

The Multifactorial Aspect of Wood Weathering: A Review Based on a Holistic Approach of wood Degradation Protected by Clear Coating

Antoine Cogulet, Pierre Blanchet,* and Véronic Landry

Wood is an abundant and renewable natural resource. Its use is promoted as a way to reduce the carbon footprint in building construction. Wood structures are degraded by their environment due to weathering. This review is a meta-analysis of the main factors of degradation that belong to this phenomenon. The impact of irradiation, the role of water, oxygen, temperature, and colonization by fungi are explained. To protect against these factors, the use of coatings is the most common solution. Since currently the trend is to maintain the grain and the natural color of the wood, the use of transparent coatings is favored. This review presents the main technologies used in clear wood coatings. The durability of this protection against weathering is approached. The whole of knowledge gathered has made it possible to begin a discussion on the multifactorial aspect of wood weathering. Schemes were created to synthesize the synergistic and antagonistic effects between the degradation factors.

Keywords: Wood weathering; Clear wood coating; Multifactorial degradation; Fungi; Photodegradation

Contact information: N. S. ERC Industrial Research Chair on Eco-responsible Wood Construction, Wood and Forest Sciences Department, Pavillon Gene-H.-Kruger, 2425, Rue de la Terrasse, Université Laval, Québec (Québec), G1V 0A6, Canada; *Corresponding author: pierre.blanchet@sbf.ulaval.ca

INTRODUCTION

The wood decking market for 2018 in the United States is estimated at 6.5 billion USD. This market represents an increase of 2.4% annually in demand for wood (Freedonia 2011). In order to support this trend, it is necessary to provide to consumers sustainable, durable, and aesthetic practical wood products. However, it has been estimated in the state of California that the annual amount attributable to the deterioration of wooden buildings is 364 million USD (Freedonia 2011; Kutz 2012). This reflects an inability to protect wood against weathering. The term weathering describes all types of surface degradation that occur on wood due to a wide range of environmental factors. The most common factors are presented in Table 1. A distinction between abiotic and biotic factors can be made. Not all of these phenomena lead to degradation, but they are essential to other degradation processes. Thus, temperature or oxygen will not cause degradation by themselves, but they allow biological degradation to occur or have an influence on photodegradation (Hon 1979; Hon *et al.* 1982; de Meijer and Militz 2001).

These phenomena work using different mechanisms, however, they lead to the same result of a performance loss of wood and coatings. Strategies to protect wood against weathering include wood modifications or the application of coatings (Nuopponen *et al.* 2004; Williams 2005; Hill 2007; Baur and Easteal 2013). The latter is the most widespread, especially due to its economic- and convenience-based advantages.

Table 1. Phenomena that Occur during Weathering (Williams 2005)

Weathering Factor	Impacts
Irradiation	Photo-oxidation of the polymers present in wood, Destruction of lignin leading to delamination, Generation of secondary chromophores leading to wood photo yellowing
Water	Surface leaching; Stress in the material leading to fractures, splits, and checks
Fungi	Wood colouration, Depth degradation, Patterns of degradation differ in terms of species
Atmosphere	Oxygen, pollutants
Wind	Wind-driven rain, hail, and particle-like sand; Leads to erosion

A first distinction can be made between waterborne coatings and solvent-borne coatings. Due to the latest regulations concerning VOCs emission from paints, this review will only focus on waterborne coatings. Acrylic and polyurethane coating technologies are often selected due to their stability against weathering (Weiss 1997; Chiantore *et al.* 2000; Chiantore and Lazzari 2001; Singh *et al.* 2001; Rosu *et al.* 2009; Shukla *et al.* 2009). Lately, alkyd resin technologies have been formulated by making emulsions in water. The new architectural trends, as well as growing interest from customers, aim to maintain the natural wood appearance. Unfortunately, this transparency means the permeability of the protection to the visible light.

Additives can be incorporated into coatings to provide extra protection against photodegradation. However, up to now, clear protections do not offer the same durability as opaque protection. This difficulty to provide long term durability with clear protection can have an impact on the increasing trend of the use of wood as a building material.

It is essential to better understand the degradation mechanisms when wood is exposed to outdoor conditions. Research to understand the loss of performance of exterior wood has generally involved separate laboratory experiments on each weathering factor. While this strategy has led to a better understanding of wood degradation, it does not accurately reflect reality. Interactions can be easily imagined between the factors shown in Table 1. As a result, some papers emphasize the synergistic effects of photodegradation and biological degradation. Included among these effects, there is the ability of fungi to use lignin byproducts generated from the photodegradation (Schoeman and Dickinson 1996, 1997). Except for the present study, there have been no relevant reports on the multifactorial effect of weathering. Thus, there is a strong need for studies that take into account synergistic and antagonistic effects between weathering factors. A “holistic approach” of the degradation pathways of wood finished with clear coatings should be considered.

To better understand this failure to offer an efficient and sustainable transparent solution to protect the wood, new insights in the knowledge available on this topic have to be considered. For this reason, this review describes the main factors involved in both wood and clear coating degradation. An emphasis on the photodegradation mechanisms and their impacts has been realized regarding the importance of this factor in the weathering process. By summarizing this information, graphics showing synergetic and antagonistic effects between the weathering factors were suggested. Taking into account interactions between degradations could help researchers for improving wood protection with clear coatings.

DEGRADATION OF WOOD AND WOOD CLEAR COATING DUE TO WEATHERING

The next subsections discuss the mechanisms of how the biotic and abiotic factors degrade the wood and its clear protection. Impacts of photodegradation on wood and its clear protection will be first discussed. Then, description of the others abiotic factors is approached. The last part of this section treats of wood degradation and its clear protection by fungi.

Wood Irradiation

Generality

Irradiation of wood leads to photodegradation phenomena. The degradation occurs directly after exposure of the material to light. It depends on the photon energy as calculated by Eq. 1,

$$E = \frac{h * c}{\lambda} \quad (1)$$

where h is the Planck constant, c is the speed of light in a vacuum (m/s), and λ is the wavelength (nm).

Short wavelengths are more energetic than longer ones. The shortest wavelengths hitting the earth's surface fall in the UV spectrum range from 290 nm to 400 nm after absorption by the ozone layer. It is possible to reproduce photodegradation under laboratory settings using lamps and to accelerate the degradation rate by using shorter wavelengths (Rosu *et al.* 2009; Pintus and Schreiner 2010; Pintus *et al.* 2016).

Reproduction of weathering with tougher conditions than natural exposure allows testing the durability and the resistance of samples as well as study degradation mechanisms. In artificial weathering, conditions are controlled, which allows a normalized degradation. In contrast, natural weathering depends on the geographic area, weather, years, and even the specific days of study.

Xenon and fluorescence lamps are the most commonly used. Tolvaj and Mitsui (2005) suggested using xenon arc lamps with filters to reproduce the natural spectrum of the sun. Fluorescence lamps can reproduce the UV spectrum of the sun but also produce more energetic light that allows an acceleration of the degradation (Tolvaj and Mitsui 2005). Additionally, lasers can be used to study a specific wavelength or localization (Barta *et al.* 2005; Pandey and Vuorinen 2008). These studies have elucidated some of the wood photodegradation mechanism.

Wood photodegradation mechanism

Although photodegradation has been studied since the 1960s (Tarkow *et al.* 1966), its mechanism is not fully understood. Photodegradation starts with the absorption of a photon. The molecule is in an excited state with respect of the second law of photochemistry, Stark-Einstein (Rabek 1994; Williams 2005). The chemical groups targeted are chromophoric and phenolic groups, which lead to the formation of free radicals (Moore and Owen 2001). Leary (1994) describes several pathways of degradation that are water and oxygen dependent. These begin by chromophoric group excitations from lignin and end with the generation of quinones and free radicals.

Free radicals

The presence of free radicals has been discovered by the use of electron spin resonance on the photodegraded samples (Hon and Ifju 1978). In its native state, wood does not contain free radicals; their presence is a clear indication of degradation (Hon *et al.* 1980). Moreover, these studies have clarified the relationship between light wavelength and free radical formation. These are produced by the cleavage of aldehydes and ketones following a Type I Norrish reaction. Cleavage occurs on the C α linkage and generates two free radicals. Free radicals can migrate through the wood, causing deeper degradation (Feist and Hon 1984).

Depth of photodegradation

Photodegradation is mainly a surface phenomenon. Penetration of light into wood depends of wood density and the length of exposure (Kataoka and Kiguchi. 2005). Experiments were performed to determine the depth of degradation after light irradiation. Different results have been reported in terms of the wood species and the type of lamp used. Hon and Ifju (1978) found a degradation depth of 75 μm for UV and 200 μm for visible light. Kataoka and Kiguchi (2001) reported deeper modifications after long-time exposure, around 500 μm for lignin and 700 μm for carbohydrates on *Cryptomeria japonica* (D. Don) after 1500 h of exposure under a xenon lamp. They confirmed in another study the role of the length of exposure in depth profiling the degradation. Logarithmic behavior has been observed between exposure time and depth of degradation (Kataoka and Kiguchi 2001; Kataoka and Kiguchi 2005). Despite the interspecies variability, these studies show a lesser penetration of photons belonging to UV than photons belonging to visible light (Kataoka and Kiguchi 2001).

Wood polymer degradation

The presence of aromatic and phenolic functions in lignin, such as chromophoric compounds, leads to strong absorption between 280 nm and 400 nm (Kutz 2005; Williams 2005) In addition to a change in wood colour, the loss of lignin, which is hydrophobic, makes the surface of wood more hydrophilic (Williams 2005)). Evans *et al.* (1992) made the analysis of the leachate of a *Pinus radiata* (D. Don) photodegraded surface and found the presence of mannose and xylose, which suggests the degradation of hemicellulose (Evans *et al.* 1992).

Unlike lignin, holocelluloses are sensitive to the global spectrum of light (Derbyshire and Miller 1981), which leads to depolymerization and weight loss (Pandey 2005b). Photons from visible light are less energetic than those from UV (Eq. 1), so damages occur more slowly. Evans *et al.* (1996) have studied natural weathering of *P. radiata* (D. Don) in Australia. Surface delignification was measured within 4 h and a significant depolymerization within 4 d. Even if the rate of cellulose modification is slower, the damages are deeper due to the better penetration of visible light in wood.

Macroscopic Impacts of the Irradiation

On wood

The surface aspect of wood is impacted as it becomes rough and stringy with the formation of microscopic checks. Due to swelling and shrinkage, these defects can grow in large macroscopic cracks (Feist and Hon 1984).

More specifically the main target of the photodegradation of wood is the lignin and especially its chromophoric groups. Lignin comprises up to 76% of the middle lamella and

is involved in the cohesion between wood cells. Its photodegradation leads to a loss of cohesion between tracheids (Volkmer *et al.* 2013). This phenomenon translates into cell delamination (Singh and Dawson 2003).

The generation of new chromophoric compounds leads to a wood modification that is correlated with the wavelength, temperature, time, and intensity (Pandey 2005b). The wood colour goes from its natural colour to a birefringent silver patina, which corresponds to the natural colour of the cellulose (Feist and Hon 1984).

With the contribution of some fungi, a grey colour appears on delignified wood. Some fungi, especially black stain fungi, produce organic pigments, such as melanin, which give a grey colouration. Some extractives have chromophoric structures and can also be involved in the colour change (Pandey 2005a).

Photodegradation is different in hardwood and softwood. Both Colom *et al.* (2003) and Pandey *et al.* (2005b) found greater degradation for softwood than hardwood under xenon lamps for 24 weeks and 4 weeks, respectively.

On coating

In coating, pigments and dyes are also degraded (Allen 1994; Pintus *et al.* 2016). A loss of gloss can be observed due to the binder degradation and the formation of a rough surface (Christensen *et al.* 1999; George *et al.* 2005). Some pigments can be more photo-resistant than the binder. The destruction of the binder leaves the particles, like pigments, non-bound to each other. This leads to a phenomenon called “chalking”, which describes the friable layer on the surface (Pappas and Fischer 1974). The coating can become more brittle due to chemical changes, and cracks can appear (Johnson and McIntyre 1996). A decrease of the film thickness linked to weight loss is also a consequence of photodegradation (Schmid 1988). On polyurethane varnish, photo yellowing is also a consequence of photodegradation, where an increase in the carbonyl group, such as quinone, is noticed (Singh *et al.* 2001; Rosu *et al.* 2009).

Different colour scales allow for the analysis of colour changes in a chromatic coordinated system. Colour modification attributed to weathering can be followed for both the wood and coating. Schnabel and Petutschnigg (2011) found colour stabilization after 200 days of natural weathering at Kuch (Austria) for *Picea abies* (Karst) and *Larix decidua* (Mill.). This report corroborated the observations of Agresti *et al.* (2013), who observed colour changes after 504 h under xenon lamps for *Populus tremula* (L.).

Clear Coatings Irradiation

Wood and coatings age following the same phenomena (Table 1). Aging of both occur at the same time but with different consequences (Williams 1983). Coatings are prone to photodegradation, but depending on the coating composition, the durability will not be the same. As an example, the nature of the pigments and dyes significantly impacts the UV resistance of the coating (Allen 1994; Pintus and Schreiner 2010; Pintus *et al.* 2016).

A wide range of coating types can be applied over wood. Each formulation shows a different behavior towards photodegradation. However, due to their polymeric nature, they are prone to photo oxidation and cross-linking reactions, as shown in Fig. 1 (Gryn'ova *et al.* 2011).

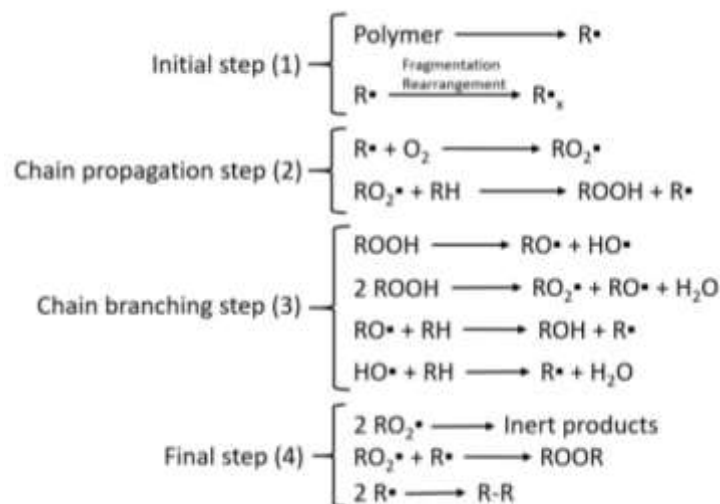


Fig. 1. Mechanism of polymer photo oxidation (Gryn'ova *et al.* 2011)

The mechanism can be divided into four steps:

1. Initial step: photon absorption by the polymer generating free radicals;
2. Chain propagation step: reactions between oxygen and free radicals to create peroxy radicals (RO₂•). They react with the polymer to form a polymer hydroperoxide (ROOH) and a polymer alkyl radical (P•);
3. Chain branching step: hydroperoxides are broken into oxy (RO•) and hydroxyl (HO•) radicals;
4. Final step: cross-linking reaction between free radicals (Gryn'ova *et al.* 2011; Pintus *et al.* 2016).

The glass transition temperature (T_g) of coatings changes after photodegradation, which can impact the paint film resistance against dimensional variations (Hunt and Lansing 1935; Koleske 2012).

In the case of clear coatings, the loss of protection is due to delamination rather than destruction of the polymeric matrices (Singh and Dawson 2003; Evans *et al.* 2015). This review will not focus on the chemical modification of the polymer itself. The loss of coating performance will be discussed as part of the global degradation of the material.

Water Action on Wood and Wood Clear Coating

Wood is a hygroscopic material in equilibrium with air relative humidity (RH). It can undergo dimensional variations. Wood is anisotropic, such that the modifications occurring are different regarding orientation. Changes are more important in the tangential than in the radial direction. Stresses due to moisture content variation in internal and external wood can lead to swollen grain and splits. Damages appear after several wet/dry cycles, at least from 20 to 30 cycles (Williams *et al.* 2001b,c).

Water can also cause erosion of the wood surface at an average speed of 50 μm per year (Williams *et al.* 2001b). This varies strongly depending on the exposure angle; the erosion being related to photodegradation. The light energy is stronger at 45° than at 90°. Between 45° and 0° there is no significant difference of energy, but at 0° there is no

leaching due to the flow. The accumulation of lignin breakdown products from photodegradation can protect the wood and decreases both the degradation and wood erosion (Evans 2008). Furthermore, the rate of erosion depends on the nature of wood as well as the density or the species (Williams *et al.* 2001b ; Orton *et al.* 2004). Arnold *et al.* (1991) compared the erosion rate after 2400 h under UV irradiation or xenon lamp irradiation and they found a good correlation. They concluded that the erosion strongly depends on water and not light. A study, realized by Anderson *et al.* (1991) used xenon lamps with or without the contribution of water. Differences in the rate of wood degradation confirmed the role of water in the photodegradation process.

Water is a highly effective solvent; heavy rain can leach the surface of wood and carry products from photodegradation and hydrolysis. These phenomena contribute to the erosion and weight loss (Hon 1983; Horn *et al.* 1994). The extractives can be leached as well, which makes the wood less water repellent (Williams 2005).

Coatings can also undergo damages due to the flow of water on its surface. Some compounds, like pigments or hydrophobic compounds, can be leached. This modifies the permeability of the coating and favors water exchanges (de Meijer and Militz 2001). Water is also known for hydrolysis of organic compounds (Evans and Evans 1990; Evans *et al.* 1992). Holocellulose and hemicellulose's constituents were found after an analysis of leachate from streaming water. After photodegradation, the lignin in its natural state protects hemicellulose, and tends to make it more exposed to hydrolysis. Humidity is also a critical factor of a microorganism's growth, like fungi.

Other Abiotic Factors

Temperature

Temperature is an important parameter in the material aging process. Material temperature is influenced by the air temperature and exposure to light (especially infrared). Depending on the wood colour, the degree of light absorption is more or less intense and contributes to an increased sample temperature.

The glass transition temperature of the coating (T_g) is a critical factor; it determines the temperature range in which the material transitions from brittle to rubbery. It is a reversible phenomenon. Usually the coating age increases the T_g and causes more fragility, especially prior to dimensional variations (Podgorski *et al.* 1996).

Oxygen

Exposure to oxygen contributes to aging *via* the oxidation of synthetic polymers in coating binders (acrylics, polyurethanes, *etc.*) or natural wood polymers. Some unstable species, such as peroxide or hydroperoxide, are created by the reaction between free radicals from photodegradation and oxygen (Hon 1976, 1979; Hon *et al.* 1982). The oxygen singlet corresponds to a high energy form of oxygen. This molecule reacts with phenolic compounds in lignin, resulting in depolymerization and lignin modification (Bonini *et al.* 1998; Barclay *et al.* 2003; McNally *et al.* 2005; Cogulet *et al.* 2016).

Biotic Factors

Generality

Depending on the environment, many organisms colonize and degrade wood. Fungi are especially found on wood with a protection failure of the coating due to biological degradation. They are ubiquitous and have an impact on the quality and the lifetime of wood before and after commercial utilization. The first observations of a biotic factor on

wood were conducted at the end of the nineteenth century by Schacht, then Mobius (Schacht 1863; Williams *et al.* 2001a). With microscopic observations, Mobius highlighted that the grey colour is associated with fungi.

Fungi are eukaryotes and heterotrophs, meaning they must find an external source of organic material. Lignocellulosic compounds and saccharides found in parenchyma and also wood extractives are used as nutrients by some fungi (Horvath *et al.* 1976). At the anatomic scale, fungi consist of one body or thallus subdivided into many substructures called hyphae. A mycelium that can be seen at the macroscopic scale is composed of several thallus. There are two fungal morphologies: filamentous and yeast-like. Filamentous fungi can be divided by internal cross-walls called septa, and yeast-like fungi exist as blastospores or a mix between filamentous and yeast-like, *i.e.*, pseudomycelium (Fig. 2). Fungal infection starts with hyphae penetration in the cell walls, which allows the secretion of an enzymatic cocktail that oxidizes the aromatic chain compounds and makes them easier to digest (Bousslimi *et al.* 2014).

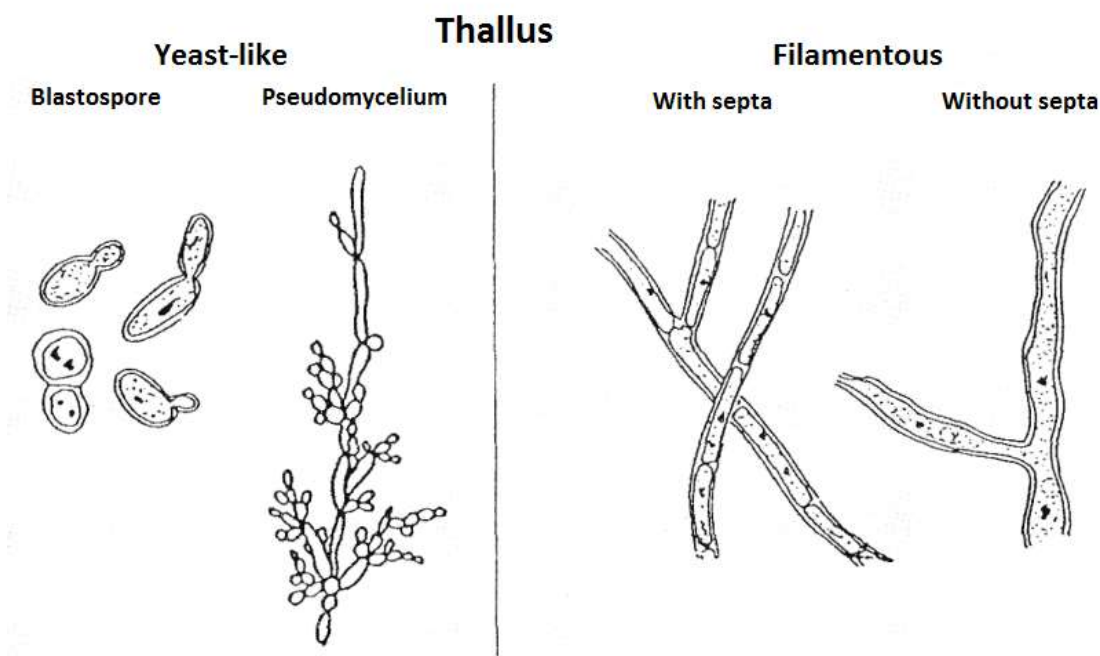


Fig. 2. Yeast-like and filamentous fungi (Kendrick 1985)

Opportunistic fungi

Opportunism in the present review describes the ability of some fungi to grow on weathered wood, for example, to metabolize photodegradation products (Schoeman and Dickinson 1997). The majority of *fungi* isolated from infected wood are *Ascomycota*. There are four species that represent 70% of the fungal flora on photodegraded wood: *Aureobasidium pullulans*, *Hormonema dematioides*, *Epicoccum nigrum*, and *Phoma spp.* (Seifert 1964; Dickinson 1971; Bardage and Bjurman 1998a). Other species belonging to the *Clasosporium* and *Scerophoma* can also be found. They are all ubiquitous and can be carried by rain or wind. The strategies used to grow favourably on photodegraded wood are not the same for each species, but they all lead to colour changes. They are called “black stain fungi” and give a grey colouration on delignified wood, and black or brown colouration on lignified wood.

A. pullulans and *H. dematioides* synthesize melamine. It is a high molecular weight compound with a dark brown or black colour that protects against UV radiation. These fungi modulate their melamine production to match the UV radiation intensity. *A. pullulans* is the main fungus colonizing photodegraded wood (Shirakawa *et al.* 2002). This species produces blastospores that promote its adhesion to wood cells (Bardage and Bjurman 1998b). *E. nigrum* produces black sporododia, which are aggregates of spores that protect against UV radiation. *Phoma* spp. produces pycnide, which protects spores until their liberation. They appear as black dots on wood.

Environments favourable to fungi

Fungi require oxygen, moderate temperature, nutrients, a certain pH, vitamins, and minerals, but water is the main growth factor.

When wood moisture content is slightly superior to the point of wood saturation, water can be found in lumens. This water is available for fungi and can be used to promote its growth as well as to secrete enzymes into the wood (Zabel and Morrell 1992). Even though the wood moisture content is below to the point of wood saturation, an external source of water such as a water leak or an infiltration is enough to promote their growth. Each fungus has its own metabolic and ecology requirement, but it seems necessary to have humidity between 35% and 50% and a temperature between 25 °C and 35 °C (Kendrick 1985).

WOOD PROTECTION BY COATING

Generality

One of the purposes of a coating application is to increase the wood resistance against its environment. However, the aesthetic appearance is also important, as it is the main purchasing factor for customers. The customer sees the coating as an extension of his house (de Meijer 2001). A coating contains a resin, a solvent and/or diluent, additives, and pigments and/or dyes.

Currently, environmental rules and worker safety are becoming more stringent. For coatings, it translates into new volatile organic compound (VOC) regulations that favor water-soluble coatings. This technology cannot block water exchange between the atmosphere and wood, but does regulate it (Ahola *et al.* 1999). Three kinds of resins are mainly used for exterior waterborne wood coatings: acrylic, polyurethane, and alkyd.

Acrylic coatings are widely used for outdoor paints, as they are very resistant to hydrolysis and show good resistance against UV light (Prane 1986). Their adhesion to wood substrates as well as their quick drying are two other advantages. They are prepared by polymerization of both acrylic and methacrylic acids with acrylate and methacrylate monomers. They are modified with oils for better adhesion on wood that is naturally photodegraded (Evans *et al.* 1996). This kind of coating lets the wood “breathe” due to its porosity. Unfortunately, Bardage and Daniel (1997) demonstrated that micropores can be large enough to allow fungi colonization (Bardage and Daniel 1997).

Polyurethane coatings are often crafted as two-component systems with an isocyanate and a compound with active hydrogen (*e.g.*, polyol). Hybrid formulations containing polyurethane and acrylic technologies use the hydroxyl group from acrylic resin as active hydrogen. They have good resistance to weathering and also against mechanical deterioration like scraping (Weiss 1997; de Meijer *et al.* 2001).

Traditional alkyd coatings were solvent-borne and contained mineral spirits or aromatic solvents. They offer advantageous properties such as high gloss, penetration in wood and auto-oxidative curing (Goikoetxea *et al.* 2010; Athawale and Nimbalkar 2011). To respect new regulations on VOCs emission, efforts were given to provide solvent-free alkyd emulsion in water. Since emulsions are inherently unstable over time, it is necessary to seek the suitable surfactant to promote formation of small droplets as well as to prevent flocculation and coalescence (O'stberg *et al.* 1995; Wang and Jones 2000).

Alkyd resins can be combined with acrylic resins to obtain a blend of their properties (Athawale and Nimbalkar 2011). Therefore, disadvantages of alkyd resins such as low acid and alkali resistance can be overcome (Wang *et al.* 2000; Saravari *et al.* 2005).

There is increasing research into the use of silicone to improve the weather resistance of coatings. The linkages in silicon materials, such as Si-C and Si-O, are strong and allow good weathering resistance. In addition, because they are synthetics, they are not prone to biological degradation. Silicon coatings also have good scratch resistance. This technology has been studied in wood coatings as an additive or as the resin itself.

This review does not discuss wood modification or wood preservatives. Despite their uses and efficiency in wood protection, this review focuses on issues involved in clear coatings.

Clear Coating Performance Loss

The loss of clear coating performance results in the failure of wood protection or the loss of the aesthetic aspect. Clear coating durability is a real issue for the wood industry. In the 1950s, the California Redwood Association (USA) and the Western Pine Association (USA) performed tests on the durability of some clear coatings. The best performing coating offered 18 months of protection. The majority failed after 8 months (Sarvis 1953; Estrada 1967). Currently, despite the advances in clear coatings for wood substrates, warranties do not exceed 5 years.

Even if the reasons for the loss of performance in wood coatings are multifactorial, an emphasis can be done on their permeability to visible light (MacLeod *et al.* 1995; Miniutti 1967; Singh and Dawson 2003). Despite the introduction of UV protectors, clear coatings often fail prematurely. Evans *et al.* (2015) recently reviewed the different strategies used for enhancing their durability. Different aspects were studied, from the modification of the coating formulation to the different wood modifications with an overview on the use of additives in the coating as UV protectors.

The light permeability of clear coatings leads to photodegradation of the wood surface with all of the consequences describe above. The generation of free radicals from lignin degradation affect the wood-coating interface. Thus, even though linkages between the coating and wood are still under study, it is well accepted that mechanical anchorage remains the strongest adhesion mechanism. These links are degraded by free radicals and can cause delamination in the absence of degradation of the coating (Fig. 3). In addition to the loss in the coating adherence, the first layer of cells lose their coherence due to middle lamella degradation as a consequence of lignin photodegradation (Fig. 5) (Estrada 1967; MacLeod *et al.* 1995; Singh and Dawson 2003; Evans *et al.* 2015b).

Other factors can lead to protection loss, such as the stresses induced by the coating after abiotic degradation, especially the modification of the T_g and dimensional variations, causing fractures, fails, and other defects. In addition, an unappropriated application of the coating, or an application on a surface already photodegraded or poorly prepared will decrease the coating service life (Williams and Feist 2001; Jirouš-Rajković *et al.* 2007).



Fig. 3. Delamination of clear coating on wood (Evans *et al.* 2015b)

Synthetic polymers, such as those found in coating formulations, are relatively resistant to microbes. They are often high molecular weight compounds that are difficult to digest by microorganisms (Shirakawa *et al.* 2002). However, some pigments can feed fungi or in contrast, have antifungal activities (Chen *et al.* 2009).

Aureobasidium pullulans, the main fungus in photodegraded wood, is unable to grow on glass samples coated with paint; it needs lignin breakdown products to grow (Horvath *et al.* 1976). There are many theories explaining the presence of mold on painted surfaces. As per its ubiquitous nature, *Aureobasidium pullulans* can be present either on the surface before paint application or on the paint surface. Some fungi enter the coating either *via* micropores or by direct penetration by specialized hyphae (Bardage and Daniel 1997). Transpressorium is a characteristic structure found in black stain fungi like *A. pullulans*. This structure enables it to penetrate the woody cells and can be used to penetrate the coating (Schmidt 2006). At the interface, fungi spread their hyphae and easily grow. In fact, the film prevents lixiviation of the surface and keeps breakdown products from photodegradation and hydrolysis at the interface.

As previously stated, a critical factor affecting fungi growth is wood moisture content. Waterborne coatings do not allow a total blocking of water exchanges (Bagherzadeh and Mousavinejad 2012). At best, they regulate the exchange between wood and atmosphere. A thicker coating results in better protection against fungi because it blocks hyphae penetration (Morris and Morse 2008).

MULTIFACTORIAL ASPECTS OF DEGRADATION

State-of-the-art

All of the degradation mechanisms presented in this review occur at the same time when the wood is exposed to its environment. Numerous synergistic or antagonist interactions can be imagined between them. Studies already emphasized some interactions, the easiest one being the role of the temperature, which increases the rate of photodegradation and hydrolysis (Mitsui *et al.* 2001). Fundamental studies, such as those realized by Schoeman and Dickinson (1997), on the ability of some fungi to metabolize the lignin breakdown products from the photodegradation open the way toward new comprehensions.

For clear coatings, the permeability to visible light and the variability in the efficiency of UV protectors lead to the accumulation of simple sugar and phenolic compounds at the wood/coating interface. With the coating and bare wood, the protective layer prevents lixiviation of these compounds by rain. Thus, they are trapped at the interface as nutrients for fungi. This may explain why it is common to find strong colonization by black stain fungi on wood coated by a clear coating.

As early as 1986, the synergetic effects between different phenomena associated with weathering were emphasized (Fig. 4) (Sell and Feist 1986). Nevertheless, technological advances and knowledge in the field of wood degradation elucidate the multifactorial aspect of this process. Furthermore, some conclusions can be made from the review of the different degradation factors that occur during weathering.

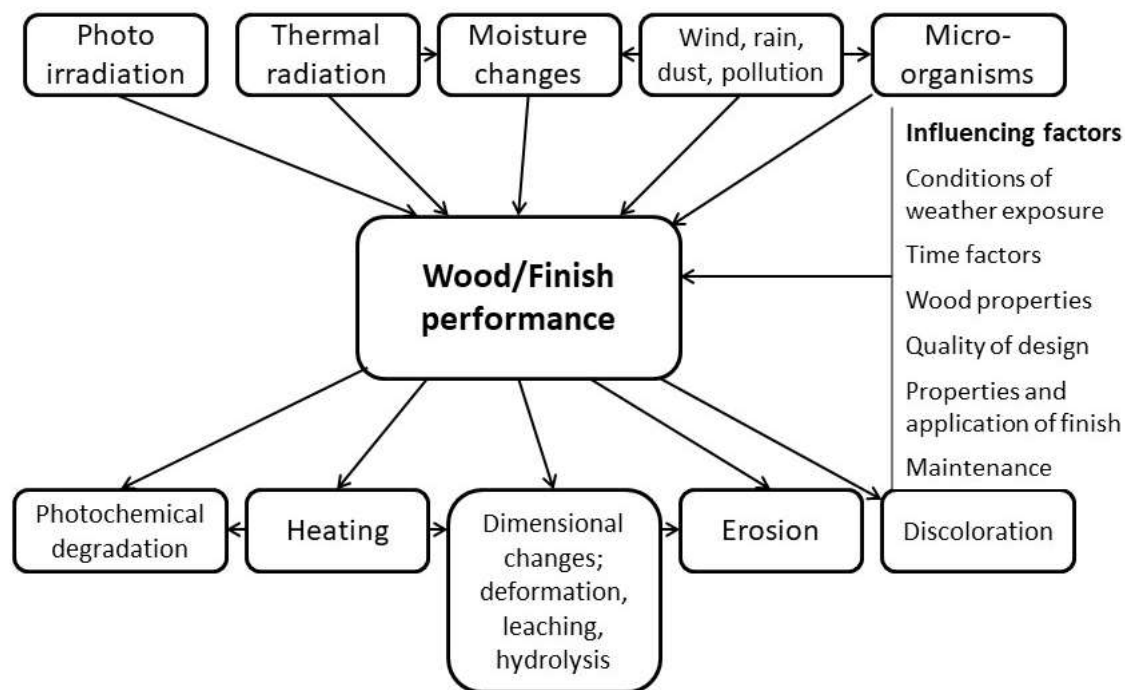


Fig. 4. Interaction between different mechanisms of degradation for the wood/coating (Sell and Feist 1986)

Moving Forward

New schema describing the interactions that can occur during wood and clear coating degradation are necessary. The complexity of these interactions impedes the elaboration of a unique, clear and simple schema. Figure 5 divides the three main causes of the loss of performance of a clear protection for wood into a) photodegradation, b) water degradation, and c) fungal degradation. The goals of these schema are twofold: on the one hand they gather the knowledge presented in this review, and on the other hand, they give the possible consequences of degradations from one factor to another. Readers have to keep in mind that these schemas are projections from the knowledge summarized in this review. They must therefore serve as a track for the development of new protocols taking into account the multifactorial aspect and should not be taken for granted.

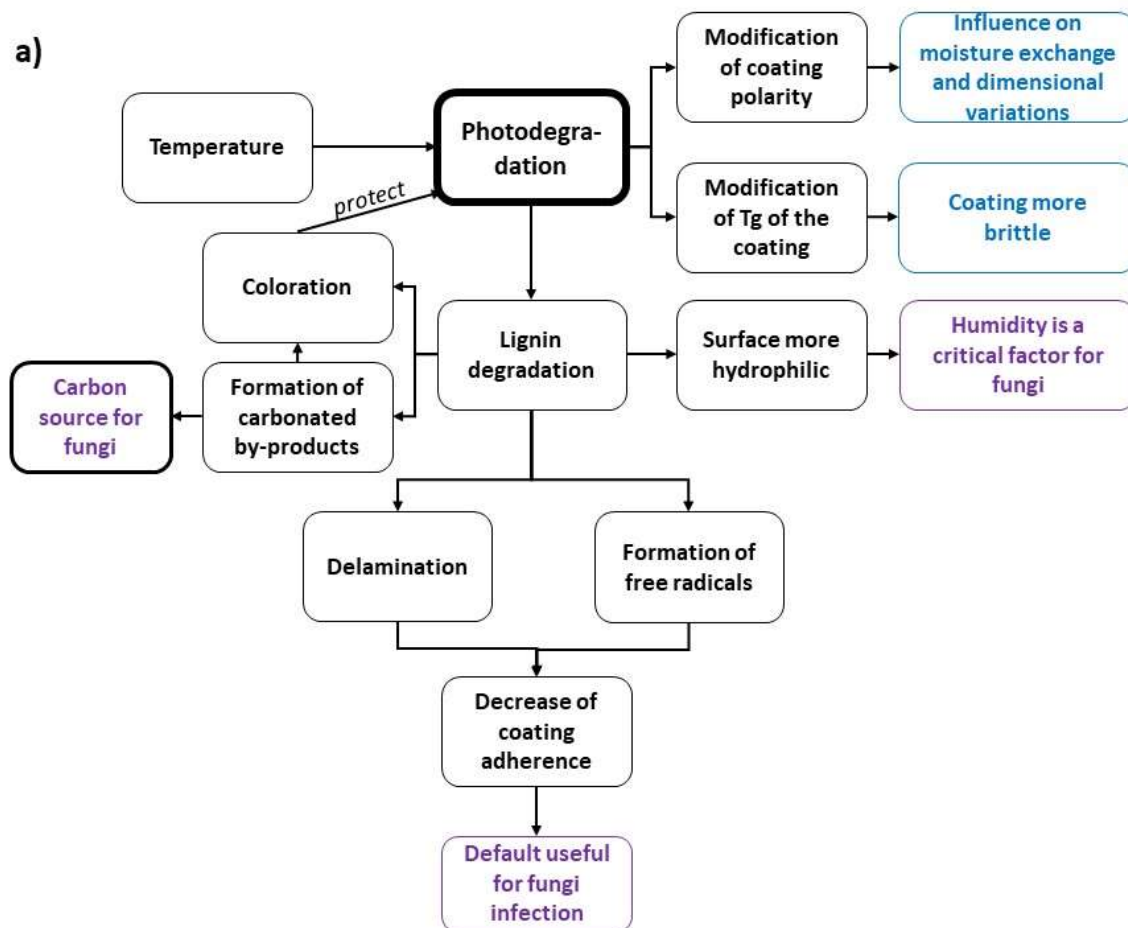


Fig. 5 (a). New approaches of the multifactorial aspect of the wood and clear coating weathering by a) photodegradation, b) water degradation, and c) fungal degradation

Explanation of Fig. 5a.

Photodegradation seems to lead to the most serious consequences to the wood clear coating durability. This is mainly due to the permeability of this technology to visible light (Sarvis 1953; Estrada 1967; Evans *et al.* 2015b). Interaction between light and lignin leads to delamination phenomenon as well as formation of free radicals (Hon *et al.* 1980; Gryn'ova *et al.* 2011; Seo and Weon 2012). The potential degradation of the anchoring points of the coating on wood by free radicals, coupled with the cohesion loss between wood cells, leads overall to a decrease in the coating adhesion (Evans *et al.* 2015a). This can be observed through images of clear coatings peeling from wood surface (Estrada 1967; Evans *et al.* 2015). This consequence can promote the introduction of water and hyphae through the protection. Lignin photodegradation generates by products that can be metabolized by black stain fungi (Schoeman and Dickinson 1997; Bardage and Bjurman 1998). This is true if the wood is protected by a coating. In this case, by-products are stuck at the interface between wood and coating.

The coating itself undergoes modifications due to the photodegradation. T_g can be modified due to the photodegradation (Hunt and Lansing 1935; Larché *et al.* 2010; Koleske 2012). A higher T_g is associated with a lower flexibility of the coating. This phenomenon can be associated with a modification of the coating polarity and consequently on its

regulation of water exchanges. Greater water exchange increases the defects in coating associated with wood swelling (de Meijer and Militz 2001; Podgorski *et al.* 1996; Williams 2005). The temperature has an influence on the rate of degradation, either faster or slower (Daglen *et al.* 2007; Porcal *et al.* 2015).

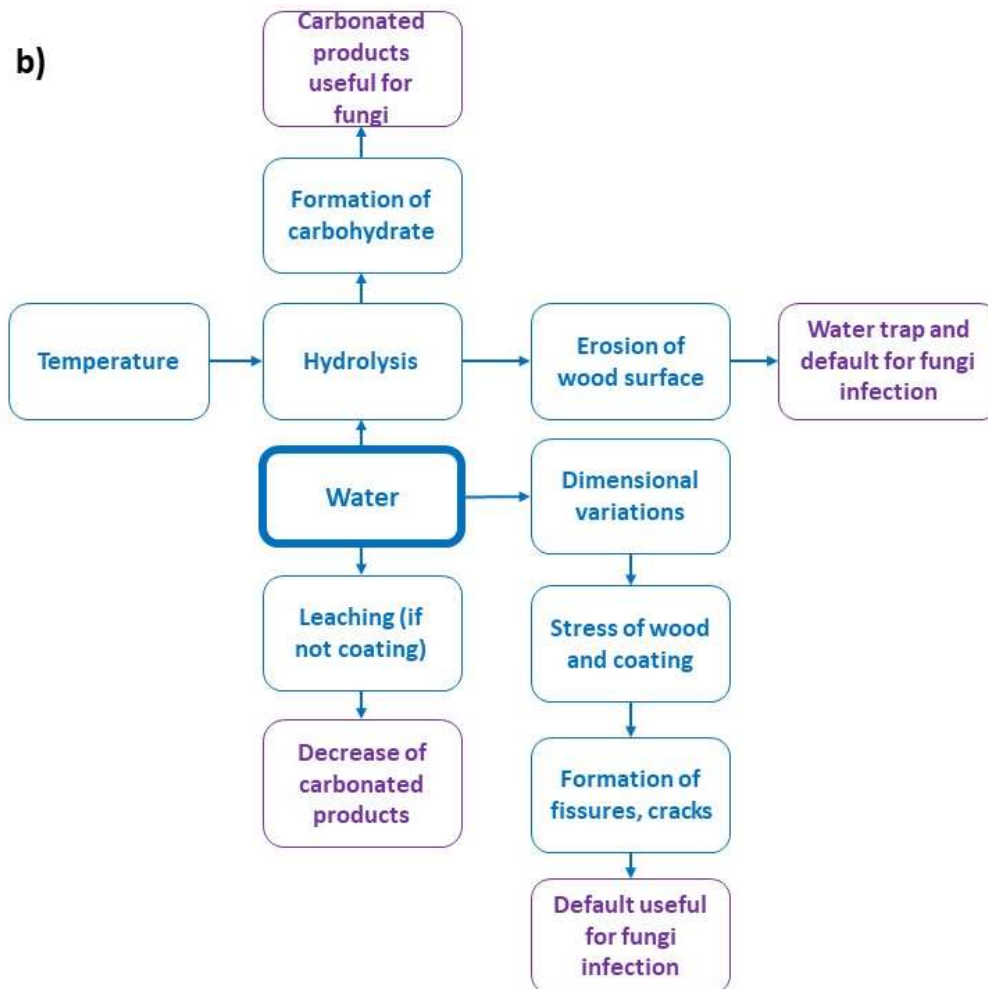


Fig. 5(b). New approaches of the multifactorial aspect of the wood and clear coating weathering by a) photodegradation, b) water degradation, and c) fungal degradation

Explanation of Fig. 5b.

Water causes dimensional variations. With or without a coating, swelling and shrinkage create stress in the wood. In the case of wood coated by a clear protection, if the coating is not flexible enough, cracks, fissures can appear. These defects can become gates to let pass even more water through the coating which further aggravates this phenomenon. These gates can also be used by fungi to colonize wood as well. Other defects can be created by erosion.

Water can be trapped by the whole of these defects and can promote fungal growth. If the wood is not coated, or if water is trapped at the interface between wood and coating, hydrolysis phenomenon occurs (Katzen and Othmer 1942). Carbohydrates are therefore created and form a source of carbon for fungi growth. If the water comes from the rain,

leaching may occur that removes all the by-products on the wood surface and are no longer available for fungi growth. The temperature has an influence on the rate of degradation, either faster or slower (Daglen *et al.* 2007; Porcal *et al.* 2015).

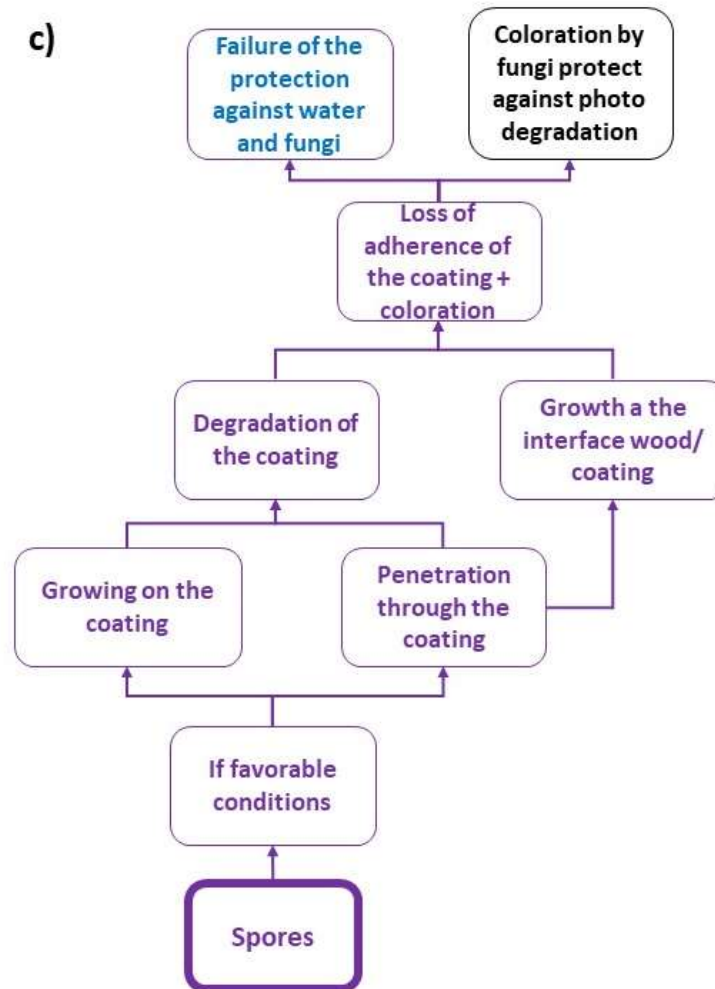


Fig. 5(c). New approaches of the multifactorial aspect of the wood and clear coating weathering by a) photodegradation, b) water degradation, and c) fungal degradation

Explanation of Fig. 5c.

Fungal degradation begins with a spore contamination of the surface. If conditions are favorable (water, temperature, nutrients), germination can occur and fungi develop hyphae to colonize the sample. Either the colonization remains on the coating surface or it manages to go through the protection to reach the wood. In both cases, coating undergoes degradations. If the colonization spreads at the interface between the wood and the coating, a detachment of the protection can take place. Therefore decreasing the coating adhesion on wood. Black stain fungi give a dark coloration during colonization. Colored fungal colonies protect the wood against photodegradation by acting as a physical barrier. In addition, if fungi are able to colonize, then water can as well. Since water is a critical factor for fungi growth, colonization becomes even stronger.

Concluding remarks

The degradation of wood siding and decking follow the logic of a “slippery slope”. Each mechanism of degradation contributes to other mechanisms, accelerating the degradation of the material.

Further studies are needed to clarify the multifactorial aspect. For example, it is unclear if the growth of fungi causes a physical pressure at the interface between the wood and coating, leading to a decrease of the coating adherence. Furthermore, some fungi use lignin breakdown products. Does their use lead to a faster or stronger growth? How do fungi gain the ability to enter the protective layer, and is this ability affected by weathering?

CLOSING THOUGHTS

1. Wood undergoes physical, chemical, and biological degradation, which together are classified as weathering phenomena that recycle nutrients from wood to the biosphere. The main strategy for protecting wood is through the use of coatings. Different coating technologies offer different levels of protection. New trends tend to use clear coatings in order to let the wood’s natural appearance be visible. However, protection provided by those technologies are weaker in durability than opaque coatings.
2. The origins of weathering are known, and mechanisms of degradation are partially understood. Even though it is needed to further understand the phenomena involved in the loss of performance of clear coatings, it is important to take into account the interaction between weathering factors in order to go further in the understanding of wood weathering.
3. There are known interactions between photodegradation and biological degradation. However, there is still a lack of knowledge about fundamental aspects of weathering. It is possible to resolve the problem of wood durability by experimenting with new protection methods and developing new protection strategies that take into account the interactions. Further studies are needed to explain the multifactorial aspects.

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