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(54) MINERALIZING OF WOOD OR WOODEN MATERIAL USING CALCIUM ACETATE

MINERALISIERUNG VON HOLZ ODER HOLZWERKSTOFF UNTER VERWENDUNG VON CALCIUMACETAT

MINÉRALISATION DU BOIS OU DE MATÉRIAU EN BOIS À L’AIDE D’ACÉTATE DE CALCIUM

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WO-A2-2018/065335 GB-A- 244 178
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- **KRAMB JASON ET AL: "Modeling of the catalytic effects of potassium and calcium on spruce wood gasification in CO2", FUEL PROCESSING TECHNOLOGY, ELSEVIER BV, NL, vol. 148, 1 March 2016 (2016-03-01), pages 50-59, XP029519221, ISSN: 0378-3820, DOI: 10.1016/J.FUPROC.2016.01.031**

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Description

Field of disclosure

[0001] The invention relates to a method for producing a mineralized wood or mineralized wooden material.

Background, prior art

[0002] Various methods exist to render wood or wooden material fire resistant. However, many of these methods suffer from high cost, making them economically unfeasible, or the environmental hazards associated with the materials involved. Additionally, many of the current methods lead to significant swelling of the wood or wooden material. This swelling is undesired as it may lead to alteration of the mechanical properties of the wood or wooden material. Additionally, treatment of the wood or wooden material is often accompanied by significant changes in the coloration of the wood or wooden material. These changes in coloration may also manifest upon subsequent surface coating of the wood or wooden material. Additionally, treatment of wood or wooden material is often accompanied by significant weight gain of the material. While the increased weight may be a desirable feature for limited applications, increased weight of the wood or wooden material is generally undesirable.

[0003] Given the prevalence of wood or wooden material as a major building material for the construction of houses, including multi-story houses, fire resistance of wood or wooden material is of high importance. Accordingly, different processes have been developed to render wood or wooden material more fire resistant. These processes rely on substances which result in delayed ignition, reduced heat release rate and slower spread of flames. They act on different levels, most of the time combined: promotion of char formation at lower temperature than wood usually degrades, free-radicals trapping in the flame, dilution of combustible gases coming from wood with non-combustible gases, reduction of heat content of the volatile gases, or coating protection of the wood surface. The most commonly used fire retardants for wood products are inorganic salts, of which some can absorb moisture promoting decay and destruction of metal joints. Because these salts are typically water soluble and easily leached out of wood, water-insoluble organic fire retardants have been developed, which are mainly based on amino resin systems polymerized after impregnation into wood. Unfortunately, fire retardants, despite reducing the combustion potential of wood, can also unfavorably affect following properties of wood: mechanical strength, hygroscopicity, stability, toxicity, adhesive and mechanical properties, and receptivity to coatings. Moreover, they are used in relatively large doses, which impacts the cost of the structure. The smoke emissions, together with carbon monoxide increased concentration during fire might happen as well, as it is the case with the widely used monoammonium phosphate. Intumescent coatings are easier to apply and less costly but their susceptibility to cracks, abrasion and wear results in the loss of efficiency. Methods for treating wood are disclosed in WO 2018/065335, GB 244 178 and in KRAMB JASON ET AL: "Modeling of the catalytic effects of potassium and calcium on spruce wood gasification in CO2".

Summary of disclosure

[0004] Although many processes have been developed to render wood or wooden material increasingly fire resistant, the resulting wood or wooden material often suffers from adverse side effects. These side effects include increased moisture absorption and swelling in a humid atmosphere, resulting in a considerable increase in weight. The propensity to undergo swelling under humid conditions and shrinking under dry conditions is undesirable because it leads to formation of cracks and deformations, thus limiting the structural stability of the wood or wooden material. Given the widespread use of wood or wooden material for the construction of houses across the globe, including places with varying humidity, moisture resistance is of prime importance.

[0005] A further disadvantage of wood or wooden materials containing additives to increase fire resistance are the adverse effects of the additives, such as salt deposits, on subsequent steps involving further processing of the wood or wooden material. As an example, processing of wood or wooden material containing such additives with a circular saw may lead to corrosion on the circular saw or other instruments involved in processing of the wood or wooden material as a result of the additives, including salt deposits.

[0006] Additionally, certain process for increasing fire resistance and/or for protecting the wood employ toxic components or precursors. which may be transformed into toxic compounds upon exposure to extreme temperatures.

[0007] It is therefore the general objective of the present invention to advance the state of the art with respect to wood protection. In advantageous embodiments, the disadvantages of the prior art are overcome fully or partly. Preferably, an environmentally friendly and non-toxic method to improve the fire resistance of wood and wooden materials is provided. This new method ideally also minimizes undesired swelling of the wood or wooden material upon treatment. Finally, the new method would ideally lead to minimal changes in the coloration of the wood or wooden material, including after subsequent surface coating using common surface coating agents such as linseed oil. In further advantageous embodiments, toxic components and/or the generation of toxic compounds, particularly under extreme temperatures such as in a fire, are avoided. The invention aims at providing a method for the protection of wood and wooden materials by mineralization. This method relies on water soluble reactants penetrating the material in a stepwise fashion and reacting with each other to form water insoluble salts. These salts, often present in crystalline form, are generated in situ within the cells themselves, in the cell walls, in the pits and in the middle lamellas.

Detailed Description of the invention

[0008] The general objective is achieved in a first aspect of the invention by a method comprising (i) a first impregnation step, comprising a first impregnation of wood or wooden material with an aqueous solution of potassium oxalate, (ii) a first drying step, comprising drying of the wood or wooden material, (iii) a second impregnation step, comprising a second impregnation of wood or wooden material with an aqueous solution of calcium acetate, (iv) and a second drying step, comprising drying of the wood or wooden material. Using the salt solution system potassium oxalate / calcium acetate has the advantage that toxic components are avoided. For example, halogen ions such as chloride or bromide may under extreme temperatures, i.e. under fire exposure generate toxic gases such as HCl or HBr. Therefore, the inventive method provides wood or wooden material which is safer. Additionally, calcium acetate can be used as an aqueous solution and therefore its handling is easier and safer than handling of gaseous materials. Furthermore, the generated calcium oxalate significantly improves the fire resistance of the mineralized wood or wooden material.

[0009] As the skilled person understands, drying may be achieved by exposing the impregnated wood or wooden material to increased temperatures, for example by using hot air or an oven. Alternatively, drying may be achieved by maintaining the wood or wooden material at ambient temperature until a certain water content is reached. Additionally, or alternatively, drying may be achieved by application of an underpressure, i.e. applying a vacuum.

[0010] Furthermore, impregnation may be achieved by any suitable method, such as dipping, particularly under pressure, spraying or spreading. However, preferably, impregnation is achieved by filling an autoclave with wood or wooden material and the corresponding solution and applying a pressure. Typically, the first and second impregnation are separate impregnation steps. The intermediate drying step makes the second impregnation step significantly more efficient.

[0011] Typically, the concentration of potassium oxalate dissolved in the solution lies in the range of 20%-100%, preferably 90%-100% of its saturation concentration.

[0012] In some embodiments, the concentration of calcium acetate dissolved in the solution may lie in the range of 1 5-90%, preferably 65-90% of its saturation concentration. As the skilled person understands, the saturation concentration is the maximum possibly quantity of a substance that can dissolve in the solvent, i.e. in water. Such a concentration has been found beneficial, as a calcium acetate solution with a concentration below the saturation concentration penetrates the wood or wooden material faster and deeper, i.e. the impregnation is more effective. Furthermore, the concentration is high enough to enable sufficient generation of calcium oxalate.

[0013] In certain embodiments, the first and/or the second impregnation comprises a phase of overpressure during which the pressure is selected in the range of $5\text{-}10\times10^5$ Pa (5-10 bar), preferably 8 bar, and the temperature is selected to be in the range of 15-50 °C, preferably in the range of 15-25 °C, more preferably 20°C.

[0014] In some embodiments, the duration of the phase of overpressure in the first and/or the second impregnation step is $\geq$ 1 hour, typically 1-24 h, preferably 2-8 h.

[0015] In further embodiments, the first and/or the second impregnation is preceded by a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably of $1\text{-}3\times10^4$ Pa (100-300 mbar), preferably for 30 minutes, preferably at 20 to 60 °C. The term underpressure as used herein refers to a pressure below atmospheric pressure, preferably to a pressure of up to 300 mbar.

[0016] In further embodiments the first and/or second drying step comprises a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably for a time period lying in the range of 30 minutes to 4 hours, more preferably 45 minutes to 3 hours, preferably at a temperature of 20-70 °C, more preferably 30-60 °C, and preferably at an underpressure of $1\text{ -}3\times10^4$ Pa (100-300 mbar), more preferably 100-150 mbar.

[0017] In certain embodiments, the wood or wooden material is dried to a wood moisture of 612%, preferably 8% in the second drying step.

[0018] A second aspect of the present disclosure, not according to the invention, comprises wood or wooden material which is mineralized in a method according to any of the embodiments described herein, which is characterized in that it comprises calcium oxalate deposits and is essentially free of chloride deposits, such as potassium chloride, calcium chloride or the like.

[0019] Essentially free of potassium chloride means that the content of chloride ions of the total salt content in the wood or wooden material is below 5%, i.e. below 1%, i.e. below 0.1 %, i.e. below 0.01 %, preferably 0%.

[0020] In some embodiments, wood or wooden material which is mineralized according to the present invention contains potassium acetate deposits. In a further preferred embodiment, the molar ratio of the potassium acetate deposits and the calcium oxalate deposits is in the range of 1.5:1 to 3:1, preferably 2:1.

[0021] In further embodiments, the content of calcium oxalate in the wood or wooden material which is mineralized in a method according to the present invention lies in the range of 10-20 weight percent, preferably 13-16 weight percent, more preferably 1 5-16 weight percent.

[0022] In some embodiments, the wood or wooden material comprises European oak, beech or maple, mixtures thereof or consists thereof.

[0023] In certain embodiments, oak is used as wood or wooden material for the mineralization method described herein, wherein the content of calcium oxalate in the mineralized wood lies in the range of 12-17 weight percent, preferably 15-16 weight percent.

[0024] In some embodiments, the critical heat flux, as determined according to ISO 9239-1 (version of 2010-11), exceeds 10.5 kW/m^2 for mineralized oak, wherein the content of calcium oxalate lies in the range of 12-17 weight percent, preferably 15-16 weight percent.

[0025] In some embodiments, the burning distance, as determined according to ISO 9239-1 (version of 2010-11), lies between 100 mm and 10 mm, preferably between 30 mm and 20 mm, for mineralized oak, wherein the content of calcium oxalate lies in the range of 12-17 weight percent, preferably 15-16 weight percent.

[0026] In certain embodiments, the tangential swelling coefficient at 20 °C and in the presence of 65% relative humidity lies in the range of 1%-3%, preferably 2.0%-2.6%, more preferably 2.2% and 2.4%, for mineralized oak, wherein the content of calcium oxalate lies in the range of 12-17 weight percent, preferably 15-16 weight percent.

[0027] In some embodiments, beech is used as wood or wooden material for the mineralization method described herein.

[0028] In certain embodiments, maple is used as wood or wooden material for the mineralization method described herein.

[0029] The mineralization with calcium oxalate is based on two separate impregnation steps. In the first step, the material is impregnated in an aqueous solution with potassium oxalate ($C_2O_4K_2$). After impregnation, the material is dried and then impregnated with calcium acetate ($Ca(CH_3COO)_{2}$.). The potassium oxalate already present in the material to be mineralized and the calcium acetate form calcium oxalate $\{CaC_2O_4\}_{solid}$, which is practically not soluble in water, and potassium acetate as by product.

[0030] In a preferred embodiment for mineralizing wood or wooden material, a molar ratio of 1:1.12 of potassium oxalate/calcium acetate was employed.

[0031] The molecular weight of $K_2C_2O_4$-$6H_2O$ is 184.23 g/mol, the water solubility 38.7 g/100g H_2O. The molecular weight of $Ca(CH_3COO)_2$ is 158.166 g/mol, the water solubility 34.7 g/100g in H_2O at 20°C. In a preferred embodiment, the potassium oxalate solution was prepared by dissolving 360 g Potassium oxalate hydrate in 1| H_20 and the calcium acetate solution was prepared by dissolving 309 g calcium acetate monohydrate in 1| H_2O.

Calcium acetate

[0032] Calcium acetate, in its anhydrous form, is a white solid at room temperature. It is a hygroscopic compound and forms solutions in water dissociating in calcium and acetate ions. It is commercially available in anhydrous and hydrous form as $Ca(CH_3COO)_2 \cdot H_2O$. The properties will evidently depend on its hydration degree. For the tests performed calcium acetate monohydrate was employed.

[0033] As far as safety and the environmental impact are concerned, calcium acetate and its aqueous solutions may be considered as harmless. Indeed, calcium acetate is commonly employed as food additive (E 263). Calcium acetate is therefore suited for wood impregnation and does not pose a significant danger in the event that the impregnated wood or wooden material displays residual calcium acetate.

Potassium oxalate

[0034] Potassium oxalate is a salt of oxalic acid and is commercially available as a colorless solid. In aqueous solutions it can dissociate to form oxalate and potassium ions. Oxalate ions can be combined with calcium, magnesium, and iron ions to form less soluble or insoluble salts. Potassium oxalate is commercially available in anhydrous form or as its monohydrate. In the current experiments, the monohydrate ($K_2C_2O_4 \cdot H_2O$) was used. Once the oxalate anion has reacted with the cation from the calcium acetate solution, it forms a heavy soluble salt (CaC_2O_4) that is retained in wood or wooden material, providing the protection effect.

Wood, wooden material and other cellulosic materials

[0035] The three hard-wood species commonly used as decorative wood for interior applications are European oak (*Quercus spp.*), beech (*Fagus sylvatica*) and maple *(Acer spp.).* They are representative species of European hardwood and grow across European countries.

[0036] The woods preferably used in the method according to the invention include: European oak, beech and maple.

[0037] European oak (*Quercus spp.)* is a hardwood belonging to the division of angiosperms. As it is characteristic for hardwoods, oak is composed by vessel elements, fibers (tracheids), parenchyma and ray cells. Vessels are arranged in a ring porous structure. Density varies from 0.43 - 0.69 - 0.96 g/cm^3. Characteristic for oak is a high amount of water extractives (up to 12%) including a high amount of tannins. European oak heartwood (*Quercus spp.)* is classified as heavily treatable. Treatability is the ease with which a wood can be penetrated by a liquid.

[0038] Beech (*Fagus sylvatica*) is a hardwood belonging to the division of angiosperms. As it is characteristic for hardwoods, beech is composed by vessel elements, fibers (tracheids), parenchyma and ray cells. Vessels are arranged in a non-specific pattern, resulting in a semi-porous to diffuse porous distribution. Growth ring limits are demarked by dark colored late wood. Density varies from 0.48 - 0.68 - 0.88 g/cm^3. Beech (*Fagus sylvatica*) is classified as easily treatable.

[0039] Maple *(Acer spp.)* is a hardwood belonging to the division of angiosperms. As it is characteristic for hardwoods, maple is composed by vessel elements, fibers (tracheids), parenchyma and ray cells. Vessels are arranged in a non-specific pattern, resulting in a semi-porous to diffuse porous distribution. The density of maple varies from 0.53 - 0.63 - 0.79 g/cm^3. Maple *(Acer spp.)* is classified as easily treatable.

Fire tests

[0040] The samples are placed vertically into the holding device and the burner is installed in front of the sample tilted 45°. The distance of the burner from the unprotected edge of the sample is 16mm. The flame has a length of 20mm. With this experimental set up the samples get flame treated for a fixed time depending on the material. Then the burner with the flame gets removed. The evaluation of the burning test is done via the time the sample burns after removing the flame and the dimension of the burning pattern on the surface.

[0041] The following paragraph describes the process steps of mineralisation at an industrial level for flooring according to one embodiment of the present invention. To guarantee the process safety the industrial application of this specific mineralisation will be done in two autoclaves with systems to monitor the vacuum-pressure cycle.

1.Supply of the wood material: In a preferable embodiment, the material thickness does not exceed a thickness between 2 and 5 mm, the length and width can vary. In one example, the thickness of the wood was 4 mm. The moisture content prior to treatment is between 8%-12%)

2.Filling the first autoclave with the wood or wooden material (oak, beech or maple)

3.Application of vacuum of ca. 100 mbar for 30 min at 20°C

4.Filling the autoclave with the solution of potassium oxalate

5.Application of pressure of ca. 8 bar for ca. 4 h at 20°C

6.Empty the autoclave and transport the wood material to the dryer

7.Drying the wood in a conventional kiln to a moisture content of ca. 20%

8.Filling the second autoclave with the dried wood material

9. Application of vacuum of ca. 100 mbar for 2h at 20 °C

10. Filling the second autoclave with the calcium acetate solution

11. Application of pressure of ca. 8 bar for ca. 4 h at 20°C

12. Drying the mineralized wood to 12%-16%

Parameters

[0042] The wood or wooden material obtained from mineralization may be characterized by different parameters, including the following:

The weight percentage gain (WPG) is defined as follows:

$$WPG = \frac{weight_{treated} - weight_{abs.dry}}{weight_{abs.dry}} x100; \%$$

[0043] The color changes of the wood after treatment were determined according to the CIEL*a*b* model (DIN EN ISO 11 664-4, version of 2012-06). The following parameters were determined:

$$absolute\ color\ changes\ (\Delta E) = \sqrt{(L_{untreated} - L_{treated})^2 - (a_{untreated} - a_{treated})^2 + (b_{untreated} - b_{treated})^2}$$

$$lightness\ changes\ (\Delta L) = lightness_{treated} - lightness_{untreated}$$

$$chroma\ changes\ (\Delta C) = \sqrt{(a_{untreated} - a_{treated})^2 + (b_{untreated} - b_{treated})^2}$$

[0044] The area bulking (AB) is defined as:

$$AB = \frac{width_{treated,tangential} - width_{untreated,tangential}}{width_{untreated,tangential}} \times \frac{width_{treated,radial} - width_{untreated,radial}}{width_{untreated,radial}} \times 100; \%$$

[0045] The moisture excluding efficiency (MEE) is defined as:

$$MEE = \frac{equilibrium\ moisture\ content_{untreated} - equilibrium\ moisture\ content_{treated}}{equilibrium\ moisture\ content_{untreated}} \times 100; \%$$

[0046] The swelling coefficient tangential is defined as:

$$swelling_{tangential} = \frac{width_{treated\ at\ certain\ moisture\ content} - width_{treated;abs.zero}}{width_{treated;abs.zero}} \times 100; \%$$

[0047] Thermogravimetric analysis was performed using a TG50 instrument (Mettler Toledo). The weight of the tested mineralized wood powder varies between 10-15 mg.

[0048] The fiber saturation level is defined as the moisture content of wood which is determined at a theoretical relative humidity of 100%. The fiber saturation point represents the wood moisture content at which the cell wall cannot increase its moisture content any further.

[0049] The wood moisture content is defined as the current amount of water in the wood based on the absolute dry weight of the wood.

[0050] The absolute dry weight of the wood (abbreviated as abs. dry) is defined as the mass which occurs after drying the wood at 103 °C until weight constancy. Weight constancy is defined as a weight change less than 0.1 % in 6 hours.

$$Moisture\ Content = \frac{weight_{wood\ at\ the\ current\ moisture\ content} - weight_{absolute\ \ dry}}{weight_{absolute\ dry}}$$

[0051] The wood equilibrium moisture content is defined as the moisture content which occurs if the wood is exposed under stable temperature and relative humidity.

[0052] The parameters described above were determined for oak (*Quercuss spp.*) mineralized according to the process described above (see process steps of mineralisation at an industrial level). The parameters for oak are as follows:

$$\text{WPG} = 22{,}6\% \ (\pm 0{,}6\%)$$

$$\text{Bulking}_{\text{area}} \ (\text{tangential x radial}) = 2{,}11\% \ (\pm 0.27\%)$$

[0053] Color changes of the wood, determined according to CIEL*a*b*:

$$\Delta E = 10{,}7 \ (\pm 1{,}8)$$

$$\Delta L = -8{,}5 \ (\pm 3{,}0)$$

$$\Delta C = 5{,}7 \ (\pm 2{,}0)$$

Moisture excluding efficiency (at 20 °C and 65 % relative humidity and atmospheric pressure) = -16,4% (±4,7%)

Swelling coefficient in tangential direction (at 20 °C and 65% relative humidity and atmospheric pressure) = 2,75% (±0,27%)

[0054] On set temperature of the thermal degradation, as determined by thermogravimetric analysis = 245 °C

[0055] Critical heat flux, as determined according to DIN EN ISO 9239-1 (version of 2010-11): 11.0 kW/m^2 in product direction and 11.0 kW/m^2 in direction perpendicular to the first direction

[0056] The mineralized oak was subjected to a modified ISO norm 11925-2 test, where the specimens were conditioned at 20 °C and 65% relative humidity instead of 23 °C and 50 % relative humidity involving exposure to an ignition source for 30 seconds. The time of burning after elimination of the ignition source was determined to be 0 seconds, as reproduced with 5 specimens).

[0057] The following parameters, as defined above, were determined for beech (*Fagus sylvatica*) mineralized according to the process described above (see process steps of mineralisation at an industrial level). The parameters for beech are as follows:

On set temperature of the thermal degradation, as determined by thermogravimetric analysis = 240 °C

[0058] The critical heat flux of the mineralized beech is 8.0 kW/m^2 (length) and 7.5 kW/m^2 (perpendicular), as determined according to ISO 9239-1 (version of 2010-11).

[0059] The burning distance of the mineralized beech, as determined according to ISO 9239-1 (version of 2010-11), is 220 mm (length) and 160 mm (perpendicular).

[0060] The following parameters, as defined above, were determined for maple *(Acer spp.)* mineralized according to the process described above (see process steps of mineralisation at an industrial level). The parameters for maple are as follows:

On set temperature of the thermal degradation, as determined by thermogravimetric analysis = 240 °C

[0061] The critical heat flux of the mineralized maple is 10.0 kW/m^2 (length) and 10.5 kW/m^2 (perpendicular), as determined according to ISO 9239-1 (version of 2010-11).

[0062] The burning distance of the mineralized maple, as determined according to ISO 9239-1 (version of 2010-11), is 200 mm (length) and 150 mm (perpendicular).

[0063] Further processing of the mineralized wood or wooden material, particularly oak, obtained from mineralization as described herein does not lead to corrosion on the steel devices that are used either for performing the mineralization process or for further processing of the mineralized wood or wooden material. As an example, a stainless steel bath used for mineralization of the wood or wooden material did not show any signs of corrosion. As another example, a circular saw used for further processing of the mineralized wood or wooden material did not show any signs of corrosion after the further processing.

[0064] A further advantage of the mineralized wood or wooden material obtained from the mineralization method outlined above is that the mineralized wood or wooden material displays remarkable color fastness. In particular, the untreated wood or wooden material hardly differs from the mineralized wood or wooden material in either color or color structure. Additionally, mineralized wood or wooden material, particularly oak, that has been subjected to subsequent surface coating using common surface coating agents such as linseed oil also hardly differs from the respective untreated wood or wooden material in either color or color structure.

Brief description of the figures

[0065]

Fig. 1	shows the burning distances of oak mineralized according to the invention (middle row), oak mineralized with potassium oxalate and calcium chloride (bottom row) and non-mineralized oak (top row labelled "Untreated"), as determined according to DIN EN ISO 9239-1 (version of 2010-11). As can be readily seen, mineralization with the method according to the invention, i.e. with potassium oxalate / calcium acetate is superior to other salts, such as calcium chloride / potassium oxalate, thus demonstrating the increased fire resistance.
Fig. 2	shows the adsorption isotherms (at 20 °C) of calcium oxalate mineralized oak specimens compared to untreated oak (based on 27 specimens for each variation);
Fig. 3	shows the tangential swelling of mineralized oak specimens compared to untreated oak (based on 27 specimens for each variation) exposed to various relative humidities at 20 °C. (Specimens dimensions: 4 mm × 20 mm × 50 mm; tangential, radial, longitudinal);
Fig. 4	shows the thermal gravimetric analysis (TGA) of mineralized oak and untreated oak (3 measurements for each variation à 15 mg) under nitrogen atmosphere;
Fig. 5	shows the flame paths of a mineralized oak specimen (labelled "Formulation 2") and an untreated oak specimen (labelled "untreated"), as determined according to a modified ISO 11925-2 test, where the specimens were conditioned at 20 °C and 65% relative humidity instead of 23 °C and 50 % relative humidity.

Claims

1. A method for mineralizing wood and wooden material comprising:

  i) a first impregnation step, comprising a first impregnation of wood or wooden material with an aqueous solution of potassium oxalate,
  ii) a first drying step, comprising drying of the wood or wooden material,
  iii) a second impregnation step, comprising a second impregnation of wood or wooden material with an aqueous solution of calcium acetate,
  iv) a second drying step, comprising drying of the wood or wooden material.

2. A method according to claim 1, **characterized in that** the concentration of potassium oxalate dissolved in the solution lies between 20% and 100%, preferably 90% to 100% of its saturation concentration.

3. A method according to claim 1 or 2, **characterized in that** the concentration of calcium acetate dissolved in the solution lies in the range of 1 5%-90%, preferably 65%-90% of its saturation concentration.

4. A method according to any of the preceding claims, **characterized in that** the first and/or the second impregnation comprises a phase of overpressure during which the pressure is selected to be in the range of $5\text{-}10 \times 10^5$ Pa (5-10 bar), preferably 8×10^5 Pa (8 bar), and the temperature is selected to be in the range of 15-50 °C, preferably in the range of 15-25 °C, more preferably 20 °C.

5. A method according to claim 4, **characterized in that** the duration of the phase of overpressure in the first and/or the second impregnation step is ≥ 1 hour, typically 1-24 h, preferably 2-8 h.

6. A method according to any of the preceding claims, **characterized in that** the first and/or the second impregnation is preceded by a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably of $1\text{-}3\times10^4$ Pa (100-300 mbar), preferably for 30 min, preferably at 20 to 60 °C.

7. A method according to any of the previous claims, **characterized in that** the first and/or second drying step comprises a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably for a time period lying in the range of 30 minutes to 4 hours, more preferably 45 minutes to 3 hours, preferably at a temperature of 20-70 °C, more preferably 30-60 °C, and preferably at an underpressure of $1\text{-}3\times10^4$ Pa (100-300 mbar), more preferably 100-150 mbar.

8. A method according to any of the preceding claims, **characterized in that** the wood or wooden material is dried to a wood moisture of 6%-12%, preferably 8% in the second drying step.

Patentansprüche

1. Verfahren zur Mineralisierung von Holz und Holzmaterial, umfassend:

   i) einen ersten Imprägnierungsschritt, der eine erste Imprägnierung des Holzes oder des Holzmaterials mit einer wässrigen Lösung von Kaliumoxalat umfasst,
   ii) einen ersten Trocknungsschritt, der das Trocknen des Holzes oder Holzmaterials umfasst,
   iii) einen zweiten Imprägnierungsschritt, der eine zweite Imprägnierung des Holzes oder Holzmaterials mit einer wässrigen Lösung von Calciumacetat umfasst,
   iv) einen zweiten Trocknungsschritt, der das Trocknen des Holzes oder des Holzmaterials umfasst.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Konzentration des in der Lösung gelösten Kaliumoxalats zwischen 20 % und 100 %, vorzugsweise 90 % bis 100 %, seiner Sättigungskonzentration liegt.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Konzentration des in der Lösung gelösten Calciumacetats im Bereich von 15%-90%, vorzugsweise 65%-90% seiner Sättigungskonzentration liegt.

4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die erste und/oder die zweite Imprägnierung eine Überdruckphase umfasst, während der der Druck im Bereich von $5\text{-}10\times10^5$ Pa (5-10 bar), vorzugsweise 8×10^5 Pa (8 bar), und die Temperatur im Bereich von 15-50 °C, vorzugsweise im Bereich von 15-25 °C, besonders bevorzugt 20 °C, gewählt wird.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet, dass** die Dauer der Überdruckphase im ersten und/oder zweiten Imprägnierschritt ≥1 Stunde, typischerweise 1-24 h, vorzugsweise 2-8 h beträgt.

6. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der ersten und/oder der zweiten Imprägnierung eine Vakuumphase vorausgeht, während der das Holz oder der Holzmaterial einem Unterdruck, vorzugsweise von $1\text{-}3\times10^4$ Pa (100-300 mbar), vorzugsweise für 30 min, vorzugsweise bei 20 bis 60 °C, ausgesetzt wird.

7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der erste und/oder zweite Trocknungsschritt eine Vakuumphase umfasst, während der das Holz oder Holzmaterial einem Unterdruck ausgesetzt wird, vorzugsweise für einen Zeitraum, der im Bereich von 30 Minuten bis 4 Stunden, besonders bevorzugt 45 Minuten bis 3 Stunden liegt, vorzugsweise bei einer Temperatur von 20-70 °C, besonders bevorzugt 30-60 °C, und vorzugsweise bei einem Unterdruck von $1\text{-}3\times10^4$ Pa (100-300 mbar), besonders bevorzugt 100-150 mbar.

8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Holz oder Holzmaterial im zweiten Trocknungsschritt auf eine Holzfeuchte von 6-12%, vorzugsweise 8%, getrocknet wird.

Revendications

1. Procédé de minéralisation du bois et des matériaux en bois comprenant :

    i) une première étape d'imprégnation, comprenant une première imprégnation du bois ou du matériau en bois avec une solution aqueuse d'oxalate de potassium,
    ii) une première étape de séchage, comprenant le séchage du bois ou du matériau en bois,
    iii) une deuxième étape d'imprégnation, comprenant une deuxième imprégnation du bois ou du matériau en bois avec une solution aqueuse d'acétate de calcium,
    iv) une deuxième étape de séchage, comprenant le séchage du bois ou du matériau en bois.

2. Procédé selon la revendication 1, **caractérisé en ce que** la concentration d'oxalate de potassium dissous dans la solution est comprise entre 20 % et 100 %, de préférence entre 90 % et 100 % de sa concentration de saturation.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** la concentration d'acétate de calcium dissous dans la solution est comprise entre 15 % et 90 %, de préférence entre 65 % et 90 % de sa concentration de saturation.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première et/ou la seconde imprégnation comprend une phase de surpression au cours de laquelle la pression est choisie dans la gamme de $5\text{-}10\times10^5$ Pa (5-10 bar), de préférence 8×10^5 Pa (8 bar), et la température est choisie dans la gamme de 15-50 °C, de préférence dans la gamme de 15-25 °C, plus préférentiellement 20 °C.

5. Procédé selon la revendication 4, **caractérisé en ce que** la durée de la phase de surpression dans la première et/ou la deuxième étape d'imprégnation est ≥ 1 heure, typiquement 1-24 h, de préférence 2-8 h.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première et/ou la seconde imprégnation est précédée d'une phase de vide, au cours de laquelle le bois ou le matériau en bois est exposé à une dépression, de préférence de $1\text{-}3\times10^4$ Pa (100-300 mbar), de préférence pendant 30 min, de préférence à une température de 20 à 60 °C.

7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première et/ou la deuxième étape de séchage comprend une phase de vide, au cours de laquelle le bois ou le matériau en bois est exposé à une dépression, de préférence pendant une durée comprise entre 30 minutes et 4 heures, plus préférentiellement entre 45 minutes et 3 heures, de préférence à une température de 20 à 70 °C, plus préférentiellement entre 30 et 60 °C, et de préférence à une dépression de 1 à 3×10^4 Pa (100 à 300 mbar), plus préférentiellement entre 100 et 150 mbar.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le bois ou le matériau en bois est séché jusqu'à une humidité du bois de 6 % à 12 %, de préférence 8 %, lors de la deuxième étape de séchage.

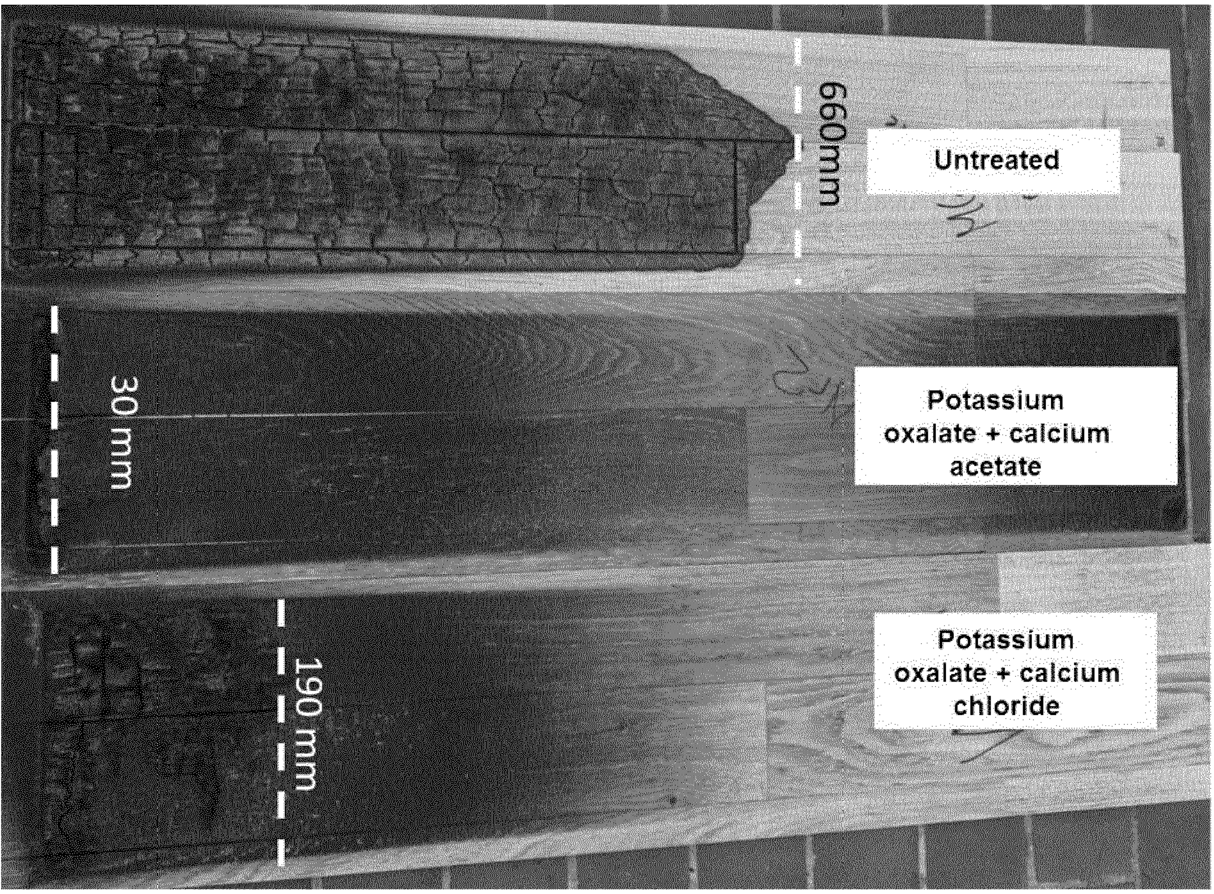
660mm
Untreated
30 mm
Potassium oxalate + calcium acetate
190 mm
Potassium oxalate + calcium chloride

Fig. 1

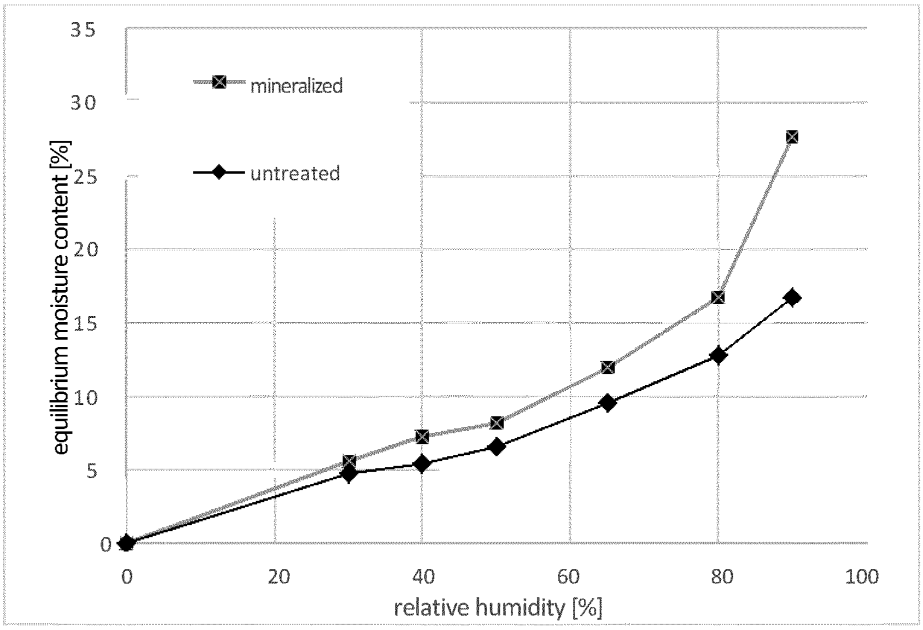
35
30
25
20
15
10
5
0
equilibrium moisture content [%]
mineralized
untreated
0
20
40
60
80
100
relative humidity [%]

Fig. 2

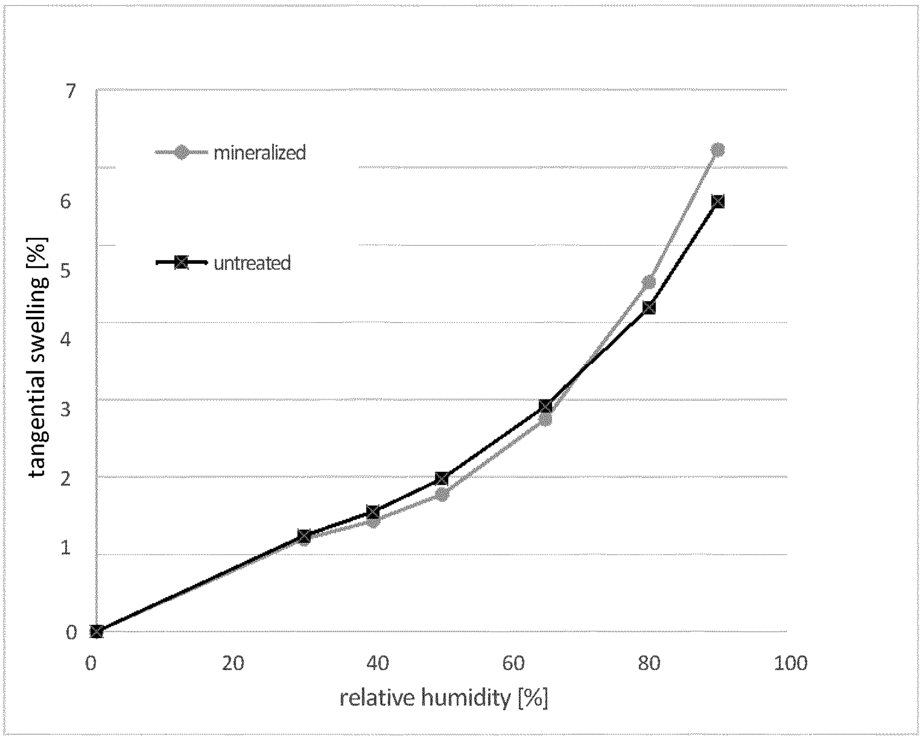
7
6
5
4
3
2
1
0
tangential swelling [%]
mineralized
untreated
0
20
40
60
80
100
relative humidity [%]

Fig. 3

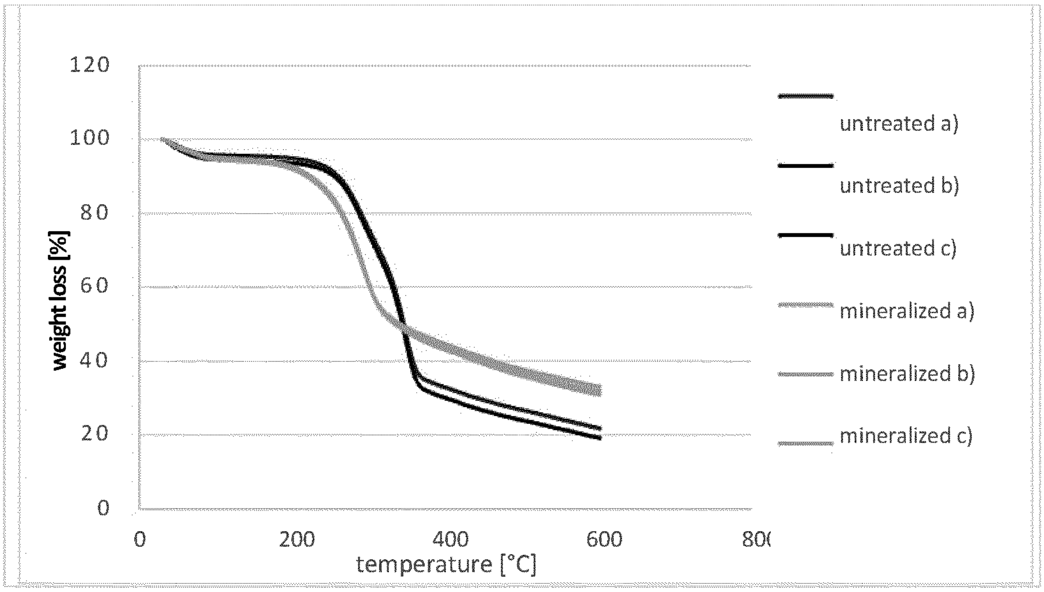
120
100
80
60
40
20
0
weight loss [%]
0
200
400
600
80(
temperature [°C]
untreated a)
untreated b)
untreated c)
mineralized a)
mineralized b)
mineralized c)

Fig. 4

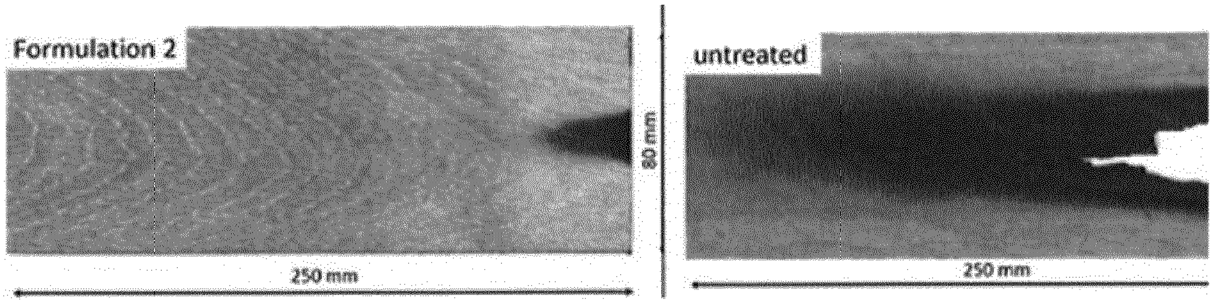
Formulation 2
250 mm
80 mm
untreated
250 mm

Fig. 5

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2018065335 A **[0003]**
- GB 244178 A **[0003]**

Non-patent literature cited in the description

- **KRAMB JASON et al.** *Modeling of the catalytic effects of potassium and calcium on spruce wood gasification in CO2* **[0003]**