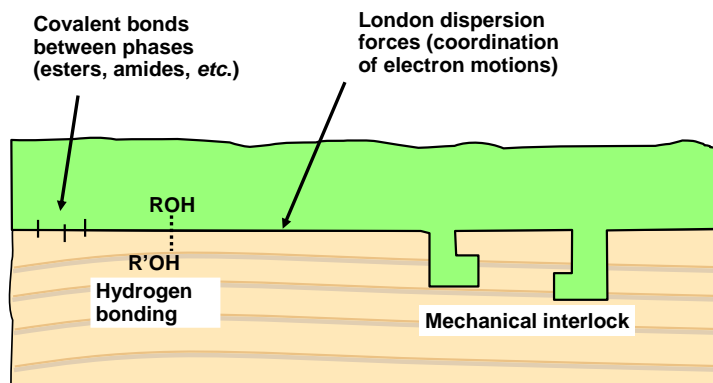


Fig. 16. Key contributions to the adhesion of a wood coating, on a molecular scale

Testing of Wood Coating Adhesion

Several approaches to assessment of finish layer adhesion have been described in recent publications, and many of these can be described as pull-off methods or assessments based on microscopic observations (Budakçi and Sönmez 2010). Ahola (1991) described “torque tests” in which the shear stress required to remove finish levels was quantified. It was found that pre-weathering, before application of the coating to the wood, had a negative effect on the strength of adhesion, after exposure of the coated surface to further weathering. Follow-up work showed that such adverse effects of pre-weathering could be reduced by prompt application of a pigment stain to the wood, thus allowing the film-forming coating layers to be applied somewhat later (Ahola 1995). Van den Bulcke *et al.* (2006) used pull-off tests to further study the effects of weathering on coating adhesion. Dilik *et al.* (2015) used a pull-off test to assess the forces needed to pull polyurethane-based paint layers from the coated particleboard or medium density fiberboard surfaces. Vitosyte *et al.* (2013) used a pull-off test to evaluate effects of surface roughness on adhesion to an ash wood surface. Karaman *et al.* (2023) used computer modeling to predict levels of adhesion of waterborne polyurethane finish to oak, chestnut, and pine wood surfaces, as assessed by ASTM D4541.

Knaebe and Williams (1993) describe an improved test based on fracture toughness, which was said to give more convenient and reliable results in comparison to available shear block, lap shear, and tensile test procedures. de Meijer and Militz (2000a) describe a “new method” involving an adhesive tape to allow measurement of the force needed to peel layers of finish from wood. In general, coating formulations achieving better wetting of the wood substrate, as well as greater penetration into the pore structure, were found to give higher resistance to peeling.

Further information regarding adhesion can be obtained by microscopy and related methods. Rijckaert *et al.* (2001) used fluorescence microscopy to evaluate the penetration of various adhesives into the pores of wood surfaces (Van den Bulcke *et al.* 2003). Kanbayashi *et al.* (2019) describe an application of Raman spectrometry, by means of confocal microscopy, to reveal the precise location of resins and pigments from coatings within the microstructure of wood. In this way, it is possible to answer questions related to whether the coating has entered the pore structure.

In view of the diversity of test methods that have been used to quantify the adhesion of coating layers to wood surfaces, no one test method stands out. Choice of an appropriate method can be expected to depend on the specific interests of the investigators. While various pull-off tests tend to be quick and easy to evaluate, they generally do not mimic the conditions likely to result in flaking of wood coatings in actual applications. Conditioning steps before testing, such as artificial weathering (Kropat *et al.* 2020), may be just as important as the specific test method that is used for quantification of resistance to detachment.

Initial Wetting of Wood by Finish

Wood wettability as necessary but not sufficient

The ability of a film of coating to adhere to a wood surface depends upon both chemistry and structure. One can envision a series of steps, starting with spreading of the liquid formulation, by means of a brush, roller, or spraying, *etc.* Wetting of the wood by the formulation can be regarded as a necessary but not sufficient criterion for achieving strong adhesion. If there are air gaps, *i.e.* bubbles or lack of molecular contact, they can provide starting points for peeling or crack development in the coating. Features of roughness, including pores, can provide a mechanical interlocking effect with the applied finish. But all of these aspects that can contribute to good adhesion can be defeated, at least in part, if the wood surface is covered by a sufficient amount of waxy, monomeric extractives, such as triglyceride fats, fatty acids, and other wood resins. These may serve as a weak boundary layer between the finish and the underlying wood.

As illustrated in Fig. 17, a first step in figuring out whether wettability may be playing a determinative role with respect to adhesion of the coating can involve the measurement of contact angle of the fresh formulation. Such measurements have been carried out in various cases (Krystofiak *et al.* 2016; Miklečić *et al.* 2022). The work of Miklečić *et al.* (2022) helps to address concerns of an expected greater difficulty of spreading waterborne formulations onto wood, especially in cases where the wood has a hydrophobic surface. Indeed, the contact angles measured for waterborne formulations were reported to be about three times greater than the corresponding measurements for solvent-based finishes.

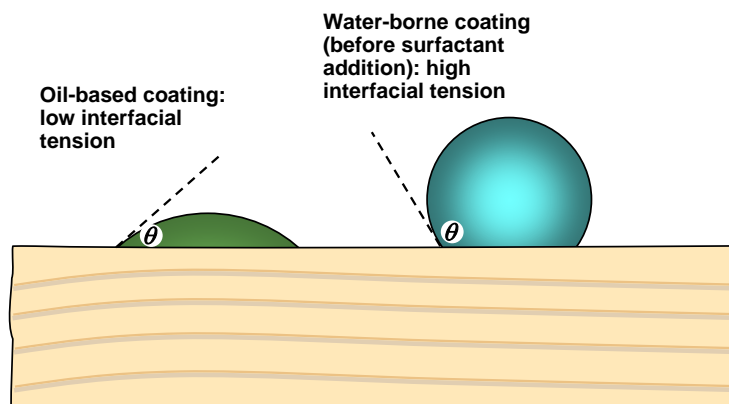


Fig. 17. General expectation of favorable wetting of wood surfaces by solvent-based formulations, in contrast to uncertainties about wetting by waterborne formulations, especially in the absence of surfactants

In principle, the presence of a film of water on a wood surface might be expected to block interaction with oil-based formulations. Such an effect is consistent with a recommendation that a wood surface to be painted ought not to have a moisture content higher than 12% (Williams *et al.* 1996). Rather, even if the surface has been prewetted to address concerns related to undesired swelling of the wood by waterborne coatings, the wood should be dried (and possibly resanded) before application of the finish. An exception to this rule is in cases of waterborne finishes and aqueous staining of some wood surfaces, where sometimes it can be an advantage to work with a water-dampened wood surface (Flexner 1994).

Although contact information, obtained with fresh formulations of coatings, can be used to judge initial wettability, the results of such tests will not necessarily be indicative of success. For instance, in the work of Krystofiak *et al.* (2016), the wettability information was used to draw conclusions regarding the work of adhesion and other parameters in the final coating; it can be argued that such estimates could be inaccurate due to the fact that the most of the liquid medium, which plays a big role during the initial spreading of the formulation, will have evaporated by the time the coating has solidified. Thus, even though the necessary condition of achieving good contact with the surface can be supported by contact angle information, there are further aspects of the full process of curing that cannot be accurately revealed, in typical cases, by such tests.

Thermal modification and wettability

Due to the increasing popularity of thermally modified wood, studies have been carried out regarding such treatment on the wettability of such products by coating formulations. Such work is highlighted in Table 3. As can be seen, although most of the listed studies showed decreased wettability and/or decreased coating adhesion strength on the heat-treated woods, some of the results were the opposite. Figure 18 illustrates the most common observations. Though at relatively low temperatures, heating may cause hydrophobic extractives to come to the surface (Klinc *et al.* 2017), higher temperatures can be expected to thermally degrade both the extractives and the hemicellulose (Pratiwi *et al.* 2019). The wettability of wood heated in the presence of steam increased (Quintos *et al.* 2023). By contrast, decreased wettability and adhesion can be expected in cases where the heat treatment causes a net accumulation of hydrophobic monomers to the wood surface (Chang *et al.* 2019).

Table 3. Reported Effects of Thermal Treatment of Wood on its Wettability and Adhesion Characteristics

Highlights of the Report	Citation
Heat treatment of wood at 225 °C did not adversely affect penetration of finishes into the wood.	Jämsä <i>et al.</i> 1999
Heat-treatment of ash wood in the range 192 to 212 °C resulted in an increase of water contact angle from 61 to about 99 degrees.	Herrera <i>et al.</i> 2015
Heat treatment of pine, oak, and chestnut woods at 130, 180 and 230 °C resulted in decreased adhesion strength.	Kesik <i>et al.</i> 2015
Microwave heating above 80 °C was found to bring wood resins to the surface, thus interfering with the adhesion of some finishes.	Klinc <i>et al.</i> 2017
Heat treatment decreased the wettability of cedar and acacia woods. Other aspects of heat treatment were generally favorable.	Chang <i>et al.</i> 2019
Heat treatment of short-rotation teak wood at 220 °C resulted in degradation of hemicellulose as well as extractives, but a higher proportion of lignin. Coating adhesion generally was improved by the heat treatment.	Pratiwi <i>et al.</i> 2019
Heat treatment of beech wood at 145, 165, and 185 °C decreased the pull-off strength of polyester-based finish.	Taghiyari <i>et al.</i> 2019
Heat treatment of pine wood specimens at 150, 170, and 190 °C caused the contact angle to increase. The elastic modulus at the interface with a waterborne acrylic lacquer was relatively low, suggesting a weak zone of adhesion.	Wu <i>et al.</i> 2020
Heating of untreated teak wood at 220 °C appeared to slightly decrease the surface free energy.	Basri <i>et al.</i> 2022
Heat treatment of pine at increasing temperatures generally hurt the adhesion strength of two waterborne paints; in the case of beech, two different paint products showed contrasting results – one with increasing and one with decreasing adhesion following heating.	Karamanoglu <i>et al.</i> 2022
Fresh sanding or milling of thermally modified wood improved the adhesion of both solvent-borne and waterborne finishes, suggesting that the thermal treatment might be drawing a higher proportion of hydrophobic material to the surface.	Miklečić <i>et al.</i> 2022
Heat treatment of densified poplar wood made it more hydrophobic.	Cheng <i>et al.</i> 2023
Heat treatment of beech and pine wood at 170, 190 and 210 °C resulted in decreased adhesion strength of varnish.	Pelit <i>et al.</i> 2023
Heat treatment of bolo wood, in the presence of steam, increased the adhesion of both lacquer (with nitrocellulose) and polyurethane (both oil-based and waterborne formulations).	Quintos <i>et al.</i> 2023
Heat treatment of surface-densified wood for flooring and furniture resulted in weaker adhesion of the film.	Cheng <i>et al.</i> 2024

In light of the effects of heat treatment, as just shown, it is reasonable to ask whether related effects might be obtained just by waiting a long time. Observations related to that concept were reported by Kiliç and Sögütlü (2022) for a large number of adhesives on oak, chestnut, and pine. No significant differences were found with respect to aging time. Another reasonable question to ask is how heat treatment following wood coating will affect coating adhesion. Such a question was addressed by Atar *et al.* (2015), who evaluated the pull-off strength of various varnishes from beech, oak, poplar, and pine woods. Heat treatment after coating significantly decreased the pull-off strength.

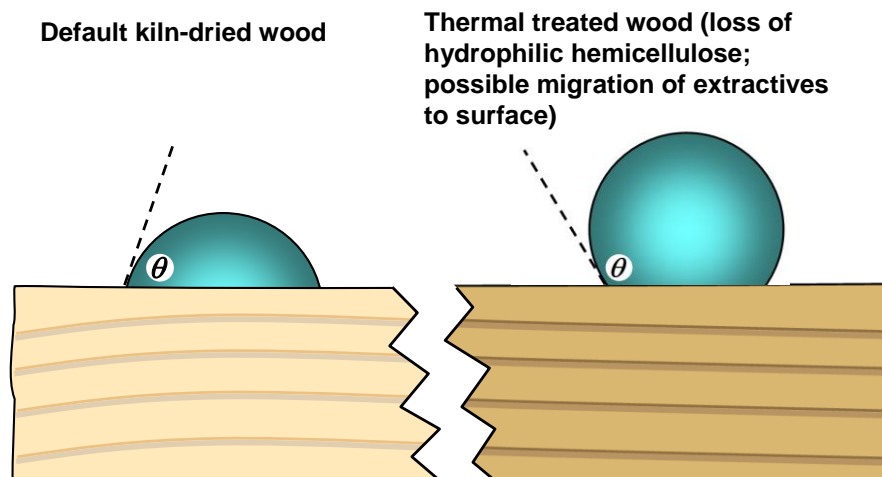


Fig. 18. Typical effects of thermal treatment of wood on its wettability by waterborne finish formulations

Plasma after heat treatment

It is well known that plasma treatment, depending on the gas components, energy level, and various other factors, can greatly affect wettability conditions of surfaces. In particular, corona treatment, involving relatively low-energy plasma with air, is known to oxidize various surfaces and increase their wettability (Zigon *et al.* 2018). Table 4 lists various studies evaluating the effects of various plasma treatments of wood surfaces on the subsequent wettability or adhesion with coating formulations. The main expected effect of corona treatment is illustrated in Fig. 19, where the contact angle decreases after treatment. The effect can be attributed to the increased number of hydrophilic functional groups, such as -OH and -COO. The high affinity of water for such groups means that waterborne formulations will spread better on the corona-treated wood. Waterborne formulations often do not spread well and fail to penetrate pores on hydrophobic surfaces, such as waxy wood, thereby leading to poor adhesion.

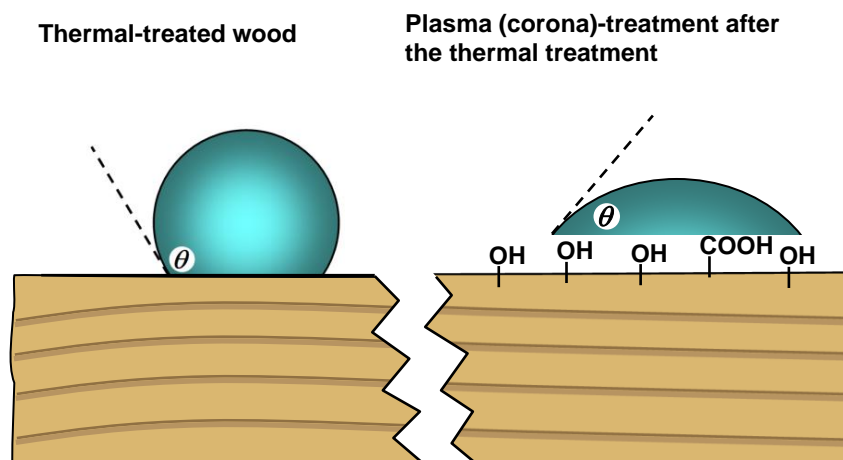


Fig. 19. Expected effect of corona treatment (relatively mild plasma treatment in air) on the wettability of wood by aqueous formulations

Table 4. Reported Effects Plasma Treatment of Wood before Finish Application on its Wettability and Adhesion Characteristics

Highlights of the Report	Citation
The review article mentions examples of the use of plasma treatments to improve the durability of coatings subsequently applied to the wood.	Podgorski & Roux 1999
Results of plasma treatment of spruce and maple wood were highly dependent on the type of gas, and also the effects were transient, decreasing with time after treatment. An argon plasma was found to improve the wettability of the wood and increase adhesion of a waterborne UV-curable polyurethane/polyacrylate coating to a sugar maple surface.	Riedl <i>et al.</i> 2014
Plasma pretreatment gave rise to deeper penetration of solvent-borne polyurethane coatings on spruce wood and thereby improved resistance to accelerated weathering.	Haase <i>et al.</i> 2019
Low-temperature plasma treatment of beech wood increased the wettability and improved the adhesion of a waterborne UV-cured primer.	Peng & Zhang 2019
Plasma treatment removed oil from the surface of oil-heat treated wood. The wettability improved, but there was not a significant effect on the adhesion of a white acrylic coating.	Jamali & Evans 2020
Air plasma treatment of wood increased adhesion of water-based varnish. Optimum treatment conditions were found.	Hazir 2021; Hazir <i>et al.</i> 2021
Atmospheric plasma increased the wettability of beech and spruce wood. The treatment promoted the penetration into beech wood, but it did not have such an effect in the case of spruce wood.	Zigon <i>et al.</i> 2021
Atmospheric plasma increased the wettability of wood, but it did not significantly improve the adhesion of the coatings that were considered. It was noted that the coatings tended to perform well on wood that had been pretreated with an organic solvent.	Zigon <i>et al.</i> 2022

Wood weathering and wettability

Exposure to weather likewise has been found to decrease the adhesion of various coatings, but the reasons appear to be different. Studies reporting such results are listed in Table 5. As illustrated in Fig. 20, it has been shown that weathering generally removes the lignin from the outermost millimeter of the wood surface (Kropat *et al.* 2020), thus tending to render the surface more hydrophilic, but weaker.

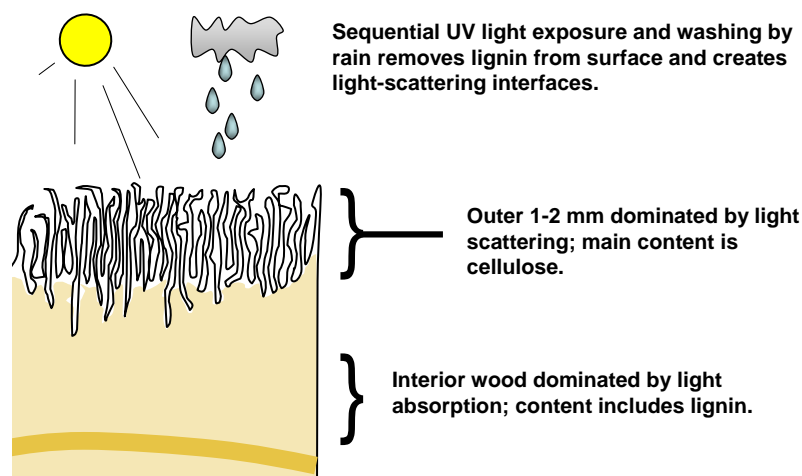


Fig. 20. Summary of the effects of natural weathering (with UV light and intermittent rain) on the surface of exposed wood. Figure modified from an original copyrighted by Kropat *et al.* (2020)

In most of the cases listed in Table 5 the authors did not conduct wettability tests. However, the findings of Basri *et al.* (2022) are consistent with the higher polarity and hydrogen bonding ability of cellulose, compared to the lost lignin.

Table 5. Reported Effects Weathering of Wood before Finish Application on its Wettability and Adhesion Characteristics

Highlights of the Report	Citation
Repeating of weathered painted wood can be done with most coating formulations, as long as the surface has been suitably prepared.	Bottcher 1984
Even brief exposure of wood to outdoor weather was found to unfavorably affect the durability of coatings.	Kleive 1986
Short-term exposure of western red cedar to weather drastically decreased the adhesion of primer coats.	Williams <i>et al.</i> 1987
Preweathered wood panels showed reduced adhesion of paints, based on tests following additional weathering.	Ahola 1991
Exposure of wood to weather for periods of 1 to 16 weeks had an increasingly negative effect on paint/wood bond strength, leading to cracking and flaking.	Williams & Feist 1993, 1994
Preweathering adversely impacted coating adhesion strength, as measured by the torque test.	Ahola 1995
Increased time of preweathering before finish application tended to decrease the service life of the paint.	Williams & Feist 2001
Thermal modification of pine and spruce resulted in lower adhesion of three contrasting types of coatings. The authors did not find a strong coloration with wettability.	Altgen & Militz 2017
Preweathering resulted in weakening of a polyurethane coating at two points, both within the weak weathered layer of wood and at the interface.	Vidholdová <i>et al.</i> 2017
Weathering of moderately heated polar wood caused increased wettability by water.	Herrera <i>et al.</i> 2018
Woods having relatively high content of resins were found to result in poor adhesion of coatings after relatively brief preweathering.	Kettner <i>et al.</i> 2020
Weathering of untreated teak wood increased the calculated surface free energy from 46.9 to 57.4 mJ/m ² .	Basri <i>et al.</i> 2022
UV irradiation of thermally modified wood adversely affected the adhesion of both solvent-borne and waterborne finishes.	Miklečić <i>et al.</i> 2022

Yet another strategy to modify the wetting and adhesion characteristics of wood surfaces involves the addition of resin. Thus, Kielmann and Mai (2016a,b) found that treatment with phenol-formaldehyde resin increased the adhesion of coating. Less blistering, flaking, and cracking were observed during subsequent weathering.

Even if a coating formulation adequately wets of wood surface, an additional requirement is that the macromolecules in the facing surfaces have sufficient mutual solubility so that they can become sufficiently integrated in a three-dimensional manner at the interface (Hansen 2007). Without such three-dimensional integration of polymer segments from the two materials, weak adhesion can be expected. In the case of weathered wood, one can expect a strong contrast between the hydrophilic nature of the cellulose-enriched material at the wood surface and the much less polar resins of typical wood coating formulations. By contrast, lignin is much less hydrophilic and contains aromatic groups that can be expected to match much better to coating resins in terms of the Hansen solubility parameters.

Chemical modification and wettability

Chemical modification of a wood surface, such as acetylation, has the potential to more profoundly affect wettability. As illustrated in Fig. 21, the abundance of -OH groups on typical wood surfaces provides a suitable location for esterification reactions. For example, Pandey and Srinivas (2015) applied acetylation and benzylation to rubberwood surfaces. After coating with a polyurethane-based finish, there was improved resistance to weathering. The effect was attributed to a high resistance to moisture of the esterified wood surfaces. Alade *et al.* (2024) observed improved adhesion of pine wood to oil-based coating following its esterification with acetic anhydride, etherification with 1,3-dimethylol-4,5-dihydroxyethyleneurea, or esterification with a sorbitol/citric acid formulation. However, a waterborne coating formulation showed improved adhesion only with the sorbitol/citric acid formulation. Though such results may point in the direction of various useful strategies, one needs to bear in mind that chemical derivatization of wood surfaces is inherently more challenging and expensive than other wood treatments considered in this article.

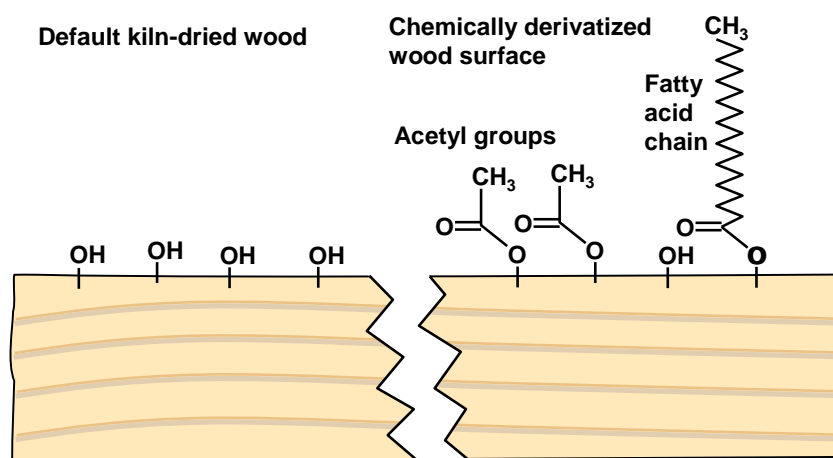


Fig. 21. Illustration of chemical derivatizations with either acetic acid or long-chain fatty acids to provide esterified wood surfaces having much higher hydrophobic character

Surfactants and wettability

In principle, it would make sense to add wetting agents to decrease the contact angle of waterborne coating formulations when they are applied to wood surfaces (Flexner 1994). A wetting agent generally can be described as a surface-active agent that is insoluble in water but having a sufficient content of hydrophilic groups to interact strongly with water at an interface. Ekstedt (2003) evaluated the effect of using such additives in the case of alkyd emulsion paints. Excessive levels of such surfactants resulted in high water absorption by the applied paint layers. Thus, it will be important to keep the amounts of such wetting agents at a relatively low level, as needed to promote the initial wetting of the wood.

Flow into Pores

Evidence of flow into pores in the wood surface

In order for the resins in a coating formulation to be able to establish a firm connection to wood (especially in the case of a primer coating), it is important that the mixture wets not only the outer surface, but also the surfaces of pores, such as those of vessels, tracheids, and spaces created by the microscopic-scale tearing action of milling or sanding. In other words, adequate adhesion of the first coating layer to the wood may require an optimized degree of penetration into the wood.

Van den Bulke *et al.* (2003) used laser confocal microscopy to quantify penetration of waterborne coatings into the pores of wood. A range of different penetration depths were observed for a series of different solvent-borne and waterborne formulations, with no clear differences based on which class of coating was being applied. Though the authors drew a curve through their data, purporting to show a very strong positive relationship between penetration depth and maximum adhesive force before failure, a linear regression would have shown a weak relationship. Rijckaert *et al.* (2001) used confocal microscopy with fluorescent material to compare the penetration of several different coatings. Notably, certain oil-based formulations penetrated to a much greater degree in comparison to the waterborne coating formulations that were evaluated. Such a difference is predicted by the lower surface tension of most nonpolar liquids, which generally results in lower contact angles on solid surfaces, as well as contributing to better wettability (Hubbe *et al.* 2015a). Related work has been reported by Kanbayashi *et al.* (2019), who combined confocal microscopy with Raman spectrometry to be able to identify chemical components in the images.

Erich *et al.* (2006) and Bessières *et al.* (2013) used X-ray tomography to assess the degree to which different solvent-borne, waterborne, or powder coatings penetrated into the pore structure of wood surfaces. The ability of the different resins to flow into pores were found to be governed by resin type, the solids content, and the methods used for drying. de Meijer *et al.* (1998, 2001) similarly concluded that flow into pores was affected by the resin type, pigmentation, solids content, and drying speed. Passages allowing inward flow of the formulation included tracheids and ray cells of softwoods. Tyloses in the wood also were found to block the penetration of freshly applied coating. Czarniak *et al.* (2022) used scanning electron microscopy (SEM) to evaluate paint penetration. They observed no improvement in penetration following plasma treatment of the surface, and they used the SEM evidence to help explain their results. It seems possible that the plasma-induced chemical changes may have been mostly on the outer surfaces and not affecting the wettability of pore surfaces as much. Singh and Dawson (2006) and Singh *et al.* (2007) showed that the resolution of SEM images showing that such features can be enhanced by

use of osmium tetroxide (OsO_4), which strongly blocks electrons. They showed that wood coatings can penetrate even into nano-size pores in the wood.

Kibleur *et al.* (2022) showed that a method called dual-energy computed tomography (DECT) can be used to obtain accurate 3D images of coatings or resins on wood surfaces. This X-ray method was shown to be able to differentiate between the resin, the pigment, and the wood in the obtained images.

Progress in obtaining real-time measurements of the penetration of alkyd, emulsified alkyd, and linseed oil into wood have been obtained by a microautoradiographic method (Nussbaum *et al.* 1998). It was shown that solvent-borne primers and waterborne alkyd emulsion primers had similar rates of permeation into wood.

Mechanical interlock

According to a mechanical interlocking mechanism of adhesion, it is reasonable to expect that the adhesion of a coating to a wood surface would show a positive correlation to penetration into the pore structure. This idea is consistent with the penetrating nature of primers, which are intended to achieve a strong attachment to the wood surfaces (Allen 1984). de Meijer and Militz (2000a,b) found a positive correlation between greater penetration of wood and increased cohesive failure of the coating during subsequent testing of the adhesion. In other words, the attachment to the wood was found to be stronger than the internal strength of the coating itself.

Evidence supporting the mechanical interlock concept of adhesion of coatings onto wood has been obtained from a study involving the effects of sanding. Sögütli *et al.* (2016) found a positive correlation between roughness (achieved with coarser sandpaper) and coating adhesion for three different varnish types. de Moura and Hernández (2005) reported that the adhesion of a high-solids polyurethane coating on sugar maple was favorably affected by sanding. The better adhesion was attributed to surface roughness resulting from the tearing out of fibrils by the abrasive action of the sandpaper. The authors' explanation appears to be consistent also with the idea that the torn-out features could contribute to pores, as discussed in the previous subsection. Cool and Hernández (2016) likewise found that better adhesion was found when the wood surface had such features as open lumens and fibrillation. Such features were affected by the method of preparing the wood, such as oblique cutting, face milling, and helical planing. Helical planing gave the best adhesive strength. Vitosyte *et al.* (2013) found correlations between increased roughness of a birch wood surface and increased adhesive strength to an acrylic polyurethane varnish; such results are in qualitative agreement with a mechanical interlock mechanism.

Lucas-Washburn predictions

In principle, the permeation of a fluid into a porous material can be estimated based on the equations of Lucas (1918) and Washburn (1921), as discussed by de Meijer *et al.* (2001b). As shown in Fig. 22, these equations are based on a simplified model in which cylindrical, smooth pores of uniform diameter are used to represent the porosity of the material. The contact angle governing wetting within the pores is assumed to be the same angle as measured on the exterior of the material.

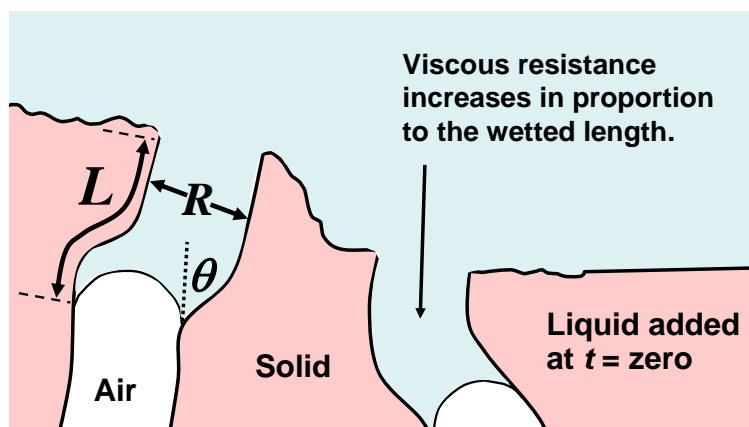


Fig. 22. Simplified physical model assumed for derivation of the Lucas-Washburn equations for prediction of the rates of wetting of porous solids based on the pore radius, the contact angle, and the fluid viscosity

The capillary force giving rise to penetration into the model pores is resisted by the viscous drag associated with Poisseuille-type laminar flow, which increases in proportion to the distance of penetration into the model pore. The integrated form of the Lucas-Washburn equation predicts a proportionality between the distance penetrated and the square-root of time. The Lucas-Washburn can be written in a derivative form or in an integrated form as shown below,

$$dL/dt = \gamma_{LV} R \cos \theta / (4\eta L) \quad (1)$$

$$L = [(R \gamma_{LV} \cos \theta) t / (2\eta)]^{1/2} \quad (2)$$

where R is the equivalent radius of the pores (based on the cylindrical pore model), η is the dynamic viscosity, v is the average velocity of fluid flow into the capillary, L is the distance of permeation at time t , and t is the elapsed time after the initial wetting.

The viscosity term in the Lucas-Washburn equation can offer a likely explanation for observations reported by Cheng *et al.* (2016), who found that addition of a certain kind of nanofibrillated cellulose to a paint formulation had a negative effect on its adhesion to wood. Tamantini *et al.* (2023) reported similar results when cellulose nanocrystals were added to a waterborne acrylic wood coating. It is known that nanocellulose addition to an aqueous system can give a very strong increase in the coefficient of viscosity (Hubbe *et al.* 2017). Accordingly, the adverse effect on adhesion might be due to less distance of penetration of the formulation into the pores. Yona *et al.* (2001a) argued that penetration into pores was prevented by clogging and blockage of pores in the systems that they studied.

The contact angle term of the Lucas-Washburn equation might account for some other effects that have been observed. Xie *et al.* (2006), among various others, observed more favorable adhesion to wood with a solvent-borne coating formulation compared with a waterborne formulation. It is well known that solvent-borne fluids have very low angles of contact with typical wood surfaces. So, except for the effects of wetting agents, as mentioned earlier, the Lucas-Washburn equation can be used to explain some instances of poorer adhesion of waterborne coatings, especially if the wood is relatively hydrophobic. Work reported by Ghofrani *et al.* (2016) likewise supported the Lucan-Washburn equation, as well as the degree of penetration into pores, as an explanation for differences in adhesion

of coatings. They found that removal of extractives, using a mixture of water and ethanol, resulted in improved adhesion. Such findings are consistent with the expected increase in capillary force, drawing the fluid into the pores. This is because removal of the hydrophobic material by the solvent mixture results in a lower contact angle, which is more favorable for wetting.

Resin Interactions with Wood

The next kind of hypothesis that can be considered is that the strength of adhesion may be significantly dependent on the development of bonds of a chemical nature. In principle, such bonds may be of two forms. One option is that the bonding may involve the diffusional entanglement among polymer segments, as was discussed earlier in this article. The other is that chemical bonding, such as covalent bonds, hydrogen bond interaction between ionic groups of opposite charge, or chemical complexation of various types may be significantly contributing to the observed adhesion.

Diffusional bonding with wood

Diffusional mixing of polymer segments, such as those belonging to adjacent latex particles, were already considered in Fig. 12, which is inspired by the work of Cabrera *et al.* (2022). Such an interdiffusion of polymer segments in an interfacial region was proposed by Shi *et al.* (2012) to account for adhesion between polymer fibers at a nano-scale. Krongauz (2021) found evidence of such a mechanism in the autohesion at the interface between plasticized poly(vinyl chloride) surfaces. Such a mechanism may be especially appropriate when envisioning what happens when a fresh layer of finish is being applied on top of another layer, especially when the time between the applications is a matter of hours or days. Such relatively prompt applications of successive coatings has been recommended as a way to favor good inter-layer adhesion (Cassens and Feist 1986). Presumably, a relatively fresh coating will have polymer segments facing the surface that retain a greater degree of mobility, especially when wetted and partly solubilized by the active solvents (Flexner 2005) present in the fresh coating. In such cases the main forces of interaction may be relatively weak, but cumulative van der Waals interactions (Gong *et al.* 2008; Klatt *et al.* 2017). Thus, Gong *et al.* (2008) demonstrated the participation of van der Waals forces during the initial approach of latex particles to each other during the curing of a coating. Klatt *et al.* (2017) calculated such forces for adhesion of a specific polymer film onto a rough surface. As discussed earlier, it can be expected that diffusional bonding will be strongly favored with the solubility parameters of the polymers associated with the wood (especially the lignin component) and the resins in the coating formulation have similar Hansen solubility parameters (Hansen 2007).

Molecular interactions

More energetic interactions, beyond the ubiquitous van der Waals interactions, have been shown to affect bonding at interfaces in many cases, including the anchoring of coatings onto wood. For instance, Kúdela and Liptáková (2006) carried out calculations that showed a dominant contribution of polar interactions in the adhesion of coating materials to wood. Probst *et al.* (1997) calculated the work of adhesion at the interfaces between primer and wood and primer and a top layer of polyester varnish. The interactions considered included not only van der Waals forces but also hydrogen bonding and electrostatic interactions. These authors also considered the detailed conformational shapes of different polymers, affecting their abilities to come into efficient molecular contact with

each other. The electrostatic forces were shown more explicitly by Renneckar and Zhou (2009) for nanoscale layer-by-layer disposition of polyelectrolyte monolayers onto wood. Though the effects were demonstrated clearly, it can be argued that that type of coating is not representative of the state-of-the-art of wood coating methods.

A covalent bonding effect with the wood surface can be achieved by reaction with a silane reagent, thus achieving a sol-gel curing effect (Tshabalala and Gangstad 2003; Tshabalala *et al.* 2011; Cheumani-Yona *et al.* 2015, 2021; Slabejová *et al.* 2018; Yona *et al.* 2021a,b; Qu *et al.* 2023; Zhang *et al.* 2023). Though the relatively weak Si-C bonds present within such a film structure can represent a point of vulnerability, the films can make up for that by having a three-dimensional glass-like structure. It has been shown that treatment with a silane coupling agent can provide a suitable anchoring point for subsequent layers of coatings on wood (Zhang *et al.* 2022, 2023; Tao *et al.* 2024). Zheng *et al.* (2020) demonstrated a system in which a silane coupling agent improved the performance of an acetate-butyrate modified acrylic waterborne coating, presumably by a crosslinking effect.

Weak Boundary Layer Issues

All of the mechanisms of interfacial adhesion described above can fail in cases where the wood surface already is covered by weakly adsorbed monomeric substances such as waxes and wood resins. Monomeric wood extractives are often present at wood surfaces, especially after the passage of time, and their amount will depend on the wood species (Allen 1984; Williams *et al.* 1996; Kimerling and Bhatia 2004; Cordeiro *et al.* 2023). Such substances have been found to gradually diffuse and accumulate at the surface exposed to air (Hiltunen *et al.* 2008; Englund *et al.* 2009). This effect is illustrated in Fig. 23. Such an effect helps to explain why adhesion to a coating layer is often improved by fresh sanding of the surface (Cool and Hernández 2011; Cordeiro *et al.* 2023), thus removing the surface accumulation.

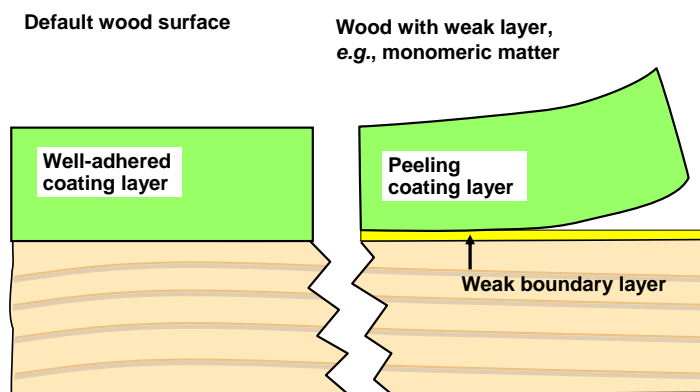


Fig. 23. Expected effect of a “weak boundary layer”, often consisting of monomeric compounds accumulated on a surface and getting in the way of intended adhesion

A strikingly different kind of weak layer between a coating layer and the surface of wood can result from the gradual breakdown of the lignin due to ultraviolet light, which to some extent will be able to pass through the finish. Kanbayashi *et al.* (2023) demonstrated such an effect by artificial weathering of cedar wood that had been coated with four common types of exterior finishes. Subsequent confocal Raman spectrometry revealed the degradation of lignin near to the paint interface, leaving the film vulnerable to detachment.

DEVELOPMENT OF FILM PHYSICAL PROPERTIES

Overview

In order to perform its function, an applied film of coating on wood needs to reorganize itself in response to evaporation and permeation processes. By such means it needs to solidify and develop strength, it needs to develop its hydrophobic or hydrophilic surface attributes, it will develop its appearance attributes, and it might even be designed so that it acquires a self-healing ability. Such issues will be considered in this section.

Self-assembly Overview

At the moment that a fresh layer of coating has been applied to a wood surface, or on top of previous such layers, various processes can take place that are no longer under human control. Rather, the dissolved polymers, particles, and emulsified matter within the formulation will move around in various ways during such processes as evaporation, diffusion into pores, and reorientation of amphiphilic compounds at phase boundaries. The sorting-out processes involved in such diffusional movements, especially if it leads to somewhat organized and beneficial effects, has been called self-assembly (Hubbe *et al.* 2023).

A key principle of self-assembly is illustrated in Fig. 24. As shown, it is proposed that certain of the component parts of the system to be assembled have a tendency to fit together in a prescribed favorable fashion. What is generally required for self-assembly to happen is a suitable level of mobilization of the parts, such that they are able to assume a large number of intermediate conditions on the way to adopting an intended structure.

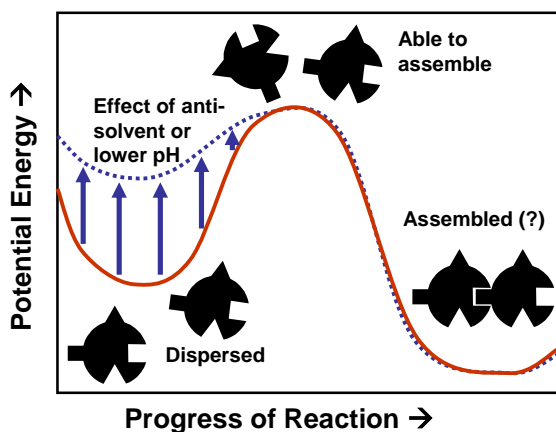


Fig. 24. Schematic illustration of a self-assembly process, which depends on the presence of a certain level of chaotic energy and the sampling of different possible fits. Figure reused from Hubbe *et al.* 2023; copyright by the authors

As one example of how interactions at the nanoscale can affect the properties of coating layers, it has been shown that incorporation of ZnO nanoparticles was able to increase the glass transition temperature of an acrylic stain, once it had been evaporatively cured (Cristea *et al.* 2010). The effect was attributed to the ability of the nanoparticles to induce an increased level of crystallinity within the polymer material during its curing. Another example involved the development of a highly ordered pattern of latex spheres in a coating on wood, such as to present so-called “structural colors” that do not require any

chromophoric materials or selective absorption of light (Liu *et al.* 2020). Song *et al.* (2024) reported the preparation of uniform lignin/titanium dioxide nanoparticles, by confined self-assembly, and their subsequent usage as an additive in polyurethane wood coatings. It is also possible to directly utilize self-assembled lignin nanoparticles (Trovagunta *et al.* 2024) as an additive in wood coatings (Song *et al.* 2022).

Hardness

The hardness of a wood coating can be important in various applications where the surface needs to be able to resist effects of tableware, footwear, and writing with a pen, to name a few. In principle, hardness can be regarded as being dependent on both the nature of the cured resin and any reinforcing particles in the formulation, as well as how the particles are arranged. Figure 25 illustrates some of the general principles that can be used to achieve increases in hardness in a formulated coating. There are a great variety of resin types used in wood coatings; though their properties are to some extent known, there is likely to be variation between and within different brands that nominally have the same identification. Likewise, the hardness of recycled versions of plastics to be used in wood coating formulations will need to be evaluated (Godinho *et al.* 2021). The hardness of a coating can be expected to change over time, due either to further curing or to other effects, such as weathering. Notably, Gunduz *et al.* (2019) found that certain coatings actually became harder in the course of weathering. The application of a coating, such as a varnish, often increases hardness (Pelit *et al.* 2023), which is consistent with the filling in of pore spaces need to the wood's surface; however, the authors found cases in which a soft coating had the opposite effect of rendering the coated surface less hard. In general, factors that tend to increase the glass transition temperature and the crystallinity index of the cured resin in a coating can be expected to give higher hardness (Veigel *et al.* 2014).

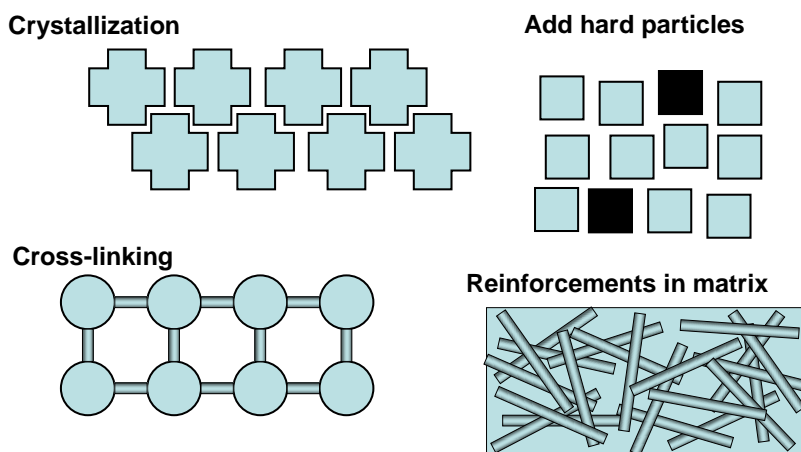


Fig. 25. Some basic ways to achieve increases in hardness of a formulated coating

Role of crosslinking

Crosslinking can be regarded as a primary tool by which to increase the hardness of a wood coating. This is a particularly important issue in the coating of floors and furniture, which can encounter scuffing and impacts during normal usage. A notable feature of UV-cured coatings, which are popular for factory-prepared furniture and ready-to-use flooring, is that they provide extensive crosslinking (Hermann *et al.* 2021). Such

systems are also known for their potential to achieve high hardness (Landry *et al.* 2015). Hermann *et al.* (2021) showed that high crosslink density, as needed to achieve high hardness, can be achieved by optimization of the mix of monomers and oligomers employed.

Addition of reinforcing materials to the formulation

A further strategy that can be used to promote hardness is to optimize the type and level of mineral content, noting the high hardness of certain minerals. For instance, Zhou *et al.* (2023) reported achievement of high hardness and scuff resistance when adding nano silicon carbide, a very hard mineral, to a UV-curing formulation for flooring. However, Ersoy *et al.* (2021) showed, somewhat surprisingly, that a strong contribution to hardness can be achieved with calcium carbonate, which is relatively low in cost. To go yet further in that unexpected direction, Yan *et al.* (2022a) found that incorporation of the relatively soft material rice husk powder, formulated with melamine, increased the hardness after curing of a mixture that included shellac microcapsules and a waterborne primer. Such findings appear to teach that the reinforcement itself may be as important to the development of hardness as is the hardness of the materials used for reinforcement. Landry *et al.* (2010) reported some hardness increases when using clay mineral at the 3% level in acrylate formulations; however, under many of the tested conditions there was no benefit to hardness when adding the mineral to the formulation. A related approach is to consider the highly platy nano-scale material graphene oxide; Xu *et al.* (2022) showed that its incorporation into a waterborne polyurethane paint formulation led to significant increases in hardness, which might be attributed to their efficient reinforcement in a type of nanocomposite.

Plasticizers, glass transition temperature, and flexible resins

A potential downside of high hardness is a possible associated tendency for brittleness. Thus, it can be important to consider strategies that can be used to decrease the cured hardness of a coating. One of the key tools by which this can be done is by incorporation of a plasticizer (Cox 2003; Flexner 2005). In very general terms, a plasticizer can be defined as a non-crystalline compound having low volatility that has good solubility with the rest of the components in the formulation. For example, Flexner (2005) noted the common usage of cellulose acetate butyrate in nitrocellulose-based lacquer as a means to reduce the brittle character to an optimal extent.

Another approach to decreasing the hardness of a coating is to use an inherently flexible resin component (He *et al.* 2022). This can mean selecting a resin having a lower glass transition temperature (Nejad and Cooper 2010, 2017). In general, latex-type waterborne coatings are likely to be more flexible, and thus more resistant to cracking, than their oil-based counterparts (Williams *et al.* 1996).

Self-healing Attributes

Capsules in a coating formulation component

A recurring problem associated with wood coatings is their eventual development of cracks, peeling, or other damage. Several investigators have considered the possibility of developing a type of coating that has the ability to cure itself after being subjected to such damage. Highlights of such studies are provided in Table 6. A common feature of most such systems that have been considered is that they contain microcapsules filled with active coating formulation. Thus, in principle, when an event occurs causing damage to the

coated surface, some of the local capsules will be ruptured, allowing for some filling of the crack or damaged zone.

Table 6. Progress in the Development of Self-Healing Wood Coatings

Highlights of the Report	Citation
Microcapsules based on UF and MF thermoset resins that contained healing agents based on an epoxy system were mixed with diverse kinds of coating formulations. Performance was demonstrated by means of a simulated hailstorm.	Schreiner <i>et al.</i> 2017
Urea-formaldehyde/epoxy resin microcapsules were prepared with different ratios of core to wall material and added to waterborne wood coatings. Good repair ability was observed.	Yan <i>et al.</i> 2019
The self-healing system was based on acrylate formulations having -OH groups on oligomers and monomers. It was important to have low steric hinderance in the self-healing formulation.	Paquet <i>et al.</i> 2020
Incorporation of an interior layer consisting of microcapsules increased the resistance to scuffing. Other properties were less encouraging.	Slabejová <i>et al.</i> 2020
Urea-formaldehyde resin was used to form the walls of capsules that were incorporated into waterborne coatings formulations. Cracking was inhibited and the system lays groundwork for a self-healing system.	Yan & Peng 2020
Waterborne acrylic core vs. epoxy core microcapsules were prepared and added to waterborne wood coating. The system was able to be cured at room temperature.	Yan <i>et al.</i> 2020a
The core-wall ratio was optimized for a self-healing system with waterborne acrylic resin encapsulated in a urea-formaldehyde wall. A core-wall ratio of 0.55:1 worked best.	Yan <i>et al.</i> 2020b
Shellac-filled microcapsules with urea-formaldehyde walls were added to waterborne paint formulation. Self-healing was observed.	Yan & Wang 2020
The middle layer of a coating system contained microcapsules. The broken microcapsules were able to fill artificially made cracks.	Lagana <i>et al.</i> 2021
Different healing modes were found following abrasion vs. scratching. Results were sensitive to the cross-link density and glass transition temperature.	Paquet <i>et al.</i> 2021
Self-healing capability was incorporated into a coating formulation that also was resistant to fire.	Sun <i>et al.</i> 2021
Waterborne coating was prepared with self-healing microcapsules for an interior layer; some healing was observed after scratching.	Tao <i>et al.</i> 2021
A superhydrophobic and also self-healing version of a waterborne coating was prepared using an encapsulated silane reagent as a repair agent.	Wu <i>et al.</i> 2021
Microcapsules containing a waterborne coating formulation were added to a waterborne primer. The study laid further groundwork for a self-healing system.	Yan & Peng 2021
Self-healing formulation in microcapsules was added to a water-based topcoat formulation. Some healing effect was observed.	Yan <i>et al.</i> 2021a
A waterborne primer was prepared with shellac microcapsules enclosing a waterborne coating formulation to impart self-healing ability. Self-healing depended on the details of formulation.	Yan <i>et al.</i> 2021b
A self-healing system with water-based formulation encapsulated in urethane-formaldehyde walls was evaluated on linden wood. Up to 20% of repair was observed.	Yan <i>et al.</i> 2021c

Lac resin microcapsules and fluorane microcapsules were used together in a water-based primer or top coat. A self-repair efficiency of about 10% was observed.	Yan <i>et al.</i> 2021d
A gelatine-based microcapsule system was used to deliver fire retardant ability and self-healing.	Zhang <i>et al.</i> 2021
Tung oil microcapsules were included in a urea formaldehyde resin; the coating was able to heal microcracks formed after its application to a wood surface.	Pan <i>et al.</i> 2022
Adding microcapsules with tung oil increased the toughness of paint films; the best performance was with a core-wall ratio of 0.78:1.	Peng & Yan 2022
Self-healing capsules were added to a shellac formulation. There was no chemical reaction between the coating components and the encapsulated components.	Qin & Yan 2022
Waterborne coating formulations were prepared with shellac-based capsules. The extent of self-healing was up to about 36%.	Wang <i>et al.</i> 2022
Microcapsules were prepared with a range of core-wall ratio, emulsifier concentration, reaction temperature, and rotation speed. The core-wall ratio was found to be the most important variable. Cellulose inclusion was able to toughen the capsules.	Xia <i>et al.</i> 2022
Shellac microcapsules coated with rice husk powder was used with waterborne primer, laying the groundwork for a self-repairing system.	Yan <i>et al.</i> 2022a
Fluorane thermochromic microcapsules were prepared, in addition to waterborne acrylic resin-filled microcapsules. They were added to a waterborne coating, where they exhibited both color change and a repair efficiency of about 58%.	Yan <i>et al.</i> 2022b
This article describes the colloidal principles underlying the use of microcapsules for self-healing coatings on wood.	Chang <i>et al.</i> 2023
Healing efficiency as high as 92% was reported for vanillin-derived aromatic Schiff base polyurethane that was designed with reversible bonding within its backbone chain.	Chen <i>et al.</i> 2023
An optimum level of magnetic carbonyl iron powder microcapsules was found for core:wall ratios between 0.65:1 and 0.70:1.	Li & Yan 2023
Repair performance was as high as about 34% for capsules with melamine-formaldehyde walls and carbon nanotubes and carbonyl iron powder self-healing mixture.	Wu <i>et al.</i> 2023
Shellac microcapsules were combined with carbonyl iron powder and carbon nanotubes to achieve both self-healing ability and conduction of electricity in the coatings.	Xia <i>et al.</i> 2023
A core formulation of shellac solution with rosin plasticizer was encapsulated in melamine resin. Repair efficiencies were in the range of about 18 to 28% after breakage and reassembly of the coating.	Zhu <i>et al.</i> 2024

As illustrated in Fig. 26, self-assembly offers a different strategy by which to design self-healing systems. As shown, such mechanisms depend on the component parts of the system to be in a state of activation, making it possible for the system to sample many different arrangements of structure. The final structure, after a period of trial and error, can be governed by preferential rules of fitting, making some arrangements more energetically favorable. It is worth noting that none of the studies listed in Table 6 employed this kind of strategy. A possible reason is that typical coatings on wood may be so completely immobilized as to block such self-healing effects.

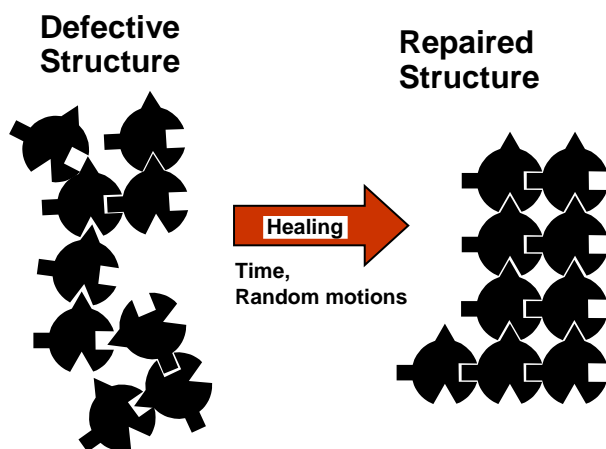


Fig. 26. Self-healing principle that is inherent in certain self-assembly mechanisms. Figure reused from Hubbe *et al.* 2023; copyright by the authors

COMPROMISES INHERENT IN ECO-FRIENDLY FINISHES

Challenges for Waterborne Finishes

As stated at the outset of this article, the decades since the late 1990s have witnessed a dramatic shift in wood coating formulations, going from exclusively oil-based mixtures to the present dominance of waterborne systems, especially in products designed for use by the general public. Various challenges, as well as successes, involving such systems already have come up in the course of considering different topics in this review article. The purpose of this section is to take stock of the present state of the art. Due to the advantages in terms of low volatile organic solvents and easy cleanup with soap and water, it can be expected that waterborne coatings for wood will continue their dominant position for the foreseeable future.

Among the issues that seem most in need of research input, relative to the performance of waterborne coating formulations in general, are the undesired swelling of the wood, the relatively high permeability of typical waterborne coatings, and opportunities to further improve the environmentally friendly character of such coating formulations.

Undesired Swelling of the Wood during Coating

Fiber-rise issues

As has been noted in this review, an inherent problem associated with the usage of waterborne coating formulations is related to the swelling of the wood when it is wetted by water (Flexner 1994, 2005; Cox 2003; Landry *et al.* 2013). For instance, Fig. 27 illustrates a problem called “fiber-rise,” in which the swelling of wood fibers in water causes them to protrude from a sanded surface of the wood. As shown, such protruding fibers often can exceed the thickness of the cured coating, which can result in a loss of gloss and a defective appearance. The practical effect is that the grain pattern of the wood can be raised in the course of its wetting by a water-based coating formulation (Landry *et al.* 2013). Ways to mitigate the problem are often labor-intensive and requiring extra time. For instance, the wood surface can be pre-wetted, allowed to dry overnight, sanded, and only then coated with a first waterborne layer (Flexner 2005). Although the mentioned procedure can be expected to decrease effects associated with the raising of the grain of the wood, it is not

likely to completely resolve the problems. The topic of the swelling of cellulosic materials, including wood itself, was recently reviewed (Hubbe *et al.* 2024). A key issue highlighted in that review is the fact that the swelling of wood is strongly anisotropic, which results in a much greater expansion perpendicular to the grain direction.

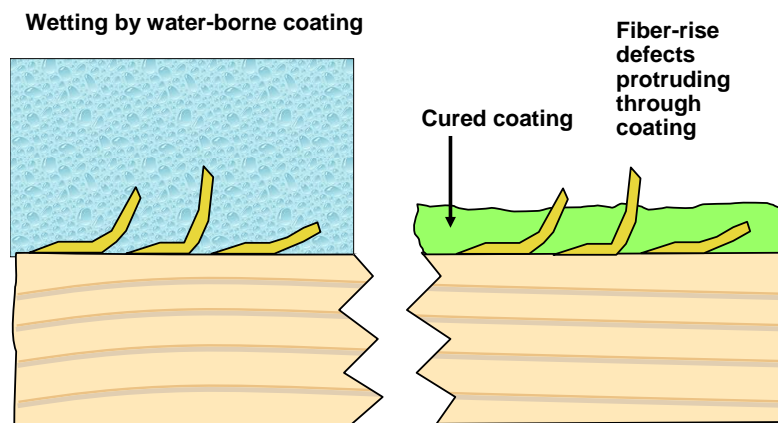


Fig. 27. Illustration of fiber-rise caused when a sanded wood surface is wetting by a waterborne finish formulation

With an aim to strike a balance between a high quality of the coating, including its smoothness and adhesion to the wood, along with the minimization of environmental harm, it appears that one of the most promising approaches may be to optimize a suite of ethanol-based primer formulations that can be applied to the wood first. Ethanol is relatively benign, and it has been used successfully for the application of some stains, thus achieving less distortion and “fiber rise” problems at that stage of wood treatment (Cox 2003). Although in such applications it is clear that ethanol can be an effective means of distributing certain stain compounds, especially some of those that already can be distributed by water, it is unclear whether ethanol can be used as a substitute fluid carrier for the resins or resin-oil blends that are associated with many modern wood finishes. In particular, it may be inherently problematic to distribute a latex formulation in that way. Rather, the opportunity might lie in the development of a more narrowly focused class of primers to be used in cases where the goal is to minimize wood swelling in the course of applying the second and later coating layers, which can be expected to be waterborne in a high proportion of cases. Solubility principles (Hansen 2007), as outlined earlier, might be used as a means of narrowing down candidate resins suitable for such alcohol-borne primers.

Permeability

The relatively high permeability of many waterborne coatings for wood has been noted as an ongoing concern (Allen 1984; Ekstedt 2003; Donkers *et al.* 2013; Volkmer *et al.* 2015; Hysek *et al.* 2018). There appears to be a need for coating products that can achieve much higher barrier performance, relative to vapor exchange, while still retaining the environmental benefits of using water as the main solvent and carrier (Gezici-Koç *et al.* 2019). A more effective barrier to water vapor can be expected to decrease the extent of periodic swelling and shrinkage in response to changes in weather (Gezici-Koç *et al.* 2019). A particular challenge may reside in the fact that wetting of a coating layer, as in

the case of rain, may render it yet more permeable to water vapor, presumably due to its swelling (Hysek *et al.* 2018).

A further incentive to developing coating formulations that offer greater resistance to permeation is that such coatings might simultaneously provide a better answer to observed problems with the bleeding of wood resins through waterborne coating layers (Allen 1984; Cassens and Feist 1986; Williams *et al.* 1996; Williams and Feist 1999; Kimerling and Bhatia 2004; Williams *et al.* 2005; Englund *et al.* 2009; Darmawan *et al.* 2018; Wu *et al.* 2020; Coniglio *et al.* 2023a,b; Dvorak *et al.* 2023). Wood resins rising to the surface may become more important, depending on the likely growth in popularity of some thermally modified wood products (Altgen and Militz 2017). Presently it appears that one of the best ways to address such issues is with a prime coating of pigmented shellac (Allen 1984), which falls into the category of an oil-based formulation.

One path by which developers of future waterborne coating formulations could take as a strategy to reduce vapor permeability would be to employ highly platy particles. Such materials might include exfoliated sodium montmorillonite, which has been shown to have an especially high ratio of plate diameter to thickness (Ploehn and Liu 2006). It can be dispersed in water and has been shown to be effective for developing vapor barrier properties (Bangar *et al.* 2023). Work by Cristea *et al.* (2010) already has shown that the incorporation of very different kinds of mineral particles, nano TiO₂ and ZnO₂, already can achieve some of the desired effect of decreasing the permeability of the coating. One of the challenges that needs to be faced during such developmental efforts is the possibility that vapor may be preferentially transported in a layer at the surface of the solid particles (Donkers *et al.* 2019). But presumably if the particles have a sufficiently high aspect ratio, such effects may be less important than the increased tortuosity, *i.e.* a much higher path length that diffusing molecules need to take in order to diffuse through the coating layer (Wolf and Strieder 1990; Ghanbarian *et al.* 2013; Simões da Silva *et al.* 2022).

Another angle by which future coating formulations might be optimized to address concerns of coating layer permeability is by focusing on the water uptake of the coating layer itself. Work by Gibbons *et al.* (2020) showed strong correlations between such water uptake and the surface tension and solids content of the coating formulations. Presumably, the degree of swelling of the coating itself, upon exposure to water, can be addressed by increased crosslinking and perhaps by increased hydrophobic composition.

Eco-friendly Coatings

Though the emergence of waterborne coatings for wood can be regarded as an important step forward in the direction of minimizing environmental impacts, there appear to be many opportunities for further progress in the direction of minimizing adverse environmental impact. These include further efforts to reduce volatile organic carbon (VOC) emissions and the replacement of some petroleum-sourced components with plant-based components. Figure 28 emphasizes some of the key goals with respect to achieving a high level of sustainability when using wood products, noting that wood coatings will play a role in such issues.

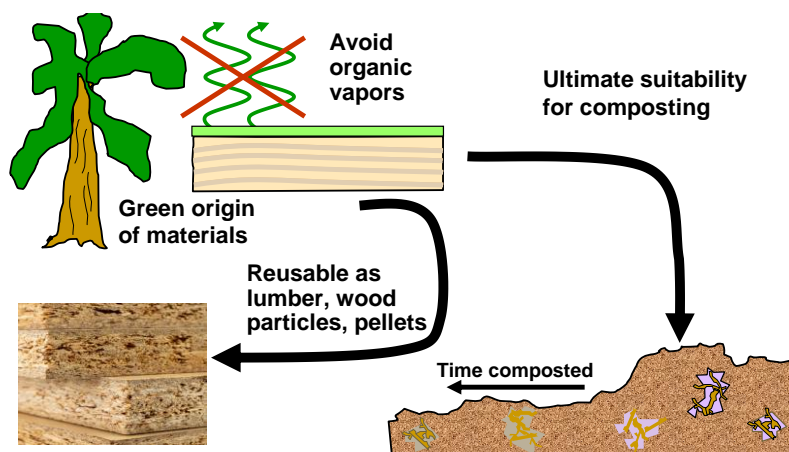


Fig. 28. Overall view of sustainability goals for wood products, including any effects related to the coatings. Part of this figure adapted from Hubbe (2023)

Plant-sourced components in coating formulations

Some progress in the development of coatings based on plant materials is highlighted in Table 7. In addition to plant-based approaches, there has been a specific concern to replace toxic isothionate products. A class of non-isothionate polyurethanes has been described by Zareanshahraki and Mannari (2021). Another such issue concerns the kinds of plasticizing agents used in lacquer coating products made with polyester resin and drying oils (Alves *et al.* 2023). The glycol ethers used for that purpose are known to be more toxic than alternatives such as propylene glycol ethers (Flexner 2005).

Table 7. Progress in the Development of Plant-based Wood Coatings

Highlights of the Report	Citation
Polymerized whey proteins were used in the formulation of coatings. A biocide was used to slow down mold growth.	Wright <i>et al.</i> 2006
Fatty acid methyl ester from vegetable oil was used as a component in waterborne wood coatings.	Philipp & Eschig 2012
Soybean-based coatings are reviewed. These include epoxy, alkyd, urethane, and UV-curable systems.	Ren & Soucek 2014
Biobased waterborne polyurethanes were prepared from partially or fully dimerized fatty acid polyols.	Poussard <i>et al.</i> 2016
Condensed tannins were used as additives in acrylic-based clear coatings to stabilize wood color.	Grigsby 2018; Grigsby & Steward 2018
A life cycle assessment of wood flooring treatments supports the development of coating products with bio-based components.	Montazeri & Eckelman 2018
A fatty amine was prepared from mahua vegetable oil to be used in a polyurethane system.	Raychura <i>et al.</i> 2018
Lignin, as a plant-based polyol, was proposed to be incorporated into a polyurethane system to be used in various applications.	Alinejad <i>et al.</i> 2019
Hemicelluloses were used as stabilizers for alkyd resins in paints.	Mikkonen <i>et al.</i> 2019
Jatropha oil was used as the source material for preparation of a polyurethane resin system, which exhibited high hardness of the coating but poor adhesion to the wood.	Mudri <i>et al.</i> 2020
Cellulose acetate butyrate (CAB), a bio-based product, was used in the development of a waterborne acrylic resin system.	Zheng <i>et al.</i> 2020
Natural indigo pigment was used as a colorant and for its contribution to resistance to weathering.	Jordan <i>et al.</i> 2021

Gelatin was the source material for a biodegradable, self-healing coating for wood.	Zhang <i>et al.</i> 2021
Soy flour was used as the basis for preparing an adhesive for wood.	Zhang <i>et al.</i> 2022
This review article considers replacement of petroleum-based chemicals in wood coating formulations.	Landry <i>et al.</i> 2023
A new binder for coatings was developed with cashew nut shell liquid <i>via</i> oxidative coupling of the alkyldiene chain.	Ranarijaona <i>et al.</i> 2023
Polyurethane coatings were prepared by thermochemical liquefaction of two wood types to make alkylphenol polyols.	Silva <i>et al.</i> 2023

CONCLUDING STATEMENTS

A series of hypotheses were introduced at the beginning of this article. Now, after having reviewed published literature, these hypotheses can be reconsidered.

1. Understanding wood's degradation and the factors that affect it can provide a foundation for understanding the role of protective finishes.

Support for this hypothesis mainly lies outside of the present work, which did not focus on reviewing wood degradation. Much is known about wood weathering from research that has been considered in earlier review articles (Feist 1982; Cogulet *et al.* 2018; Kropat *et al.* 2020). In addition, coating systems designed for exterior usage on wood will be considered in a future review article by the present authors.

2. By blocking all or most rainwater from wetting the wood itself, a finish is able to decrease the swings of cyclical changes in moisture content that would have been experienced by unprotected wood exposed to outdoor weather.

This hypothesis has been well supported by findings reported in the literature, especially the work of Lu and Lin (2008), de Meijer and Militz (2001a,b), Gezici-Koç *et al.* (2019), and Bobadilha *et al.* (2020).

3. By absorbing UV light, a suitably formulated finish can avoid or slow down the photodegradation of lignin near the surface of the wood, thus helping to maintain the integrity of the wood surface.

This hypothesis is well supported by numerous studies involving the addition of UV-absorbing additives in wood coatings. Such treatments will be considered in greater depth in a future review article by the present authors.

4. By presenting a suitably hard and contiguous film at the wood surface, the finish can protect the wood from scratching and abrasion.

This hypothesis is well supported by findings cited in this article, especially with respect to the development of hardness in wood coatings.

5. By drying and curing in a way that develops smoothness, the finish can contribute to a glossy appearance, and the level of gloss can be adjusted by formulation of the finish mixture.

This hypothesis, while agreeing with common experience, was not specifically addressed in the present work. Rather, it will be a key focus of a future review article by the present authors that deals with the coating of wood for indoor applications.

6. Surface preparation steps and many other details are foundational to achieving film and reliable adhesion of the finish to the wood to achieve an expected service life of multiple years or even decades in some cases.

As discussed in this article, key preparation steps will include fresh milling or sanding. One of the effects of such mechanical preparation is the exposure of surfaces not blocked by monomeric wood resins, which in some cases can present a weak interface, preventing the establishment of good adhesion. Also, published findings indicate that a moderately coarse final sanding is likely to provide better mechanical anchoring of the finish, especially in cases where there might be a problem.

7. To perform its various functions, an effective layer of finish will need to have undergone a curing process, which can involve evaporation of one or more carrier fluids (drying), oxidation and other chemical changes, and even covalent crosslinking in some cases.

This hypothesis is well supported by the reviewed findings. Curing processes that involve evaporation can be understood as also involving the self-assembly of polymeric segments and particulate components. Diffusional motions during evaporation of the carrier fluid are understood to be essential to achieve the needed density and interweaving among polymer segments to establish strong films and adhesion to the wood. In some other cases, curing can involve the establishment of chemical bonds.

8. To be able to spread effectively onto either wood or a previous layer of finish, the next layer to be spread needs to be formulated with a suitable surface tension, as well as having resins able to spread and interact with the functional groups facing the surface.

The present review of the literature did not find evidence of cases in which a fresh layer of coating formulation was not able to spread adequately onto another widely used type of wood coating. On the other hand, there will still be a need for studies that address ways to overcome poor wetting, spreading, and permeation of coating formulation onto and into the pore spaces of wood specimens having hydrophobic surfaces, often as a result of wood resins.

7. A final hypothesis to be considered in this article can be attributed to Flexner (1994, 2005). The background for this hypothesis involves the design of waterborne wood finishes. The general expectation of a waterborne finish is that it ought to perform its various roles equally well in comparison to traditional oil-borne formulations. The hypothesis states that a well-performing waterborne finish formulation will contain not only water, but also a minor amount of a slower-to-evaporate vehicle, which in addition needs to be a good solvent for the polymeric binder in the finish. Such a system can be expected to permit intermixing among polymer segments of adjacent macromolecules, thus resulting in a contiguous film.

While this hypothesis appears to be sound, it does not appear to have been the focus of critical studies. Due to the likely importance of such a mechanism relative to the further development of waterborne coatings for wood, it is recommended that further research should focus on confirming and explaining the role of solvent components that are less volatile than water and able to bring about tackiness of resin

components either in a continuous manner or especially in the situation where their concentration has been increased due to the evaporation of water during the curing process.

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