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(54) **MINERALIZING OF WOOD AND CELLULOSIC MATERIALS**

MINERALISING OF WOOD AND CELLULOSIC MATERIAL

MINÉRALISATION DU BOIS ET DE MATIÈRES CELLULOSIQUES

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(56) References cited:
EP-A1- 2 937 193
GB-A- 191 306 179
JP-A- 2001 001 306
SU-A1- 1 541 056
US-A1- 2002 094 937
US-A1- 2002 110 677

- **CHANGYU LIU ET AL: "Fabrication of superhydrophobic wood surfaces via a solution-immersion process", APPLIED SURFACE SCIENCE, ELSEVIER, AMSTERDAM, NL, vol. 258, no. 2, 18 August 2011 (2011-08-18), pages 761-765, XP028313931, ISSN: 0169-4332, DOI: 10.1016/J.APSUSC.2011.08.077 [retrieved on 2011-08-25]**
- **Laboratory Forest Products: "The fiber saturation point of wood", , 1 June 1944 (1944-06-01), XP055682581, Retrieved from the Internet: URL:https://www.fpl.fs.fed.us/documnts/fpltn/fpltn-252.pdf [retrieved on 2020-04-03]**
- **THALER N ET AL: "Bioincising of Norway spruce wood using wood inhabiting fungi", INTERNATIONAL BIODETERIORATION & BIODEGRADATION, ELSEVIER, AMSTERDAM, NL, vol. 68, 10 November 2011 (2011-11-10), pages 51-55, XP028397570, ISSN: 0964-8305, DOI: 10.1016/J.IBIOD.2011.11.014 [retrieved on 2012-01-10]**

EP 3 519 147 B1

Description

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

[0002] More particularly, the invention relates to mineralized wood and wooden material suitable for indoor and outdoor use and methods for making such materials. Various attempts have been heretofore madeto protect wood, wooden material and other cellulosic material against fungi and to improve its fire resistance/reaction to fire. Many of the methods developed were either too costly to be economically feasible or not environmentally safe.

[0003] The chemical protection of wood against wood destroying fungi is divided into two different approaches: a) the prevention of the colonization and b) the killing of fungi after they have already colonized wood. According to this, different chemicals are used. In the following, only the application of active agents which can prevent a colonization of wood will be discussed.

[0004] In general wood preservatives have to meet certain requirements. They have to be efficient against the target organism and the active agents need to be fixed and stabilized in the wood in order to avoid a leaching and evaporation. The ecological impact needs to be as small as possible and its effect should not be a risk for the environment and humans.

[0005] The known products can be divided into three groups: i) water based salts, ii) solvent based formulations, and iii) creosotes. Basically, water solved metal salts are not stable in wood and are therefore only used for indoor applications. Apart from some essential additives they consist of 80-100% of the active agent. They are easily washed out and already after one rain fall, the whole effect of the substance can be lost if the application was done by brushing or dipping. The main substances are fluoride, silicate or borate. The different salt formulations can further be differentiated by the solubility and penetration behavior.

[0006] For outdoor uses the above mentioned salt formulations need to be fixed with chrome. Within 4-6 weeks after the application chrome salts react with certain wood components. Thereby leaching can be significantly reduced. The fixation of chrome salts in wood is based on the reduction of chrome (VI) to chrome (III). With chrome (III) the fluorine or copper salts react to insoluble chemical combinations and become very weather resistant. Parallel to the fixation of the salts the color of the wood changes as well from yellow-orange to olive-green. The chrome functions mainly as fixing agent. Certain chrome compounds (chrome (VI), for example zinc chromate) are very toxic to animals and humans.

[0007] The addition of copper in the salt formulations provides additional protection against soft rot. These salts can be used for impregnation of wood in very wet conditions and in soil contact. The expected rates of leaching for copper-chrome combinations are about 5%. Common water soluble metal salts are: Chrome-fluoride-salts, Chrome-fluoride-boron-salts, Chrome-copper-salts, Chrome-copper-boron salts and Chrome-copper-fluoride salts.

[0008] The use of creosotes is restricted to special applications. Railway sleepers represent the main field for impregnation with creosotes. The efficiency of the creosotes depends on their composition. Products with high concentrations of polycyclic aromatic compounds with 4-6 rings show the best efficiency. A coating of creosote treated wood is not possible. Depending on certain circumstances creosotes can migrate and pollute the surface. Creosote impregnated parts need to be treated as hazardous waste after their lifetime.

[0009] Solvent based preservative formulations are used for indoor and outdoor applications with no ground contact. The common fields of application are usually class of utilization 1 - 3 (regarding EN 335, for example class 3 windows and doors). The basic components are organic solvents, biocide active substances, binders and pigments. These products are mainly water stable and cannot be leached out but they do not show the necessary performance in earth contact. The concentration of the active substances is normally between 0.5 - 5 % because they are highly efficient. The active agents in solvent based preservatives belong to the same groups like the biocide agents in herbicides, but they differ in certain points significantly. The aspects of special interest for this type of wood preservatives are: penetration depth, low evaporation of the active agent, no crystallization at the surface, smelling behavior, binder and pigment concentration. Frequently used organic biocide systems are: Permethrin, Deltamethrin, Dichlofluanid, Propiconzol and Tebuconazol.

[0010] All of the above mentioned agents exhibit a certain protection behavior, however they all transform the wood into a toxic material.

[0011] Beside the degradation via fungi wood can also be destroyed by fire. Therefore a comprehensive fire protection is necessary and becomes more and more important especially for multi-story houses made from wood. To influence the fire resistance wood can be treated with different systems of fire retardants.

[0012] A treatment with these substances results 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 retard-

ants, 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. EP2937193A1 discloses a method for mineralising wood to improve its fire resitance comprising impregnating the wood with a first solution of a first metal salt, followed by impregnation with a second solution of a second salt.

[0013] It is therefore an objective of the present invention to overcome these and other disadvantages characterizing the prior art and provide an environmentally friendly and non-toxic method to protect wood and wood containing materials against fungi and to improve their fire resistance.

Summary of the Invention

[0014] The purpose of this invention is to provide a method for protecting wood and wooden material by mineralization. Due to the novel mineralization method, the water soluble reactants penetrate the material stepwise and water insoluble salts, preferably in crystalline form, are generated in situ within the cells themselves, in the cell walls, in the pits and in the middle lamellas.

[0015] A further purpose of this invention is to provide mineralized products, i.e. wood, wooden material, in such a way as to allow their intended functions while also providing one or more of the following properties or functions: i) protection against fungi, ii) improving their biological resistance, iii) improving moisture and weather resistance, iv) reducing flammability, v) improved fire resistance.

Detailed Description of the Invention

[0016] The purpose of this invention is to provide an improved method for mineralization of wood and wooden material, for example materials containing wood, such as windows, tables and doors, the 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 of wood or wooden material iii) a second impregnation step, comprising a second impregnation of wood or wooden material with an aqueous solution of calcium chloride and iv) a second drying step, comprising drying of the wood or wooden material.

[0017] Typically, the concentration of potassium oxalate dissolved in the solution is 100% of their saturation concentration. Additionally, the concentration of calcium chloride dissolved in the solution may be 100% of its saturation concentration. It is preferred that the first and/or the second impregnation comprises a phase of overpressure during which the pressure is selected in the range of 5 - $10x10^5$ Pa (5-10 bar) and the temperature in the range of 15 to 50°C. According to a further preferred embodiment, the duration of the phase of overpressure in the first and/or the second impregnation step is ≥ 1 hour, typically 1-24 h, preferably 4-8 h .

[0018] According to a further preferred embodiment, 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 for 30 minutes at 40 to 60 °C and preferably to an underpressure of 1 - $3x10^4$ Pa (100-300 mbar).

[0019] According to a further preferred embodiment the wood or wooden material is dried above the fiber saturation level of 28-35%, preferably 30% in the first drying step. A fiber saturation level of 100% (fiber saturation point) is the point in the drying process at which only water bound in the cell walls remains and all other water having been removed from the cell cavities.

[0020] The first drying step comprises preferably a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably for 30 minutes at 40 to 60 °C and preferably at an underpressure of 1 - $3x10^4$ Pa (100-300 mbar).

[0021] Typically, the wood or wooden material is dried to a wood moisture, preferably a wood moisture of 12 to 16% in the second drying step. The wood moisture is calculated by the formula $(m_s-m_d)/m_d$ *100, wherein m_s is the mass of the sample and m_d is the mass of the sample after drying in an oven at 103 °C until mass constancy.

[0022] Wood or wooden material which is mineralized in a method according to the present invention is characterized in that calcium oxalate of low or no solubility in water is deposited in the wood or wooden material, preferably in crystalline form.

[0023] Preferably the untreated wood or wooden material gains 40 - 50 %, by mineralization with calcium oxalate.

Mineralization with calcium oxalate

[0024] The mineralization with calcium oxalate is based on two impregnation steps. In the first step, the material is impregnated in an aqueous solution with potassium oxalate $C_2O_4K_2$. After impregnation with the anion, the material is dried and then impregnated with calcium chloride $CaCl_2$ (cation). The potassium oxalate already present as anion in the material to be mineralized and the calcium chloride form calcium oxalate $\{C_2O_4Ca\}_{solid}$, preferably in crystalline form, which is practically not soluble in water, and KCl.

[0025] In this reaction, the molar ratio between both reactive compounds is 1:1. For each reactive compound preferably a solution of equimolar content is prepared.

The molecular weight of $C_2O_4K_2 \cdot H_2O$ is 184.23 g/mol, the water solubility 38.7 g/100g H_2O. The molecular weight of $CaCl_2 \cdot 6H_2O$ is 219.08 g/mol, the water solubility 81.3 g/100g H_2O. For equimolar solutions 387 g potassium oxalate is dissolved per 1L H_2O and 460 g calcium chloride per 1L H_2O.

Calcium chloride ($CaCl_2$)

[0026] Calcium chloride is an ionic halide in solid state at room temperature. $CaCl_2$ is a hygroscopic compound and forms solutions in water dissociating in calcium and chloride ions. It can be commercially found in pure state, but more commonly as hydrated compound for example as mentioned above as $CaCl_2 \cdot 6H_2O$, or as $CaCl_2 \cdot 4H_2O$, $CaCl_2 \cdot 2H_2O$ or $CaCl_2 \cdot H_2O$. Properties will evidently depend on its hydration degree. For the tests performed $CaCl_2 \cdot 6H_2O$ was employed.

[0027] From the safety and environmental side, calcium chloride and its solutions represent the same risks as other common non-toxic chlorides, e.g. NaCl, LiCl and KCl. Therefore its solutions can be considered as harmless to plants and soil, hence environmentally friendly for wood impregnation, if some residues of this compound remain.

Potassium oxalate ($C_2O_4K_2$)

[0028] Potassium oxalate is a salt of oxalic acid. Its appearance is that of transparent and colorless crystals. 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 water-soluble or insoluble salts. Potassium oxalate is commercially available as anhydrous and monohydrate salt. In the current experiments, the monohydrate ($C_2O_4K_2 \cdot H_2O$) was used. Once the oxalate anion has reacted with the cation from the calcium chloride solution it forms an insoluble salt (C_2O_4Ca) that is retained in wood, providing the protection effect.

Wood, wooden material.

[0029] Two wood species commonly used in construction are beech (Fagus sylvatica) and pine (Pinus sylvestris). They are representative species of European hardwood and softwood and grow in important volume in Switzerland and other central European countries. Furthermore, they are listed as suggested species in the norm EN 113, for biological tests of impregnated wood. These two wood species were used in the experiments described below.

[0030] 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.

[0031] Pine (Pinus sylvestris) is a softwood belonging to the division of conifers. Pine is mainly composed by tracheids, as is characteristic for softwoods and has well differentiated thick walls in late wood and thin walls in early wood. Density varies from 0.3 - 0.49 - 0.86 g/cm^3 (in the early zone).

[0032] Further types of wood preferably used in the method according to the invention are: silver fir, maple, cotton wood and alder.

[0033] Wood which fulfils the requirements for wood according to the norm EN 113 is preferably used and mineralized in the method according to the present invention. The main requirements of the norm EN 113 are:

a) Wood quality: wood should have straight grains and no knots. Pine should be exclusively of sapwood and poor in resin. Beech should not have red heart.

b) The number of annual rings in the width direction must be 2.5 - 8 per cm for pine, and 2 - 6 per cm for beech.

c) The direction of the rings in the cross section could have any direction but should not be tangential to the width direction of the cross section.

d) The proportion of latewood in the cross section should not be more than 30%.

e) Moisture content in wood should be 12%.

f) Wood must not have floated in water, not have been dried over 60°C and neither have been chemically treated.

g) The density of samples must not vary more than ± 10% from the mean value for samples that will be treated and not more than ± 20% for samples that will be used for control.

h) The stated size of specimens is 50x25x15 mm^3.

Leaching: brief description of the EN84 procedure

[0034] In order to evaluate and quantify the mineralization process (i.e. the retention of impregnated insoluble material in treated specimens) leaching tests were performed. The description of the leaching process can be found in the standard EN84. A summary of the main points to be considered for the current tests is presented below.

a) Specimens to be leached include untreated samples (control) besides the ones that are mineralized.

b) Every material species and treatment must be

separated in different leaching baths. The quantity of deionized water is 100mL per sample of 50x25x12mm^3. As for impregnation, specimens need to be completely covered and weights need to be added to avoid samples to float.

c) First, specimens submerged into the deionized water bath undergo a vacuum (40 mbar) during 20 min. Then, they stay at atmospheric pressure during 2 hours. Afterwards this first water bath is poured and changed.

d) Samples are then transferred to a room at 20 ± 2 °C and 65 ± 5 % RH. Here, samples remain during 14 days, and water is changed 9 times. The first change must be done after 1 day and the following after 2 and 3 days.

Biological tests

[0035] The biological tests were done on the basis of the European Standard EN 113 (European Standard, 1996) with some modifications in order to allow accelerated tests. Two series of biological tests have been carried out in order to evaluate the resistance of the mineralized woods, wooden materials and other cellulosic materials against fungi and biological degradation.

[0036] According to the literature (Bravery and Dickinson, 1978) it is possible to employ smaller wooden blocks in order to accelerate the duration of the test to 6 to 10 weeks, depending on the size of the samples (EN 113 incubation time is 16 weeks). This method has been used for the present tests.

[0037] Fungi used in the tests were Coniophora puteana, Coriolus versicolore and Poria placenta.

[0038] For characterization two methods were employed. For gravimetry the weight of wood specimens was measured at several points of the experimental process. Since the reactives/products of impregnation/mineralization have a significant weight and concentration, the gained weights in wood and other specimens treated were perfectly measureable. Obviously, specimens with bigger sizes give more accurate results than small ones, since the volume of samples and absorbed materials are already more representative. For microscopy (as the second method) analysis were done with raster electron microscope, Hitachi TM 1000 with a Wolfram Cathode (Voltage: 15kV) as electron source and a backscattering electron detector with a magnification of 20-10'000.

[0039] The samples were prepared in several different ways. For each mineralization type, samples were boiled or simply humidified on the surface. With this approach it was possible to estimate stability against leaching. The cutting was done with a sliding microtome and single use knifes. To understand the changes due to the impregnation procedure and due to the degradation by fungi, reference samples were prepared as well.

Evaluation of treatment efficiency

[0040] The weight loss percentages of mineralized samples was determined after attack with different fungi according to EN 113 and before leaching.

[0041] In all treatments, impregnated samples suffered less weight loss after fungi attack (not higher than 4% for the majority of treated samples) than control samples that were placed in the same fungi infested petri dishes.

Fire tests

[0042] The fire tests were performed according to EN ISO 11925-2. 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.

Brief Description of the Figures

[0043]

Fig. 1 shows a schematic flow chart of the mineralization method according to the present invention;

Fig. 2 shows a schematic flow chart of an preferred embodiment of the mineralization method according to the present invention comprising vacuum phases preceding the first and the second impregnation;

Fig. 3 compares the solid content of Pine and Beech samples treated by methods T1, T2 and T3 before and after leaching, (T1 calcium oxalate, T2 calcium methylsiliconate, T3_gas polymethyl silicic acid polymerized with pressurized CO_2, T3_liq polymethyl silicic acid polymerized with liquid CO_2);

Fig. 4 shows the weight loss of samples mineralized with calcium oxalate and control samples after exposure to fungi (following EN 113) before leaching, illustrating a clear trend showing that impregnated samples provide a protection effect of wood against fungi attack. Furthermore, Fig, 4 shows that Coniophora puteana cultures are more active than Coriolus versicolor cultures. P-T1-CN (Pine Calcium oxalate Coniophora puteana), P-T1-CR (Pine Calcium oxalate Coriolus versicolor), B-T1-CN (Beech Calcium oxalate Coniophora puteana), B-T1-

CR (Beech Calcium oxalate Coriolus versicolor);

Fig. 5 shows the weight loss of samples mineralized with Calcium methyl siliconate and control samples after exposure to fungi (following EN 113) before leaching. Fig. 5 illustrates a clear trend showing that impregnated samples provide a significant protection effect of wood against fungi attack. P-T2-CN Pine Calcium methyl siliconate Coniophora puteana, P-T2-CR Pine Calcium methyl siliconate Coriolus versicolor, B-T2-CN Beech Calcium methyl siliconate Coniophora puteana, B-T2-CR Beech Calcium methyl siliconate Coriolus versicolor;

Fig 6 shows burning time after removal of the flame for different mineralized wood samples of fir and beech, following EN ISO 11925-2 (treatment 1 calcium oxalate, treatment 2 Calcium methyl siliconate, treatment 3 polymethyl silicic acid). As can be seen, all treatments 1-3 significantly improve the fire resistance of the wooden samples;

Fig. 7 to Fig. 11 show pine and beech samples mineralized with Calcium methyl siliconate and Calcium oxalate and polymethyl silicic acid.

Fig 7 shows REM images of an untreated reference beech sample before (a) and after (c) fungi attack as well as of untreated reference pine sample before (b) and after (d) fungi attack (Coniophora puteana). In beech the degradation caused by Coniophora puteana (c) becomes obvious by the holes between the cells, in pine, (d) the degradation by the same fungi leads to cracking of the cell walls.

Fig 8 shows REM images of beech treated with calcium chloride and potassium oxalate after leaching for 9 days and boiling for 4 hours (11 7°C). Calcium oxalate crystals are produced in the lumen of the cells. Mainly the vessels are filled with calcium oxalate (a, c), but also in the lumen of the fibers and parenchyma cells (b) Oxalate crystals are present. The reaction product not always fills the whole cell lumen but it covers the cell wall surface (a, d).

Fig 9 shows REM images of pine treated with calcium chloride and Potassium oxalate after leaching for 9 days. The oxalate crystals can be detected in the late and early wood tracheids (a,b). Mainly the cell walls (e) are covered but sometimes the whole lumen is filled (c,d). A high concentration of reaction product is present in the bordered pits (f). As the REM samples were taken from the center of the wood piece, and the calcium oxalate is distributed over the whole sample, Figure 9 demonstrates that the impregnation takes place in the whole sample and in almost every cell.

Fig 10 shows REM images of beech treated with calcium chloride and potassium methyl siliconate after leaching for 9 days and boiling 4 hours (117°C). The lumen of the cells and the fibers are filled, the crystals form a solid bloc (a, b). The cell wall layer is also infiltrated and intensively covered with the reaction product (c (leached and boiled), d (only leached)). The cavities of the radial parenchyma cells are less filled in comparison to the bigger lumen of the vessels (e).

Fig 11 shows REM images of pine treated with calcium chloride and potassium methyl siliconate after leaching for 9 days. Siliconates are visible in the early and late wood tracheids (a). Some of the cells are completely filled with the siliconate crystals (b) and sometimes the cell wall is covered by a layer of these crystals (e). The membranes of the bordered pits are often infiltrated and mineralized by the impregnation products (c, d).

[0044] The following paragraph describes the process steps of mineralization at an industrial level for facade claddings according to one embodiment of the present invention. The procedure can be applied for the mineralization with calcium oxalate and calcium methyl siliconate, the latter not forming part of the invention.

[0045] To guarantee the process safety the industrial application of this specific mineralization will be done in two autoclaves with systems to monitor the vacuum-pressure cycle.

1. Supply of the wood material: dimensions 120x20x2500mm (moisture content between 12-16%)
2. Filling the first autoclave with the wood material (beech or pine),
3. Filling the autoclave with the solution of the anion (Potassium methyl siliconate or Potassium oxalate)
4. Application of vacuum of ca. 100 mbar for 2 h
5. Application of pressure of ca. 8 bar for ca. 4 h and temperature in the range of 15 -25 °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. 30%
8. Filling the second autoclave with the dried wood material
9. Filling the second autoclave with the cation solution (Calcium chloride)
10. Application of vacuum of ca. 100mbar for 2h

11. Application of pressure of ca. 8bar for ca. 4h and temperature in the range of 15 - 25 °C
12. Drying the mineralized wood to 12-16%

[0046] The following paragraph describes the process steps of mineralization at an industrial level for facade claddings not according to the invention. The procedure can be applied for the mineralization with polymethyl silicic acid. The industrial application of the mineralization will be done in one autoclave with a system to monitor the vacuum-pressure cycle.

1. Supply of the wood material: dimensions 120x20x2500mm (moisture content between 12-16%)

2. Filling the autoclave with the wood material (beech or pine),

3. Filling the autoclave with the solution of the anion (Potassium methyl siliconate)

4. Application of vacuum of ca. 100 mbar for 2h

5. Application of pressure of ca. 8 bar for ca. 4h and temperature in the range of 15 - 25 °C

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

7. Drying the wood in a conventional kiln to a moisture content of about 30%

8. Filling the autoclave with the dried wood material

9. Application of CO_2 in gaseous state with ca. 2 bar for 10 h. and temperature in the range of 15 -25 °C

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 chloride,
   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 is 100% of its saturation concentration.

3. A method according to claim 1 or 2, **characterized in that** the concentration of calcium chloride dissolved in the solution is 100% 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 in the range of 5 - $10x10^5$ Pa (5-10 bar) and the temperature in the range of 15 -50 °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.

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-$3x10^4$ Pa (1 00-300 mbar) and preferably for 30 min at 40 to 60 °C.

7. A method according to any of the preceding claims, **characterized in that** the wood or wooden material is dried to the fiber saturation level of 28-35%, preferably 30%, in the first drying step, wherein a fiber saturation level of 100% represents the fiber saturation point, the point in the drying process at which only water bound in cell walls remains and all other water having been removed from the cell cavities.

8. A method according to any of the previous claims, **characterized in that** the first drying step comprises a vacuum phase, during which the wood or wooden material is exposed to underpressure, preferably for 30 minutes at 40 to 60 °C and preferably at an underpressure of 1 -$3x10^4$ Pa (1 00-300mbar).

9. A method according to any of the preceding claims, **characterized in that** the wood or wooden material is dried to a wood moisture, preferably a wood moisture of 12 to 16% in the second drying step.

Patentansprüche

1. Verfahren zum Mineralisieren von Holz und Holzmaterial, umfassend:

   i) einen ersten Imprägnierschritt, umfassend eine erste Imprägnierung von Holz oder Holzmaterial mit einer wässrigen Lösung von Kaliumoxalat,
   ii) einen ersten Trocknungsschritt, umfassend Trocknen des Holzes oder Holzmaterials,

iii) einen zweiten Imprägnierschritt, umfassend eine zweite Imprägnierung von Holz oder Holzmaterial mit einer wässrigen Lösung von Calciumchlorid,
iv) einen zweiten Trocknungsschritt, umfassend Trocknen des Holzes oder Holzmaterials.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Konzentration von Kaliumoxalat, das in der Lösung gelöst ist, 100 % von dessen Sättigungskonzentration beträgt.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Konzentration von Calciumchlorid, das in der Lösung gelöst ist, 100 % von dessen Sättigungskonzentration beträgt.

4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die erste und/oder die zweite Imprägnierung eine Überdruckphase umfasst, während welcher der Druck im Bereich von 5 bis $10x10^5$ Pa (5 bis 10 bar) und die Temperatur im Bereich von 15 bis 50 °C gewählt wird.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet, dass** die Dauer der Überdruckphase in dem ersten und/oder dem zweiten Imprägnierschritt ≥ 1 Stunde beträgt.

6. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der ersten und/oder der zweiten Imprägnierung eine Vakuumphase vorangeht, während welcher das Holz oder Holzmaterial Unterdruck ausgesetzt wird, vorzugsweise bei 1 bis $3x10^4$ Pa (100 bis 300 mbar) und vorzugsweise für 30 Minuten bei 40 bis 60 °C.

7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Holz oder Holzmaterial in dem ersten Trocknungsschritt auf das Fasersättigungsniveau von 28 bis 35 %, vorzugsweise 30 % getrocknet wird, wobei ein Fasersättigungsniveau von 100 % den Fasersättigungspunkt wiedergibt, den Punkt in dem Trocknungsprozess, bei dem nur in Zellwänden gebundenes Wasser verbleibt und alles andere Wasser aus den Zellhohlräumen entfernt worden ist.

8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der erste Trocknungsschritt eine Vakuumphase umfasst, während welcher das Holz oder Holzmaterial Unterdruck ausgesetzt wird, vorzugsweise für 30 Minuten bei 40 bis 60 °C und vorzugsweise bei einem Unterdruck von 1 bis $3x10^4$ Pa (100 bis 300 mbar).

9. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Holz oder Holzmaterial in dem zweiten Trocknungsschritt auf eine Holzfeuchtigkeit, vorzugsweise eine Holzfeuchtigkeit von 12 bis 16 % getrocknet wird.

Revendications

1. Procédé de minéralisation de bois et de matériau en bois comprenant :

i) une première étape d'imprégnation, comprenant une première imprégnation de bois ou de 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 de bois ou de matériau en bois avec une solution aqueuse de chlorure 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 100 % de sa concentration de saturation.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** la concentration de chlorure de calcium dissous dans la solution est 100 % de sa concentration de saturation.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première et/ou la deuxième imprégnation comprend une phase de surpression pendant laquelle la pression est sélectionnée dans la plage de 5 à 10×10^5 Pa (5 à 10 bar) et la température dans la plage de 15 à 50 °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.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première et/ou la deuxième imprégnation est précédée par une phase sous vide, pendant laquelle le bois ou le matériau en bois est exposé à une sous-pression, de préférence de 1 à 3×10^4 Pa (100 à 300 mbar) et de préférence pendant 30 min à 40 à 60 °C.

7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le bois ou le matériau en bois est séché au niveau de saturation des fibres de 28 à 35 %, de préférence 30 %, dans

la première étape de séchage, dans lequel un niveau de saturation des fibres de 100 % représente le point de saturation des fibres, le point dans le processus de séchage auquel seule l'eau liée dans les parois cellulaires est présente et toute autre eau ayant été éliminée des cavités cellulaires.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la première étape de séchage comprend une phase sous vide, pendant laquelle le bois ou le matériau en bois est exposé à une sous-pression, de préférence pendant 30 minutes et à 40 à 60 °C, et de préférence à une sous-pression de 1 à 3 $\times$ 10^4 Pa (100 à 300 mbar) .

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le bois ou le matériau en bois est séché à une humidité de bois, de préférence une humidité de bois de 12 à 16 % dans la deuxième étape de séchage.

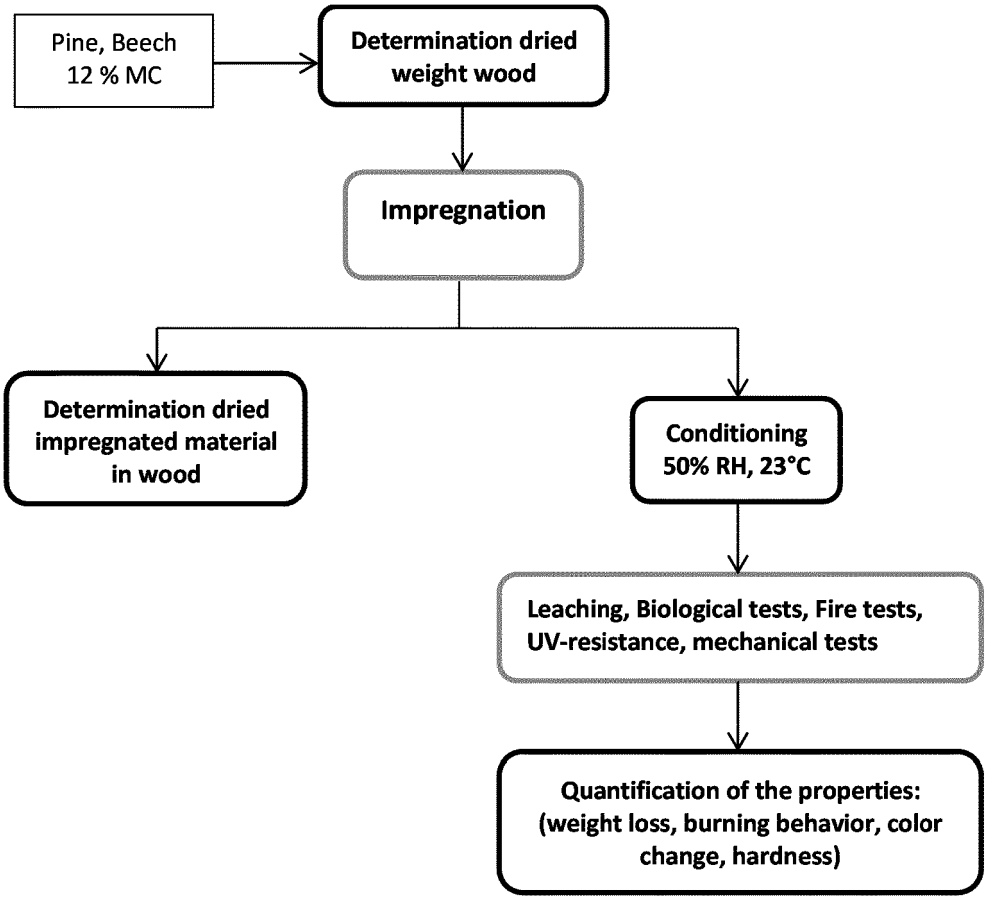

Pine, Beech
12 % MC
Determination dried weight wood
Impregnation
Determination dried impregnated material in wood
Conditioning 50% RH, 23°C
Leaching, Biological tests, Fire tests, UV-resistance, mechanical tests
Quantification of the properties: (weight loss, burning behavior, color change, hardness)

Fig. 1

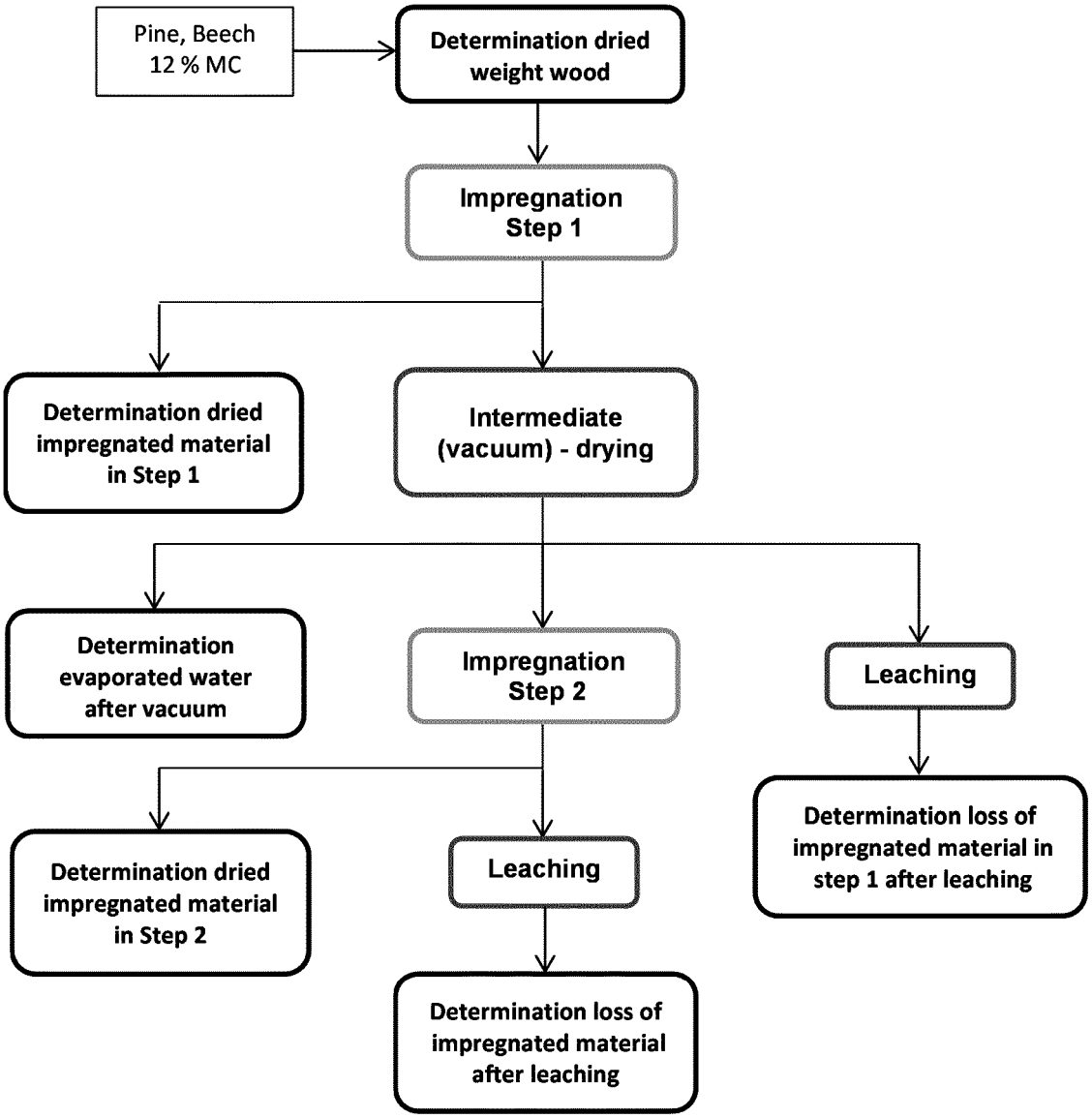
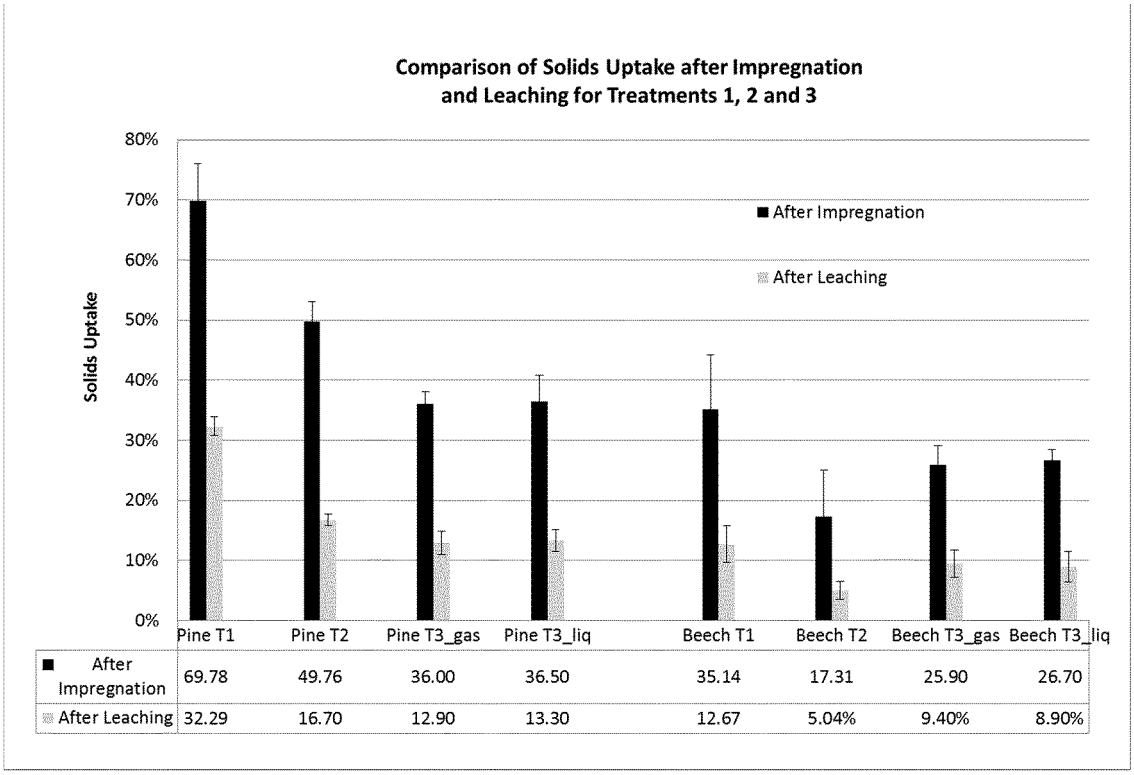
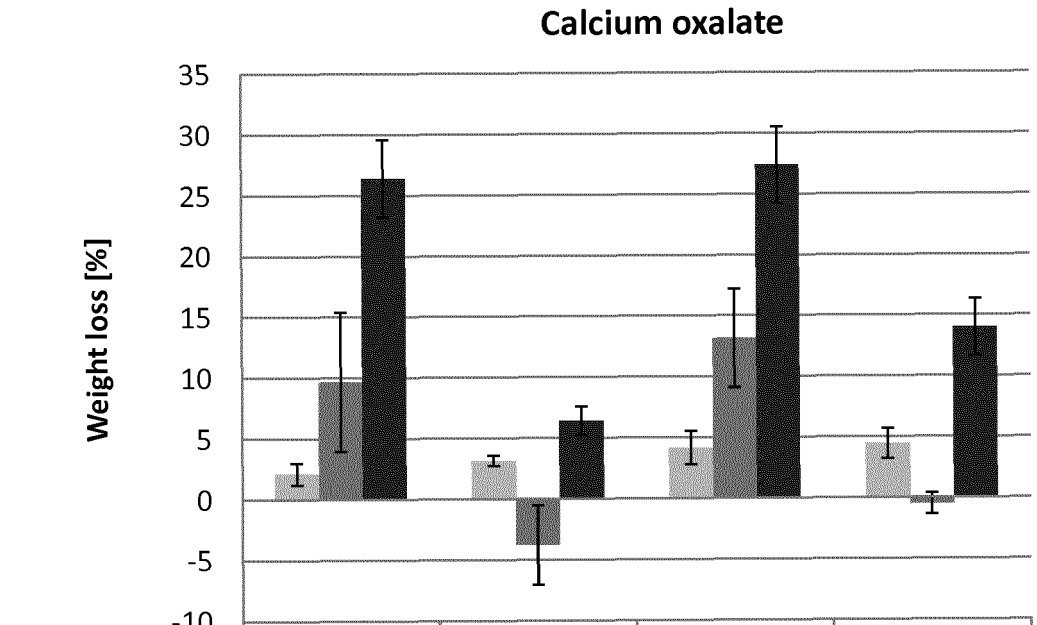

Pine, Beech
12 % MC
Determination dried weight wood
Impregnation Step 1
Determination dried impregnated material in Step 1
Intermediate (vacuum) - drying
Determination evaporated water after vacuum
Impregnation Step 2
Leaching
Determination loss of impregnated material in step 1 after leaching
Determination dried impregnated material in Step 2
Leaching
Determination loss of impregnated material after leaching

Fig. 2



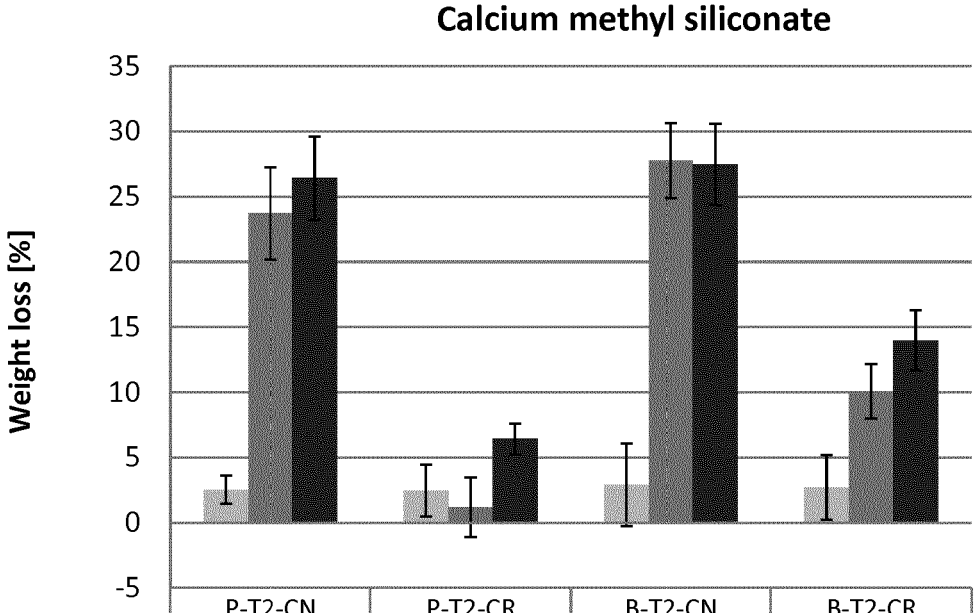
	Pine T1	Pine T2	Pine T3_gas	Pine T3_liq	Beech T1	Beech T2	Beech T3_gas	Beech T3_liq
After Impregnation	69.78	49.76	36.00	36.50	35.14	17.31	25.90	26.70
After Leaching	32.29	16.70	12.90	13.30	12.67	5.04%	9.40%	8.90%

Fig. 3



	P-T1-CN	P-T1-CR	B-T1-CN	B-T1-CR
Impregnated (P1)	2.1	3.1	4.2	4.5
Control (P21)	9.7	-3.8	13.1	-0.5
Virulence (P22)	26.4	6.4	27.4	14.0

Fig. 4



	P-T2-CN	P-T2-CR	B-T2-CN	B-T2-CR
Impregnated (P1)	2.5	2.5	2.9	2.7
Control (P21)	23.7	1.2	27.8	10.1
Virulence (P22)	26.4	6.4	27.4	14.0

Fig. 5

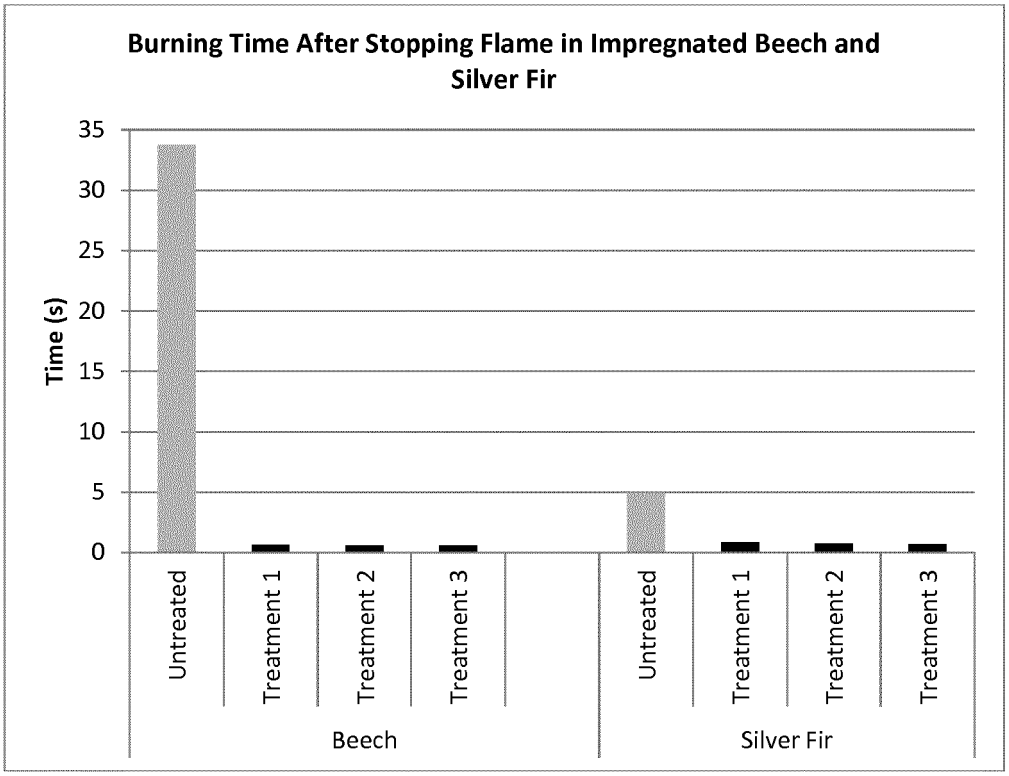

Burning Time After Stopping Flame in Impregnated Beech and Silver Fir
Time (s)
35
30
25
20
15
10
5
0
Untreated
Treatment 1
Treatment 2
Treatment 3
Untreated
Treatment 1
Treatment 2
Treatment 3
Beech
Silver Fir

Fig. 6

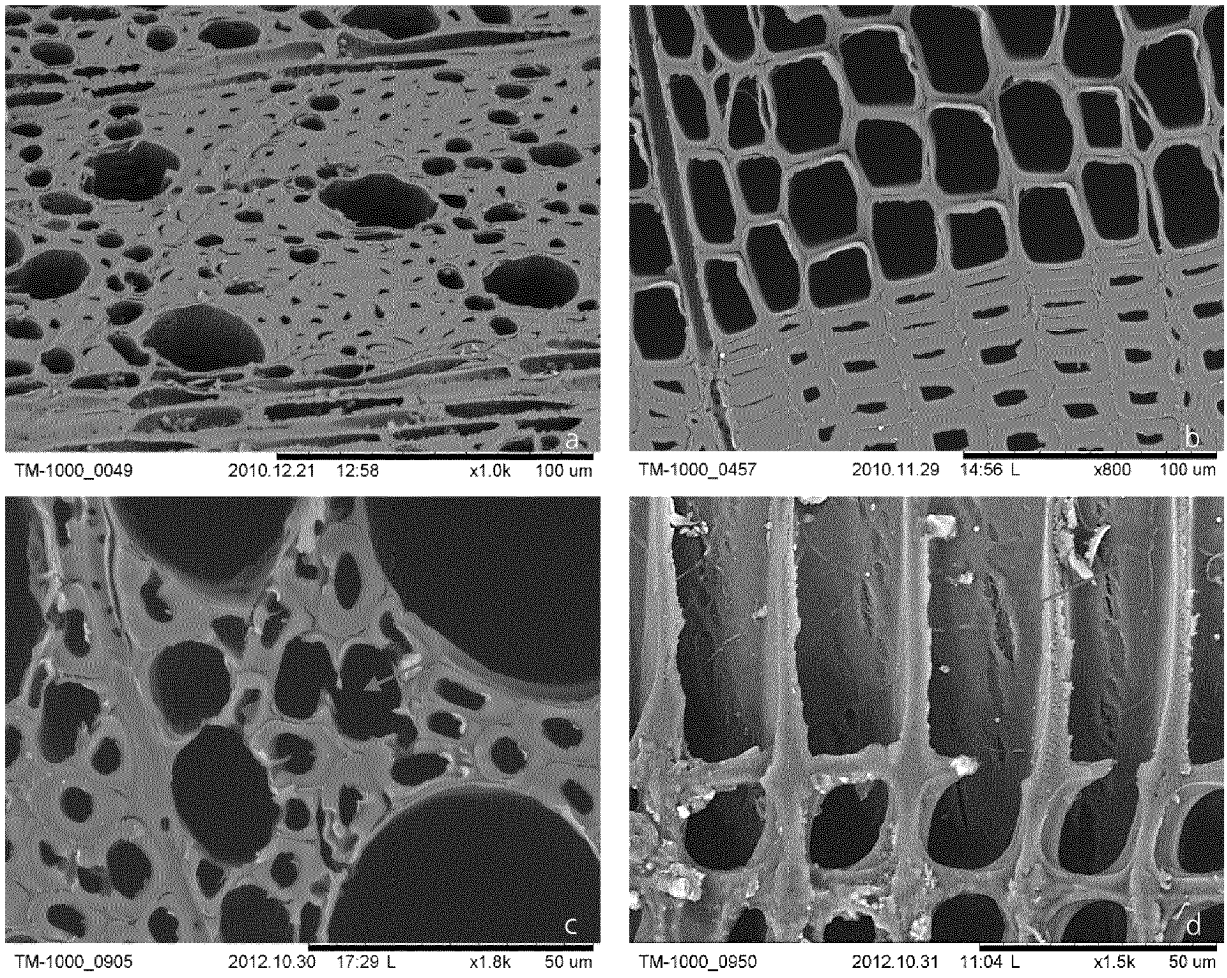

a
TM-1000_0049 2010.12.21 12:58 x1.0k 100 um
b
TM-1000_0457 2010.11.29 14:56 L x800 100 um
c
TM-1000_0905 2012.10.30 17:29 L x1.8k 50 um
d
TM-1000_0950 2012.10.31 11:04 L x1.5k 50 um

Fig. 7 a-d

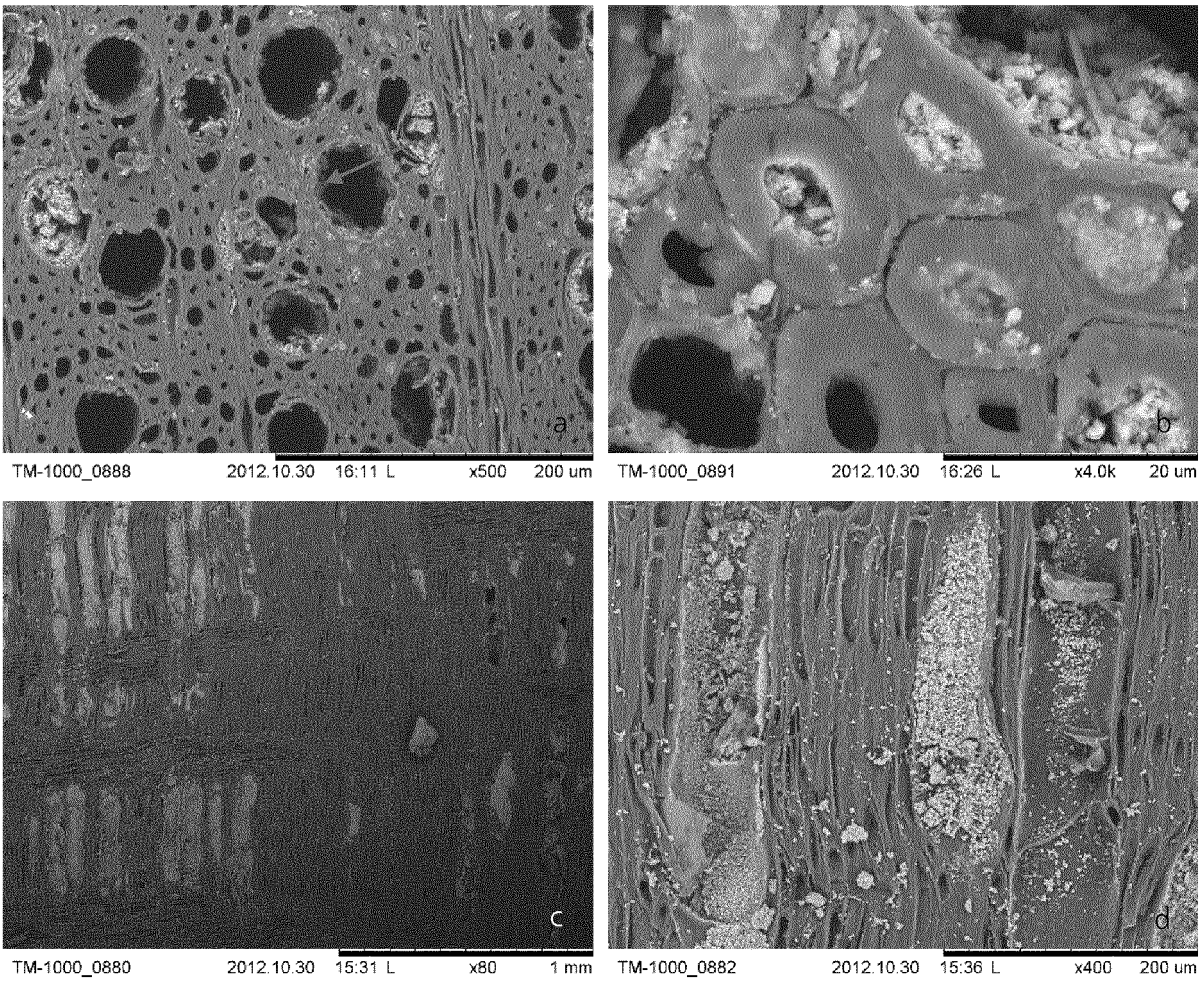

a
TM-1000_0888 2012.10.30 16:11 L x500 200 um
b
TM-1000_0891 2012.10.30 16:26 L x4.0k 20 um
c
TM-1000_0880 2012.10.30 15:31 L x80 1 mm
d
TM-1000_0882 2012.10.30 15:36 L x400 200 um

Fig. 8 a-d

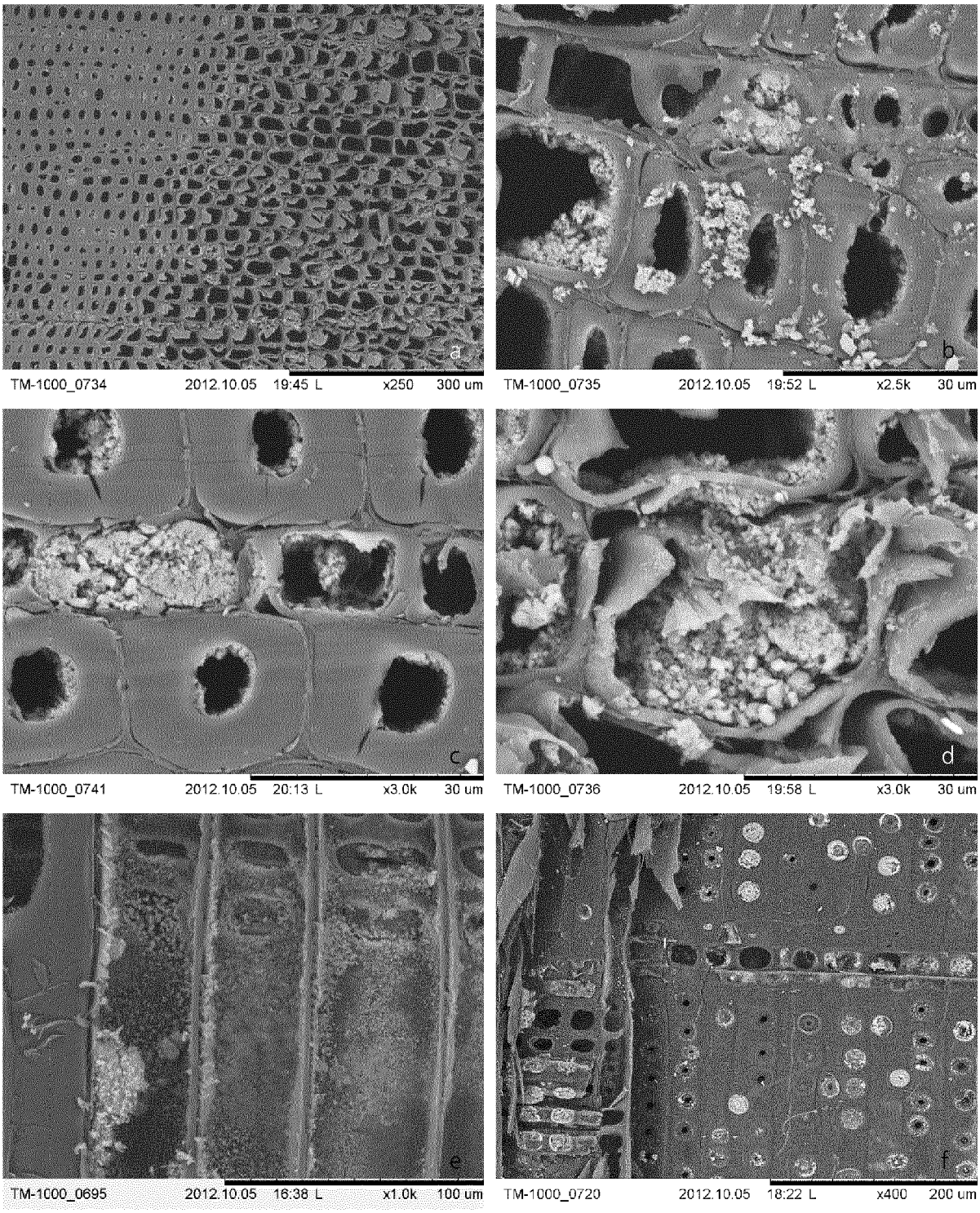

a
TM-1000_0734 2012.10.05 19:45 L x250 300 um
b
TM-1000_0735 2012.10.05 19:52 L x2.5k 30 um
c
TM-1000_0741 2012.10.05 20:13 L x3.0k 30 um
d
TM-1000_0736 2012.10.05 19:58 L x3.0k 30 um
e
TM-1000_0695 2012.10.05 16:38 L x1.0k 100 um
f
TM-1000_0720 2012.10.05 18:22 L x400 200 um

Fig. 9 a-f

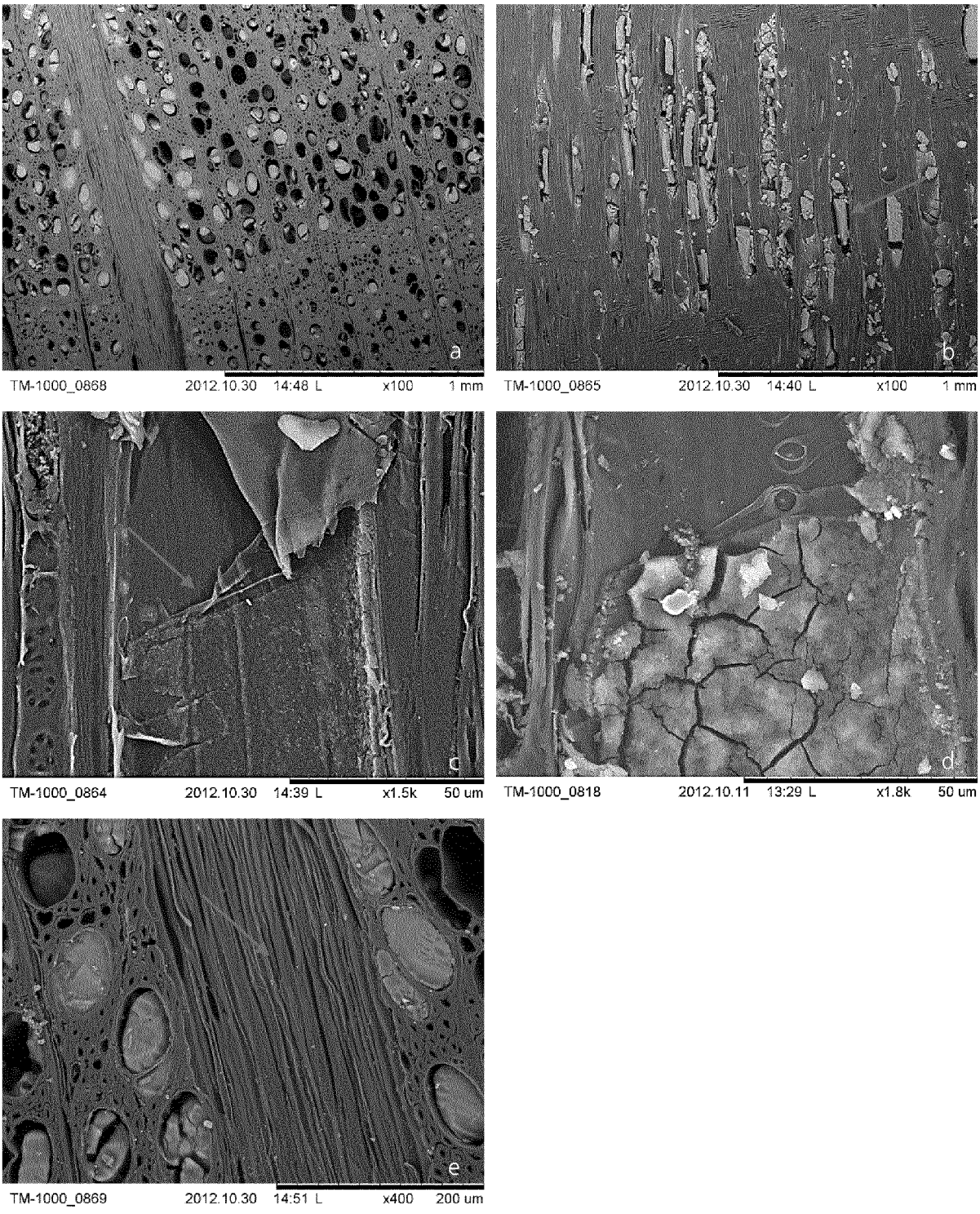

a
TM-1000_0868 2012.10.30 14:48 L x100 1 mm
b
TM-1000_0865 2012.10.30 14:40 L x100 1 mm
c
TM-1000_0864 2012.10.30 14:39 L x1.5k 50 um
d
TM-1000_0818 2012.10.11 13:29 L x1.8k 50 um
e
TM-1000_0869 2012.10.30 14:51 L x400 200 um

Fig. 10 a-e

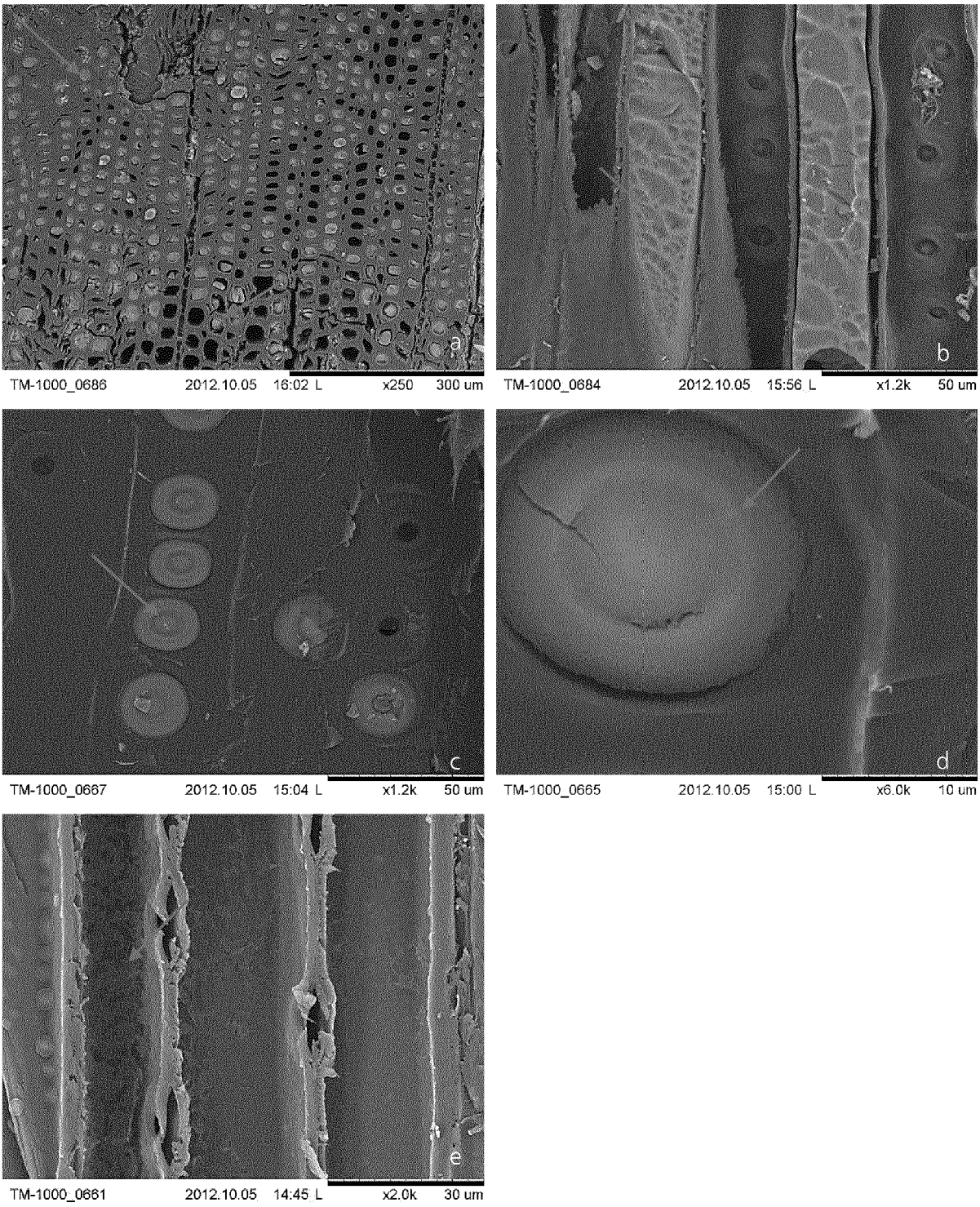

a
TM-1000_0686 2012.10.05 16:02 L x250 300 um
b
TM-1000_0684 2012.10.05 15:56 L x1.2k 50 um
c
TM-1000_0667 2012.10.05 15:04 L x1.2k 50 um
d
TM-1000_0665 2012.10.05 15:00 L x6.0k 10 um
e
TM-1000_0661 2012.10.05 14:45 L x2.0k 30 um

Fig. 11 a-e

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 2937193 A1 **[0012]**