

WOOD PROTECTION AND MAINTENANCE

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Wood technology – wood preservation

Start Course

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My background is wood science. I am specialist in wood chemical technology, wood protection, preservation and modification, as well as its utilization;

Manager and participant of numerous scientific projects on a national and international range;

Member of Polish Committee for Standardization, Polish Association of Building Mycology and numerous international organizations, e.g.:

- COST (European Cooperation in Science and Technology),
- IRG-WP (International Research Group on Wood Protection),
- WSE (Northern European Network for Wood Science and Engineering).

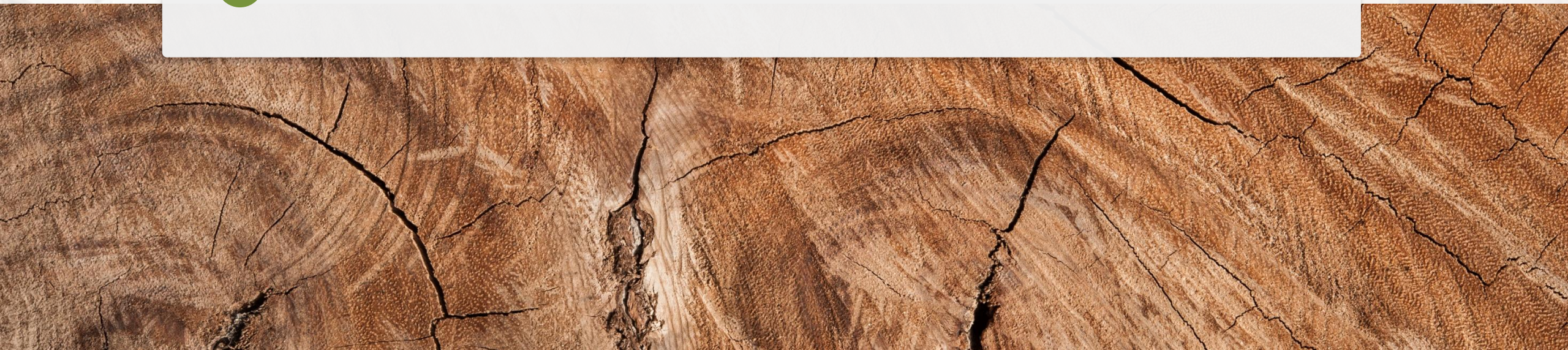
The creator of patent applications and implemented technologies in wood protection and modification.

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Wood Protection and Maintenance

1. Wood Durability and Lifetime of Wooden Products
2. Abiotic Degradation of Wood
3. Biological Degradation of Wood
4. Chemical Protection of Wood





1. Wood Durability and Lifetime od Wooden Products

1.1 Basic information about wood structure and its properties

Wood and wooden composites

The structure of wood and wooden composites and their exposure in conditions suitable for the action of abiotic factors and/or the activity of biological pests are the basic prerequisites for potential damage of wooden products and constructions.

Wood is a biopolymer, created by a genetically encoded system of photosynthetic and subsequent biochemical reactions in the cambial initials of trees.

Trees consist of approximately 70–93 vol.% of wood, with the rest being bast, bark and needles or leaves.

Wood is the internal, lignified part of the stem, branches and roots. The characteristics of wood include: (1) anisotropy, typical in three anatomical directions – longitudinal, radial and tangential; (2) inhomogeneity, influenced by the sapwood and heartwood, the early wood and late wood, and so on; (3) specificity, given by the wood species; and (4) variability, given by the growth conditions of the tree of a given wood species.

Wood is a traditional material, used for producing wooden buildings, furniture, work and sport tools, as well as art works. It is currently an irreplaceable raw material for the production of bio-based composites with the targeted combination of wood particles in various stages of disintegration and pretreatment with a complementary system of adhesives, waxes and other additives

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The structure of wood and wooden composites is defined at four levels:

- primary (i.e. molecular/chemical structure);
- secondary (i.e. anatomical/submicroscopic structure);
- tertiary (i.e. morphological/microscopic structure);
- quaternary (i.e. geometric/macroscopic structure).

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A basic preview of the geometric structure of wood

The geometric structure of wood defines

- The external appearance – shape, volume, colour, the ratio of tangential, radial and facial areas, the proportion of sapwood, heartwood and/or mature wood, the proportion of early and late wood in annual rings, the roughness and overall quality of the surfaces, and so on.
- The macrosopic inhomogeneities – knots, compression or tension wood, juvenile wood, false heart, resin chanals, and so on, together with their type, frequency and state of healt (e.g. damage by rot).

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A basic preview of the geometric structure of wood

The geometric structure of wood depends on

- The morphological structural level (i.e. the proportional and spatial distribution of various types od cel elements in the wood);
- The growth defects and anomalies in the wood;
- The mechanical and other loads/treatments of the wood.

A basic preview of the morphological structure of wood

The morphological structure of wood defines

- The individual cells – type, shape, dimension, slenderness factor, orientation to the pith (longitudinal, radial), thickness of the cel wall, thinning in the cel wall (type, frequency, location) and so on.

- The grouping of cells – proportion and location of parenchymatic, libriform, vessel, tracheid and other cell-types in the wood tissues.

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A basic preview of the morphological structure of wood

The morphological structure of wood depends on (1/3)

Wood of coniferous species has a simple and fairly regular morphological structure. Approximately 90–95% of wood volume is formed of early and late tracheids. Tracheids have a conductive and strengthening function. They are 2–5 mm long (late are approximately 10% longer) and 0.015–0.045 mm wide. Their cell walls, with a thickness of 0.002– 0.008 mm, contain a fairly high number of pit pairs, usually 60–100 in early tracheids and 5–25 in late tracheids. Pit-pairs with a diameter of 0.008–0.03mm are mainly at the end of tracheids on their radial walls.

Opened pit-pairs provide interconnection between tracheids, which is used in the transport of liquids into the wood at its chemical protection and modification. Parenchymatic, thin-walled cells form stock tissue with living protoplasm. They are located in radially oriented pith beams and in longitudinally oriented parenchymatic fibres and resin channels. Resin channals are lacking in some coniferous species (i.e. they are not present in fir or yew wood).

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A basic preview of the morphological structure of wood

The morphological structure of wood depends on (2/3)

Wood of broadleaved species has a more complicated morphological structure compared with coniferous wood. Libriform fibres, present in a volume of 36–76%, have a strengthening function. They are relatively short, from 0.3 to 2.2 mm, with a width from 0.005 to 0.03 mm. They have a weak connection with other types of cells due to the small number of simple pit or half-pit thinned areas. Vessels, present in a volume of 20–40%, have a conductive function. Their conductive function is important for the transport of nutrients during a tree's growth, as well as for transport of preservatives and modifying substances into wood. In ring-porous species (ash, elm, hickory, oak), large vessels in early wood have a diameter from 0.2 to 0.5 mm, whilst small vessels in late wood are from 0.016 to 0.1 mm. The length of vascular systems are usually up to 0.1 m, but in some wood species this can even be several metres (e.g. as long as 7 m in oak). They are created from a long, vertical line of vessels connected via openings – simple, reticular or ranking perforations.

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A basic preview of the morphological structure of wood

The morphological structure of wood depends on (3/3)

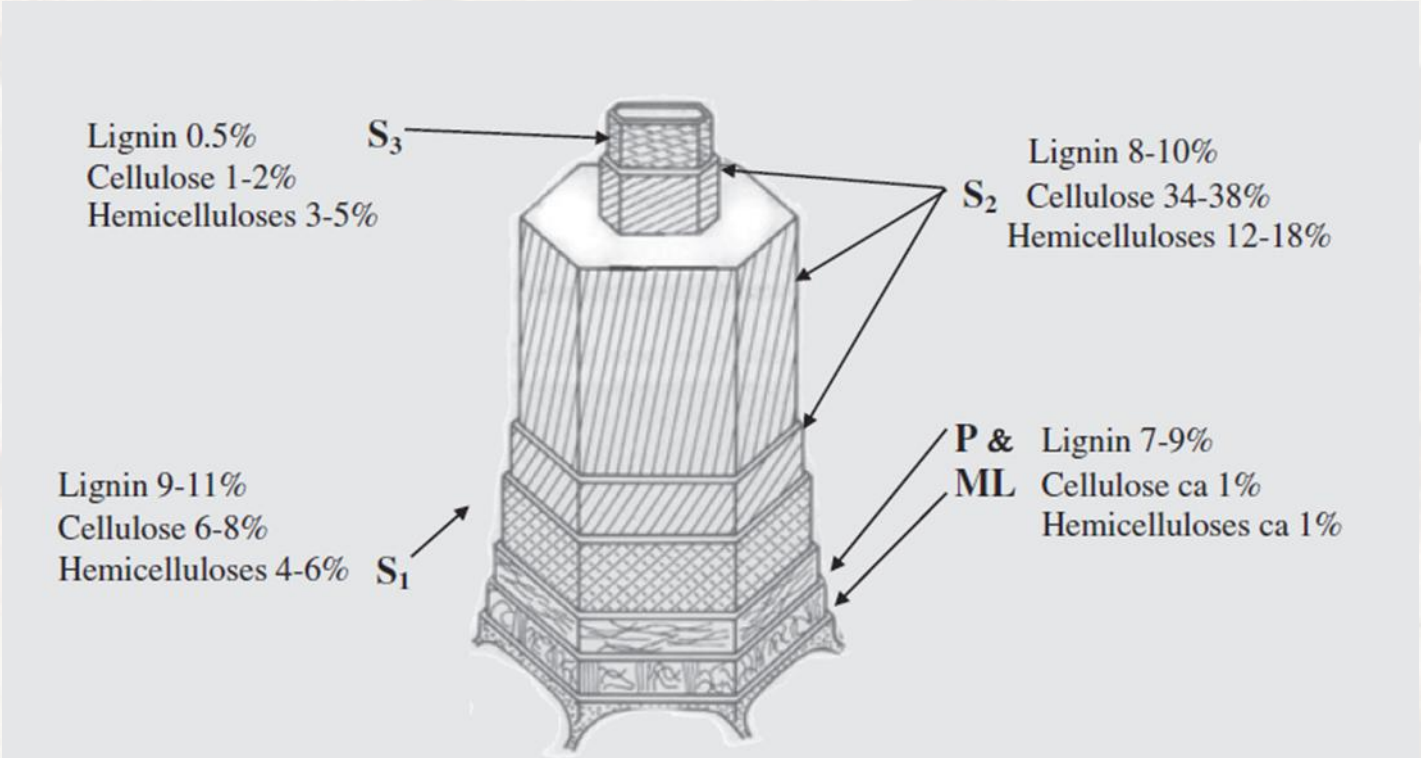
Cell walls of vessels have circular and spiral thickenings. The conductive function of vessels decreases under the influence of tyloses (i.e. when blocked by outgrowth from the surrounding paratracheal parenchyma). Parenchymatic cells, present in a volume of 2–15%, mainly have a storage function. Longitudinal, paratracheal parenchymata (single-sided, group, vasicentric, etc.) group around the vessels and vessel tracheids and connect to them via single sided pit pairs. Longitudinal, apotracheal parenchymata do not come into contact with the vessels. In radially oriented pith beams, several parenchymatic cells are combined with a rectangular shape, horizontal or vertical, either in morphological unity (homogeneous beam) or in morphological diversity (heterogenic beam).

A basic preview of the anatomical structure of wood

The anatomical structure of wood defines

The structure of the cell walls of wood's cells:

- Layering (i.e. the individual layers ML, P, S_1, S_2, S_3;
- Proportion and localization of the structural polymers (cellulose, hemicelluloses and lignin) and extractives in the individual layers of the cel wall.



A basic preview of the anatomical structure of wood

The anatomical structure of wood depends on

The wood species and the type of cell:

- Elementary fibrils, formed usually of 40 macromolecules of cellulose, are the basic elements of the cells' walls with a cross-section of ca 3.4nm x 3.8 nm. Microfibrils consist of 20-60 elementary fibrils. Macrofibrils consist of cellulose microfibrils as well as of hemicellulose fillings and lignin microlayers.
- Microfibrils and macrofibrils form substantial lamellae that are the structural base for individual layers of a cel wall (i.e. the ML, P, S_1, S_2, S_3):
  - ML – middle lamella, mainly formed of lignin granules;
  - P – primary wall, with a thickness of 0.06-0.09 µm, formed of a high proportion of lignin and cellulose fibrils orientated randomly into a multilayered network;
  - S – secondary wall, with a thickness of 1-6 µm, formed of three separate layers, S_1, S_2, S_3; three layers differ in thickness, orientation of fibrils and the proportion and structure of lignin and polysaccharides; for example in the tracheids of conifers the ratio of layers $S_1/S_2/S_3$ is around 12/78/10.

A basic preview of the anatomical structure of wood

The anatomical structure of wood affects

The permeability of the wood:

- Cell walls of wood are able to transmit gases and polar liquids. This is due to their microporous structure with vacant pores size 1-80 nm, as well as due to hydroxyl (-OH), carbonyl (C=O) and other polar groups of lignin and polysaccharides. Macromolecules of polysaccharides in the cell walls repel each other in the presence of polar liquid molecules (e.g. water), which also continuously increase the porosity of the cell wall to a maximum size of ~80 nm. Therefore, its permeability for diffusion and capillary transports continually increases.
- Micropores in the cell walls of wood – gaps in elementary fibrils (~1 nm), capillaries in microfibrils (~10 nm), capillaries in microfibrils (<80 nm), pores in a pit membranę (<150 nm).

The mechanical properties of the wood:

- For example, cell walls with a greater proportion of the S_2 layer, and also therefore cellulose, provide wood with a greater tensile strenth along the fibres.

A basic preview of the molecular structure of wood

The molecular structure of wood defines

The types and chemical structure of wood components – cellulose, hemicelluloses and lignin located in the cell walls, and extractives (accompanying substances) located in the cell walls or also in the lumens.

The physical-chemical status of wood components – the degree of polymerization, conformation and configuration structures (spatial grouping into globules, rods, helixes), the supramolecular status (crystalline, amorphous), the physical status (glassy, plastic, viscoelastic), the ability to form intramolecular bonds (hydrogen bonds, van der Waals interactions)

A basic preview of the molecular structure of wood

The molecular structure of wood depends on

The wood species, the type of cell, and the specifics of its composition (Eriksson et al., 1990; Fngel&Wegener 2003):

- Cellulose is a linear poliymer consisting of 1,4-β-α-glucopyranose units. These are either arranged into crystaline units (elementary fibrils) or are in an amorphous state.
- Hemicelluloses form branched macromolecular systems of mannanes (in coniferous wood), xylanes (in broadleaved wood) and other polysaccharides.
- Lignin in coniferous woods is a guaiacyl-type based on coniferyl phenyl-propane units (i.e. 15% -OCH_3 groups/C_9). Lignin in broadleaved woods is a mixture of guaiacyl-type and syringyl-type, at which lignin of syringyl-type is based od synapyl phenyl-propane units (i.e. 20-21% -OCH_3 groups/C_9).
- Terpenes are accompanying biologically effective substances in the wood of more durable coniferous species. Tannis, flavonoids and some other substances play this role in the wood of more durable broadleaved species.

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A basic preview of the molecular structure of wood

The molecular structure of wood affects

The preservation and modification of the wood:

- Diffusion and fixation proces of preservatives and modifying substances in wood depend not only upon their physical and chemical properties but also upon the molecular structure of the cell walls in the wood;
- Modification of the molecular structure of wood (acetylation, etherification, etc.) can increase resistance to biological pests, and the dimensional stability and strength properties can be improved.

The durability od the wood:

- Hemicelluloses are the overall most unstable component of the wood, mainly againts high temperatures and hydrolysis in the presence of scids in the wnvironment or enzymes produced by wood-decaying fungi;
- Lignin is not stable when facing oxidation induced by ultraviolet (UV) radiation in exterior, or by peroxidases and other enzymes of white-rot fungi;
- Accompanying substances affect the resistance of wood to biological damage; various woods contain different amounts of (1) easily biodegradable substances (e.g. starch, pectin, glycosides and lipids) and (2) substances biologically effective against wood-decaying fungi, moulds or wood-boring insects (e.g. tannins, flavonoids, stilbenes, terpenes and resin

A basic preview of the properties of wood

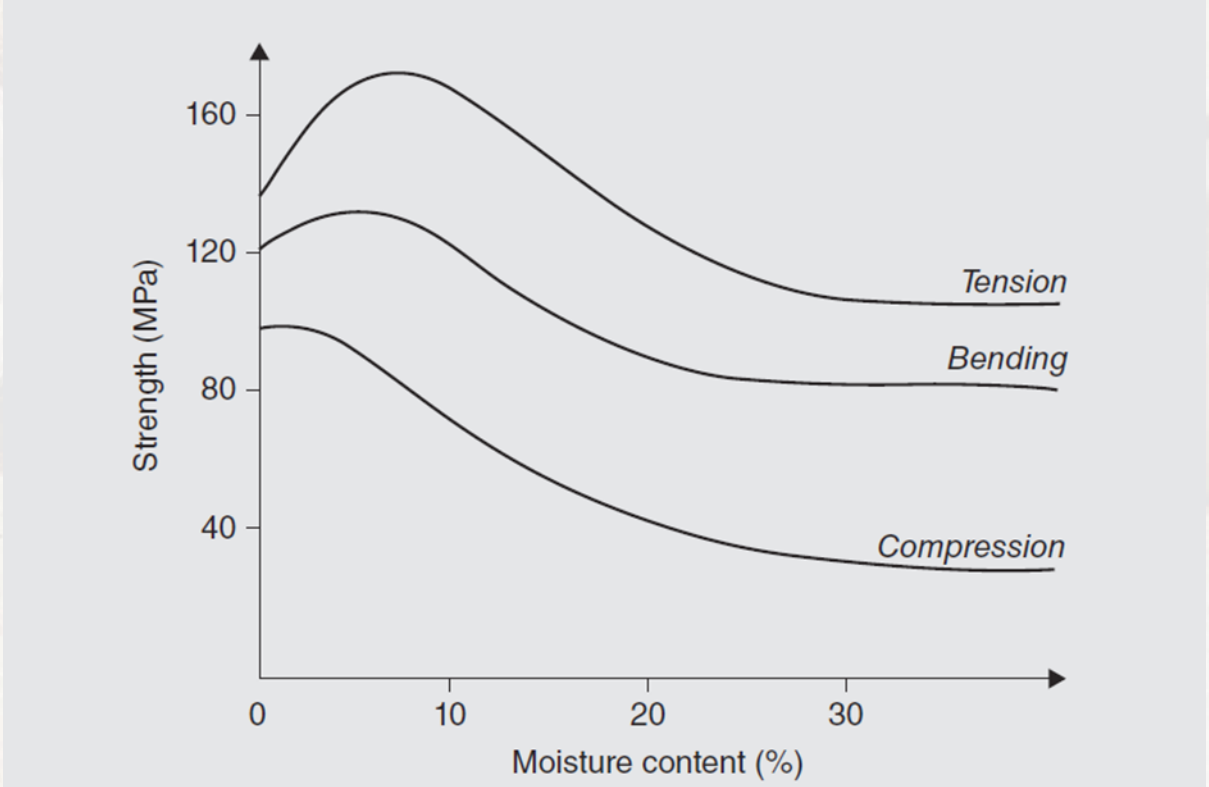
Density

The wood of broadleaved species commonly used in Europe for products and construction (beech, birch, black Locust, elm, hornbeam, linden, maple, oak, poplar, etc., 440-800 kg/m^3) is usually more dense than the wood of commonly used coniferous spacies (cedar, Douglas fir, fir, larch, pine, spruce, 370-530 kg/m^3). The density of wood is decreased after being damaged by fire, fungal rot or insect galleries. However, the opposite trend (i.e. an increase of density) is not uncommon in subfossil wood or wood attacked by alkalis.

A basic preview of the properties of wood

Strength properties

Wood has a relatively high strenght in relations to its density when compared with other materials used in construction. The strength properties of wood (compression, tension, bending, hardness, etc.) depend upon its density and structire, which assist us in selecting a suitable type of wood for a particular use. Depolymerization of polysaccharides in decayed or otherwise damaged wood decrease its strength, mainly in its wet state, where the suport strenghtening effects of hydrogen bonds and van der Waals interactions already do not apply.



A basic preview of the properties of wood

Thermal properties

Wood has relatively good thermal insulation properties. However, it does not resist temperatures over 150°C for a long time and may ignite. Despite the fact that it is flammable, during fires it is often more stable in terms of shape and strength than metals or plastics are.



A basic preview of the properties of wood

Moisture properties

The humanity of wood adapts to climatic condition of its exposure. During long-term exposure to air with a relative humidity of 95-99%, wood greatly humidifies and its equilibrium moisture content settles around 28-30%; that is, the fibre saturation point (FSP). The wood also easily receives liquid water via capillary forces, and its maximum moisture depends upon its porosity/density; for example, beech with a density of 600 kg/m^3 has a maximum moisture of ~120%, whereas for spruce with density of 400 kg/m^3 it is as much as ~200%.

The swelling and shrinkage of wood are processes connected with receiving of bound water until it reaches the FSP (wood swells) and vice versa with its drying when water is released (wood shrinkage). The dimensions of wood change as well as when its moisture changes from FSP to 0%; for example, for common wood species the maximum shrinkages are in a longitudinal direction α_L = 0.15-0.65%, a radial direction α_R = 2,5-6,7% and in tangential direction α_T = 8,3-14,7%.

The moisture properties of wood also affect its strength, durability and use; that is, (1) strength of wood usually decreases with increased moisture within the range from 0% to the FSP; (2) resistance of wood to biological damage is usually lower at higher moistures; and (3) frequent and marked changes in the moisture content of wood lead to shape deformation and the creation of cracks.



1. Wood Durability and Lifetime od Wooden Products

1.2 Types and principles of wood degradation

Wood degradation

Damages and degradation of wood (1/2)

Wood is more or less susceptible to various forms of degradation.

In wood degradation, the dominant role is played by its molecular structure.

However, its higher structural levels – anatomical, morphological, and geometric – also play significant role.

Wood can already be damaged:

- During its growth in trees,
- Subsequently at harvesting,
- During storage and transport of logs and timbers,
- After processing on products and constructions.

Changes in structural levels of wood are caused by abiotic agents or energies and biological pests. Subsequently, its strength, hygroscopic, thermal, aesthetic and other properties are also changed, and usually impaired.

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Wood degradation

Damages and degradation of wood (2/2)

The intensity and scope of the structural and property changes of wood depend upon the type and mechanism of the degradation process.

- In the case of some degradation types (e.g. due to weathering or moulds), just surface damage of wood occurs.
- In contrast, in the case of fire, fungal decay or feeding by wood-damaging insects, wood is degraded to a greater depth, often in full.

Damage that begins at the molecular structure of wood is the most important. All degradation effects in the molecular structure of wood – in its polymers, caused by atmospheric factors, high temperatures, aggressive chemicals and fungal decay – are reflected also at its anatomical and morphological structural levels (e.g. with regard to damage of cell walls and entire tissues), and usually also at its geometric level (e.g. more intensive degradation of sapwood or early wood), and of course in its properties as well. Damage that begins only at the upper structural levels of wood is usually less important for changes in its properties. For example, small changes in the density and strength of wood can occur as a result of microscopic and macroscopic cra created by moisture stresses due to badly regulated drying, although without great changes in its

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1.3 Natural durability of wood

Wood in comparison with stone, clay, brick, concreto, metals, plastics

Advantages

- Permanently renewable material source (e.G. It has low impact on the environment and low energetic demands for processing in total);
- Easily workable;
- High strength in relation to density;
- Low thermal conductivity;
- Aesthetically pleasing qualities in products.

Disadvantages

- Weathering
- Flammability
- Biodegradability.

Durability of wood

Variables

The natural durability of wood is its inherent resistance to various abiotic factors and biological pests (abiotic and biological degradation).

The natural durability of a defined wood species (and also of a defined type of wooden composite) may be only supposed – it may not be exactly defined.

The cause is the complementary effects of many variables.

The most significant of these are:

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- Differences in the structure of the individual wood species;
- The environment around the wooden product;
- The natural durability of individual wood species is known from practice;
- The natural durability of wood is based on practical knowledge and experiments;
- The natural durability of individual wood species is influenced also by the pest's interest about the wood, or by the ability of a specific chemical compound to be attacked in the wood.

Natural durability of wood predetermined by its structure

Source: R., L. (2013) Wood Protection, Handbook, TU Zvolen, Slovakia, 134 p. Reproduced by permission of TU Zvolen.

Structural level of wood	Wood durability
Molecular	
• Accompanying substances:	
Tannins (e.g. black locust, chestnut, oak)	higher resistance to fungi and insects
Resins (e.g. Douglas fir, larch, pine)	higher resistance to fungi and insects lower resistance against ignition
Inorganic substances (e.g. containing Na, K, Ca, Mg, P, S) comprised mainly in the wood of fast-growing species (e.g. poplar, alder)	lower resistance against fungi
• Crystalline cellulose	higher resistance against fungi
• Lignin	higher resistance against combustion lower resistance against UV radiation
Anatomical	
• Both polysaccharides and lignin in cell walls	impeded transfer of enzymes of fungi and bacteria in cell walls
Morphological	
• Parenchyma cells	easily attacked by bacteria and fungi (since they comprise nutrients)
• Vessels	easily permeable for fungi hyphae (also for liquids and gases)
• Libriform fibres	easily attacked by some decay-causing fungi (compared with vessels)
• Opened pits in cell walls	easier transfer of enzymes in wood easier changes of wood moisture
Geometric	
• More frontal surfaces	worse durability
• More sap-wood	worse durability
• More early wood	usually worse durability
• Rougher surface	usually worse durability

Classes of natural durability of selected wood species in their contact with ground – against rot (modified from EN 350-2)

Durability classes 1 to 5 are relative; that is, usable only for mutual comparison of durability of the individual types of wood.

Durability classes are applicable only to heartwood.

Sapwood of all broadleaved and coniferous species is classified in class 5 (non-durable), unless other data are available

a B

Durability class	Commercial name	Scientific name	B or C[a]	Density (kg/m³)	Occurrence
	Birch	*Betula pubescens*	B	660	Europe
	Hornbeam	*Carpinus betulus*	B	800	Europe
	Lime tree	*Tilia cordata*	B	540	Europe
	Maple	*Acer pseudo-platanus*	B	640	Europe
	Poplar	*Populus* sp.	B	440	Europe

Durability class	Commercial name	Scientific name	B or C[a]	Density (kg/m³)	Occurrence
1 Very durable	Greenheart	*Ocotea rodiaei*	B	1030	South America
	Jarrah	*Eucalyptus marginata*	B	830	Australia
	Mansonia	*Mansonia altissima*	B	620	West Africa
	Okan	*Cylicodiscus gabunensis*	B	920	West Africa
	Padouk	*Pterocarpus soyauxii*	B	740	West Africa
	Teak	*Tectona grandis*	B	680	Asia
	Walaba	*Eperua falcata*	B	900	South America
1–2	Black locust	*Robinia pseu-doacacia*	B	740	Europe
	Kapur	*Dryobalanops aromatica*	B	700	South-East Asia
2 Durable	Bubinga	*Guibourtia demeusii*	B	830	West Africa
	Chestnut	*Castanea sativa*	B	590	Europe
	Oak	*Quercus robur (Q. petraea)*	B	710	Europe
	White cedar	*Thuja plicata*	C	370	North America
3 Medium durable	Douglas fir	*Pseudotsuga menziesii*	C	530	North America
	Turkey oak	*Quercus cerris*	B	770	Europe
	Walnut	*Juglans regia*	B	670	Europe
3–4	Larch	*Larix decidua*	C	600	Europe
	Pine	*Pinus sylvestris*	C	520	Europe
4 Less durable	Elm	*Ulmus* sp.	B	650	Europe
	Fir	*Abies alba*	C	460	Europe
	Spruce	*Picea abies*	C	460	Europe
5 Non-durable	Ash	*Fraxinus excelsior*	B	700	Europe
	Beech	*Fagus sylvatica*	B	710	Europe



1.4 Methods of wood protection for improvement its durability

Methods of wood protection for improvement its durability

Protection of wood

Protection of wood can be performed by applying various methods throughout the various stages:

- protection of growing trees (i.e. in the forest) against physiological pests and other factors, which is provided by foresters (i.e. forest and tree protection);
- protection of harvested wood (i.e. on round-wood yards) and during first stage processing to sawn timber, veneers, chips and other intermediate products (i.e. the physical – totally wet conditions or quick drying) and possibly also short-term chemical wood protection;
- protection of new wooden products (i.e. use of suitable structural designs and selection of suitable chemical, modifying and other processing) – all these methods of preventive and supplementary wood protection are based on physical, structural, chemical and/or modification technologies;
- protection of older wooden products – that is, maintenance of wood, or conservation and reconstruction of markedly degraded wood, typically of

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1.5 Service life prediction of wooden products

Service life

Definitions

Wooden products and constructions wear in time both:

- physically (i.e. due to the impact of defects caused by various wood-degrading factors) and
- morally (i.e. due to the changed demands of humans regarding their functionality, aesthetic aspects, etc.).

The service life means the period of time after installation during which a building or its parts meets or exceeds the performance requirements (ISO 15686). Similarly, the service life of log cabins, trusses, ceilings, windows, doors, furniture and other products made of wood is defined by the time for which they should meet the function, technical and aesthetic requirements under the supposed conditions of application.

Their service life can be defined also as the time after which they get to a so-called terminal condition (i.e. they become unusable). The service life is a variable value since it is determined from supposed exposure conditions that are not always fully implemented.

Moisture content of wood is frequently used as an input variable to modelling conditions and the resulting risk of decay, and then also of the service life prediction of wooden products.

Lifetime of wooden products

Definitions

The lifetime of materials and structures is defined as the:

• physical useful lifetime – reflecting the real technical condition;

• ethical lifetime – relating mainly to aesthetic aspects and the satisfaction of functional demands of the present user (e.g. stylishness, spatialization and/or higher demands for thermal and acoustic insulation);

• economical lifetime – considering the time within which the costs of maintenance, operation and depreciation are still economical with regard to usability.

Lifetime of wooden products

Entire product vs. wooden elements (1/2)

The useful lifetime is not usually the same for the entire wooden product or wooden structure; it means for all the wooden elements in a log cabin, truss, and so on. For example, in log cabins, the most suitable humidity conditions for action of biological pests are created in the lowest beams, which are more often in contact with rain or capillary water.

Shortening of the physical lifetime of products/structures can be caused mainly due to the following effects:

• failures in a project (i.e. errors in static, material composition, structural protection, etc.);

• failures in execution (i.e. technological errors);

• failures during usage (i.e. increased aggressiveness of environment, increased mechanical load, poor or insufficient maintenance);

• unforeseeable events (i.e. fire, storm, etc.);

• amendments in standards and regulations (i.e. innovations in static standards, new safety regulations, etc.).

Lifetime of wooden products

Entire product vs. wooden elements (2/2)

The useful lifetime, or service life:

- wooden buildings or bridges is usually from 40 to 200 years,
- trusses from 60 to 400 years,
- windows from 30 to 70 years,
- untreated sleepers from 3 to 5 years,
- sleepers preserved with creosote from 25 to 50 years.

In Eurocode, the suggested minimum design service life of a building's elements varies from 10 to 100 years. However, the age of well maintained wooden historical buildings and their components is often greater; for example, there are log-cabin-churches more than 200 years old and there are windows greater than 100 years old.

Factor method

ISO 15686

The service life prediction or planning of wooden constructions and wooden products can be performed by the factor method (ISO 15686).

The factor method is used to obtain an estimated service life of a component or a design object by modifying a reference service life by considering the differences between the object-specific and the reference in-use conditions under which the reference service life is valid:

$$ESL_{WP} = f(A, B, C, D, E, F, G) = RSL_{WP} \times (A \times B \times C \times D \times E \times F \times G)$$

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Factor method

Subjectivity

In practice the computation of ESL_{WP} by the factor method is sometimes connected with a certain subjectivity and sometimes also with less professionalism:

• It is not a really scientific method;

• Need for intensive preparatory work – for example, many-year observations in terrain and/or model experiments, with the aim to reliably define all specific effects influencing the individual factors A to G;

• There can be a subjective overestimation of the importance of a certain factor and the underestimation of another;

• There can be ambiguities in the mutual interactions of the individual factors A to G.

Life cycle assessment of wooden products

Life cycle assessment (LCA) is a technique for assessing the environmental aspects and potential impacts associated with a product and has been used by industry in many situations; for example, to help reduce overall environmental burdens across the whole life cycle of goods and services, to improve the competitiveness of a company's products or to communicate with governmental bodies. It can also be used in decision-making, as a tool to improve material composition and design of the product, the selection of optimal technologies, and so on. The benefit of LCA is that it provides a single tool that is able to provide insights into the upstream and downstream trade-offs associated with environmental pressures, human health and the consumption of resources.

The LCA of wooden products and constructions is usually better for comparing with those made from steel, aluminium, concrete or other materials.

The individual factors of LCA are evidently better for borate-treated lumber structural framing in comparison with galvanized steel framing:

(1) there are 3.7 times less fossil fuel use and 38 times less water use;

(2) there are 1.8 times lower greenhouse gases, 3.5 times lower acid rain, 2.8 times lower smog and 3.3 times lower emissions;

(3) they are candidates for energy recovery as a renewable fuel source.

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Similarly, in a comparison of wooden and plastic PVC windows, in a mild exposure scenario the service life of plastic windows should be beyond 35 years and wooden windows 60–65 years, at which time the recycling of wooden

Calculation of estimated service life (ESL) of wooden bridges

Source: R., L. (2005) Investigation of wooden constructions – the basis for their renovation. In: Restoration and Reconstruction of Constructions, 27th Conference WTA, pp. 23–30. Brno, Czech Republic. (In Slovak.)

Wooden bridge with a roof – very good lifetime

Microclimate in construction details is rarely suitable for fungal rot. — $D = 0.8$

The bridge is not exposed to direct water precipitations. — $E = 1$

The bridge is not exposed to more significant mechanical stresses, emissions, and so on. — $F = 1$

Regular inspection with diagnosis of damage (every third year), and the execution of both suitable maintenance and improvement interventions. — $G = 2$

$ESL_{WP} = RSL_{WP} \times (A \times B \times C \times D \times E \times F \times G) = 40 \times (2.25 \times 1 \times 1 \times 0.8 \times 1 \times 1 \times 2) \approx 144$ years

Wooden bridge without a roof – good lifetime

Glued lamellae prepared from Norway spruce (*Picea abies*), which according to EN 350-2 is less durable wood species against wood-decaying fungi (class 4) and is also prone to degradation by wood-damaging insects (class SH). The individual lamellae are first treated with stable and highly efficient biocide (fungicide and insecticide) against pests using vacuum-pressure technology, and then bonded with stable water-resistant adhesive. The glued lamellae are also treated with a water-repellent paint. Finally, biocide cartridges are inserted to the end (frontal) sections of glued lamellae. — $A = 3$

The bridge is not roofed. However, the details are structurally correctly designed, with possible drain of rainwater. — $B = 0.5$

Proper input humidity of wood when producing glued lamellae (moisture content of wood $w = 15\,\%$). — $C = 1$

Microclimate in details of bridge is sometimes (e.g. after rains) suitable for fungal rot. — $D = 0.6$

The bridge is exposed to rainfall, alternation of rainy and sunny weather, thermal differences between day and night, and so on. This all enables the swelling and shrinkage of wood, and gradually creation of cracks. Environment for activity of fungi and insects is also suitable. — $E = 0.6$

The bridge is not exposed to more significant mechanical stresses, emissions, and so on. — $F = 1$

Regular inspection with diagnosis of damage (every third year), and suitable maintenance (exchange of biocide cartridges, new paints, etc.) and improvement interventions (replacement or reinforcement of damaged elements by prostheses, etc.) carried out. — $G = 2$

$ESL_{WP} = RSL_{WP} \times (A \times B \times C \times D \times E \times F \times G) = 40 \times (3 \times 0.5 \times 1 \times 0.6 \times 0.6 \times 1 \times 2) \approx 43.2$ years

Wooden bridge with a roof – very good lifetime

Solid larch (*Larix decidua*) heartwood, which according to EN 350-2 is from moderately durable to less durable against wood-decaying fungi (class 3–4) and durable against wood-damaging insects (only sapwood is susceptible to attack – class S). The individual wooden elements of bridge (note: elements dimensionally greater than lamellae and thus harder to impregnate) treated with stable biocide (fungicide and insecticide) against wood pests using a long-term dipping technology. Finally, all surfaces of wood elements painted with a water-repellent coating. — $A = 2.25$

The bridge is both roofed and structurally correctly designed. — $B = 1$

Proper input humidity of wood for the production of bridge elements ($w = 18\,\%$). — $C = 1$



2. Abiotic Degradation of Wood

2.1 Wood damaged by weather factors

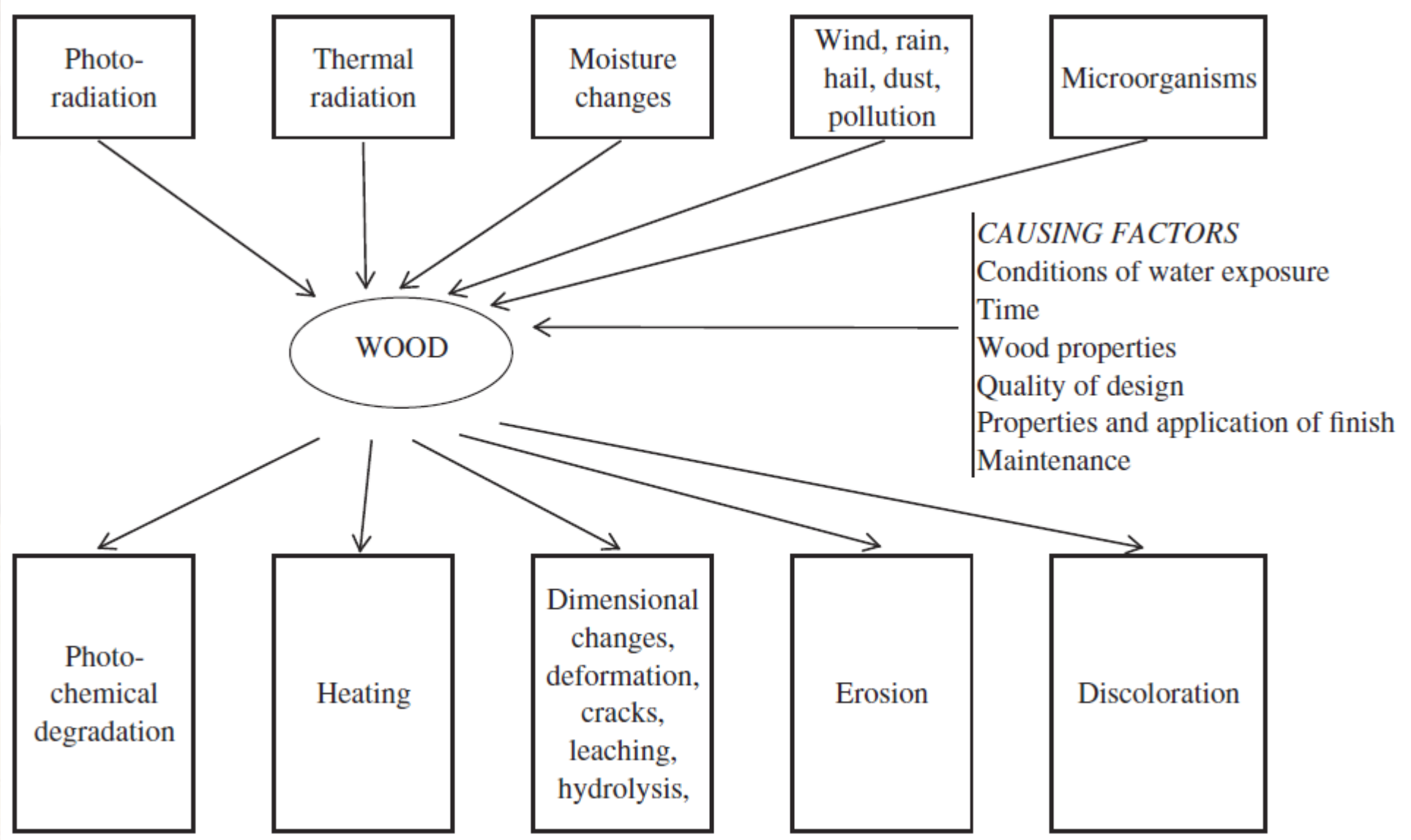
Abiotic degradation of wood in interior and exterior environments

Source: R., L. (2013) Wood Protection, Handbook, TU Zvolen, Slovakia, 134 p. Reproduced by permission of TU Zvolen.

a Intensity of the chemical corrosion of wood depends on the type and concentration of the aggressive chemical (emissions, solutions of acids, etc.).

	Mode and intensity of wood degradation			
	Interior		Exterior	
Abiotic factor	Mode	Intensity	Mode	Intensity
Thermal				
(a) intense	Fire	Significant	Fire	Significant
(b) moderate	Darkening	Significant	Darkening	Significant
	Strength decrease	Moderate	Strength decrease	Moderate
Radiation (UV, visible, IR)				
		Moderate		Significant
	Photo-oxidation	'On surface'	Photo-oxidation	'On surface'
	Colour changes	'On surface'	Colour changes	'On surface'
Water				
			Leaching out of photo-oxidized lignin	Significant 'on surface'
			Hydrolysis lasting many years	Moderate 'fossilization'
Sand, etc.				
			Fibrillation and roughening	Significant 'on surface'
Drying/ mechanical				
	Cracks	Moderate	Cracks	Moderate
	Surface wear	Moderate	Surface wear	Moderate
Chemical				
	Fibrillation and roughening	—[a]	Fibrillation and roughening	—[a]
	Colour changes	—[a]	Colour changes	—[a]
	Strength changes (decrease)	—[a]	Strength changes (decrease)	—[a]

Scheme of factors causing weather impact on wood and their effect on changes in wood



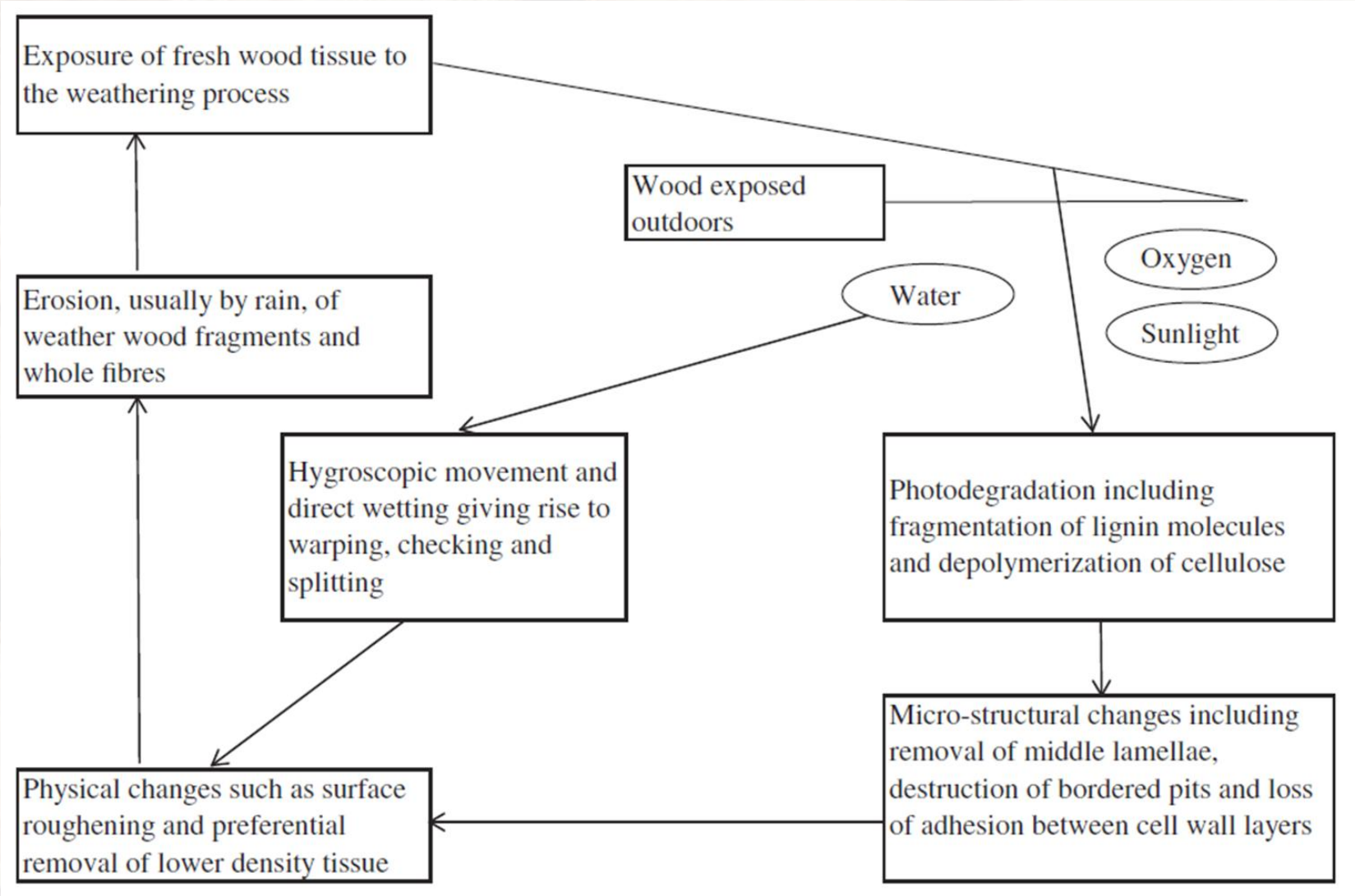
Cyclic sequence of damaging processes during atmospheric corrosion of wood in external environment

Source: Reproduced by permission of Feist, W. C. (1990) Outdoor wood weathering and protection. In:

Archaeological Wood – Properties, Chemistry, and Preservation (eds. R. M. Rowell, J. R. Barbour), Adv

Chem Ser 225, Am Chem Soc, pp. 263–298.Washington DC, USA. Copyright c 1990, American

Chemical Society





2.2 Wood damaged thermally and by fire

Chemical composition

Wood easily ignites and burns. The cause is its chemical composition, since it is comprised:

- 49–51% carbon,
- 43–44% oxygen,
- 6–7% hydrogen.

The high energy content in the covalent bonds of wood polysaccharides and lignin was accumulated during photosynthesis (i.e. during production of glucose from carbon dioxide and water) and during subsequent endothermic reactions (i.e. during transformation of glucose to polysaccharides and lignin). This chemical energy can be retrospectively released from wood by supplying the necessary activation energy. Thus, the ignition and burning of wood is the opposite process to that of the origin of wood, and its components with high values of chemical energy are gradually split up into flammable gases and then further to carbon dioxide and water.

Thermal wood decomposition

The thermal degradation of wood is a set of chemical reactions (depolymerization, dehydration, etc.) initiated by its heating, and achieving the activation energy.

At temperatures below 66 ◦C, the chemical reactions of wood in air do not in fact take place.

At temperatures from 66 to 110 ◦C, some of them may take place depending upon the duration of wood heating, but they usually have only a negligible importance for the structure and properties of wood from a practical point of view.

More apparent thermal disruption of the components of wood takes place only at temperatures exceeding 150 ◦C, when hemicelluloses are decomposed at first, then cellulose, while the most thermally stable is lignin.

The general knowledge on the thermal decomposition of wood polymers is implied by DTA, NMR, FTIR:

Hemicelluloses are already decomposed at temperatures above 150 ◦C, though with more significant exothermic degradation above 200 ◦C.

Cellulose is significantly depolymerized at temperatures above 300 ◦C, from which levoglucosan (1,6-anhydro-β-d-glucopyranose) is generated and subsequently transformed to flammable gases.

Lignin is significantly exothermically decomposed only at temperatures of 300–400 ◦C or higher. At these temperatures there is

Click to learn more

e of alkyl–alkyl

Click to learn more

ts of phenyl-propa

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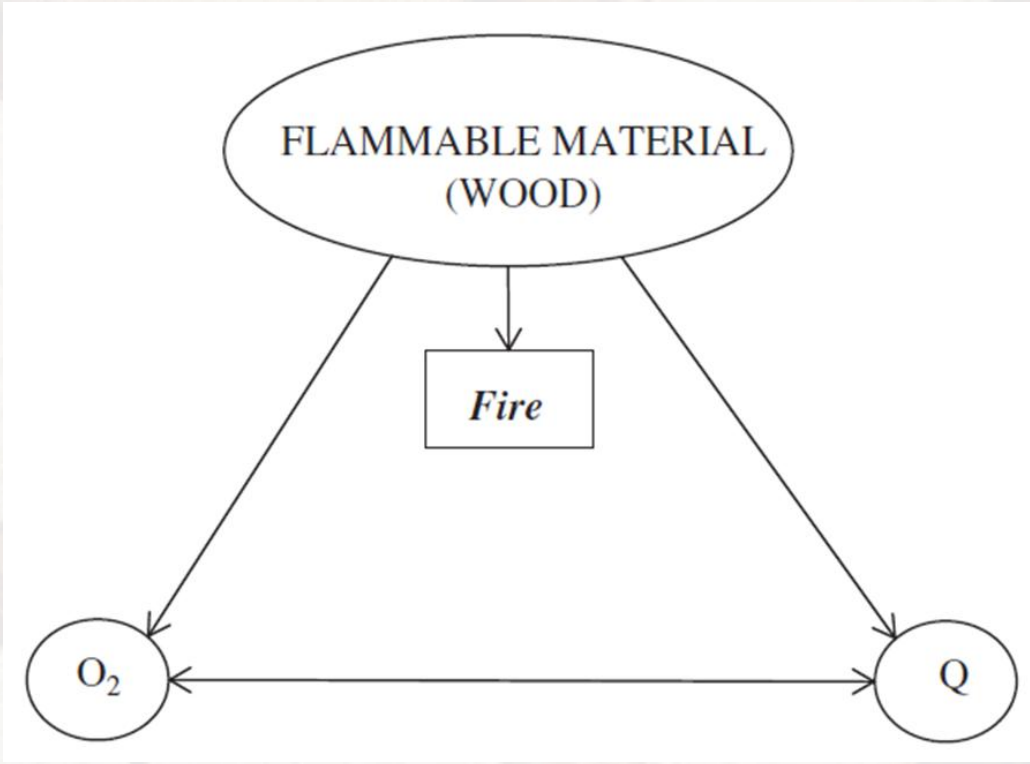
l bonds, ether bonds and C–C bonds in the aromatic nucleus of the phenyl-propane units.

Combustion triangle

Burning wood

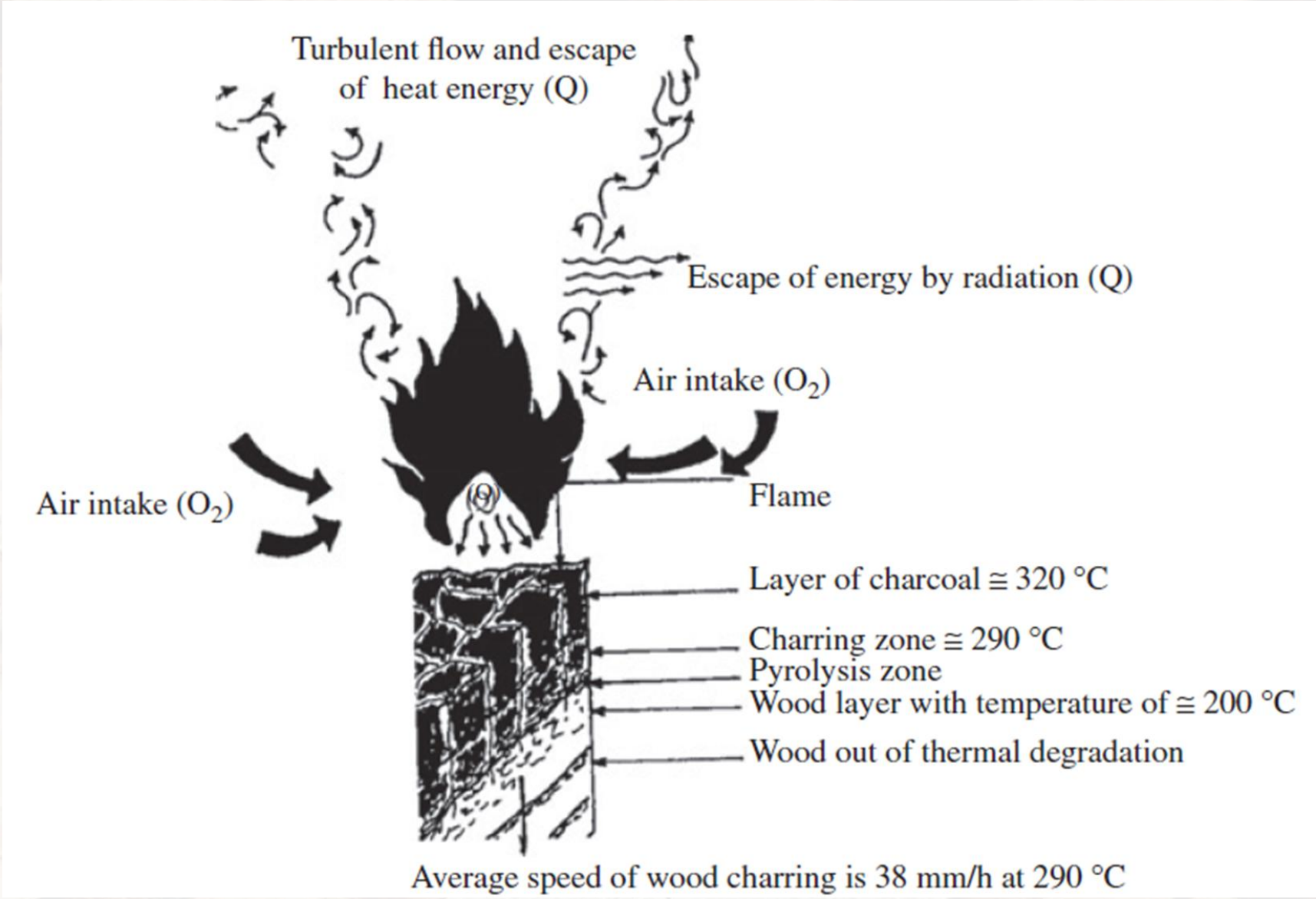
Combustion triangle interconnects the three factors that are needed for ignition and burning processes:

- flammable material, in which is accumulated sufficient chemical potential energy (e.g. wood, coal, oil);
- oxygen (O2), which is a common component of air;
- activation energy Q, which is produced from a flame or radiating thermal source.



When the combustion triangle is disrupted (e.g. due to absence of oxygen or presence of fire retardants), the flame burning of wood is significantly slowed down and charcoal production is preferred. Subsequently, the charcoal created on the wood surface becomes a natural fire retardant barrier to further burning of the wood.

Basic mechanism of wood burning



Source: R., L. (2013) Wood Protection, Handbook, TU Zvolen, Slovakia, 134 p.

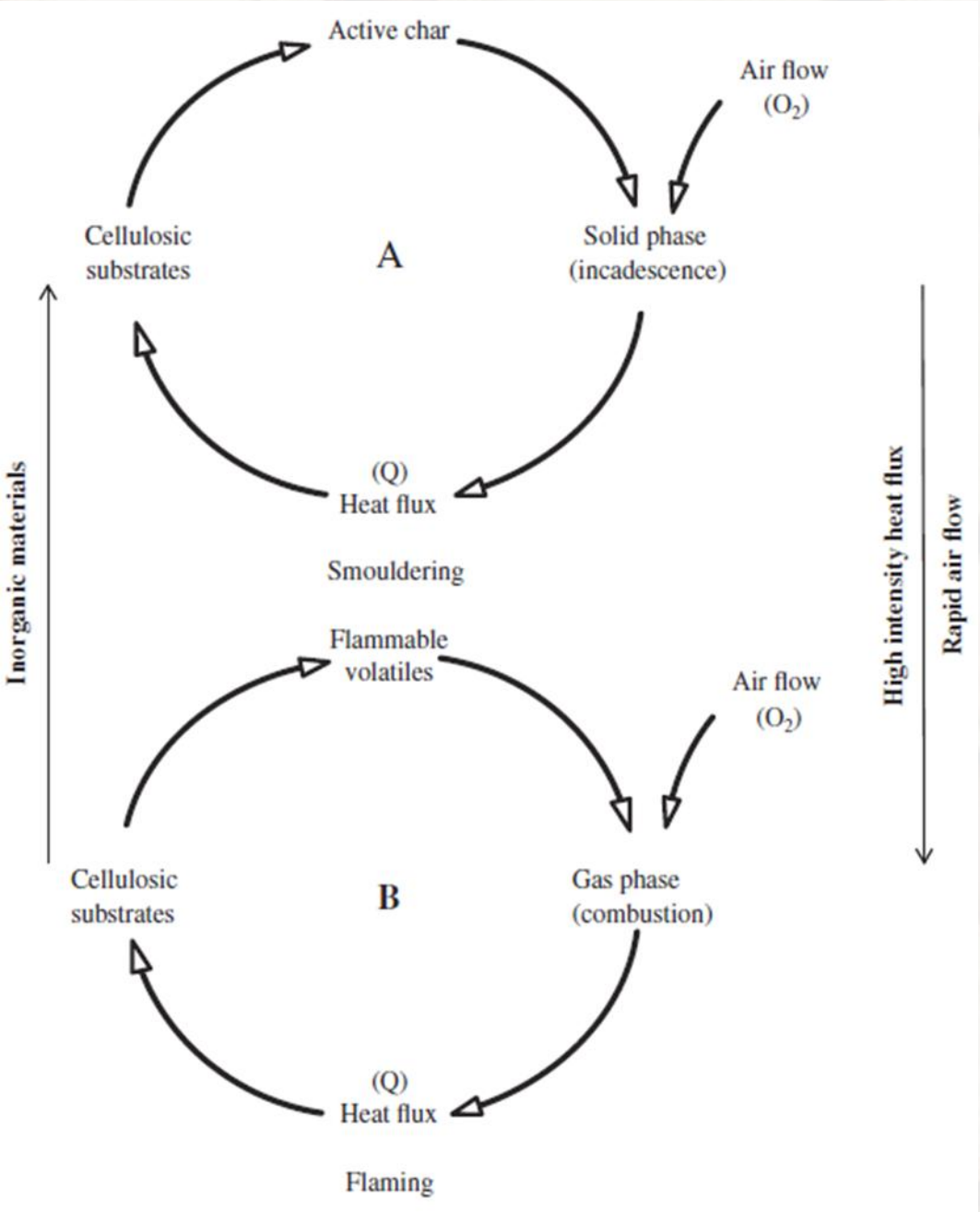
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Thermal decomposition of wood

Thermal decomposition of wood and its burning depend upon the supply of heat, air flow and presence of inorganic additives in wood:

(A) preference for the production of charcoal;

(B) preference for the production of flammable gases



Source: Reproduced by permission of Shafizadeh, F. (1984) The chemistry of pyrolysis and combustion. In: The Chemistry of Solid Wood (ed. R. M. Rowell), pp. 489–529. Adv Chem Ser 207, Am Chem Soc, Washington, USA.
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Wood trusses damaged by a fire – charcoal on wooden elements

Source: R., L. (2013) Wood Protection, Handbook, TU Zvolen, Slovakia, 134 p. Reproduced by permission of TU Zvolen





Process of wood burning

The burning of wood and wooden materials takes place in three stages:







initiation (i.e. combustion of wood by its ignition or inflammation)

propagation – that is, flame spreading on wood surfaces, an intense thermal decomposition of wood (pyrolysis, as a mixture of exothermic reactions or also some endothermic reactions), and the actual burning of flammable gases originated from the thermally decomposed wood (burning, as exothermic thermo-oxidation reactions of flammable gases with

termination (i.e. incandescence of wood charcoal)

Wood combustion

Combustion of wood occurs by its ignition or flashing, both in the presence of oxygen and initiation energy from thermal sources having sufficient input energy (IE) per area unit of wood surface A, usually ~104 W/m2. The initiation energy input depends upon the type of energy source; that is, in the case of a radiant source it must be ~100–150% greater than for a flame source.



The temperature of wood combustion

Ignition or inflammation

The temperature of wood combustion – that is, ignition (by a radiant source) or inflammation (by a flame source) – is usually in the range from 200 to 400◦C and is affected by several factors:

- Heating time – its prolongation decreases the temperature of wood combustion (e.G. The ignition time is 12–40 min for radiant heating of wood to 200 ◦C, but it is only from 1.5 to 3.5 min for heating to 300 ◦C);
- Moisture of wood – moist or wet wood is substantially harder to light up than dry wood is (causes: liquid water increases thermal conductivity of wood and thus also heat dissipation from its surface to its internal zones; water vapour is generated during heating, thus heat is consumed for phase transformations; flammable gases are diluted by water vapour);
- Ratio of wood surface to its volume – wood with greater ratios of surface to volume catches fire more easily (cause: assortments smaller as for shape, e.G., With less thickness, can be heated and ignited faster);
- Roughness of wood surface – products with rougher surfaces with greater contact area (e.G. Sawn) will ignite faster than smoothly worked ones (e.G. Planed);
- Wood density – denser wood is harder to set fire to (causes: thermal conductivity of wood grows with its density and so

Flame spreading

Flame spreading and burning of wood follows after the fire initiation.

Flame spreads most promptly on surfaces of a dry wood with lower density and higher roughness. The speed of wood burning depends upon the internal conditions of the wood (e.g. moisture, density), and also upon the external conditions in its vicinity (e.g. wind).

The role of outside energy source needed for wood combustion is taken over by wood itself or by other flammable materials; that is, materials from which another heat necessary for fire development is generated by exothermic reactions. Wood does not burn immediately to ash, but it gradually burns away and in a time τ (min) – depending on the speed of wood burning $\beta 0$ (mm/min) – is changed to the carbonated layer of charcoal with a thickness of dchar:

$$d_{char}\ (mm) = \beta 0 \tau$$

The speed of wood burning away depends upon several factors. For example, on fire, spruce wood with a density of 350–440 kg/m^3 shows an average speed of burning away $\beta 0$ = 0.65–0.8 mm/min. However, beech wood, with a lower content of lignin and a higher density of 700 kg/m^3, reaches the same speed of burning away. For wooden composites, the speed of burning away depends also upon their composition and type of adhesive; for example, $\beta 0$ for glulam spruce wood bonded with phenol-formaldehyde adhesive is 0.68 mm/min and for beech plywood 0.77 mm/min. This implies that the speed of burning away depends not only upon the density of the wood, but also on the thickness and type of woodenmaterial (plywood, particleboard, etc.), and also in relations to its chemical composition, thermal conductivity, permeability for gases, and so on (White & Nordheim, 1992; EN 1995-1-2).

Incandescence of wood

Creation of charcoal

Incandescence of wood and creation of charcoal is the last stage of thermal degradation of wood. The carbonized layer 'charcoal' acts as natural fire retardant because:

- its density is just ~20% of the original wood density and therefore it also has approximately five times lower thermal conductivity, and
- it is no longer decomposed to flammable organic gases during
  - the incandescence. However, this carbonized layer forms flamma
  - monoxide gas in an exothermic oxidation reaction with oxygen a
  - subsequently the nonflammable carbon dioxide:

$$C + \frac{1}{2}O_2 \rightarrow CO + 110.74\ \text{kJ mol}^{-1}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + 284.75\ \text{kJ mol}^{-1}$$

When a layer of charcoal peels away, thermal decomposition and flame wood burning are restored. Wood burns in several cycles of 'initiation–propagation–termination'.

Parameters

Wood burning

Wood burning is characterized by the following parameters:

- Ignition (combustion) temperature;
- Speed of flame spreading;
- Intensity of thermal decomposition (speed of wood burning away);
- Smoking;
- Production of a layer of charcoal.

The parameters of burning depend upon several factors in the proximity of wood, as well as directly in the wood:

- External
- Internal

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Flammability

Wooden materials and constructions

Flammability is a material value that is evaluated by laboratory and large dimensional tests. Nowadays, in Europe, construction materials, including wood, are classified according to the European standard EN 13501-1 into seven classes: A1, A2, B, C,D, E and F. They are based on several testing methods and their mutual combination:

- Flammability test by EN ISO 1182, means 'burns–does not burn' at 750 ◦C;
- Flammability test by EN ISO 1716, based on caloric value, measuring heat of combustion in pure oxygen in a calorimetric bomb;
- Single burning item test by EN 13823, which measures speed of fire development, lateral flame spreading, creation of smoke and burning drops;
- Flammability test by EN ISO 11925-2, which measures flame spreading.

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Fire retardants

Reducing flammability

Fire retardants reduce the flammability of wood and other flammable materials

Fire retardants of wooden materials suppress the thermal decomposition and burning of wood by the following physical and chemical effects.

- They create a mass insulation layer, which restricts the ingress of oxygen to the wood and the directionally opposite transfer of the flammable gases from the wood.
- They create a thermal insulation layer, which prevent the ingress of heat from the external thermic sources to the wood; that is, either from the synthetic intumescent paints after their foaming and carbonization, or from the wood itself, which in the presence of catalytic substances is converted to charcoal.
- They dilute flammable gases with inflammable gases, which leak from the wood during its thermal decomposition.
- They reduce the concentration of oxygen in the zone of active pyrolysis, whereas they supresses the course of exothermic thermo-oxidation reactions directly in the wood and also in the flammable gases escaping above its surfaces.
- They activate endothermic reactions, in particular dehydration reactions, and at the same time support the generation of a thermal insulation layer of charcoal, and in contrast suppress the generation of flammable gases.

Physical effects of fire retardants

Restriction of mass transfer

Restriction of mass transfer by creation of mass-nonpermeable layers (of oxygen to the wood and of flammable gases, such as methane and alcohols, from the wood:

- on the outside surfaces of wood (e.g. by meltable water-glasses, based on sodium and potassium silicates, or also by intumescent paints);
- inside the wood on the S_3 layers of its cell walls (e.g. by meltable borates, such as H_3BO_3 and $Na_2B_4O_7 \cdot 10H_2O$).

Physical effects of fire retardants

Restriction of heat transfer

Restriction of heat transfer by intumescent thermal-insulation solid foams created from intumescent paints or foils on wood surfaces at temperatures above 150 ◦C. Intumescent foams have a microporous structure, which is a strong, nonflammable, and has a thermal-insulation effect. These foams protect the surfaces of wood for a rather long time (sometimes up to 30 min) against fire or radiant heat impact. Their expansion factor – that is, the relation of the thickness of the solid foam to the initial thickness of the paint – is ~50 : 1. In practice, at least 5 mm thickness of foam is desirable, which can be achieved by 300–500 g of paint per square meter of wood.

Intumescent paints and foils contain the following components, which at high temperatures create nonflammable gases and solid foam:

$$\begin{matrix}\text{Macromolecular substance}\\ \text{Foaming agent}\\ \text{Catalyst and other additives}\end{matrix} \xrightarrow{t(^\circ\text{C})} \begin{matrix}\text{(a) Nonflammable gases}\\ \text{(b) Condensed phase in the form of solid foam}\end{matrix}$$

Physical effects of fire retardants

Dilution of flammable gases

Dilution of flammable gases released from wood with inflammable gases H_2O, NH_3 or CO_2 with the aim to inhibit exothermic oxidation reactions in molecules of the flammable gases. The probability of collisions and reactions of molecules of flammable gases with molecules of oxygen is reduced in the presence of inflammable gases, whereas the propagation of exothermic reactions is also reduced. However, the inflammable gases, such as water vapour, carbon dioxide or ammonia may not be released prematurely, but at the moment of the thermal decomposition of wood connected with the generation of flammable gases. The sources of inflammable gases are, for example:

- hydrated aluminium sulphate – $Al_2(SO_4)_3 \cdot 18\ H_2O \rightarrow H_2O$
- ammonium dihydrogen phosphate or ammonium sulphate – $NH_4H_2PO_4$ or $(NH_4)2SO_4 \rightarrow NH_3$
- potassium carbonate or sodium carbonate – K_2CO_3 or $Na_2CO_3 \rightarrow CO_2$

Chemical effects of fire retardants

Oxidizable substances creating chemical bonds with oxygen

Oxidizable substances creating chemical bonds with oxygen decrease the concentration of oxygen molecules in the zone of active pyrolysis of the wood and block the burning process. Halides – for example, chlorides (Cl−) and bromides (Br−) – are mainly used for these purposes, as they are oxidized by oxygen to higher oxidation levels:

$$Cl^- + 0.5O_2 \rightarrow ClO^- + 0.5O_2 \rightarrow ClO_2 + 0.5O_2 \rightarrow ClO_3^- + 0.5O_2 \rightarrow ClO_4^-$$

Chemical effects of fire retardants

Catalytic dehydration of polysacharydes and carbonization of wood

Catalytic dehydration of polysaccharides and carbonization of wood –molecules of water are created from the polysaccharides during their endothermic dehydration, while the polysaccharides are also carbonized and so less are transformed to flammable gases. The dehydration of polysaccharides is catalysed by substances based on phosphoric acid; for example, $(NH_4)2HPO_4$, $NH_4H_2PO_4$, K_3PO_4, or tri-arylphosphates. A similar dehydration effect on wood components is attributable also to salts of other strong inorganic acids (e.g. sulphuric acid and hydrochloric acid) or to boric compounds (e.g. H_3BO_3 and $Na_2B_4O_7{\cdot}10H_2O$).



3. Biological Degradation of Wood

3.1 Wood damaged by bacteria

Bacteria

Colonization and utilization

Various bacteria colonize:

- Living wood;
- Harvested wood;
- Processed wood.

(in different ways and with different intensities)

Bacteria are ubiquitous in nature and can utilize a wide range of substrates for their nutrition, from simple sugars and complex molecules to highly toxic substances. Therefore, it is not surprising that certain types of bacteria can inhabit standing trees and also colonize and attack harvested wood and wood products placed in service. Whereas, fungi play a dominant role in wood decay, certain groups of bacteria can also degrade lignin-containing cell walls.

Bacteria

Characteristic features

- Common bacteria are subtle, measuring 0.4–5 µm in size and are rod, sphere, helix, or comma shaped.
- In living trees they attack the phloem cells.
- Bacteria penetrate into a deadwood via xylem parenchyma cells of ray tissues and resin canals. Subsequently, they enter libriform fibres, vessels, tracheids and other wood cells, mainly using pits in cell walls for their penetration.
- Bacteria live on pectin, monosaccharides and other easily accessible nutrients and may prepare the wood for fungi.
- The strength of wood is reduced only by some species of bacteria that are able to attack not only the non-lignified pits in tracheids or other tissues but also the cell walls of wood cells.
- Wet wood having a certain amount of oxygen (i.e. logs protected with water in basins or spraying), wooden products above the ground or in contact with the ground (e.g. sleepers, utility poles and palisades) can be attacked by aerobic bacteria – for example, Bacillus brevis, B. firmus, B. subtilis, Cellulomans flavigena.
- Wet wood totally soaked with water (i.e. wood placed long-term in water or in wet ground – cooling towers, sea harbour structures or archaeological wood) can be attacked by anaerobic bacteria – for example, Acetivibrio cellulolyticus, Clostridium thermocellum, Clostridium papyrosolvents.

Bacteria

Classification

Wood-colonizing bacteria have been classified into four groups:

- Bacteria living off the accompanying substances in ray tissues of wood, able to impair the non-lignified pits in cell walls and thus increase the permeability of wood, though without the impact on its strength.
- Bacteria destroying cell walls and reducing the strength of wood – erosion, cavitation and tunnelling bacteria.
- Bacteria acting only in wood primarily or concurrently attacked by another biological pest, or in the wood primarily delignified by abiotic factors; for example, in archaeological wood.
- Antagonistic bacteria suppressing the development and activity of other biological pests in wood. Among these are well-known Bacillus spp., Pseudomonans spp. and Streptomyces spp., used for biological modification of wood.

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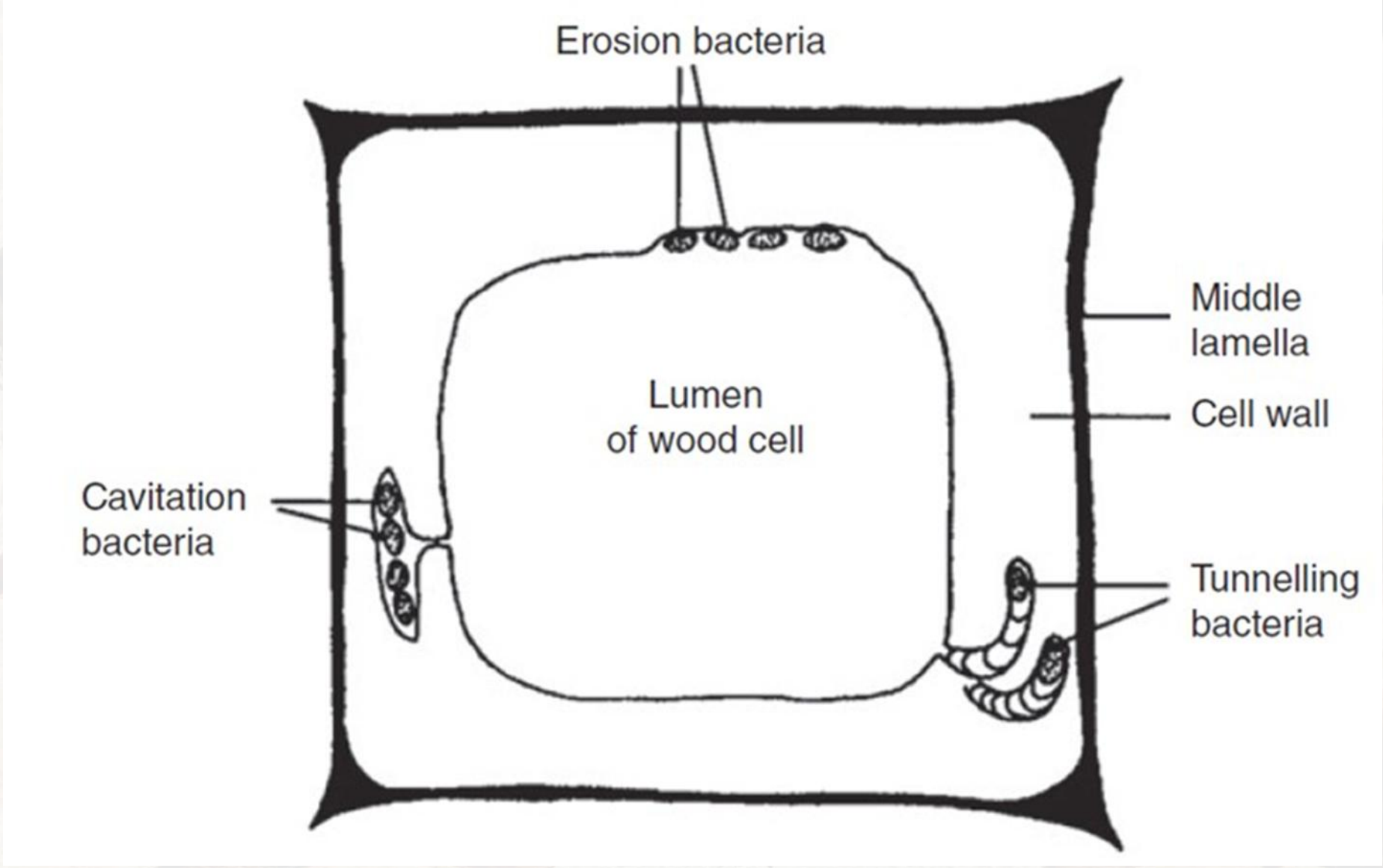
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Overview of bacterial decomposition of wood cell walls

- Erosion bacteria;
- Tunnelling bacteria;
- Cavitation bacteria.



Colonization

The pattern of colonization of wood is similar for TB and EB.

WDB enter wood tissues generally via rays. Cell walls of ray parenchyma in many wood species are not lignified,
and thus can be more easily degraded compared to lignin-containing cell walls.

Ray parenchyma are also a source of abundant readily hydrolyzable food for bacteria.
Bacterial entry into ray contact cells (tracheids, vessels) is likely to be via pits.

Pit membranes consist of cellulose, hemicelluloses, and pectins, and in sapwood is not lignified,
and thus can be readily degraded by WDB.

TB have the capacity to degrade highly lignified middle lamella, direct penetration through the common cell wall is also likely.

EB, on the other hand, can degrade the secondary cell wall but not the middle lamella.
Thus, cell-to-cell movement by EB can only occur via pits.

Stages of TB entry into cell wall

TB attack the cell wall from the cell lumen where they initially multiply.

TB attachment to the cell wall is facilitated by an extracellular slime, which helps retain the bacterium in contact with the cell wall.

TB undergo remarkable shape changes from the initial point penetration through progressive stages of entry into the cell wall. The point penetration is typically associated with a pear-shaped form, with partial cell wall entry achieved by the pointed front of the bacterium, where cell wall degrading elements (enzymes, radicals) may become more concentrated.

The S_3 layer is the first point of contact and bacterial attachment.

In many wood species this layer is more highly lignified than the S_2 layer, and this may have a relation to the initial pear shape, as this is the first cell wall structure to be breached prior to complete [illegible]econdary cell wall.

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Slime

- The slime is specific to bacterial species, which also differ in the amount of slime they can produce. Chemical characterization suggests that bacterial slime is composed of polyanionic polysaccharides.
- Extracellular slime production in response to contact with a solid substrate is not only a feature of bacteria but also of fungi.
  - the proposed functions for the slime produced by fungi and bacteria are the protection from desiccation and other environmental stresses, concentration of substrates, efficient delivery of enzymes, and immobilization of heavy metals such as copper.
- The degradation patterns produced by bacteria are strikingly different from the decay patterns produced by fungi.
- Compared to white and brown rot fungi, wood-degrading bacteria (WDB) are regarded to possess greater tolerance to toxic chemicals, for example, heartwood extractives and wood preservatives (copper-chrome-arsenate, pentachlorophenol), as they can degrade preservative-treated wood exposed in service under a range of conditions, such as in contact with soil and as part of cooling towers.
- Tunneling bacteria can also degrade a range of lignocellulosic substrates with high lignin content, such as the:
  - tropical hardwood species Alstonia scholaris and Homalium foetidum,
  - stems of the fern Pteridium,

WDB

WDB are widely present in nature in terrestrial and aquatic environments.

While tunneling bacteria (TB) seem to require the presence of oxygen for their activity, erosion bacteria (EB) can tolerate conditions with extremely low levels of oxygen.

Wooden objects placed in situations where they become saturated with water resulting in anoxic conditions or in environments supporting limited oxygen availability are predominantly attacked by erosion bacteria (EB)

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Enzymes, Vesicles, Radicals

Microbial enzymes are rather large molecules and cannot penetrate sound wood cell walls, which contain nanoscale pores (about 2 nm in kiln-dried wood). Wood-degrading basidiomycete fungi have developed a mechanism for circumventing this barrier. The tiny radicals generated loosen the cell wall, thus facilitating enzyme penetration.

Much of the description presented for TB also applies to EB. Because of the inability to obtain EB in pure culture, it has not been possible to characterize EB-produced enzymes. One of the striking differences between TB and EB is that while TB tunnels generally contain little or no degraded cell wall residues, substantial amounts of lignin residues are left in EB-degraded regions of the cell wall, suggesting differences between TB and EB in their lignin degrading capabilities. The presence of membranous vesicles also during EB degradation points to similarities between TB and EB in the roles vesicles may play in facilitating delivery of wood-degrading agents to cell wall degradation sites. EB are also likely to deploy radicals to facilitate cell wall degradation, as proposed for TB.

Biological damage of wood by organisms - pests

Type of organism	Character of wood damage
Bacteria	No or less-intense decomposition of wood cells
Fungi	Rot of wood cells caused by wood-decaying (wood-destroying) fungi
	Moderate impairment of wood by wood-staining fungi and moulds
Insects	Damage of wood by feeding marks produced by larvae (or imagoes)
Marine borers	Damage of wood by boreholes and tunnels
Parasitic spermatophytes	Growth of plant roots in the wood of a living tree
Synanthropic vertebrate	Damage of wood by biting it out, hiding places in panels, excrement
Human	Unsuitable approach to harvesting, storage and processing of wood, as well as bad protection and maintenance of wooden products; following creation of suitable conditions for fungal-rot, insect damage, atmospheric, thermal and other forms of wood damage



4. Chemical Protection of Wood

4.1 Methodology, ecology and regulation of chemical protection of wood

Chemical protection

Wood preservatives

The chemical protection of wood = 'wood preservatives'

- Bactericides (against bacteria);
- Fungicides (against fungi);
- Insecticides (against insects);
- Fire retardants (against fire);
- Anti-weathering and anti-corrosive agents (against [illegible] and aggressive-chemical effects).

The quality of chemical protection of wood depends upon

- The sufficient efficiency, distribution and stability of the preservative in the wood;
- The minimal risk of the preservative to people and the environment.

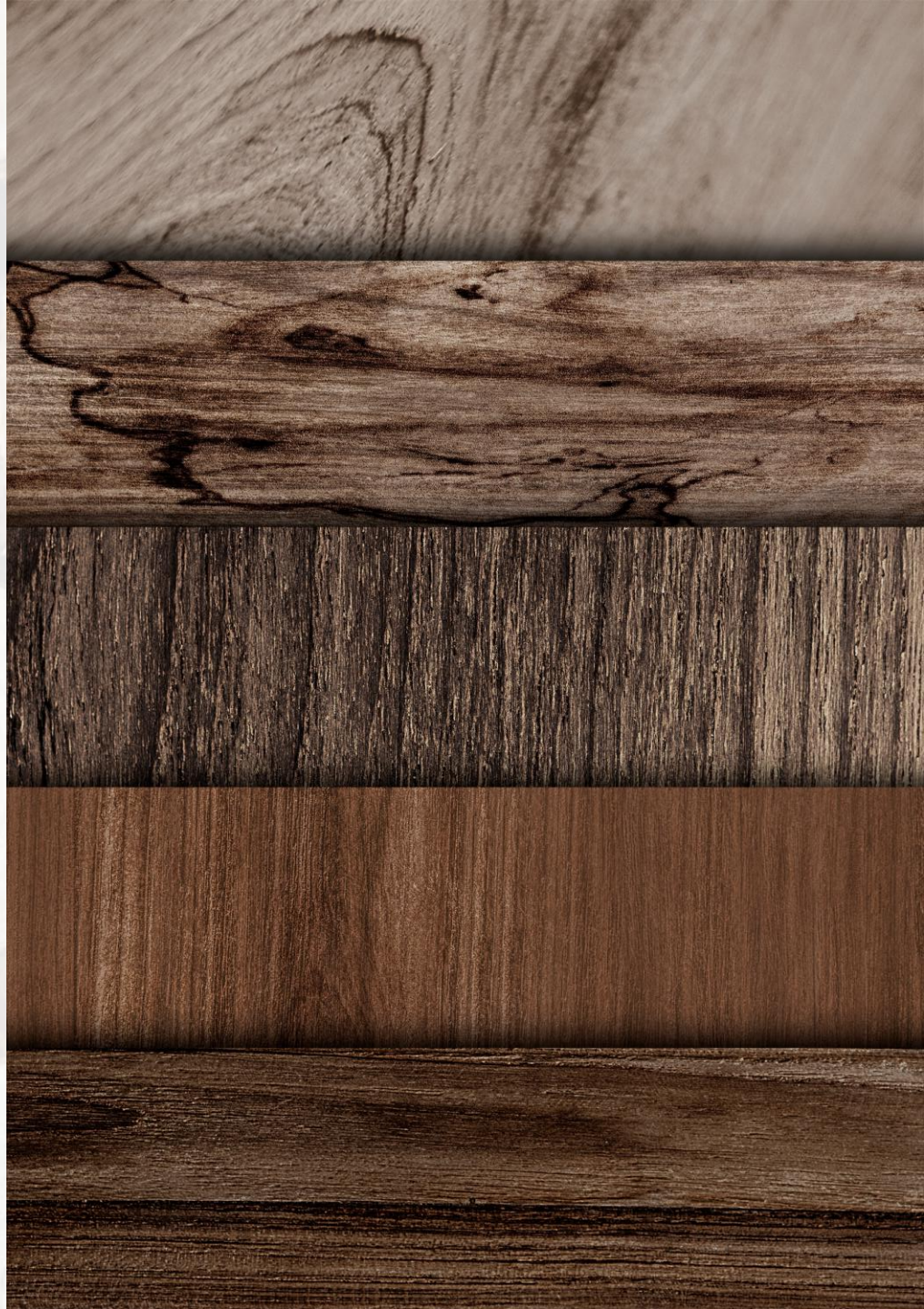
More of these factors are directly influenced by:

- The wood structure (dimension, porosity, permeability, etc.);
- The application properties of the preservative;
- The technology using of the preservative.

Methodology and legislation of chemical protection of wood

A suitable wood species and/or the type of wooden material is first selected for the wooden product based also on its natural durability

- Classes of wood durability in the presence of biological pests according to EN 350-2
- Classes of wood reaction to fire according to EN 13501-1.



Damage, resistance, protection

- The expected damage to the wooden product;
- The natural resistance of the wooden material;
- The particular chemical protection;
- The wood preservatives,

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The technology for chemical protection of the wood (1/2)

The technology for chemical protection of the wood is proposed, preferably observing the following principles:

- Only mechanically processed wood should be subject to chemical protection. If a layer of chemically treated wood is removed by subsequent sawing, planning, boring, and so on, then this section of wood has to be protected again.
- The impregnation of poorly permeable ‘refractory’ wood species (e.g. spruce and fir) can be improved by mechanical and laser perforations, or by biological and chemical pretreatments.
- The optimum moisture of wood prior to protection depends upon the technology used (pressure or diffusion driving forces).
- The particular technology of protection is given by the requirement of the depth of penetration and retention of the preservative in the wood.
- The technology of chemical protection of wood should be selected on the basis of its class of use – depending on danger of attack by biological pests (EN 335), based on the principles of EN 351-1

The technology for chemical protection of the wood (2/2)

- The depth of penetration of a preservative into the wood (for biocides prescribed by EN 351-1: from P1 to P9) depends upon the permeability of the wood as well. For example, in the case of use class 3, the biocide should penetrate from lateral areas of the well-permeable wood species (beech, hornbeam, lime, etc.) at least to 6 mm→class P5; on the other hand, for the poorly impregnable species (spruce, fir, heart of oak, etc.) there are no demands to depth of penetration→class P1.
- The technology of chemical protection of wood by fire retardants depends upon their type (i.e. intumescent paints just on the wood surface; other types also into a depth of wood by soaking or vacuum pressure technologies).
- The technology of chemical protection of wood surfaces against weather conditions is performed usually by one to three coating layers, using immersion, spraying or painting.
- Wood composites (lamella wood, plywood, laminated veneer lumber (LVL), particleboard (PB), oriented strand board (OSB), etc.) can be preserved by spraying, painting or other post manufacture treatment technologies, possibly as well as by special in-process treatment technologies during their manufacture.
- The fixation of a preservative in wood is important for those products intended for exterior use.

EN 351-1

Methodology of the chemical protection of wooden structures in accordance with EN 351-1.

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EN 460

Requirements for the chemical protection of wood-based products with fungicides efficient against wood-decaying fungi in relation to its moisture content in accordance with EN 460.

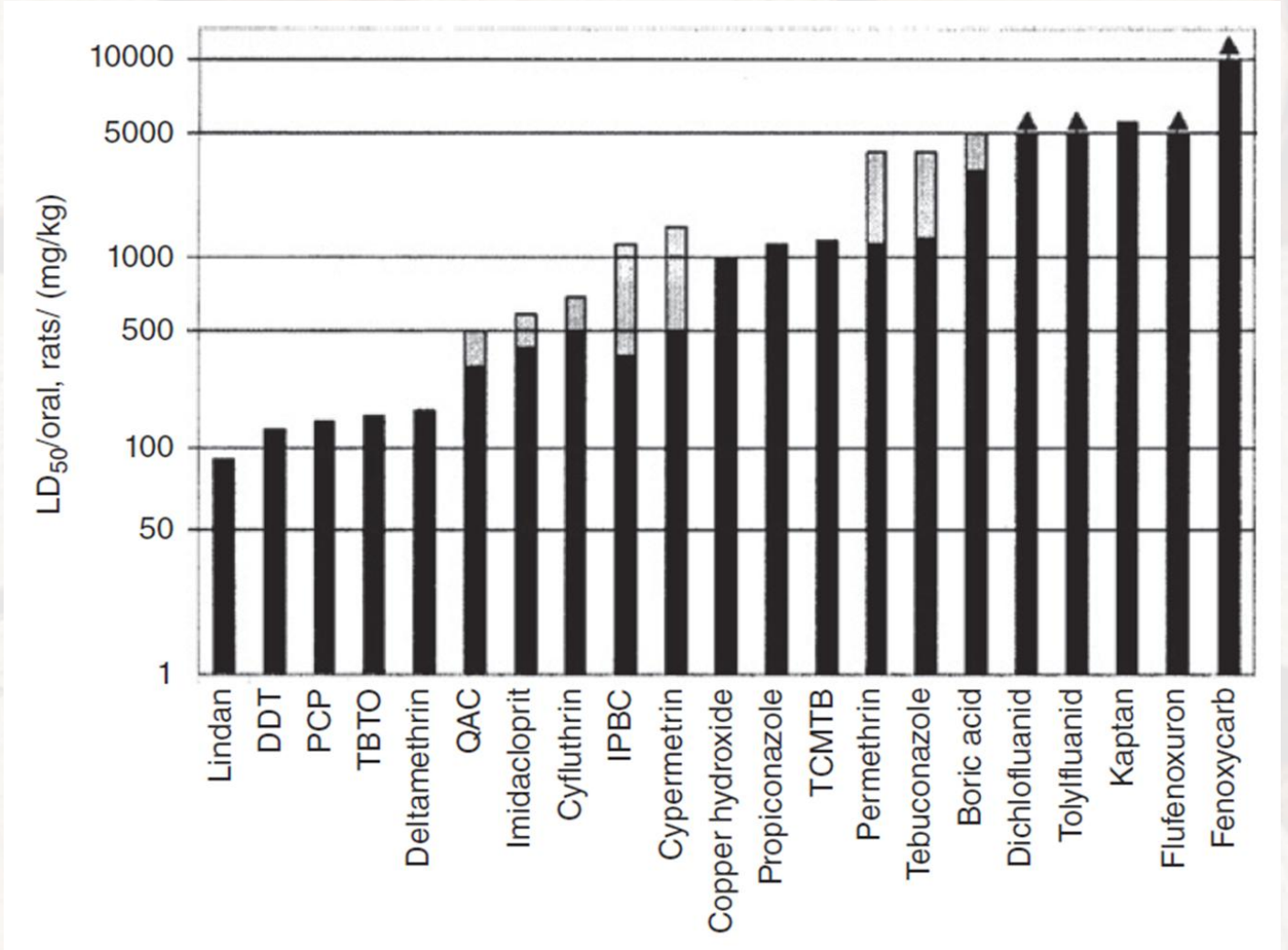
	Wood natural durability against rot according to class (EN 350-2)				
Use class of wood (EN 335)	**1**	**2**	**3**	**4**	**5**
1 (permanently: $w < 20\%$)	I	I	I	I	I
2 (from time to time: $w > 20\%$)	I	I	I	(I)	(I)
3 (more frequently: $w > 20\%$)	I	I	(I)	(I)–(X)	(I)–(X)
4 (permanently: $w > 20\%$)	I	(I)	(X)	X	X
5 (permanently: $w > 20\%$ in salty environment)	I	(I)	(X)	X	X

I: natural durability of wood is sufficient and chemical protection of wood with a fungicide is not needed;
X: wood has to be treated with a fungicide as its natural durability is not sufficient; (I) or (X): choice of fungicidal treatment of the wooden element (structure) also depends on other factors (e.g. on its static function or on its lifetime requests).

EN 335

Class of wood use (EN 335)	Technology of the preservative application
1	Not predetermined in detail (painting, spraying, etc.)
2	Not predetermined in detail (painting, spraying, etc.)
3	Minimally dipping (extraordinary painting, spraying), but optimally vacuum-pressure technologies
4	Vacuum-pressure technologies
5	Vacuum pressure technologies

Acute toxicities LD_{50} (oral, rats) of some biocides for wood protection



Toxicological and ecotoxicological standpoints of chemical protection of wood

The environmental standpoint is important not only in the technology of wood treatment, but also during its exposure and disposal of the treated wood after its useful life by incineration, composting, and so on

The toxicity of preservatives for warm-blooded organisms is assessed first of all by the acute toxicity.

This toxicological question is characterized by the lethal dose (LD), and usually by the LD_{50} (mg/kg, ppm). The LD_{50} is the dose of chemical substance in milligrams per kilogram of live weight of laboratory animals (e.g. rats) that results in 50% mortality occurring in the test population.

Preservatives with higher values of the LD50 are less toxic, both for animals and human.

Biocidal Product Directive

In Europe, biocide use, including wood preservatives, is regulated by the Biocidal Product Directive 98/8/EC. Wood preservatives used now should be relatively harmless (LD50 >15,000 mg/kg) to slightly toxic (LD50 >500 mg/kg). In addition to acute toxicity, the protective agent may not show a chronic toxicity, mutagenic, carcinogenic or teratogenic effects.

The ecotoxicity of preservatives defines their impact on the environment; that is, on the air, rivers, oceans, soils and plants. From the point of view of ecology of preservatives, but also their efficacy, it is very important also that they are stable in the preserved wood. The main problem associated with the development of environmentally friendly organic preservatives, for high hazard end uses, is the observed biotransformation of these chemicals. Certain strains of proteobacteria (e.g. Alcaligenes, Enterobacter, Pseudomonans, Ralstonia) are able to degrade some organic biocides;for example, 3-iodo-2-propynyl-butyl-carbamate (IPBC), propiconazole and chlorothalonil. Propiconazole and tebuconazole are also partly degradable by the black-stain fungus Epicoccum purpurascens

Volatile organic compounds (VOCs) are organic chemicals (solvents, active substances of preservatives, etc.) which evaporate from the preserved wood during its treatment and long-term exposure. The amount of VOCs (i.e. air pollutants) is limited by standards; for example, in Europe for coatings by the Paints Directive 2004/42/EC and EN 16402, or in the USA by the Environmental Protection Agency (EPA).

Regulation of chemical protection of wood (1/2)

The regulation of preservatives for the chemical protection of wood is a very important for their proper and safe implementation in practice. In Europe, as a result of the health and environmental demands on biocidal products determined in Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998, and also in other Commission Regulation reports of this directive (e.g.No. 2007/1451/ES), only a limited number of active substances in wood preservatives should be permitted in the European market in years 2014–2016. In Annex I to Directive 98/8/EC, there are a limited number of active substances from PT 8 (wood preservatives); for example, IPBC, potassium salt of cyclohexylhydroxydiazene 1-oxide, dialkyldimetylammonium compounds (DDACs), propiconazole, tebuconazole, thiabendazole and dichlofluanid from the fungicides.

In the USA, the EPA (Environmental Protection Agency) is responsible for regulation of biocides. Before registering a new biocide or new use for a registered preservative, the EPA must first ensure that the preservative can be used with a reasonable certainty of no harm to human health and without posing unreasonable risks to the environment. Today, the International Council-Evaluation Service (ICC-ES) issues Evaluation Reports that provide evidence that a building product complies with building codes – Acceptance Criteria (AC). Performance criteria of products containing wood preservatives are set out in AC326, arising from AWPA, ASTM and EN standard test methods.

Regulation of chemical protection of wood (2/2)

As a result of regulations for wood preservatives, the registration of new biocides and commercial products is under constant review by responsible organizations. In future, there probably will be a reduced interest for investigation of new biocidal (e.g. fungicide and insecticide) substances, mainly those on the basis of heavy metals (not only chromium, tin or arsenic, but also copper, etc.), the usage of which is already limited today.

The price for notification of existing active substances of preservatives varies from €3.3 million to €6.0 million, of which a substantial 85–90% of this price is connected with toxicology and ecotoxicology studies. Lower prices are needed for registration of existing preservatives (€0.2 million to €0.5 million) or new preservatives based on known active substances (€0.3 million to €1.4 million). However, the highest prices (from ~€20 million to €30 million) are needed for evaluation of new active substances – synthesis and analysis, their biological screening tests, and delimitation of optimal technologies for their application in practice and their verification.



4. Chemical Protection of Wood

4.2 Preservatives for wood protection

Active substances

Preservatives for wood protection comprise:

- one or several active substances;
- one or several accompanying components (i.e. solvent, stabilizer, emulsifier, fixative, pigment, coloring, etc.).

The active substances in commercial wood preservatives have various protecting effects:

- bactericides, effective against bacteria;
- fungicides, effective against wood-decaying fungi, staining fungi and moulds;
- insecticides, effective against wood-damaging insects;
- fire retardants, reducing the flammability of wood;
- inhibitors of weather corrosion, improving the resistance of wood against UV radiation, water, oxygen, and so on;

Bactericides

Bactericides eradicate bacteria that attack of wood, concrete, stone, plastics or other materials. New types of bactericides contain silver and its compounds; for example, silver chloride, silver chloride mixed with titanium dioxide (TiO2) and sodium sulfosuccinate, or silver mixed with copper oxide and zinc silicate.

Silver exhibits a broad range of antimicrobial activity against Gram-positive and -negative bacteria, but also against yeast and moulds. However, more fungicides for wood protection (e.g. quaternary ammonium compounds (QACs) are applied as bactericides as well.

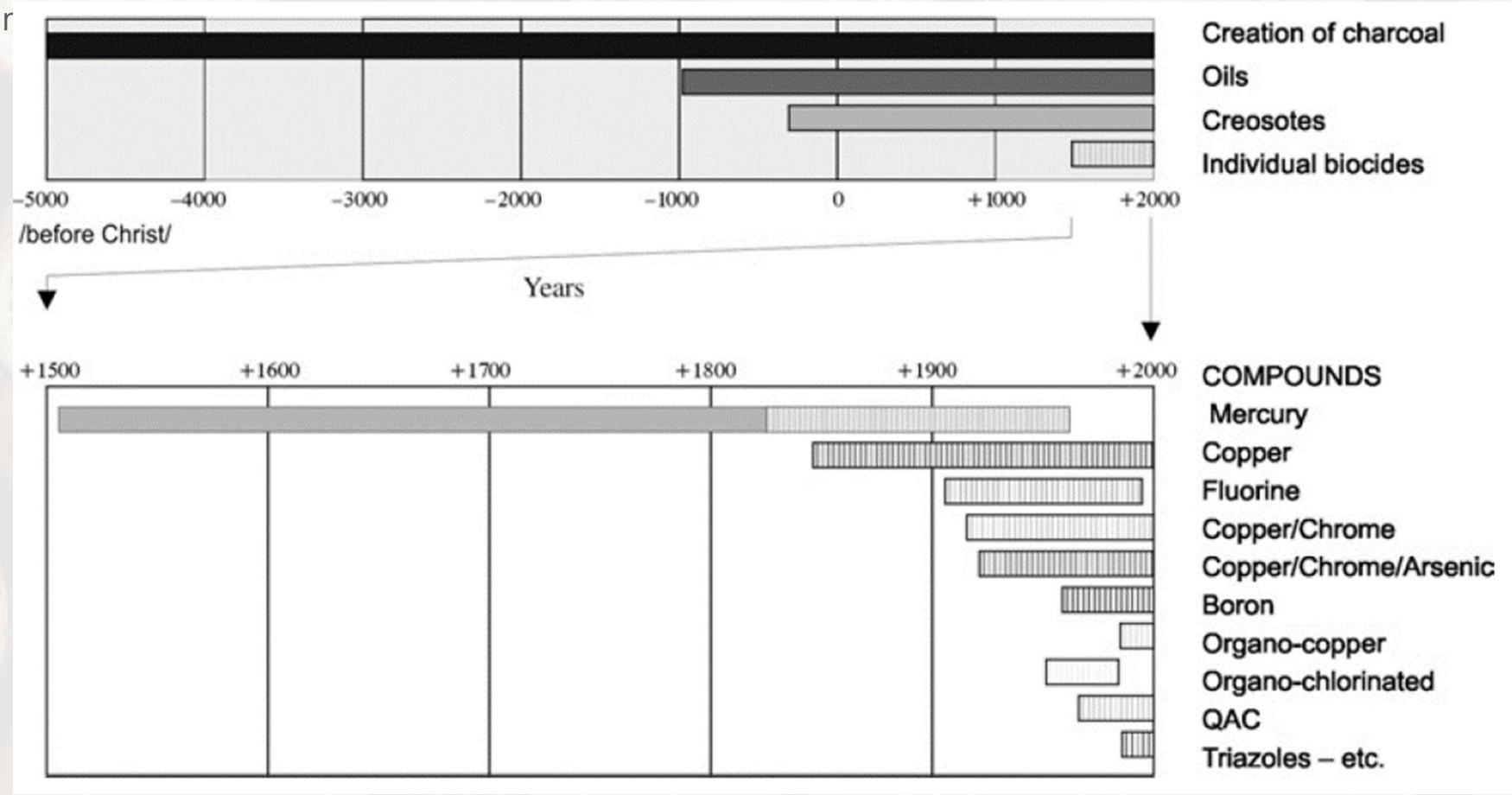
Fungicides: for decay, sap-stain and mould control

Fungicides for wood protection are classified according to their chemical structure and origin as:

- Inorganic
  - water soluble, able to be leached out from wood;
  - water soluble, fixable in wood;
- Organic
  - creosote oils (prepared by distillation of black-coal tar), containing aromatic hydrocarbons;
  - synthesized substances (e.g. organometals, QACs, carbamates, heterocycles), but also other types, usually applicable in organic solvents, water emulsions, or some of them also in aqueous solutions;
  - natural substances (e.g. chitosan).

Historic development of biocides for wood protection

Source: Pallaske, M. (2004) Chemical wood protection: improvement of biocides in use. In COST Action E22 – Environmental Optimization of Wood Protection,11 p. Lisbon, Portugal. Proceedings of the Final Cor



Inorganic fungicides

Inorganic fungicides comprise active substances based on the following chemical elements:

- copper (Cu2+);
- zinc (Zn2+);
- antimony (Sb3+);
- silver (Ag+);
- cadmium (Cd2+);
- cobalt (Co2+);
- nickel (Ni2+);
- boron (B3+).

Roll over to learn more

Those used in the past also contained arsenic (As3+ and As5+), chromium (Cr6+), and also mercury (Hg2+) long time ago.

Inorganic fungicides without fixable substances (e.g. without Cr6+) are often easily leached out from wood; that is, they are preferentially recommended for the protection of wooden products in buildings or under a shelter without exposure to rainfall water.

Creosotes

Creosotes are oils obtained by fractional distillation of black-coal tar ('tar oils' with a boiling temperature range of 200–400 ◦C).

Creosotes, as effective preservatives against biological pests, were patented in 1836 by German chemist Franz Moll and first used for wood impregnation by John Bethell in 1838.

In the 19th and 20th centuries, creosotes were the most commonly used wood preservatives throughout the world, with a worldwide production of ~16 × 106 t per year.

Creosotes contain ~96% of various nonpolar polycyclic aromatic carbohydrates (fluorene, phenanthrene, anthracene, etc.) and ~4% tar phenols (cresol, naphthol, etc.) and tar bases (quinolone, acridine, etc.).

In the past, the creosotes were applied mainly for industrial protection of wooden sleepers, utility poles, bridges and other structures for exterior use. Now, they are used to a lesser extent, substantially only for industrial treatment of special sleepers and poles, and only by vacuum-pressure technologies at temperatures above 100 ◦C.

Creosotes in Europe

In Europe, the composition and usage of creosotes is controlled by the West European Institute for Wood Impregnation (WEI). The WEI type C creosote, which contains mainly acenaphthene, fluorene, phenanthrene and anthracene, is from the environmental point of view a more friendly than older types (WEI Type A and WEI type B), because this creosote has only compounds with tapered boiling points, from ~280 to 360 ◦C; that is, without easily volatile naphthalene derivatives and also without higher condensed aromatics. For example, the maximum content of benzo(a)pyrene, whose boiling point is above 450 ◦C, and which has a strong carcinogenic effect, had to be less than 50 ppm; for example, in the WEI type C maximally from 5 to 50 ppm.

An advantage of creosotes is their stability in wood (low water leachability and low volatility), no corrosive effects on wood and metals, and affordable price. However, chemical analyses of old impregnated sleepers prove that after 25–30 years of exposure in railway routes just one-third of the original amount of oils remains in them. The disadvantages of creosotes are the dark colour, the smell, the variable chemical composition, the high viscosity (and thus also the need to heat oils forwood impregnation to temperatures of 100–140 ◦C), the moderate increase of wood flammability and particularly the health-damaging effects on humans.

The durability of wooden sleepers can be increased after pressure impregnation by creosotes three times (oak) to ten times (beech); that is, a nonimpregnated beech sleeper has a service life of ~3 years and an impregnatedone ~30 years. Retention of 30 kg/m^3 (30 kg of oil per 1 m^3 of wood) is required against wood-decaying Basidiomycota fungi causing brown and white rot, or against wood-damaging insects. However a substantially higher retention of 120 kg/m^3 is required against wood-decaying Ascomycota fungi, which cause soft rot.

Creosotes dissolved in mineral oils (carbolineum) or emulsified in water (pigmented emulsified creosote) can be used at ambient

Synthesized organic fungicides

N-Organodiazeniumdioxy-metals are organometal substances in which an atom of metal is bound to an oxygen atom present in one or more organodiazenium molecules.

The organic part of these substances is, for example, cycloalkyl, alkyl or aryl. The metal is usually potassium (K), copper (Cu), zinc (Zn), nickel (Ni), cobalt (Co) or aluminium (Al). These fungicides are applied in water solutions with the presence of suitable additives for their dissolution, or in organic solvents.

Cu-HDO other

Click to learn more

Natural organic fungicides

Natural substances

Natural substances having bactericidal, fungicidal and/or insecticidal effects.

Among the best known are:

- Essential vegetable oils (e.g. cinnamon oil, clove oil, geranium oil, neem oil, oregano oil, tea tree oil, thyme oil) and their effective compounds (e.g. 1,8-cineole, α-cadinol, α-terpinene, α-thujone, elemol, eugenol, limonene, p-cymol, thymol) obtained from convenient plant species;
- Wood extracts (e.g. Tannins, flavonoids, terpenoids) obtained from the most durable wood species;
- Extracts from chilli with the effective compound capsaicin;
- Propolis from beeswax with anantibiotic effect;
- Chitosan.



Natural organic fungicides

Essential vegetable oils



Essential vegetable oils are obtained from suitable species of plants by distillation with water vapour or by extraction with water or organic solvents. Well known are cedar oil, Egypt geranium oil (from Pelargonium graveolens), thuja oil (from Thuja occidentalis), thyme oil (from Thymus zygis), hiba oil (from Thujopsis dolabrata), tung oil (from Aleuritis fortii and Aleuritis cordata), lavender oil (from Lavandula angustifolia), neem oil (from Azadirachta indica) and clove oil (from Syzygium aromaticum), but also linseed, citrus, olive and several other types of oils. These oils are mixtures of various alcohols, aldehydes, ketones, esters, lactones, carbohydrates, terpenes and heterocycles. They are less soluble in water, but well-dissoluble in alcohols and aromatic carbohydrates. Several of them are partially volatile; that is, they act also as repellents to wood-damaging insects.

Essential oils were applied even 2000 years ago, either as concentrates or in organic solvents for the protection of construction timber. Essential oils with phenolic or aldehyde and ketone components, like thymol, eugenol, carvone and carvacrol, show better efficiency against wood-decaying basidiomycetes than those with various terpenes note that oils containing thujaplicins and some other terpenes (e.g. thyme oil and geranium oil) have good fungicide properties. Carvone, citronellol, geraniol, thymol and borneol are effective inhibitors of mould spore germination. Essential oils are effective also against bacteria, and they can be used for protection of wooden products against the

Natural organic fungicides

Wood extracts

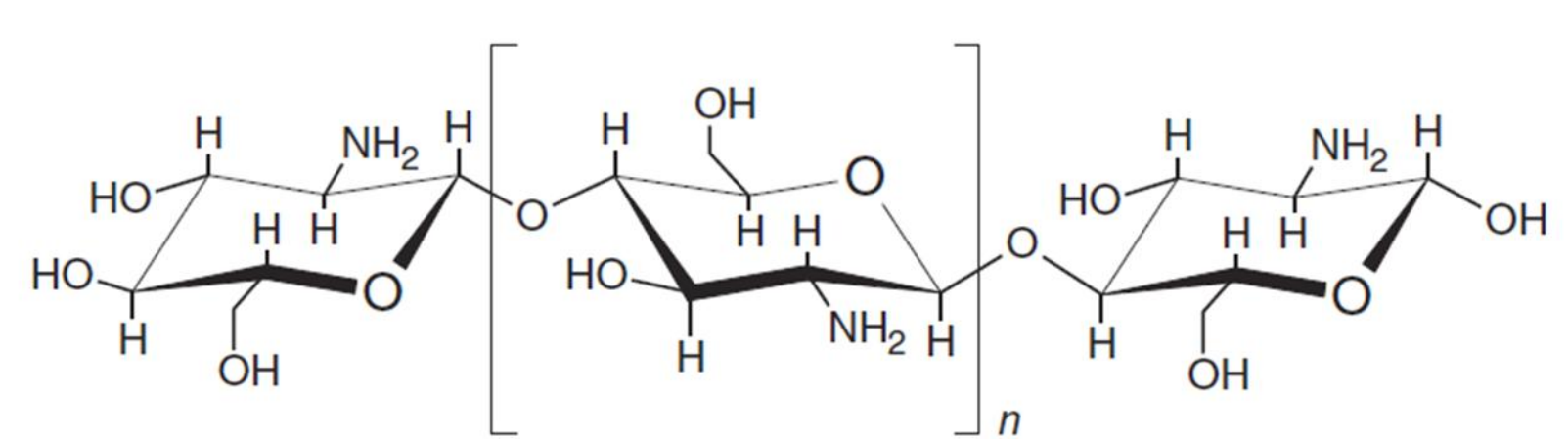
Wood extracts are obtained from splinters, sawdust and bark of highly durable wood species, such as African cherry, black locust, oak, padouk, rosewood, sequoia, teak, and others – mainly tropical species. Wood extracts in aqueous, alcoholic or other liquid solutions contain bioactive compounds: polyphenolics (e.g. flavonoids, sterols, quinones), terpenoids (e.g. diterpenoids, triterpenoids, cedrol, agathadiol, epimanool, bornyl-acetate, cedrene), alkaloids and stilbenes. Such wood extracts are used for deep impregnation or surface treatment of less durable wood species with the aim to inhibit activity of various types of wood damaging fungi. However, alteration of their chemical structure during extraction from durable woods, during treatment of nondurable woods or during exposure of treated wooden products can lead to loss of their original antifungal efficiency. Bio-efficient extracts are also obtained from the leaves of durable wood species; for example, acetone extracts from the leaves of Dalberia sissoo wood are efficient against wood-damaging fungi and bacteria.



Natural organic fungicides

Chitosan

Chitosan is a 1,4-linked heterogeneous polymer of d-glucosamine (fraction of N-acetylations FA = 0), which usually contains also N-acetyl-d-glucosamine units (FA ≠ 0). Chitosan is derived from crustacean shells, wing-cases of insects, and cellular walls of algae and fungi. It is partly water soluble under acidic conditions.



Chitosan (type $F_A = 0$, composed just of glucosamine units)

Insecticides

Insecticides for wood protection are classified according to their chemical structure and origin to:

- inorganic
  - water soluble, able to be leached out from wood;
  - water soluble, fixable in wood;
- organic
  - creosote oils, on the basis of higher aromatic carbohydrates;
  - synthesized substances (e.g. pyrethroids, heterocycles, organophosphates, juvenile hormones, chitin-inhibitors), and also repellents and pheromones;
  - natural substances (e.g. pyrethrin).

Insecticides - classification

Insecticides are classified according to their physiological effect on insects as follows:

- toxic
  - respiratory – that is, block the activity of respiratory system of insects;
  - protoplasmic – that is, cause the disintegration of live cells;
  - nervous – that is, block the activity of the central nervous system of insects;
- nontoxic
  - hormonal – that is, regulators of insect growth, development and behaviour;
  - repellents – that is, repulsing insects during their invasion to round wood yards, and so on;
  - pheromones and other attractants – that is, attracting insects to a certain place, where they are killed.

Toxic inorganic insecticides

Compounds of trivalent boron

Compounds of trivalent boron are known insecticides and fungicides effective against wood pests. They are used mainly in interiors and buildings against boring-beetles and termites; for example, H_3BO_3, $Na_2B_4O_7 \cdot 10H_2O$ and sodium octaborate.

Their insecticide effect is protoplasmic. In exteriors they can be applied in the form of diffusion cartridges for the protection of wooden windows, bridges or utility poles against wood-damaging ants.

Toxic organic insecticides

Pyrethroids

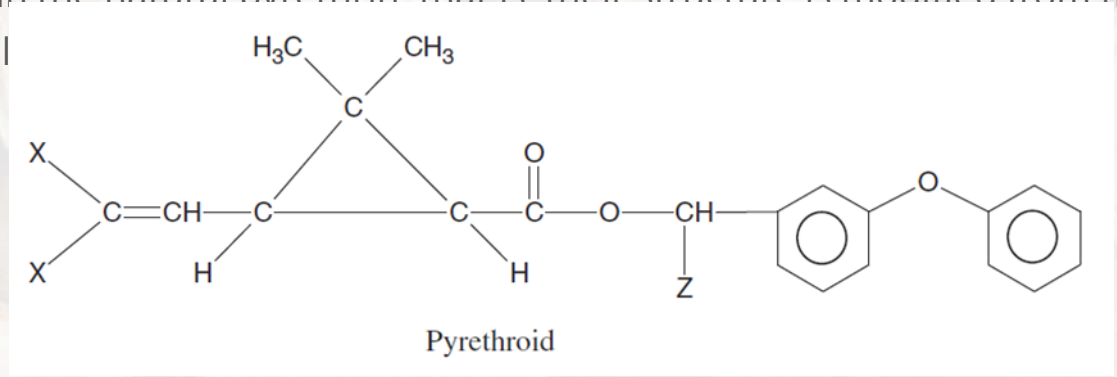
In the past, chlorinated carbohydrates (DDT, hexachlorohexane), organophosphates and carbamates were used as efficient insecticides. Nowadays, they are replaced by pyrethroids, by some types of heterocycles based on pyridine and imidazole, as well as by QACs. They are applied similar to organic fungicides, in organic solvents or in water emulsions.

Creosotes also have an insecticide effect, but their application is now very limited.

Pyrethroids (1/2)

Pyrethroids have a similar chemical structure to natural pyrethrins, obtained by extraction from flowers of thermophilic plantation-grown chrysanthemums (Chrysanthemum cinerariaefolium, Chrysanthemum coccineum, etc.) growing in particular in Kenya, Tanzania and Brazil.

To well-known synthetized pyrethroids belong permethrin, cypermethrin, cyfluthrin, deltamethrin, bifethrin, fenpropathrin and bioresmethrin. All these compounds are the dichloro- or dibromo-vinyl analogue esters of the [+]-trans-chrysanthemum acid present in the natural pyrethrin; that is, their structure is modified from the 3-phenoxy-benzyl-esters of the 2,2-dimethyl-3-(2,2-dihal



Pyrethroid

Pyrethroids block the central nervous system of insects. Their efficiencies are different; in particular, for deltamethrin : cypermethrin : cyfluthrin : permethrin against larvae of the house longhorn beetle (Hylotrupes bajulus) the efficiency is 25 : 7 : 7 : 1, and against larvae of the common furniture beetle (Anobium punctatum) it is 34 : 3 : 3 : 1.

Pyrethroids (2/2)

Pyrethroids are only slightly toxic for warm-blooded animals. In the environment they are gradually degraded due to UV light, oxygen and water; that is, the protection of wood through using them has to be regularly renewed, usually in 4- to 6-year cycles.

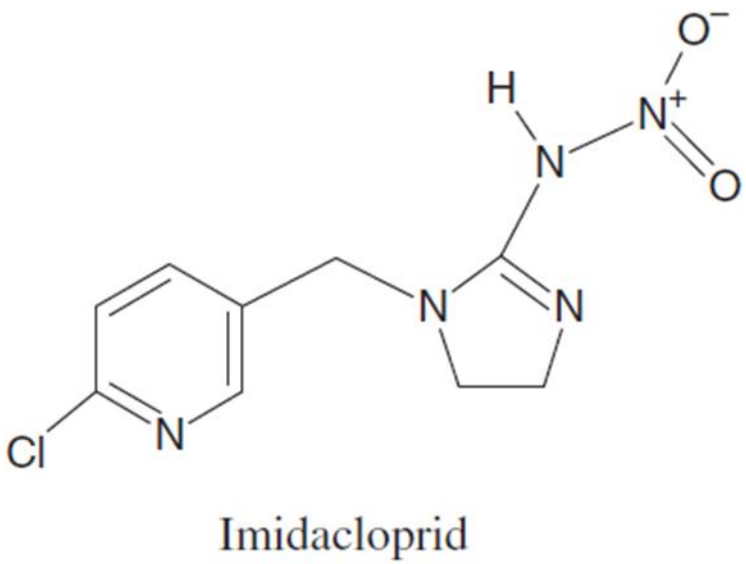
Pyrethroids moderately corrode metals (e.g. steel, aluminium and copper). In practice, they are often applied in combined biocide preservatives (insecticide+fungicide); for example, in combination with triazoles, such as tebuconazole or propiconazole.

Pyrethroids are effective against boring-beetles in use class 3, as well as against termites. They are used also for the protection of wooden composites; for example, they are added to the adhesive producing bio-stable plywood.

Derivatives of 2-imidazolidinimine

Derivatives of 2-imidazolidinimine are highly efficient against wooddamaging beetles and termites – the main compound is 1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-N-nitro-2-imidazolidinimine (imidacloprid).

It dissolves in medium polar organic solvents. However, it can also be applied in water (0.06% aqueous solution at 20 ◦C). Imidacloprid acts on the central nervous system of insects. It is medium or slightly toxic against warm blooded
rats) of 450–550 mg/kg.



Imidacloprid

Nontoxic hormonal insecticides

Hormonal insecticides, known as insect growth regulators, influence certain development stages of insects, impairing the synchronizability of their hormones.

Analogues of insect hormones – the juvenile, anti-juvenile and skin-sloughing hormones – cause killing or sexual sterilization of insects.

Their hormonal effects lie in:

- the introduction of one of the hormones (juvenile, skin-sloughing) to the insect body;
- the suppression of production of the juvenile hormones after the introduction of the anti-juvenile hormones to the insect body.

Click to learn more

Fenoxycarb

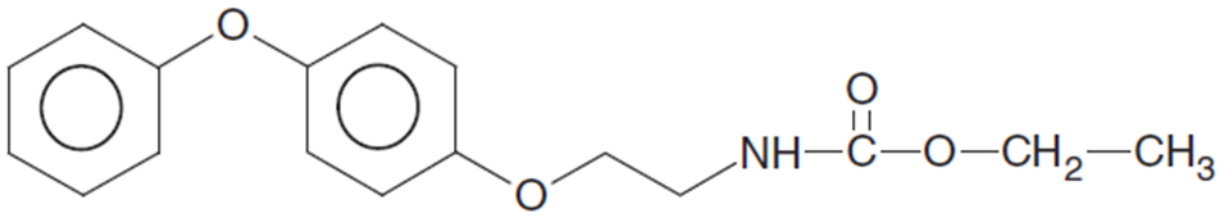
Fenoxycarb (ethyl-N-[2-(4-phenoxy-phenoxy)-ethyl]-carbamate) is a wellknown representative of the juvenile hormones.

Fenoxycarb protects wood against the house longhorn beetle (Hylotrupes bajulus), furniture beetles (Anobiidae), powder post beetles (Lyctidae) and other species of wood-damaging beetles; however, it is ineffective against termites.

It is applied in a concentration of ~0.04%.

Its required retention is ~1.0 g/m^3 in impregnated wood and ~0.05 g/m^2 in surfaces of treated wood.

It is not toxic to humans and other warm-blooded organisms (having an LD_{50} (oral, rats) ≥10000 mg/kg) and it does not corrode me ooden structures.



Fenoxycarb

Flufenoxuron

Inhibitors of chitin production slow down biosynthesis of chitin and the production

of cuticle (i.e. the external skeleton of insects). They are efficient against wood-damaging insects even in very small doses: 0.5–3 g/m^3 in impregnated

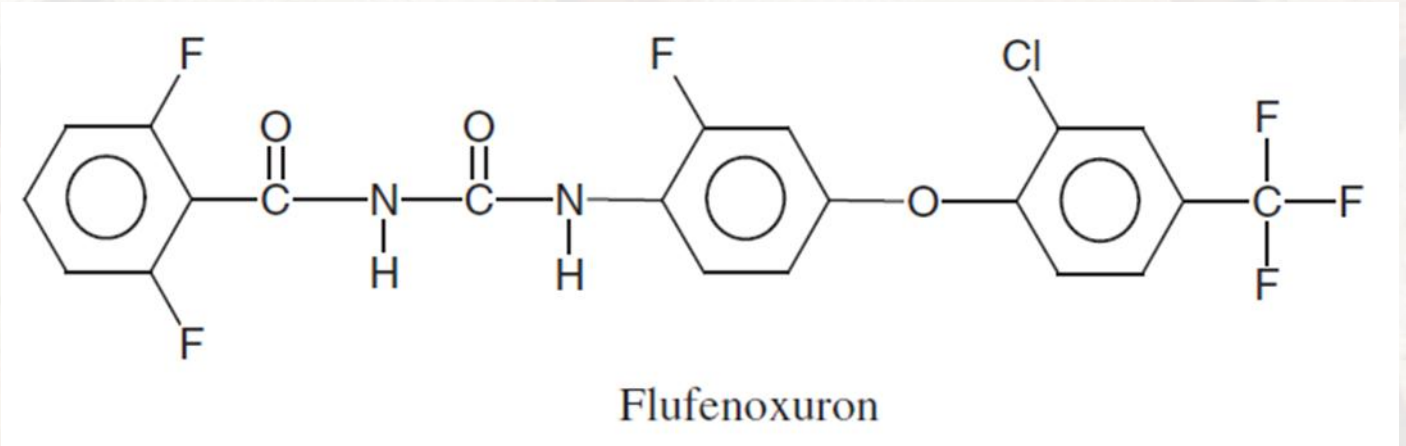
wood or 0.02–0.05 g/m^2 on wood surfaces treated by spraying or immersion.

Chitin production inhibitors are practically nontoxic for warm-blooded animals, and their ecotoxicity is negligible.

The best known ones are the derivatives of benzoyl-urea; for example, flufenoxuron.

Flufenoxuron, N-[4-(2-chlor-α,α,α-trifluor-p-tolyloxy)-2-fluor-phenyl]-

N-(2,6-difluor-benzoyl)-urea, is virtually nontoxic to humans, with an LD_{50} (oral, rats) ≥5000 mg/kg. It is stable in wood and highly resistant against weather impacts, which is contributed its minimal solubility in water and negligible volatility.



Flufenoxuron

Repellents and pheromones

Repellents are ecologically acceptable substances (e.g. some essential oils) that selectively repel some species of insects by smell or colour.

Pheromones are volatile substances produced by insects (or industrially synthesized) that affect the behaviour of individuals of the same species even in

extremely small quantities and to distance of several kilometres. Pheromones are divided into several groups, from which the best known are:

- aggregation – ensures the accumulation of the individuals of both sexes of insects at a suitable source of food;
- sexual – regulates the contact of both insect sexes;
- dispersion – motivates the behaviour of insects in time and space.

Pheromones are used mainly on round-wood yards and in forests. For example, the synthesized pheromone cis-verbenol, which is produced naturally by

female spruce bark beetles (Ips typographus), is applied in evaporators, in attracting trees, and so on. The effect of the pheromone on the selected insect

Fire retardants

Fire retardants reduce the flammability of wood and other flammable materials.

Fire retardants of wooden materials suppress the thermal decomposition and burning of wood by the following physical and chemical effects:

- They create a mass insulation layer, which restricts the ingress of oxygen to the wood and the directionally opposite transfer of the flammable gases from the wood.
- They create a thermal insulation layer, which prevent the ingress of heat from the external thermic sources to the wood; that is, either from the synthetic intumescent paints after their foaming and carbonization, or from the wood itself, which in the presence of catalytic substances is converted to charcoal.
- They dilute flammable gases with inflammable gases, which leak from the wood during its thermal decomposition.
- They reduce the concentration of oxygen in the zone of active pyrolysis, whereas they suppresses the course of exothermic thermo-oxidation reactions directly in the wood and also in the flammable gases escaping above its surfaces.
- They activate endothermic reactions, in particular dehydration reactions, and at the same time support the generation of a thermal insulation layer of charcoal, and in contrast suppress the generation of flammable gases.

Physical effects of fire retardants – mass transfer

Restriction of mass transfer by creation of mass-nonpermeable layers (of oxygen to the wood and of flammable gases, such as methane and alcohols, from the wood:

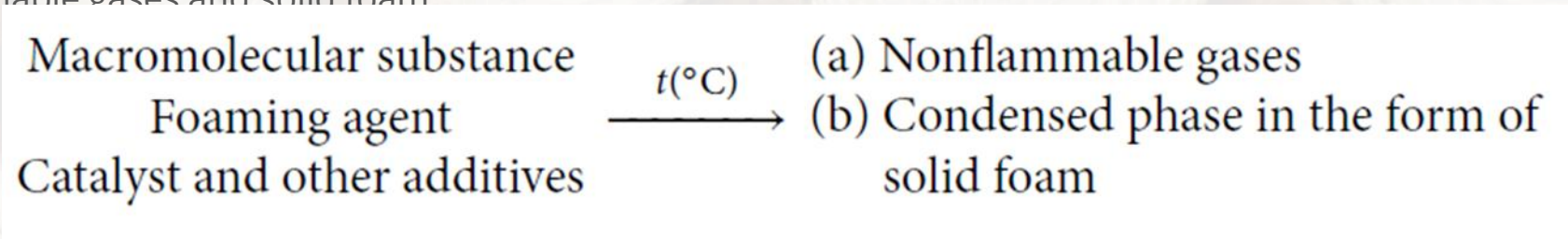
- on the outside surfaces of wood (e.g. by meltable water-glasses, based on sodium and potassium silicates, or also by intumescent paints);
- inside the wood on the S_3 layers of its cell walls (e.g. by meltable borates, such as H_3BO_3 and $Na_2B_4O_7 \cdot 10H_2O$).

Physical effects of fire retardants – heat transfer

Restriction of heat transfer by intumescent thermal-insulation solid foams created from intumescent paints or foils on wood surfaces at temperatures above 150 ◦C.

Intumescent foams have a microporous structure, which is a strong, nonflammable, and has a thermal-insulation effect. These foams protect the surfaces of wood for a rather long time (sometimes up to 30 min) against fire or radiant heat impact. Their expansion factor – that is, the relation of the thickness of the solid foam to the initial thickness of the paint – is ~50 : 1. In practice, at least 5 mm thickness of foam is desirable, which can be achieved by 300–500 g of paint per square metre of wood.

Intumescent paints and foils contain the following components, which at high temperatures create nonflammable gases and solid foam:



Physical effects of fire retardants – dilution of gases

Dilution of flammable gases released from wood with inflammable gases H_2O, NH_3 or CO_2 with the aim to inhibit exothermic oxidation reactions in molecules of the flammable gases. The probability of collisions and reactions of molecules of flammable gases with molecules of oxygen is reduced in the presence of inflammable gases, whereas the propagation of exothermic reactions is also reduced. However, the inflammable gases, such as water vapour, carbon dioxide or ammonia may not be released prematurely, but at the moment of the thermal decomposition of wood connected with the generation of flammable gases. The sources of inflammable gases are, for example:

- hydrated aluminium sulphate – $Al_2(SO_4)_3 \cdot 18\ H_2O \rightarrow H_2O$
- ammonium dihydrogen phosphate or ammonium sulphate – $NH_4H_2PO_4$ or $(NH_4)2SO_4 \rightarrow NH_3$
- potassium carbonate or sodium carbonate – K_2CO_3 or $Na_2CO_3 \rightarrow CO_2$.

Chemical effects of fire retardants

Oxidizable substances creating chemical bonds with oxygen decrease the concentration of oxygen molecules in the zone of active pyrolysis of the wood and block the burning process. Halides – for example, chlorides (Cl−) and bromides (Br−) – are mainly used for these purposes, as they are oxidized by oxygen to higher oxidation levels:

$Cl- + 0.5O_2 \rightarrow ClO- + 0.5O_2 \rightarrow ClO_2 + 0.5O_2 \rightarrow ClO-3 + 0.5O_2 \rightarrow ClO-4$

Catalytic dehydration of polysaccharides and carbonization of wood –molecules of water are created from the polysaccharides during their endothermic dehydration, while the polysaccharides are also carbonized and so less are transformed to flammable gases. The dehydration of polysaccharides is catalysed by substances based on phosphoric acid; for example, $(NH_4)2HPO_4$, $NH_4H_2PO_4$, K_3PO_4, or tri-arylphosphates.

A similar dehydration effect on wood components is attributable also to salts of other strong inorganic acids (e.g. sulphuric acid and hydrochloric acid) or to boric compounds (e.g. H_3BO_3 and $Na_2B_4O_7 \cdot 10H_2O$).

Summary

In this course you've learnt about:

- Wood Durability and Lifetime of Wooden Products
- Abiotic Degradation of Wood
- Biological Degradation of Wood
- Chemical Protection of Wood



Congratulations!

You’ve finished Wood Protection and Maintenance course.

