Methods for preparing antibacterial/antifungal compositions of wood with inorganic matter

Verfahren zur Herstellung antibakterieller/antifungaler Holzkomposite mit anorganschem Material

Méthode pour la préparation des composites antibactériens et antifongiques de bois avec de la matière inorganique

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This invention relates to methods for preparing antibacterial/antifungal inorganic matter-composited wood having an antibacterial/antifungal component incorporated therein in such a manner that the antibacterial/antifungal component is prevented from being leached out in water and the antibacterial/antifungal function is semi-permanently imparted to the wood.

The utilization of wood is often restricted by its characteristic features of "flammability," "biodeterioration" and "dimensional instability".

A number of proposals have been made for improving these properties. To impart antibacterial/antifungal and preservative functions, a variety of treatments have been proposed and practiced in the art.

One of the currently available preservative (antibacterial/antifungal) treatments is the application of creosote oil which has long been employed. The creosote oil is a mixture of aromatic hydrocarbons as a main component and numerous compounds. The creosote oil-treated wood found application as railroad ties and utility poles. As a wood preservative, creosote oil has the advantages of low cost, ease of penetration and effective preservative action and the disadvantages of giving off evil-smelling and eye and skin-irritant fumes. When dissolved out, creosote oil can contaminate the surrounding soil and leach into rivers or lakes where it is toxic to fish. In many aspects, creosote oil imposes a heavy burden on the environment.

The exterior wood which is most frequently used at present is CCA-impregnated wood. CCA is a water-soluble chemical agent containing copper (Cu), chromium (Cr) and arsenic (As) as active components. It is in widespread use over the world because wood treated therewith exhibits excellent performance. However, the inclusion of such elements as copper and arsenic draws concerns about the safety of this chemical agent. In some countries, the use of CCA is restricted. Since CCA-treated wood pieces are often used for play apparatus in parks and schools, the influence of CCA on human bodies through skin contact is also a concern. With respect to oral toxicity, the toxicity of CCA must be carefully examined because CCA-treated wood pieces are used as outdoor play apparatus for children.

While acid rain now becomes one of the causes of global environmental damage, it is expected that CCA chemicals can be leached out of the wood with aci rain. When CCA-treated wood is burned for disposal, arsenides are sublimated from the CCA agent as diarsenic trioxide and released into the air, and oxides of copper and chromium are released as microparticulates. From the safety standpoint, the Environmental Protection Agency of USA rules that CCA-treated wood must not be burned in the open air or fireplaces. In the UK, it is required that if one makes a fire in the open air using CCA-treated wood, the distance from houses must be at least 100 meters.

Since creosote oil and CCA impose heavy burdens on the environment as mentioned above, careful consideration must be made on their use in the present day when global environmental problems are highlighted. It is DDAC (didecyldimethylammonium chloride) that enjoys a rapidly growing share as a preservative agent for impregnation. This agent contains a metal salt. An increasing demand for DDAC is expected since DDAC avoids the problem associated with the disposal of wood which is of most concern in the case of CCA. Regrettably, the effect of DDAC does not last long and its semi-permanent fixation has not been realized. Alternatively, metal salts of naphthenic acid are used as a preservative of the surface treatment type and also as a chemical agent for pressure impregnation. They are known to be fully safe, but the retention of their effect is yet a problem. For this reason, the metal naphthenates are mainly used for the treatment of foundations (see "Wood Science Series 5 - Environment," Kaisei-sha, 1995). The social demand for antibacterial/antifungal and bactericidal properties is very high as demonstrated in Japan during the prevalence of group food poisoning by pathogenic E. coli bacillus 0-157 in 1996. It is urgently required to develop a wood treating agent capable of retaining its effect semi-permanently and remaining safe.

Making investigations to develop high functional wood which is improved in avoiding environmental pollution and leach, we found a method for modifying wood by impregnating wood with a silicon alkoxide and subjecting it to hydrolysis and polycondensation to form silicon oxide fixedly within the wood cell walls (inter- and intracellular spaces) whereby various functions such as anti-rotting, dimensional stability and flame retardance are imparted to the wood as reported in the Journal of the Japan Wood Research Society, 38, 11, 1043 (1992). This method relies on the sol-gel process of metal alkoxide, i.e the starting solution of metal alkoxide-water-alcohol-catalyst converts into a sol of metal oxide through hydrolysis and self-polycondensation of the metal alkoxide. With further progress of reaction, the solution converts into a gel. When this reaction is carried out within wood cells, inorganic matter based on metal oxide is incorporated into the wood.

However, recent research works revealed that the process of compositing wood with metal oxide depends largely on the rate of hydrolysis of the particular metal alkoxide used and that the distribution of metal oxide in wood cells varies largely with processing conditions. When compositing wood with inorganic matter using a silicon alkoxide having a low rate of hydrolysis and subsequent polycondensation, for example, if the wood used is a moisture-conditioned piece of wood (water in the wood is all bound water and present solely in cell walls), the hydrolysis and polycondensation reaction of the silicon alkoxide proceeds solely within the cell walls where bound water is present, resulting in inorganic matter-composited wood in which cell cavities are empty. This composited wood maintains the...
advantages of wood including light weight, strength and heat insulation, that is, it is a modified wood which is provided with rot resistance, dimensional stability and flame retardance while maintaining the porous feature of wood (see the Journal of the Japan Wood Research Society, 39, 3, 301 (1993)). If the wood used is a water-saturated piece i.e. not only the cell walls but also the cell cavities are full of water), there results an inorganic matter-composited wood in which not only the cell walls but also the cell cavities are filled with silicon dioxide (see the Journal of the Japan Wood Research Society, 39, 3, 301 (1993)).

If the metal alkoxide used is changed, there is obtained an inorganic matter-composited wood having a completely different distribution. If a titanium alkoxide having a high rate of hydrolysis and subsequent polycondensation is used, for example, titanium oxide forms solely in cell cavities in the case of a moisture-conditioned piece. In the case of a water-saturated piece, oxide forms solely on the outer surface of the piece, but no metal oxide is composited in the interior of the piece. See the Journal of the Japan Wood Research Society, 39, 3, 308 (1993).

Based on these findings, we further investigated the relationship between the intracellular distribution of metal oxide and the function imparted thereby, and found that selective compositing of metal oxide in cell walls is a key for a minor amount of metal oxide formed to exert effective functions (see Wood Industry, 50, 9, 400 (1995)). Such compositing is possible with inorganic matter-composited wood based on silicon oxide resulting from silicon alkoxide. Once distributed in wood cell walls, silicon oxide is not leached out in water or other solvents and semi-permanently fixed within cell walls.


The general aim herein is to provide new and useful methods for treating wood to confer antibacterial and/or antifungal properties while forming an inorganic wood composite therewith. A preferred aim is to provide an antibacterial and/or antifungal functionality that resists long-term leaching.

Based on the above-described results of our research and development works, we continued research work to develop inorganic matter-composited wood having an antibacterial/antifungal function. We have found that if silicon dioxide distributed and fixed in wood cell walls and an antibacterial/antifungal organic silicon compound form covalent bonds through Si-O-Si linkages, the antibacterial/antifungal component is semi-permanently fixed in the wood. The resulting inorganic matter-composited wood is capable of exerting a stable antibacterial/antifungal function over an extended term. More particularly, we have found a brand new technique capable of manufacturing an antibacterial/antifungal wood article in a simple and consistent manner while keeping the original texture of wood itself. That is, when wood is impregnated with silicon alkoxide, use is made of a mixed solution containing not only a silicon alkoxide, but also an antibacterial/antifungal organic silicon compound having a hydrolysable alkoxysilyl group and optionally, a water repellent organic silicon compound having a hydrolysable alkoxysilyl group. Then these compounds are subjected to hydrolysis and polycondensation, usually at various temperatures whereby the organic silicon compound forms a covalent bond with silicon dioxide and is thus fixed within the wood. The resulting inorganic matter-composited wood sustains the antibacterial/antifungal activity for a long time. When the water repellent function is imparted at the same time, the antibacterial/antifungal activity can be further improved.

In a first aspect, the invention provides a method of preparing a composite of wood with antibacterial/antifungal inorganic matter, comprising the steps of:

(i) impregnating wood with a treating solution, containing (a) silicon alkoxide of the following general formula (1):

\[
(CH_3)_a Si(OR)_{4-a}
\]  

wherein R is substituted or unsubstituted monovalent hydrocarbon group having 1 to 12 carbon atoms, and a is 0, 1, 2 or 3, and (b) antibacterial/antifungal organic silicon compound of the following general formula (2):

\[
\left\{ \frac{(OR)^b - CH_3}{(CH_3)_b - Si - (CH_2)_c - N - R^1} \right\} X^-
\]  

wherein R^1 is monovalent aliphatic hydrocarbon group having 11 to 22 carbon atoms, R^2 is alkyl group having 1 to 4 carbon atoms, X is a halogen atom, and b is 0 or 1; to fill the inter- and intra-cellular spaces of the wood cell
walls with the treating solution, and
(ii) subjecting the silicon alkoxide and the organic silicon compound within said spaces of the cell walls to hydrolysis
and polycondensation to form said composite.

[0015] In a second aspect, the invention provides a method of preparing a composite of wood with antibacterial/
antifungal inorganic matter, comprising the steps of

(i) treating wood with a siloxane oligomer of the following average compositional formula (4):

\[
(R_5^c R_6^d SiO_{(3-c)/2})^i (R_7^d R_8^d SiO_{(3-d)/2})^j (R_9^e R_{10}^f SiO_{(3-e)/2})^k (SiO_{4/2})^n
\]

wherein \(R_5^c, R_7^d, R_8^d, R_9^e, R_{10}^f\) are selected from hydrogen and monovalent hydrocarbon groups having 1 to 10 carbon
atoms which may be halogen- or cyano-substituted, \(R_6^d\) is halogen- or cyano-substituted or unsubstituted mono-
valent hydrocarbon group having 1 to 18 carbon atoms, \(R_{10}^f\) is amino-bearing monovalent organic group having 1,
to 18 carbon atoms, \(R_{10}^f\) is monovalent organic group of the general formula (5):

\[
[-(CH_2)_3 NR_{11}^{11} (CH_3)_2] + X^{-}
\]

wherein \(R_{11}^{11}\) is a monovalent hydrocarbon group of 11 to 22 carbon atoms and \(X\) is a halogen atom, \(c, d, e\) are 0 or 1, \(i, j\) and \(n\) are 0 or positive numbers, and \(k\) is a positive number, provided that \(i\) and \(n\) are not both 0.

said siloxane oligomer being terminated with hydroxyl group and/or alkoxy group of 1 to 4 carbon atoms, to im-
pregnate the wood with the oligomer, and

(ii) curing the siloxane oligomer by drying whereby the oligomer is concentrated, hydrolysed, polycondensed and
cured to form said composite with the wood.

[0016] Preferably, in the first aspect the treating solution further contains another organic silicon compound of the
following general formula (3):

\[
R_3^m Si(OR_4^4)_{4-m}
\]

wherein \(R_3^m\) is a substituted or unsubstituted monovalent hydrocarbon group having 2 to 18 carbon atoms, \(R_4^4\) is a
monovalent hydrocarbon group having 1 to 6 carbon atoms, and letter \(m\) is equal to 1, 2 or 3. More preferably, at least
one of the \(R_3^m\) groups is a group wherein some or all of the hydrogen atoms attached to carbon atoms are replaced by
fluorine atoms.

[0017] In the second aspect we have found another way to manufacture an antibacterial/antifungal wood article in
a simple and consistent manner without losing the original texture of wood itself. By treating wood with a solution of
the siloxane oligomer of the average compositional formula (4) and heating the treated wood, alkoxides and silanols
in the oligomer undergo hydrolysis and self-polycondensation whereby a sol of metal oxide is formed. Further progress
of reaction converts the sol to a gel. Through this reaction, wood is composited with inorganic matter based on metal
oxide. This method of preparing inorganic matter-composited wood can be practised without concerns for the safe
working environment because of the low vapor pressure of the siloxane oligomer used. Since the leaching of silicon
dioxide under the action of water is prevented, the composited wood exerts the antibacterial/antifungal activity over
an extended term in a stable manner.

[0018] More particularly, in the second aspect, by treating wood with a siloxane oligomer solution, subjecting the
oligomer to hydrolysis e.g. at various temperatures and further to polycondensation for eventually curing the oligomer,
a silicone resin containing an antibacterial/antifungal organic silicon compound and optionally, a water repellent organic
silicon compound is incorporated in the wood. There is obtained an inorganic matter-composited wood article having
antibacterial/antifungal activity. The water-repellent function given by the water-repellent organic silicon compound
helps the antibacterial/antifungal organic silicon compound exert its function. In a further embodiment wherein an or-
ganic silicon compound having an amino group is additionally used, the solubility of the siloxane oligomer in a solvent
is improved. Particularly when the solubility of the siloxane oligomer in water is improved, the siloxane oligomer can
be used as an aqueous solution.

[0019] By these means, there is provided a safe and practical method for preparing inorganic matter-composited
wood wherein the antibacterial/antifungal activity is improved due to the water repellence of the silicone resin. The term “antibacterial/antifungal activity” or function is used herein in a broader sense to encompass preservative and bactericidal activities as well.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

FIG. 1 is a photomicrograph of wood rotten with white rot fungus, sections (a), (b), (c), (d) and (e) corresponding to the test pieces of Comparative Example 1, Comparative Example 2, Comparative Example 4, Example 2, and Example 5, respectively.

FIG. 2 is a photomicrograph of wood rotten with brown rot fungus, sections (a), (b), (c), (d) and (e) corresponding to the test pieces of Comparative Example 1, Comparative Example 2, Comparative Example 4, Example 2, and Example 5, respectively.

FURTHER EXPLANATIONS; PREFERRED AND OPTIONAL FEATURES

[0021] The starting wood used herein is not critical. Logs, sawed lumber, sliced veneer, and plywood are included. The species of tree is not critical.

First embodiment

[0022] The first method involves impregnating wood with a solution containing a silicon alkoxide and an antibacterial/antifungal organic silicon compound.

[0023] The silicon alkoxide used herein is of the general formula (1).

\[ (\text{CH}_3)_a \text{Si(OR)}_{4-a} \] (1)

R is selected from substituted or unsubstituted monovalent hydrocarbon groups having 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms, for example, alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, decyl and dodecyl. Preferably R is selected from alkyl groups of 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl and butyl. Letter a is 0, 1, 2 or 3, preferably 0 or 1.

[0024] The silicon alkoxides of formula (1) may be used alone or in admixture of two or more.

[0025] The antibacterial/antifungal organic silicon compound having a hydrolysable alkoxysilyl group is of the following general formula (2):

\[
\left[ \text{(OR)}_{2-b} \text{CH}_3 \right] \left[ (\text{CH}_3)_b \text{Si} \left( \text{CH}_2 \right)_{2-b} \text{N} \right]_{-b}^+ \text{X}^- \] (2)

wherein R^1 is a monovalent aliphatic hydrocarbon group having 11 to 22 carbon atoms, R^2 is an alkyl group having 1 to 4 carbon atoms, X is a halogen atom, and letter b is equal to 0 or 1.

[0026] The monovalent aliphatic hydrocarbon groups of 11 to 22 carbon atoms represented by R^1 may be either saturated or unsaturated and either normal or branched hydrocarbon groups. Some or all of the hydrogen atoms attached to carbon atoms may be replaced by substituents such as hydroxyl groups and halogen atoms. Exemplary are octadecyl, lauryl, myristyl, and stearyl. Examples of the alkyl group represented by R^2 are methyl, ethyl, propyl and butyl. The halogen atoms represented by X include chlorine, bromine and iodine.

[0027] The compound of formula (2) is an organic silicon compound having a quaternary ammonium base and terminated with a hydrolysable alkoxysilyl group and having an antibacterial/antifungal function. Because of the absence of toxic heavy metal atoms, this compound does not pollute the soil and rivers and has very low toxicity to humans. Additionally, it is less irritant and less odorous.

[0028] The organic silicon compound of formula (2) can be readily prepared as a quaternary ammonium salt type compound by reacting a compound having a 3-halogenopropyl group and an alkoxyl group each directly attached to
a silicon atom, for example, 3-chloropropyltrimethoxysilane with an amine compound of the formula: R^1N(CH_3)_2 wherein R^1 is a monovalent aliphatic hydrocarbon group of 11 to 22 carbon atoms, for example, C_{18}H_{37}N(CH_3)_2 or C_{18}H_{37}N(CH_3)_2 in a suitable solvent, such as dimethylformamide, at an elevated temperature.

[0029] An appropriate amount of the antibacterial/antifungal silicon compound added is usually 0.0001 to 0.5 mol, more preferably 0.001 to 0.01 mol per mol of the silicon alkoxide of formula (1). Greater amounts of the organic silicon compound outside this range may sometimes adversely affect the antibacterial/antifungal effect. This is easily tested.

[0030] In one preferred embodiment of the invention, the treating solution further contains a water-repellent organic silicon compound having a hydrolysable alkoxysilyl group. This organic compound is preferably of the following general formula (3):

\[ R^3_{n-m}Si(OR^4)^{4-m} \]  

R^3 is selected from substituted or unsubstituted monovalent hydrocarbon groups having 2 to 18 carbon atoms, preferably 2 to 12 carbon atoms, for example, alkyl groups such as ethyl, propyl, butyl, pentyl, and hexyl. Also included are substituted hydrocarbon groups in which some or all of the hydrogen atoms attached to carbon atoms are replaced by halogen atoms, especially fluorine-containing groups such as cyanoethyl. Preferred among others are halogen-substituted alkyl groups in which some or all of the hydrogen atoms attached to carbon atoms are replaced by halogen atoms, especially fluorine-containing groups such as perfluoroalkyl and perfluorerheter groups, and cyano-substituted groups such as cyanoethyl. Preferred among others are halogen-substituted alkyl groups in which some or all of the hydrogen atoms attached to carbon atoms are replaced by halogen atoms, especially fluorine-containing groups such as cyanoethyl and perfluoroethyl groups. R^4 is selected from monovalent hydrocarbon groups having 1 to 6 carbon atoms, especially 1 to 4 carbon atoms, typically alkyl groups of 1 to 6 carbon atoms and alkenyl groups of 2 to 6 carbon atoms, for example, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, ethynyl and propenyl. Letter m is equal to 1, 2 or 3 and preferably equal to 1.

[0031] Examples of the compound of formula (3) include 3,3,3-trifluoropropyltrimethoxysilane, 2-((heptafluorobutyl)ethyltrimethoxysilane, 2-((heptadecfluorooctyl)ethyltrimethoxysilane, and 3,3,3-trifluoropropytrimethoxysilane.

[0032] An appropriate amount of the organic silicon compound (3) added is usually 0.0001 to 0.5 mol, most preferably about 0.01 mol per mol of the silicon alkoxide of formula (1). Greater amounts outside this range may sometimes fail to provide uniform water repellence. This is easily tested.

[0033] The first method for preparing an antibacterial/antifungal inorganic matter-composited wood is carried out as follows. To a solution containing one or more silicon alkoxides of formula (1) are added an antibacterial/antifungal organic silicon compound having a hydrolysable alkoxysilyl group of formula (2) and optionally, a water-repellent organic silicon compound having a hydrolysable alkoxysilyl group of formula (3). A moisture-conditioned piece of wood is impregnated with the treating solution so that the wood’s inter- and intracellular spaces are filled with the solution. The silicon alkoxide and the organic silicon compound(s) within the inter- and intracellular spaces are subjected to hydrolysis, followed by polycondensation, thereby forming silicon oxide with which the antibacterial/antifungal organic silicon compound forms a covalent bond and the optional water-repellent organic silicon compound also forms a covalent bond. The treated wood piece is finally dried.

[0034] The treating solution may also be obtained by using a mixed solution of the silicon alkoxide and the organic silicon compound or using dilutions of the respective compounds in suitable solvents such as alcohols, acetone, aliphatic hydrocarbons or aromatic hydrocarbons. Acidic or alkaline catalysts may be added or not.

[0035] In impregnating wood with the mixed solution, the wood may be in a moisture-conditioned or water-saturated state, preferably in a state conditioned to a water content of 10 to 50% by weight. The wood may be directly immersed in the mixed solution. A vacuum or pressure impregnation technique may also be used.

[0036] Typically the wood is kept immersed in the mixed solution at room temperature under a vacuum of about 1.3 to 2.0 kPa (10 to 15 mmHg) for about 1 to 7 days. Thereafter, the wood is taken out of the solution, allowed to stand at room temperature for about one day, and heated for drying at about 50 to 110°C for about 1/2 to about 2 days. In this process, the silicon alkoxide is hydrolysed at various temperatures and then polycondensed whereby it is converted into silicon dioxide which is fixed within cell walls. At the same time, the organic silicon compound(s) coexisting with the silicon alkoxide form covalent bonds with the silicon dioxide whereby they are semi-permanently fixed within the wood.

Second embodiment

[0037] The second method for preparing an antibacterial/antifungal inorganic matter-composited wood involves the steps of treating wood with a siloxane oligomer and curing the siloxane oligomer.

[0038] The siloxane oligomer is of the following average compositional formula (4):

\[ R^3_{n-m}Si(OR^4)^{4-m} \]
wherein R₅, R⁷ and R⁹ are hydrogen or halogen- or cyano-substituted or unsubstituted monovalent hydrocarbon groups having 1 to 10 carbon atoms, R⁶ is a halogen- or cyano-substituted or unsubstituted monovalent hydrocarbon groups having 1 to 18 carbon atoms, R⁸ is an amino-bearing monovalent organic group having 1 to 18 carbon atoms, R¹⁰ is a monovalent organic group of the general formula (5):

\[
[-(CH_2)_3NR^{II}_1(CH_3)_2]^*X^-
\]  

wherein R¹¹ is a monovalent hydrocarbon group of 11 to 22 carbon atoms and X is a halogen atom, letters c, d, and e are equal to 0 or 1, preferably 0, i, j and n are 0 or positive numbers, and k is a positive number; i and n are not both equal to 0. The siloxane oligomer is terminated with a hydroxyl group and/or an alkoxy group of 1 to 4 carbon atoms.

The monovalent hydrocarbon groups represented by R₅, R₇ and R⁹ include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, and decyl; alkenyl groups such as vinyl, allyl, propenyl and butenyl; aryl groups such as phenyl and tolyl; aralkyl groups such as benzyl and phenylethyl; substituted hydrocarbon groups in which some or all of the hydrogen atoms attached to carbon atoms are replaced by substituents such as halogen atoms and cyano groups, for example, fluorine-substituted alkyl groups such as 3,3,3-trifluoropropyl, 2-(heptafluorobutyl)ethyl and 2-(heptadecafluoroocetyl)ethyl, fluorine-substituted polyether groups, and cyano-substituted groups such as cyanoethyl.

Examples of the substituted or unsubstituted hydrocarbon groups represented by R₆ include the same examples as described for R₅, R₇ and R⁹ as well as long-chain alkyl groups such as lauryl, myristyl and stearyl, and substituted ones thereof in which some or all of the hydrogen atoms are replaced by fluorine. Preferably, R₆ is selected from halogen-substituted alkyl groups in which some or all of the hydrogen atoms are replaced by halogen atoms, especially fluorine-substituted alkyl groups.

R⁸ is preferably an amino-bearing monovalent organic group of the formula:

\[
[-(CH_2)_x-[NH-(CH_2)_y]_z-NH_2
\]

wherein x is 1 to 8, especially 1 to 6, y is 2 to 10, especially 2 to 6, and z is 0 to 8, especially 0 to 5. R¹⁰ is a monovalent organic group of the general formula (5):

\[
[-(CH_2)_3NR^{II}_1(CH_3)_2]^*X^-
\]  

wherein R¹¹ is preferably a long chain alkyl or alkenyl group.

Each of the units R₅₋₆SiO₃₋₂, R⁷₋₈SiO₃₋₂, and R⁹₋₁⁰SiO₃₋₂ may be a mixture of different structures.

In particular, the R₅₋₆SiO₃₋₂ unit, which is to impart water repellence to wood, is preferably composed of CH₃SiO₃₋₂ units and R'SiO₃₋₂ units wherein R' is alkyl of 5 to 18 carbon atoms or CH₃SiO₃₋₂ units and R"SiO₃₋₂ units wherein R" is fluorinated alkyl of 1 to 18 carbon atoms. Herein, the content of CH₃SiO₃₋₂ units is preferably 5 to 100 mol% of the R₅₋₆SiO₃₋₂ unit.

The letters i, j, k and n are as defined above. Provided that i+j+k+n = 1, i is preferably from 0 to 0.9999 and especially from 0.1 to 0.9 (that is, 0 ≤ i ≤ 0.9999, especially 0.1 ≤ i ≤ 0.9). Letter j is preferably 0 to 0.800 (that is, 0 ≤ j ≤ 0.800). It is noted that the R₇₋₈SiO₃₋₂ unit with suffix j is introduced when it is desired to impart water solubility to the siloxane oligomer. Letter k is a positive number and preferably from 0.001 to 0.5 and especially from 0.001 to 0.2 (that is, 0.0001 ≤ k ≤ 0.5, and especially 0.001 ≤ k ≤ 0.2). Letter n is preferably 0 to 0.9999 (that is, 0 ≤ n ≤ 0.9999). Both i and n are not equal to 0. That is, when i is 0, n is a positive number. When n is 0, i is a positive number.

The siloxane oligomer of formula (4) preferably has an average degree of polymerization of 2 to 20. If the degree of polymerization is more than 20, a longer time is required for impregnation.

The siloxane oligomer of formula (4) can be obtained by a conventional process of effecting co-hydrolysis of an antibacterial/antifungal organic silicon compound and a water-repellent organic silicon compound and/or a tetrafunctional silicon alkoxide such as tetramethoxysilane or tetraethoxysilane and optionally, an amino-bearing organic silicon compound. Alternatively, the silicon alkoxide and the organic silicon compound(s) are independently previously subjected to partial hydrolysis before they are mixed and co-hydrolysed.

The tetrafunctional silicon alkoxide used herein is usually of the following general formula (6):
wherein R^{12} is an alkyl group of 1 to 4 carbon atoms.

[0048] The antibacterial/antifungal organic silicon compound used herein is usually of the following general formula (7):

$$R^9_{-e} R^{10}_{-c} Si(OR^{13}_{-e})_3$$

wherein R^9, R^{10} and e are as defined above, and R^{13} is an alkyl group of 1 to 4 carbon atoms.

[0049] The compound of formula (7) is an organic silicon compound having a quaternary ammonium base and terminated with a hydrolysable alkoxysilyl group and having an antibacterial/antifungal function. Because of the absence of toxic heavy metal atoms, this compound does not pollute the soil and rivers and has very low toxicity to humans. Additionally, it is less irritating and less odorous.

[0050] The organic silicon compound of formula (7) can be readily prepared as a quaternary ammonium salt type compound by reacting a compound having a 3-halogenopropyl group and an alkoxyl group each directly attached to a silicon atom, for example, 3-chloropropyltrimethoxysilane with an amine compound of the formula: R^{11}_{-h} N(CH_{3})_2 where-in R^{11} is a monovalent hydrocarbon group of 11 to 22 carbon atoms, for example, C_{16}H_{33} N(CH_{3})_2 or C_{18}H_{37}(CH_{3})_2 in a suitable solvent such as dimethylformamide at an elevated temperature.

[0051] The water-repellent organic silicon compound may be of the following general formula (8):

$$R^5_{-c} R^6_{-c} Si(OR^{14}_{-c})_3$$

wherein R^5, R^6 and c are as defined above, and R^{14} is an alkyl group of 1 to 4 carbon atoms. Examples of the compound of formula (8) include methyltrimethoxysilane, methyltriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, 2-(heptafluorobutyl)ethytrimethoxysilane, 2-(heptadecafluoroctyl)ethytrimethoxysilane, 3,3,3-trifluoropropylthiethoxysilane, 3,3,3-trifluoropropylmethyltrioxide silane, and 3,3,3-trifluoropropylmethylidethoxysilane.

[0052] The amino-bearing organic silicon compound may be of the following general formula (9):

$$R^7_{-d} R^8_{-d} Si(OR^{15}_{-d})_3$$

wherein R^7, R^8, and d are as defined above, and R^{15} is an alkyl group of 1 to 4 carbon atoms. Examples of the compound of formula (9) include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-(2-aminooethyl)-3-aminopropyltrimethoxysilane, N-(2-aminooethyl)-3-aminopropyltriethoxysilane, and N-(2-aminooethyl)-3-aminopropylmethylidethoxysilane.

[0053] The alkoxy silanes of the above formulae (6) to (9) are reacted in such amounts that i, j, k and n may satisfy the above-mentioned molar fractions.

[0054] In the hydrolysis step, catalysts such as acidic catalysts, alkaline catalysts, fluoride catalysts, and transition metal compound catalysts may be used.

[0055] When wood is treated with the siloxane oligomer of formula (4), the siloxane oligomer may be used as such or after diluting with suitable organic solvents, for example, alcohols such as methyl alcohol and ethyl alcohol and ketones such as acetone and methyl ethyl ketone. However, the use of organic solvents is not recommended because strict restriction is now made on organic solvents and the use of organic solvents can lead to environmental damage. The siloxane oligomer of formula (4) according to the invention is soluble in water when j > 0 in formula (4), that is, when a siloxane unit having an amino-bearing monovalent organic group is contained. Then the siloxane oligomer can be diluted with water which is the preferred diluent.

[0056] To the siloxane oligomer described above, an additional organic silicon compound such as dimethylidethoxysilane or methylidimethoxysilane may be added and mixed for imparting flexibility to the resin. In this embodiment, when the siloxane oligomer is prepared, the additional organic silicon compound may be added to tetraethoxysilane or a partial hydrolysate thereof whereupon it is subject to co-hydrolysis. Further, to impart termite-resistant properties, a termite-resistant ingredient such as boric acid may be added. The termite-resistant ingredient may be added during the reaction to form the siloxane oligomer or post-added to the oligomer.

[0057] For the treatment of wood with the siloxane oligomer solution, the wood is preferably in a moisture-conditioned state although the state of wood is not critical. The treatment may be done by spraying, brush coating, dipping, and
After treatment with the siloxane oligomer, the wood is dried e.g. at elevated temperature in a range which does not cause pyrolysis of the wood, for example, 50 to 110°C. During the process, the solvent volatilizes off and the oligomer is concentrated, hydrolysed, then polycondensed and cured whereby the oligomer converts into a silicone resin having antibacterial/antifungal activity.

The method for preparing an antibacterial/antifungal inorganic matter-composited wood according to the invention has the advantage that since the antibacterial/antifungal and water-repellent organic silicon compounds are used along with the silicon alkoxide, the antibacterial/antifungal component is semi-permanently fixed within the wood and water repellence can be imparted to further improve the antibacterial/antifungal effect. Then wood is given an anti-rotting (antibacterial/antifungal) function while preventing the extraction or leaching of the antibacterial/antifungal component which has never been prevented in the prior art, and without obstructing the bonding and coating functions of wood during working. Thus, methods disclosed herein should enable the production on a large scale of antibacterial/antifungal wood which is suitable as members in open areas e.g. complying with the Japanese building standards, interior members and exterior members.

**EXAMPLE**

Examples of the invention are given below by way of illustration.

Physical properties of inorganic matter-composited wood were examined by the following tests.

1. **Weight percent gain**

   A test piece of wood was subjected to Soxhlet extraction with acetone and water each for 24 hours before the absolute dry weight (Wu) of the untreated wood piece was determined. Then the test piece was treated for inorganic matter compositing and dried at 105°C for 24 hours. The absolute dry weight (Wt) of the inorganic matter-composited wood piece was determined. A weight percent gain (WG) of the inorganic matter-composited wood was calculated according to

   \[ \text{WG} \% = \frac{(Wt - Wu)}{Wu} \times 100 \]

2. **Wood rotting test using white and brown rot fungi**

   For examining antibacterial/antifungal activity, a rotting test was made on inorganic matter-composited wood according to the Japan Wood Preservation Association (JWPA) Standard, No. 3 (1992), Durability Test Method for Wooden Material. After test pieces were dried and sterilized at 60°C for 48 hours, they were placed on lawns of white rot fungus *Coriolus versicolor* (L. ex Fr.) Quel (IFO 30340) and brown rot fungus *Tyromyces palustris* (Berk. et Curt. Murr.) (IFO 30390) which had been fully grown in culture dishes in a glass container. After cultivation in an incubator at room temperature (26°C) and a relative humidity of 55 to 65% for 8 weeks, the test pieces were taken out, and the fungal cells were wiped off from the surface. The absolute dry weight of the test pieces was determined. A percent weight loss by wood-rot fungus was calculated from the absolute dry weight of the test pieces before the test.

3. **SEM examination of wood-rot fungi**

   Using a microtome, a thin section was cut from the interior of the test piece obtained in the rotting test (2). After gold evaporation, the section was observed under a scanning electron microscope for observing the growth of wood-rot fungi.

4. **Subterranean rotting test**

   Test pieces of untreated wood and inorganic matter-composited wood were subjected to Soxhlet extraction with acetone and water each for 24 hours. A subterranean test of burying the test pieces in non-sterilized soil 17 cm deep from the ground surface was carried out for 9 months. A percent weight loss was calculated from the absolute dry weights of each test piece before and after the burying test, from which the progress of decay was presumed.

**Example 1**

Veneer pieces of cypress sapwood (50 mm x 100 mm x 1 mm thick) were subjected to Soxhlet extraction with
acetone and water each for 24 hours, and conditioned to a moisture content of 25%. To a reaction solution composed of tetraethoxysilane (TEOS, $\text{Si(OC}_2\text{H}_5)_4$), ethanol, and acetic acid in a molar ratio of 1:1:0.01, a 40 wt% methanol solution of 3-(trimethoxysilyl)propyl octadecyl dimethylammonium chloride (TMSAC) was added so as to give a molar ratio of 0.001 mol of TMSAC per mol of TEOS. The wood pieces were impregnated with this reaction solution at room temperature under vacuum for 3 days. Thereafter, the wood pieces were heated at 65°C for 24 hours and then at 105°C for 24 hours for ripening the resulting gel, obtaining pieces of inorganic matter-composited wood. These pieces had a weight gain (WG) of 4.6% mainly by silicon dioxide. After the 8-week wood rotting test using white and brown rot fungi, they showed weight losses of 3.0% and 4.0%, respectively. After the 9-month subterranean rotting test, they showed a weight loss of 10.4%.

**Example 2**

[0067] Pieces of inorganic matter-composited wood were obtained as in Example 1 except that the amount of TMSAC added was changed to a molar ratio of 0.005 mol of TMSAC per mol of TEOS. These pieces had a weight gain (WG) of 5.6%. After the rotting test using white and brown rot fungi, they showed weight losses of 2.4% and 2.8%, respectively. After the subterranean test, they showed a weight loss of 5.4%. The results are shown in Table 1.

**Example 3**

[0068] Pieces of inorganic matter-composited wood were obtained as in Example 1 except that the amount of TMSAC added was changed to a molar ratio of 0.01 mol of TMSAC per mol of TEOS. These pieces had a weight gain (WG) of 8.1%. After the rotting test using white and brown rot fungi, they showed weight losses of 2.9% and 0.4%, respectively. After the subterranean test, they showed a weight loss of 7.8%. The results are shown in Table 1.

**Example 4**

[0069] Pieces of inorganic matter-composited wood were obtained as in Example 1 except that 2-(heptadecafluorooctyl)ethyltrimethoxysilane (HFOETMOS) was further added to the reaction solution in a molar ratio of 0.004 mol per mol of TEOS. These pieces had a weight gain (WG) of 4.8%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 1.7%. The results are shown in Table 1.

**Example 5**

[0070] Pieces of inorganic matter-composited wood were obtained as in Example 2 except that 2-(heptadecafluorooctyl)ethyltrimethoxysilane (HFOETMOS) was further added to the reaction solution in a molar ratio of 0.004 mol per mol of TEOS. These pieces had a weight gain (WG) of 7.0%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 3.1%. The results are shown in Table 1.

**Example 6**

[0071] Pieces of inorganic matter-composited wood were obtained as in Example 3 except that 2-(heptadecafluorooctyl)ethyltrimethoxysilane (HFOETMOS) was further added to the reaction solution in a molar ratio of 0.004 mol per mol of TEOS. These pieces had a weight gain (WG) of 8.8%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 2.7%. The results are shown in Table 1.

**Comparative Example 1**

[0072] Using the same procedure and conditions as in Examples 1 to 6, pieces of untreated wood were subjected to the rotting test using white and brown rot fungi whereupon they showed weight losses of 10.7% and 7.9%, respectively. After the subterranean test, they showed a weight loss of 21.6%. The results are shown in Table 1.

**Comparative Example 2**

[0073] Pieces of inorganic matter-composited wood were obtained as in Example 1 except that TMSAC was not added to the reaction solution. These pieces had a weight gain (WG) of 6.5%. After the rotting test using white and
brown rot fungi, they showed weight losses of 11.4% and 4.3%, respectively. After the subterranean test, they showed a weight loss of 18.0%. The results are shown in Table 1.

Comparative Example 3

[0074] Pieces of TMSAC-treated wood were obtained as in Example 1 except that in the reaction solution, TEOS was omitted and the same volume of ethanol was added instead. These pieces had a weight gain (WG) of 0.1%. After the rotting test using white and brown rot fungi, they showed weight losses of 5.1% and 5.3%, respectively, indicating relatively good results. After the subterranean test, they showed a weight loss of 15.6%, indicating low antibacterial/antifungal activity against the 9-month test. The results are shown in Table 1.

Comparative Example 4

[0075] Pieces of TMSAC-treated wood were obtained as in Example 1 except that in the reaction solution, TEOS was omitted and the same volume of ethanol was added instead, and the amount of TMSAC (40 wt% methanol solution) added was increased so as to give a molar ratio of 0.005. These pieces had a weight gain (WG) of 1.0%. After the rotting test using white and brown rot fungi, they showed weight losses of 5.5% and 5.8%, respectively. After the subterranean test, they showed a weight loss of 6.8%. The results are shown in Table 1.

Comparative Example 5

[0076] Pieces of TMSAC-treated wood were obtained as in Example 1 except that in the reaction solution, TEOS was omitted and the same volume of ethanol was added instead, and the amount of TMSAC (40 wt% methanol solution) added was increased so as to give a molar ratio of 0.01. These pieces had a weight gain (WG) of 1.8%. After the rotting test using white and brown rot fungi, they showed weight losses of 1.7% and 2.2%, respectively, indicating relatively good results. After the subterranean test, however, they showed a fairly increased weight loss of 9.0%. The results are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Metal alkoxide</th>
<th>Silicon compound</th>
<th>Weight gain (%)</th>
<th>White rot fungus (%)</th>
<th>Brown rot fungus (%)</th>
<th>9-month subterranean test (%)</th>
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<tbody>
<tr>
<td>E1 TEOS</td>
<td>TMSAC</td>
<td>4.6</td>
<td>3.0</td>
<td>4.0</td>
<td>10.4</td>
</tr>
<tr>
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<td>TMSAC</td>
<td>5.6</td>
<td>2.4</td>
<td>2.8</td>
<td>5.4</td>
</tr>
<tr>
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<td>TMSAC</td>
<td>8.1</td>
<td>2.9</td>
<td>0.4</td>
<td>7.8</td>
</tr>
<tr>
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<td>TMSAC HFOETMOS</td>
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<td>0</td>
<td>0</td>
<td>1.7</td>
</tr>
<tr>
<td>E5 TEOS</td>
<td>TMSAC HFOETMOS</td>
<td>7.0</td>
<td>0</td>
<td>0</td>
<td>3.1</td>
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<tr>
<td>E6 TEOS</td>
<td>TMSAC HFOETMOS</td>
<td>8.8</td>
<td>0</td>
<td>0</td>
<td>2.7</td>
</tr>
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<td>10.7</td>
<td>7.9</td>
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<tr>
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<td>11.4</td>
<td>4.3</td>
<td>18.0</td>
</tr>
<tr>
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<td>5.1</td>
<td>5.3</td>
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<td>5.5</td>
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</tr>
<tr>
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<td>TMSAC</td>
<td>1.8</td>
<td>1.7</td>
<td>2.2</td>
<td>9.0</td>
</tr>
</tbody>
</table>

TEOS: tetraethoxysilane
TMSAC: 3-(trimethoxysilyl)propyloctadecyldimethylammonium chloride
HFOETMOS: 2-(heptadecafluorooctyl)ethyltrimethoxysilane

[0077] FIG. 1 is a collection of SEM photomicrographs of the test pieces rotten with white rot fungus of Examples 2 and 5 and Comparative Example 1, 2 and 4. FIG. 2 is a collection of similar SEM photomicrographs of the test pieces
rotten with brown rot fungus. In FIGS. 1 and 2, sections (a), (b), (c), (d), and (e) correspond to the test pieces of Comparative Example 1, Comparative Example 2, Comparative Example 4, Example 2, and Example 5, respectively. Many white and brown rot fungi are observed in (a), (b), and (c), but few in (d) and (e).

Example 7

[0078] A 1-liter flask was charged with 208 grams (1.0 mol) of tetraethoxysilane (TEOS), 2.8 grams (0.005 mol) of 2-(heptadecafluorooctyl)ethyltrimethoxysilane (HFOETMOS), 2.5 grams (0.005 mol) of 3-(trimethoxysilyl)propyl octadecyltrimethylammonium chloride (TMSAC), 0.5 gram (0.008 mol) of acetic acid, and 208 grams of methanol. With stirring at room temperature, 36 grams of deionized water was added dropwise to the flask for reaction to take place, and the reaction solution was ripened at 50°C for 1 hour. Then, 0.9 grams (0.005 mol) of 3-aminopropyltrimethoxysilane (APTMOS) was added dropwise to the flask for reaction to take place, and the reaction solution was ripened at 50°C for 1 hour. The solution was diluted with methanol to a solution containing 10% by weight of the resulting oligomer, which was used for treatment. This oligomer had the average composition:

\[
[C_8F_{17}C_2H_4SiO_{3/2}]_{0.0049}[H_2NC_3H_6SiO_{3/2}]_{0.0049}^+ \\
[C\tilde{I}][(C_3H_2)_{12}(C_{18}H_{37})NC_3H_6]^{+}SiO_{3/2}]_{0.0049}[SiO_{4/2}]_{0.9853}^-
\]

and an average degree of polymerization of about 6, and was terminated with methoxy and hydroxyl groups.

[0079] Veneer pieces of cypress sapwood (50 mm x 100 mm x 1 mm thick) were subjected to Soxhlet extraction with acetone and water each for 24 hours, and conditioned to a moisture content of 25%. The wood pieces were impregnated with the oligomer solution at room temperature under vacuum for 3 days. Thereafter, the wood pieces were heated at 65°C for 24 hours and then at 105°C for 24 hours for ripening the resulting gel, obtaining pieces of inorganic matter-composited wood. These pieces had a weight gain (WG) of 11.0% mainly by silicon dioxide. After the 8-week wood rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the 9-month subterranean rotting test, they showed a weight loss of 2.5%.

Example 8

[0080] Reaction was carried out as in Example 7 except that 5 grams (0.01 mol) of TMSAC was used and APTMOS was omitted. The reaction solution was diluted with methanol to a solution containing 10% by weight of the oligomer, which was used for treatment. This oligomer had the average composition:

\[
[C_8F_{17}C_2H_4SiO_{3/2}]_{0.0049}[C\tilde{I}][(C_3H_2)_{12}(C_{18}H_{37})NC_3H_6]^{+}SiO_{3/2}]_{0.0099}[SiO_{4/2}]_{0.9857}
\]

and an average degree of polymerization of about 8, and was terminated with methoxy and hydroxyl groups.

[0081] Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 10.5%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 2.8%.

Comparative Example 6

[0082] Using the same procedure and conditions as in Example 7, pieces of untreated wood were subjected to the rotting test using white and brown rot fungi whereupon they showed weight losses of 11.0% and 8.9%, respectively. After the subterranean test, they showed a weight loss of 22.8%.

Comparative Example 7

[0083] Reaction was carried out as in Example 7 except that TMSAC was omitted. The reaction solution was diluted with methanol to a solution containing 10% by weight of the oligomer, which was used for treatment. This oligomer had the average composition:

\[
[C_8F_{17}C_2H_4SiO_{3/2}]_{0.0050}[H_2NC_3H_6SiO_{3/2}]_{0.0050}[SiO_{4/2}]_{0.9900}
\]
and an average degree of polymerization of about 5, and was terminated with methoxy and hydroxyl groups.  

[0084] Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 9.3%. After the rotting test using white and brown rot fungi, they showed weight losses of 11.5% and 5.3%, respectively. After the subterranean test, they showed a weight loss of 18.9%.

Example 9

[0085] Reaction was carried out as in Example 7 except that TEOS was omitted. The reaction solution was diluted with methanol to a solution containing 10% by weight of the oligomer, which was used for treatment. This oligomer had the average composition:

\[ \text{[C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{SiO}_3\text{]}_0.3333 \text{[H}_2\text{NC}_3\text{H}_6\text{SiO}_3\text{]}_0.3333 - \text{[Cl - [(CH}_3)_2\text{NC}_3\text{H}_6\text{]} + \text{SiO}_3\text{]}_0.3333. \]

and an average degree of polymerization of about 4, and was terminated with methoxy and hydroxyl groups.

[0086] Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 0.5%. After the rotting test using white and brown rot fungi, they showed weight losses of 5.5% and 4.7%, respectively. After the subterranean test, they showed a weight loss of 14.9%.

Example 10

[0087] Reaction was carried out as in Example 7 except that HFOETMOS was omitted. The reaction solution was diluted with methanol to a solution containing 10% by weight of the oligomer, which was used for treatment. This oligomer had the average composition:

\[ \text{[H}_2\text{NC}_3\text{H}_6\text{SiO}_3\text{]}_0.0050 \text{[Cl - [(CH}_3)_2\text{)(C}_18\text{H}_{37}\text{)}NC}_3\text{H}_6\text{]} + \text{SiO}_3\text{]}_0.0050 \text{[SiO}_4\text{]}_0.9900, \]

and an average degree of polymerization of about 4, and was terminated with methoxy and hydroxyl groups.

[0088] Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 8.7%. After the rotting test using white and brown rot fungi, they showed weight losses of 1.5% and 2.5%, respectively. After the subterranean test, they showed a weight loss of 7.9%.

Example 11

[0089] A 1-liter flask was charged with 136 grams (1.0 mol) of methyltrimethoxysilane (MTMOS), 2.6 grams (0.01 mol) of decyltrimethoxysilane (DTMOS), 5 grams (0.01 mol) of 3-(trimethoxysilyl)propyloctadecylidimethylammonium chloride (TMSAC), 90 grams (1.5 moles) of acetic acid, and 500 grams of t-butanol. With stirring at room temperature, 27 grams (1.5 moles) of deionized water was added dropwise to the flask for reaction to take place, and the reaction solution was ripened at 50°C for 1 hour. Then, 179 grams (1.0 mol) of 3-aminopropyltrimethoxysilane (APTMOS) was added dropwise to the flask for reaction to take place, and the reaction solution was ripened at 50°C for 1 hour. The solution was diluted with t-butanol to a solution containing 10% by weight of the resulting oligomer, which was used for treatment. This oligomer had the average composition:

\[ \text{[C}_{10}\text{H}_{21}\text{SiO}_3\text{]}_0.0050 \text{[H}_2\text{NC}_3\text{H}_6\text{SiO}_3\text{]}_0.4950 - \text{[Cl - [(CH}_3)_2\text{)(C}_18\text{H}_{37}\text{)}NC}_3\text{H}_6\text{]} + \text{SiO}_3\text{]}_0.4950. \]

and an average degree of polymerization of about 5, and was terminated with methoxy, hydroxyl and t-butoxy groups.  

[0090] Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 9.5%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 2.8%.
Example 12

[0091] The procedure of Example 11 was repeated except that instead of t-butanol, deionized water was added to the reaction solution for dilution, obtaining an aqueous solution of 5% oligomer. Using this oligomer solution, pieces of inorganic matter-composited wood were obtained as in Example 7. These pieces had a weight gain (WG) of 7.6%. After the rotting test using white and brown rot fungi, they showed a weight loss of 0% for both. After the subterranean test, they showed a weight loss of 3.6%.

Claims

1. A method of preparing a composite of wood with antibacterial/antifungal inorganic matter, comprising the steps of:
   
   (i) impregnating wood with a treating solution, containing (a) silicon alkoxide of the following general formula (1):
   
   \[(\text{CH}_3)^a\text{Si}(\text{OR})_{4-a}\]  
   
   wherein \( R \) is substituted or unsubstituted monovalent hydrocarbon group having 1 to 12 carbon atoms, and \( a \) is 0, 1, 2 or 3, and (b) antibacterial/antifungal organic silicon compound of the following general formula (2):
   
   \[\left(\text{CH}_3\text{Si}(\text{OR})_2\right)_2\text{Si}^+(\text{OR})_2\text{R}_2^+\times X^{-}\]  
   
   wherein \( R^1 \) is monovalent aliphatic hydrocarbon group having 11 to 22 carbon atoms, \( R^2 \) is alkyl group having 1 to 4 carbon atoms, \( X \) is a halogen atom, and \( b \) is 0 or 1; to fill the inter- and intra-cellular spaces of the wood cell walls with the treating solution, and
   
   (ii) subjecting the silicon alkoxide and the organic silicon compound within said spaces of the cell walls to hydrolysis and polycondensation to form said composite.

2. A method of claim 1 wherein said treating solution contains a further organic silicon compound, of the following general formula (3):

   \[\text{R}_3^m\text{Si}(\text{OR})_{4-m}\]  

   wherein \( R^3 \) is substituted or unsubstituted monovalent hydrocarbon group having 2 to 18 carbon atoms, \( R^4 \) is monovalent hydrocarbon group having 1 to 6 carbon atoms, and \( m \) is 1, 2 or 3.

3. A method of claim 2 wherein in formula (3), at least one \( R^3 \) group is a group wherein some or all of the hydrogen atoms attached to carbon atoms are replaced by fluorine atoms.

4. A method according to claim 2 or 3 in which in formula (3) \( m \) is 1.

5. A method according to claim 4 in which the organic silicon compound of formula (3) is selected from 3,3,3-trifluoropropyltrimethoxysilane, 2-(heptafluorobutyl)ethyl-trimethoxysilane, 2-(heptadecafluorooctyl)ethyltrimethoxy-silane, and 3,3,3-trifluoropropyltriethoxysilane.

6. A method according to any one of claims 2 to 5 in which the amount of the organic silicon compound of formula (3) is from 0.0001 to 0.5 mol per mol of the silicon alkoxide of formula (1).

7. A method according to any one of the preceding claims in which in the silicon alkoxide of formula (1) groups \( R \) are selected from \( C_{1-4} \) alkyl groups and \( a \) is 0 or 1.
8. A method according to any one of the preceding claims in which in the organic silicon compound of formula (2), R¹ is selected from octadecyl, lauryl, myristyl and stearyl.

9. A method according to any one of the preceding claims in which the amount of the organic silicon compound of formula (2) is from 0.0001 to 0.5 mol per mol of the silicon alkoxide of formula (1).

10. A method according to claim 9 in which the amount of the organic silicon compound of formula (2) is from 0.001 to 0.01 mol per mol of silicon alkoxide of formula (1).

11. A method according to any one of the preceding claims in which the wood to be impregnated in step (i) is conditioned to a water content of from 10 to 50 wt%.

12. A method according to any one of the preceding claims in which the impregnation is by immersing the wood in the treating solution at room temperature under a vacuum of from 1.33 to 2.0 kPa (10 to 15 mmHg) for from 1 to 7 days.

13. A method of preparing a composite of wood with antibacterial/antifungal inorganic matter, comprising the steps of

(i) treating wood with a siloxane oligomer of the following average compositional formula (4):

\[
(R^5_c R^6 SiO_{3-c/2})_i (R^7_d R^8 SiO_{3-d/2})_j (R^9_e R^{10} SiO_{3-e/2})_k (SiO_{4/2})_n \tag{4}
\]

wherein R⁵, R⁷ and R⁸ are selected from hydrogen and monovalent hydrocarbon groups having 1 to 10 carbon atoms which may be halogen- or cyano-substituted, R⁶ is halogen- or cyano-substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms, R⁸ is amino-bearing monovalent organic group having 1 to 18 carbon atoms, R¹⁰ is monovalent organic group of the general formula (5):

\[
[-(CH_2)_3 NR^{11}_X (CH_3)_2] X^- \tag{5}
\]

wherein R¹¹ is a monovalent hydrocarbon group of 11 to 22 carbon atoms and X is a halogen atom, c, d, and e are 0 or 1, i, j and n are 0 or positive numbers, and k is a positive number, provided that i and n are not both 0, said siloxane oligomer being terminated with hydroxyl group and/or alkoxy group of 1 to 4 carbon atoms, to impregnate the wood with the oligomer, and

(ii) curing the siloxane oligomer by drying whereby the oligomer is concentrated, hydrolysed, polycondensed and cured to form said composite with the wood.

14. A method according to claim 13 in which R⁵, R⁷ and R⁸ are selected from methyl, ethyl, butyl, pentyl, hexyl, octyl, decyl, vinyl, allyl, propenyl, butenyl, phenyl, tolyl, benzyl, phenylethyl, and halogen and cyano-substituted forms of these.

15. A method according to claim 13 or 14 in which R⁶ is or are selected from lauryl, myristyl, stearyl, halogen-substituted forms thereof, and options as specified for R⁵, R⁷ and R⁸ in claim 14.

16. A method according to any one of claims 13 to 15 in which R⁸ is of the formula

\[-(CH_2)_x [NH-(CH_2)_y]_z NH_2\]

where x is from 1 to 8, y is from 2 to 10 and z is from 0 to 8.

17. A method according to any one of claims 13 to 16 in which in the oligomer from 5 to 100 mol% of the R⁵_c R⁶ SiO_{3-c/2} units are CH₃ SiO_{3/2} units.

18. A method according to any one of claims 13 to 17 in which in the oligomer the R⁵_c R⁶ SiO_{3-c/2} units are composed of CH₃ SiO_{3/2} units, and R'SiO_{3/2} units or R"SiO_{3/2} units where R' is C₅-₁₈ alkyl and R" is C₁-₁₈ fluorinated alkyl.
A method according to any one of claims 13 to 18 in which, in formula (4) for the siloxane oligomer:

\[ i \text{ is from } 0.1 \text{ to } 0.9; \]
\[ j \text{ is from } 0 \text{ to } 0.800; \]
\[ k \text{ is from } 0.001 \text{ to } 0.2, \text{ and} \]
\[ n \text{ is from } 0 \text{ to } 0.9999, \]

where \( i + j + k + n = 1. \)

A method according to any one of claims 13 to 19 in which the siloxane oligomer of formula (4) has an average degree of polymerisation from 2 to 20.

A method according to any one of claims 13 to 20 in which \( j > 0 \) in formula (4), the oligomer is water-soluble and is diluted with water for the impregnation of the wood.

A method according to any one of claims 13 to 21 in which in step (ii) the wood is dried at a temperature in the range 50 to 110°C to volatilise solvent, hydrolyse, polycondense and cure the siloxane oligomer.

A method according to any one of the preceding claims in which the wood is logs, sawed lumber, sliced veneer or plywood.

**Patentansprüche**

1. Verfahren zur Herstellung eines Verbundstoffs aus Holz mit einer antibakteriellen/antifungalen anorganischen Substanz, folgende Schritte umfassend:

   (i) Imprägnieren von Holz mit einer Behandlungslösung, die (a) Siliciumalkoxid der folgenden allgemeinen Formel (1):

   \[ (\text{CH}_3)_a \text{Si(OR)}_{4-a} \]

   worin \( R \) eine substituierte oder unsubstituierte einwertige Kohlenwasserstoffgruppe mit 1 bis 12 Kohlenstoffatomen ist und \( a = 0, 1, 2 \text{ oder } 3 \); und (b) eine antibakterielle/antifungale organische Siliciumverbindung der folgenden allgemeinen Formel (2) umfasst:

   \[ \left\{ \begin{array}{c}
   (\text{OR})_b \\
   (\text{CH}_3)_c \end{array} \right\} \text{Si} \left\{ \begin{array}{c}
   \text{CH}_3 \\
   \text{CH}_3 \\
   \text{N} \end{array} \right\} X^- \]

   worin \( R^1 \) eine einwertige aliphatische Kohlenwasserstoffgruppe mit 1 bis 22 Kohlenstoffatomen ist, \( R^2 \) eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist, \( X \) ein Halogenatom ist und \( b = 0 \text{ oder } 1 \); um die inter- und intrazelulären Zwischenräume der Holzzellwände mit der Behandlungslösung zu füllen, und

   (ii) Unterkontaktieren des Siliciumalkoxids und der organischen Siliciumverbindung innerhalb der Zwischenräume der Zellwände einer Hydrolyse und einer Polykondensation, um den Verbundstoff zu bilden.

2. Verfahren nach Anspruch 1, worin die Behandlungslösung ferner eine organische Siliciumverbindung der folgenden allgemeinen Formel (3) umfasst:

   \[ R^3_m \text{Si(OR)}_{4-m} \]

   worin \( R^3 \) eine substituierte oder unsubstituierte einwertige Kohlenwasserstoffgruppe mit 2 bis 18 Kohlenstoffatomen ist, \( R^4 \) eine einwertige Kohlenwasserstoffgruppe mit 1 bis 6 Kohlenstoffatomen ist und \( m = 1, 2 \text{ oder } 3 \).
3. Verfahren nach Anspruch 2, worin in Formel (3) zumindest eine R³-Gruppe eine Gruppe ist, worin einige oder alle der an Kohlenstoffatome gebundenen Wasserstoffatome durch Fluoratome ersetzt sind.

4. Verfahren nach Anspruch 2 oder 3, worin in Formel (3) m = 1 ist.

5. Verfahren nach Anspruch 4, worin die organische Siliciumverbindung der Formel (3) aus 3,3,3-Trifluorpropyltrimethoxysilan, 2-(Heptafluorbutyl)ethyltrimethoxysilan, 2-(Heptadecafluorocyclohexyl)ethyltrimethoxysilan und 3,3,3-Trifluorpropyltrimethoxysilan ausgewählt ist.

6. Verfahren nach einem der Ansprüche 2 bis 5, worin die Menge der organischen Siliciumverbindung der Formel (3) 0,0001 bis 0,5 mol pro mol des Siliciumalkoxids der Formel (1) beträgt.

7. Verfahren nach einem vorangegangenen Anspruch, worin im Siliciumalkoxid der Formel (1) die Gruppen R aus C₁₋₄-Alkylgruppen ausgewählt sind und a = 0 oder 1 ist.

8. Verfahren nach einem vorangegangenen Anspruch, worin in der organischen Siliciumverbindung der Formel (2) R¹ aus Octadecyl, Lauryl, Myristyl und Stearyl ausgewählt ist.

9. Verfahren nach einem vorangegangenen Anspruch, worin die Menge der organischen Siliciumverbindung der Formel (2) 0,0001 bis 0,5 mol pro mol des Siliciumalkoxids der Formel (1) beträgt.

10. Verfahren nach Anspruch 9, worin die Menge der organischen Siliciumverbindung der Formel (2) 0,001 bis 0,01 mol pro mol des Siliciumalkoxids der Formel (1) beträgt.

11. Verfahren nach einem vorangegangenen Anspruch, worin der das in Schritt (i) zu imprägnierende Holz auf einen Wassergehalt von 10 bis 50 Gew.-% eingestellt wird.

12. Verfahren nach einem der vorangegangenen Ansprüche, worin das Imprägnieren durch 1- bis 7-tägiges Eintau- chen des Holzes in die Behandlungslösung bei Raumtemperatur in einem Vakuum von 1,33 bis 2,0 kPa (10 bis 15 mmHg) durchgeführt wird.

13. Verfahren zur Herstellung eines Verbundstoffs aus Holz mit einer antibakteriellen/antifungalen anorganischen Sub- stanz, folgende Schritte umfassend:

   (i) Behandeln von Holz mit einem Siloxanoligomer der folgenden mittleren Zusammensetzungsformel (4):

   $$(R^5_c R^6 SiO_{(3-c)/2})_i (R^7_d R^8 SiO_{(3-d)/2})_j (R^9_e R^{10} SiO_{(3-e)/2})_k (SiO_{4/2})_n$$  (4)

   worin R⁵, R⁷ und R⁹ aus Wasserstoff und gegebenenfalls halogen- oder cyanosubstituierten, einwertigen Koh- lenwasserstoffgruppen mit 1 bis 10 Kohlenstoffatomen ausgewählt sind, R⁶ eine halogen- oder cyanosubstitu- tierte, einwertige Kohlenwasserstoffgruppe mit 1 bis 18 Kohlenstoffatomen ist, R⁸ eine aminohaltige, einwer- tige organische Gruppe mit 1 bis 18 Kohlenstoffatomen ist, R¹⁰ eine einwertige Kohlenwasserstoffgruppe der allgemeinen Formel (5) ist:

   $$[-(CH_3)_2 NR^{11} (CH_3)_2]^{+} X^-$$  (5)

   worin R¹¹ eine einwertige Kohlenwasserstoffgruppe mit 11 bis 22 Kohlenstoffatomen ist und X ein Halogenatom ist, c, d und e = 0 oder 1 sind, i, j und n = 0 oder positive Zahlen sind und k eine positive Zahl ist, mit der Maßgabe, dass i und n nicht beide 0 sind, wobei das Siloxanoligomer eine Hydroxyl-Endgruppe und/oder Alkoxy-Endgruppe mit 1 bis 4 Kohlenstoffatomen aufweist, um das Holz mit dem Oligomer zu imprägnieren, und

   (ii) Härten des Siloxanoligomers durch Trocknen, wodurch das Oligomer konzentriert, hydrolysiert, polykonden- disiert und gehärtet wird, um den Verbundstoff mit dem Holz zu bilden.

14. Verfahren nach Anspruch 13, worin R⁵, R⁷ und R⁹ aus Methyl, Ethyl, Butyl, Pentyl, Hexyl, Octyl, Decyl, Vinyl, Allyl,
Propenyl, Butenyl, Phenyl, Tolyl, Benzyl, Phenylethyl und halogen- und cyanosubstituierten Formen davon ausgewählt sind.

15. Verfahren nach Anspruch 13 oder 14, worin R⁶ aus Lauryl, Myristyl, Stearyl, halogensubstituierten Formen davon und den in Anspruch 14 für R⁵, R⁷ und R⁹ angeführten Optionen ausgewählt ist oder sind.

16. Verfahren nach einem der Ansprüche 13 bis 15, worin R⁶ die Formel

\[-(\text{CH}_2)_x\cdot\text{NH}\cdot(\text{CH}_2)_y\cdot\text{NH}_2\]

aufweist, worin x = 1 bis 8 ist, y = 2 bis 10 ist und z = 0 bis 8 ist.

17. Verfahren nach einem der Ansprüche 13 bis 16, worin im Oligomer 5 bis 100 Mol-% der R⁵ c R⁶ SiO\((3-c)/2\) -Einheiten CH₃SiO\(3/2\) -Einheiten sind.

18. Verfahren nach einem der Ansprüche 13 bis 17, worin im Oligomer die R⁵ c R⁶ SiO\((3-c)/2\) -Einheiten aus CH₃SiO\(3/2\) -Einheiten und R'SiO\(3/2\) -Einheiten oder R'SiO\(3/2\) -Einheiten bestehen, worin R' C₅-1₈-Alkyl und R" fluoriertes C₁-1₈-Alkyl ist.

19. Verfahren nach einem der Ansprüche 13 bis 18, worin in Formel (4) für das Siloxanoligomer

\[i = 0,1 \text{ bis } 0,9 \text{ ist};
\]
\[j = 0 \text{ bis } 0,800 \text{ ist};
\]
\[k = 0,001 \text{ bis } 0,2 \text{ ist}; \text{ und}
\]
\[n = 0 \text{ bis } 0,9999 \text{ ist};
\]

wobei gilt: \(i + j + k + n = 1\).

20. Verfahren nach einem der Ansprüche 13 bis 19, worin das Siloxanoligomer der Formel (4) einen mittleren Polymerisationsgrad von 2 bis 20 aufweist.

21. Verfahren nach einem der Ansprüche 13 bis 20, worin in Formel (4) \(j > 0\) ist und das Oligomer wasserlöslich ist und zum Imprägnieren des Holzes mit Wasser imprägniert wird.

22. Verfahren nach einem der Ansprüche 13 bis 21, worin in Schritt (2) das Holz bei einer Temperatur im Bereich von 50 bis 110 °C getrocknet wird, um das Lösungsmittel abzudampfen und das Siloxanoligomer zu hydrolysieren, zu polykondensieren und zu härten.

23. Verfahren nach einem der vorangegangenen Ansprüche, worin das Holz in Form von Rundholz, Schnittholz, Furnier oder Sperrholz vorliegt.

Reverdications

1. Méthode de préparation d'un composite de bois avec une matière inorganique antibactérienne/antifongique, comprenant les étapes de:

(i) imprégner le bois d'une solution de traitement, contenant (a) un alcoxyde de silicium de la formule générale (1) qui suit:

\[(\text{CH}_3)_a\text{Si(OR)}_{4-a}\]  \(\text{(1)}\)

où R est un groupe hydrocarbure monovalent substitué ou non substitué ayant 1 à 12 atomes de carbone, et a est 0, 1, 2 ou 3, et (b) un composé de silicium organique antibactérien/antifongique de la formule générale (2) qui suit:
où R\(^1\) est un groupe hydrocarbure aliphatique monovalent ayant 11 à 22 atomes de carbone, R\(^2\) est un groupe alkyle ayant 1 à 4 atomes de carbone, X est un atome d'halogène, et b est 0 ou 1; pour combler les espaces inter- et intracellulaires des parois des cellules du bois au moyen de la solution de traitement, et

(ii) soumettre l'alcoxyde de silicium et le composé de silicium organique dans lesdits espaces des parois des cellules à une hydrolyse et une polycondensation pour former ledit composite.

2. Méthode de la revendication 1 où ladite solution de traitement contient un autre composé de silicium organique de la formule générale (3) qui suit:

\[
R^3_m Si (OR^4)_{4-m}
\]  

où R\(^3\) est un groupe hydrocarbure monovalent substitué ou non substitué ayant 2 à 18 atomes de carbone, R\(^4\) est un groupe hydrocarbure monovalent ayant 1 à 6 atomes de carbone, et m est 1, 2 ou 3.

3. Méthode de la revendication 2 où, dans la formule (3), au moins un groupe R\(^3\) est un groupe où, une partie ou la totalité des atomes d'hydrogène attachés aux atomes de carbone sont remplacés par des atomes de fluor.

4. Méthode selon la revendication 2 ou 3, dans laquelle dans la formule (3) m est 1.

5. Méthode selon la revendication 4 dans laquelle le composé de silicium organique de la formule (3) est sélectionné parmi 3,3,3-trifluoropropyltriméthoxysilane, 2-(heptafluorobutyl)éthyl-triméthoxysilane, 2-(heptadécafluoroctyl)éthyl-triméthoxy-silane, et 3,3,3-trifluoropropytriméthoxysilane.

6. Méthode selon l'une quelconque des revendications 2 à 5 dans laquelle la quantité du composé de silicium organique de formule (3) est de 0,0001 à 0,5 mole par mole de l'alcoxyde de silicium de formule (1).

7. Méthode selon l'une quelconque des revendications précédentes, dans laquelle, dans l'alcoxyde de silicium de formule (1), les groupes R sont sélectionnés parmi des groupes alkyles C\(_{1-4}\) et a est 0 ou 1.

8. Méthode selon l'une quelconque des revendications précédentes dans laquelle dans le composé de silicium organique de la formule (2), R\(^1\) est sélectionné parmi octadécyle, lauryle, myristyle et stéaryle.

9. Méthode selon l'une quelconque des revendications précédentes, dans laquelle la quantité du composé de silicium organique de formule (2) est de 0,0001 à 0,5 mole par mole de l'alcoxyde de silicium de formule (1).

10. Méthode selon la revendication 9 dans laquelle la quantité du composé de silicium organique de formule (2) est de 0,001 à 0,01 mole par mole de l'alcoxyde de silicium de formule (1).

11. Méthode selon l'une quelconque des revendications précédentes dans laquelle le bois imprégné à l'étape (i) est conditionné à une teneur en eau de 10 à 50% pds.

12. Méthode selon l'une quelconque des revendications précédentes dans laquelle l'imprégnation est par immersion du bois dans la solution de traitement à température ambiante sous un vide de 1,33 à 2,0 kPa (10 à 15 mmHg) pendant 1 à 7 jours.

13. Méthode de préparation d’un composite de bois avec une matière inorganique antibactérienne/antifongique, comprenant les étapes de

(i) traiter le bois avec un oligomère de siloxane de la formule de composition moyenne (4) qui suit:
où R₅, R₇ et R₉ sont sélectionnés parmi hydrogène et des groupes hydrocarbures monovalents ayant 1 à 10 atomes de carbone qui peuvent être halogéno- ou cyano-substitués, R₆ est un groupe hydrocarbure monovalent halogéno- ou cyano-substitué ou non substitué ayant 1 à 18 atomes de carbone, R₈ est un groupe organique monovalent porteur d’ami nay ayant 1 à 18 atomes de carbone, R₁₀ est un groupe organique monovalent de la formule générale (5):

\[
[-(CH₂)₃NR₁₁(CH₃)₂]⁺X⁻
\]  

(5)

où R¹¹ est un groupe hydrocarbure monovalent de 11 à 22 atomes de carbone et X est un atome d’halogène, c, d, et e sont 0 ou 1, i, j et n sont 0 ou des nombres positifs, et k est un nombre positif, à condition que i et n ne soient pas tous deux 0, l’édit oligomère de siloxane étant terminé par un groupe hydroxyle et/ou un groupe alcoxy de 1 à 4 atomes de carbone, pour imprégner le bois de l’oligomère, et (ii) durcir l’oligomère de siloxane par séchage pour qu’ainsi l’oligomère soit concentré, hydrolysé, polycondensé et durci pour former ledit composite avec le bois.


15. Méthode selon la revendication 13 ou 14 dans laquelle R₆ est ou sont sélectionnés parmi lauryle, myristyle, stéaryle, leurs formes halogéno-substituées, et des options telles que spécifiées pour R₅, R₇ et R₉ à la revendication 14.

16. Méthode selon l’une quelconque des revendications 13 à 15 dans laquelle R₆ est de la formule

\[
-(CH₂)ₓ[NH-(CH₂)ᵧ]₂-NH₂
\]

où x est de 1 à 8, y est de 2 à 10 et z est de 0 à 8.

17. Méthode selon l’une quelconque des revendications 13 à 16 dans laquelle dans l’oligomère, de 5 à 100% en moles des unités R₅cR₆SiO(3-c)/2 sont des unités CH₃SiO₃/2.

18. Méthode selon l’une quelconque des revendications 13 à 17 dans laquelle, dans l’oligomère, les unités R₅cR₆SiO(3-c)/2 se composent d’unités CH₃SiO₃/2, et d’unités R’SiO₃/2 ou d’unités R”SiO₃/2 où R’ est alkyle C₅-18 et R” est alkyle C₁-18 fluoré.

19. Méthode selon l’une quelconque des revendications 13 à 18 dans laquelle, dans la formule (4) pour l’oligomère de siloxane;

\[
i = 0.1 à 0.9; \\
i = 0 à 0.800; \\
k = 0.001 à 0.2, \\
k = 0 à 0.9999, \\
\text{où } i+j+k+n = 1.
\]

20. Méthode selon l’une quelconque des revendications 13 à 19 dans laquelle l’oligomère de siloxane de formule (4) a un degré moyen de polymérisation de 2 à 20.


22. Méthode selon l’une quelconque des revendications 13 à 21 dans laquelle, à l’étape (ii) le bois est séché à une température dans la gamme de 50 à 110°C pour volatiliser le solvant, hydrolyser, polycondenser et durcir l’oligomère de siloxane.
23. Méthode selon l'une quelconque des revendications précédentes dans laquelle le bois est des grosses buches, du bois de charpente scié, du bois de placage tranché ou du contreplaqué.
FIG. 2