Said porous material may be selected from the group consisting of wood, textile, leather, paper, biological tissue.
Porous material comprising nanoparticles

Field of the invention

The invention pertains to a porous material having enhanced mechanical, physical, chemical and/or biological resistance. In one embodiment, the invention pertains to a wood sheet, in particular a wood veneer, having said enhanced mechanical, physical, chemical and/or biological resistance. Other suitable porous materials may be selected from textiles, leather, paper or biological tissue.

Background of the invention

Porous materials such as wooden species may exhibit desirable characteristics with regard to mechanical, physical, chemical and/or biological resistance. However, by far, not all wooden species exhibit one or more of these desired characteristics, and/or are too costive, and/or are of limited availability for application, e.g. for application in the wood processing industry.

Surface treatments of wooden materials such as impregnation or coating in order to add properties not naturally occurring in wooden species of choice are already known. Prior art in this field focuses on adding one or a combination of characteristics to wooden material such as improved mechanical, physical, chemical and/or biological characteristics.

US 5,652,065 discloses wood veneers having enhanced strength and/or stiffness wherein in the compacted wood cells of the veneer a cured rigid thermoset material, which maintains compaction of the compacted cells is interspersed. The preferred thermoset material is polyurea that is formed from a polyisocyanate resin applied to at least one major surface of the veneer followed by hot-pressing the veneer.

US 3,076,738 suggests to utilize a resin for impregnating woody material which will increase the density, strength, waterproof character and bonding affinity of the material.
The woody material can be a wood veneer or hardboard or a combination of wood veneer and hardboard. The resin is melamine aldehyde resin and sulfite dissolved in an aqueous solvent including at least about 40% as much alcohol as water by weight.

US 2002/0148051 A1 suggests to suppress changes in color of the wooden material caused by exposure to light or heat by subjecting a wooden material to a bleaching treatment and to an acetylatiating treatment. For example, a bleaching solution is applied onto the wooden material by means of a brush coating method or the like, and then the wooden material is treated for a predetermined time, for example, by soaking the wooden material in a bleaching solution for a predetermined time, while heating it as necessary.

US 5,512,323 discloses a wood treatment process to reduce or eliminate grain raising associated with the application of water-based wood finishing compositions. The method comprises the step of wetting the wood surface with an aqueous solution of an aluminum salt, and preferably drying the surface prior to applying the water-based finish composition.

US 4,145,242 relates to the treating of wood surfaces with a solution of selected boron compounds in order to preserve bondability during drying or storing. The compounds are applied in an aqueous solution to the wood surface prior to drying or storing. Wood products are such as bonded laminated lumber and particle board. Due to the treatment, the mechanical and physical properties of the wood products are improved, wherein the wood is also protected against decay and fungal attack.

US 5,683,820 discloses wood products which are impregnated with a polymerizable monomer selected from the group consisting of hexanediol diacrylate and hexanediol dimethacrylate which have an excellent indent resistance. The thus treated hardened, fire-retardant wood product is for application such as flooring where uniform hardness is desirable.

US 6,916,507 discloses methods for imparting dimensional stability and water repellence to substrates, for example, paper items, fibrous items and building materials such as
wood and brick. Typically, materials are coated or impregnated with solutions of silicone compounds, acrylic, urethane, ester, fatty and oily resins or monomers, followed by drying. In particular, silicone water repellents of the solvent dilution type are used. Preferably, the silicone compounds are amino group-containing alkoxy silanes. Using the aqueous water repellent, the method can render plywood or laminated veneer lumber termite-proof, rot-proof, mildew-proof, water resistant, moisture resistant and dimensional stable.

US 2005/0255251 A1 discloses a method of preserving wood comprising injecting into wood nanoparticles selected from copper salts, nickel salts, tin salts and/or zinc salts.

US 2006/0063911 A1 discloses a film forming composition comprising nanoparticles, a resin, a surface active material and a polymeric dispersant. The film forming composition may be used with wood objects including furniture, doors, floors to enhance scratch resistance.

US 2006/0235145 A1 discloses nano-sized silica, titanium oxide and zinc oxide compounded materials for surface modification of wood wall to improve chemical stability, resistance, and the capacity to repel and disperse water, oil, bacteria, organic dust, gas, electricity, magnetism and light (i.e., multi-phobic effects). For application, the nanosized material is sprayed onto the body surface.

US 2005/0287348 A1 discloses a method of coating a flexible and/or drawable substrate, wherein a coating composition comprising a dispersion of resin-coated nanoparticles is applied to said substrate. For example, nanoparticles are prepared by milling and are modified with a resin. Subsequently, the modified nanoparticles are applied to a substrate by injection. The substrate may be a thermoplastic material such as polypropylene, nylon or polyester.

US 2005/0008861 A1 inter alia discloses in a first step the formation of silver-coated silica nanoparticles by spraying a mixture of silica nanoparticles and silver nitrate into a thermal plasma reactor. In a second step, the obtained nanoparticles are deposited on wound wipe pads, napkins, tissue paper, towels, etc. to destroy microbes and bacteria.
US 6,753,035 B2 discloses a method of incorporating additives into wood or a wood product, the method comprising the synthesis of a nanoparticle that is, subsequent to the preparation, applied to wood or a wood product.

US 6,607,994 B2 discloses preparations useful for the permanent or substantially permanent treatment of textiles and other webs. In a first step, silane-coated nanoparticles are prepared that are in a second step applied to textiles.

WO 03/074420 discloses the preparation of metal oxide particles in a sol-gel process. In a preferred embodiment, tetraethoxysilane is hydrolyzed by ammonia to form silica nanoparticles. These particles are applied to polymers such as biomolecules.

WO 01/91925 discloses a method for incorporating additives such as fungicides and biocides into wood or a wood product, such as oriented strand board, particle board, medium density fiberboard, plywood, laminated veneer lumber, laminated strand lumber, hardboard and the like wherein said additives are incorporated into nanoparticles, which are applied to wood or a wood product. Said nanoparticles are based on organic polymers such as polyvinylpyridine, polystyrene and the like.

EP 1 762 352 discloses a method for incorporating nanoparticles such as phyllosilicates, hydrotalcites and polymeric colloids in a porous material such as wood by impregnating the porous material with said nanoparticles. The nanoparticles may be loaded with additives such as dyes, biocides, water repellants and the like.

US 2006/0235145 A1 discloses modified nanoparticles such as nanosized silica powder and fluorocarbon surfactant that are applied to a substrate such as wood wall to form stable nano-sized structure-compounded films.

EP 0 882 555 discloses a method for preparing antibacterial/antifungal compositions of wood with inorganic matter.
DE 10 2005 022 753 A1 discloses a method of treating a wood surface with tetraethoxysilane, wherein a coating is provided on the surface of said wood surface.

Objects of the invention

One problem to be solved by the present invention was to provide an improved porous material such as wood, textile, leather, paper, biological tissue, plastics, stones and metal, in particular wood, textile, leather, paper, biological tissue, more particularly a wood sheet, preferably a wood veneer, having enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances; and a method of preparing such improved materials. In particular, water and oil repellence of the porous material, i.e. hydrophobicity and oliophobicity, should be improved.

Summary of the invention

This and other problems were solved by a composite material comprising a porous material and nanoparticles, characterized in that said nanoparticles comprise a derivative of silica selected from the group consisting of alkoxy silanes and polyalkoxy silanes, wherein said alkoxy silanes and polyalkoxy silanes comprise at least one amino group.

The invention also relates to a process for producing a composite, the composite comprising a porous material and nanoparticles, comprising: soaking said porous material with a fluid comprising nanoparticles, characterized in that said nanoparticles comprise a derivative of silica selected from the group consisting of alkoxy silanes and polyalkoxy silanes, wherein said alkoxy silanes and polyalkoxy silanes comprise at least one amino group.

Within the subject application, the term "composite material" is used as defined herein-under in the section relating to the Second Embodiment. The same applies to the term "porous material".

The term "nanoparticle" as used herein is to be understood broadly. The term "nanoparticle" includes terms such as nanopowder, nanocluster, and nanocrystal particle. In par-
ticular it relates to particles with at least one dimension less than 500 nm, preferably below 300 nm, more preferably below 100 nm, even more preferably below 50 nm, or below 30 nm, with a lower limit being generally 0.1 nm, preferably 1 nm. When discussing the two embodiments in the Detailed description of the Invention, specific embodiments of such nanoparticles, which are particularly suitably used within the respective embodiment are disclosed. This applies particularly to the embodiments wherein a derivative of silica selected from the group consisting of alkoxy silanes and polyalkoxy silanes, which respectively comprise at least one amino group is used. The same applies to the term "soaking".

### Detailed description of the invention

While it is to be understood that the present invention broadly relates to the composite and process for producing same as defined above in section "Summary of the Invention". In the following said composite and method are described in detail with reference to two preferred embodiments. In the first embodiment, the invention is described by referring to a wooden surface as one embodiment of the porous material.

In the second embodiment, an improved process for applying nanoparticles to a porous material is provided to form a composite, said composite comprising said porous material and said nanoparticles.

#### First embodiment

This embodiment relates to a wooden surface, in particular to a wood sheet having a front surface, a back surface and a thickness comprising nanoparticles, wherein said nanoparticles are present on said front surface, said back surface and throughout the thickness.

The wooden surface according to the invention maintains the addressed improved characteristics even during the further processing. For example, a mechanical treatment by sanding a wooden surface, which is equipped with a lacquer or a varnish in order to protect the surface against water reduces the protection characteristics, whereas sanding the wooden surface according to the invention maintains the addressed characteristics. Lacquers and varnishes in general are also unstable against UV radiation or against
weather and/or atmospheric conditions, whereas the wooden surface according to the invention has an excellent resistance against UV radiation and weather and/or atmospheric conditions. Thus, advantageously, the wooden surface according to the invention has an extended durability over the wooden surfaces of the discussed prior art. A particular advantage of the wooden surface according to the invention is that said wooden surface after treatment with nanoparticles still maintains the natural optical and tactile characteristics of the employed wood. By contrast, the treatment of wooden surfaces as discussed in the prior art results in a disadvantageous change of the natural appearance of the employed wood. The addressed advantages of the wooden surface of the invention over the wooden surfaces of the prior art were neither foreseeable nor could be expected.

Specifically, the invention pertains to a wood sheet having a front surface, a back surface and a thickness comprising nanoparticles, characterized in that said nanoparticles are present on said front surface, said back surface and throughout the thickness, so as to confer enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances, to said wood sheet compared to an otherwise similar wood sheet that has no nanoparticles on its front and back surfaces and throughout its thickness.

The term "enhanced mechanical resistance" comprises an enhanced stiffness, rigidity and scratch resistance.

The term "enhanced physical resistance" comprises enhanced repelling properties against water, oils and fats, dust and dirt. In particular, said physical resistance is an enhanced hydrophobicity and oliophobicity.

The term "enhanced chemical resistance" comprises an enhanced resistance against all solids, fluids, gases and radiation which may cause a damage or an adverse alteration of the wood surface, e.g. an alteration caused by acids; bases; oxygen, particularly oxygen in combination with heat; radiation, in particular UV radiation.
The term "enhanced biological resistance" comprises an enhanced resistance against microorganisms and creatures which digest wood, i.e. which can destroy the wood surface and/or which may cause a fouling of the wood, for example microorganisms such as bacteria and fungi, or termites.

In a preferred embodiment, the wood sheet is a veneer.

The term "veneer" means a ply of natural wood obtained from a log or other unit of natural lumber by any suitable means. These means include slicing or peeling a log or another unit of natural lumber. The term "slicing" includes means such as flat cut, true quarter, bastard quarter, flat quarter and rift cut. The term "peeling" includes stay log-half, peeled and peeled-out of center. These processes are known in the art. Veneers that can be applied for the invention can be manufactured according to processes which are disclosed and referenced, for example, in EP 1 688 228. There are no limits to the tree's pieces from which the veneer is obtained. Non-limiting examples of wood comprise hard wood, such as sapele and amazakoue, and soft wood, such as walnut, spruce.

As can be readily appreciated, a sheet or a veneer has a front and a back surface, that is the observe and reverse surface across which extend the length and width dimensions of the veneer. The thickness dimension extends between the perpendicular to the front and back surface.

The permissible thickness range of a sheet can vary depending upon the species of tree from which it was obtained, the intended use of the sheet, and other factors. In general, the thickness can vary between 0.1 mm and some centimeters, e.g. up to 5 cm.

Veneers can be very thin, such as 0.5 mm or less, and can approach, in certain instances, about 2.5 cm in thickness. Generally, however, a veneer tends to be thin in the thickness dimension relative to one or both the length and width dimensions. From a practical standpoint, most veneers tend to have a thickness of 6 mm or less. In general, thinner veneers (such as 6 mm or less) are more practical within most species of wood.
Preferably, the thickness of the wood sheet or wood veneer is from 0.1 mm to 10 mm, more preferred from 0.2 mm to 6 mm, still more preferred from 0.5 mm to 3 mm.

According to the invention, the nanoparticles are not only present on the front and back surface of the wood sheet, but also throughout the thickness or the thickness dimension, i.e. throughout the dimension which extends perpendicular between the front and back surface of the sheet, in particular of the veneer.

In this embodiment, the term "nanoparticle" includes terms such as nanopowder, nano-cluster, and nanocrystal particles. In particular it relates to particles with at least one dimension less than 500 nm, preferably below 300 nm, more preferably below 100 nm, even more preferably below 50 nm, or below 30 nm, with a lower limit being generally 0.1 nm, preferably 1 nm.

Methods for producing nanoparticles are state of the art. In one approach, nanoparticles can be prepared by physical gas-phase condensation which involves the evaporation of a source material and the rapid condensation of vapour into nanometer-sized crystallites. Another manufacturing method is based on a chemistry-based solution-spray conversion process, that starts with water-soluble salts of source materials. The solution is then turned into an aerosol and dried by a spray-drying system. Rapid vaporization of the solvent and rapid precipitation of the solute keeps the composition identical to that of the starting solution. A third technique is to generate nanophase materials by condensation of metal vapours during rapid expansion in a supersonic nozzle.

Also attrition and pyrolysis are common methods. In attrition, macro or micro scale particles are ground in a ball mill, a planetary mill other size reducing mechanism. The resulting particles are air classified to recover nanoparticles.

In pyrolysis, an organic precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting ash is air classified to recover oxide nanoparticle.
A thermal plasma can also deliver the energy necessary to cause evaporation of small micrometer size particles. The thermal plasma temperatures are in the order of 10000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma and radio frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc which forms between the anode and the cathode. For example, silica sand can be vaporized with an arc plasma at atmospheric pressure. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced. In RF induction plasma torches, energy coupling to the plasma is accomplished through the electromagnetic field generated by the induction coil. The plasma gas does not come in contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing and other corrosive atmospheres. The working frequency is typically between 200 kHz and 40 MHz. Laboratory units run at power levels in the order of 30-50 kW while the large scale industrial units have been tested at power levels up to 1 MW. As the residence time of the injected feed droplets in the plasma is very short it is important that the droplet sizes are small enough in order to obtain complete evaporation. The RF plasma method has been used to synthesize different nanoparticle materials, for example synthesis of various ceramic nanoparticles such as oxides, carbides and nitrides of Ti and Si.

Inert-gas aggregation is frequently used to make nanoparticles from metals with low melting points. The metal is vaporized in a vacuum chamber and then supercooled with an inert gas stream. The supercooled metal vapor condenses into nanometer-sized particles, which can be entrained in the inert gas stream and deposited on a substrate or into a liquid.

Preferably, said nanoparticles used in the present invention are selected from the group consisting of carbon-based compounds, metals, metal oxides, and metal salts.
Carbon-based compounds are compounds such as carbon or organic pigments.

Metals are metals such as gold, silver, copper, nickel, and iron, silicon, aluminum, titanium, zinc, boron, ceria, zirconium, tin, antimony, indium, magnesium, calcium, or combinations thereof.

Metal oxides are oxides of the before-mentioned metals, such as silica, titanium oxide, aluminum oxide, iron oxide, zinc oxide, boron oxide.

Metal salts are salts of the above mentioned metals, such as copper salts, nickel salts, tin salts and/or zinc salts, such as copper chloride, iron chloride, zinc chloride.

Said nanoparticles may also comprise further compounds that are applied to the surfaces thereof. By means of said further compounds it is possible to confer to and enhance specific resistances of the wood sheet with regard to mechanical, physical, chemical and/or biological resistances.

Further compounds are for example derivatives of silica.

Preferred derivatives of silica are silazanes and silanes such as siloxanes and polysiloxanes, e.g. alkoxy silanes and poly(alkoxy silanes).

Particularly preferred silanes, siloxanes and polysiloxanes or alkoxy silanes and poly(alkoxy silanes) comprise one or more amino groups.

For example, said silica derivative can be an amino group-containing alkoxy silane. Such compounds are known from the prior art, for example from US 6,916,507.

A preferred amino group-containing silane has the formula $\text{H}_2\text{N-Y-Si(OR)}_3$, wherein $Y$ defines a branched or unbranched $\text{C}_1-\text{C}_2$ chain, and $R$ is a $\text{C}_1-\text{C}_4$ alkyl residue.

Fluids comprising nanoparticles comprising amino group-containing silanes are particularly preferred.
The nanoparticles may also comprise compounds such as fluorocarbons or fluoropolymers. These fluoro compounds typically comprise one or more fluorochemical radicals that contain a perfluorinated carbon chain having from 3 to about 20 carbon atoms, more preferably from about 6 to about 14 carbon atoms. These fluorochemical radicals can contain straight chain, branched chain, or cyclic fluorinated carbon, or any combination thereof. The fluorochemical radicals can optionally contain heteroatoms such as oxygen, sulfur, or nitrogen. Fully fluorinated radicals are preferred, but hydrogen or chlorine atoms may also be present as substituents. It is additionally preferred that any fluorochemical radical contain from about 40% to about 80% fluorine by weight, and more preferably, from about 50% to about 78% fluorine by weight.

Nanoparticles loaded with silicon compounds such as amino group-containing alkoxy silane and fluorocarbons are particularly preferred if hydrophobicity and/or oleophobicity are to be enhanced.

It is further possible to adsorb polymers on the surface of the nanoparticles, such as acrylates, styrene-based polymers, polybutadiene-based polymers, polyesters, polyurethanes, polyamides, and the like.

The nanoparticles employed in the present invention may also comprise bioactive or antimicrobial/fungal agents, sunblock agents, fire retardant chemicals, metallic reflector colloids, reflective particles, magnetic particles, insect repellants, fragrances.

The quantity of said nanoparticles being present on the front and the back surfaces and throughout the thickness of said wood sheet according to the invention preferably is from 0.5 g nanoparticles/m² wood sheet to 20 g nanoparticles/m² wood sheet, preferably from 1 g/m² to 15 g/m², more preferred from 2 g/m² to 10 g/m².

The process for the manufacture of a wood sheet having a front surface, a back surface and a thickness comprising particles, wherein said nanoparticles are present on said front surface, said back surface and throughout the thickness, comprises: treating the front and back surfaces and the thickness dimension of a wood sheet with a nanofluid comprising nanoparticles, wherein said nanofluid soaks said wood sheet.
The term "nanofluid" relates to fluids comprising nanoparticles. If nanoparticles are suspended in conventional fluids, such as organic fluids or water, a nanofluid is produced. The noble properties of nanophase materials come from the relatively high surface-area-to-volume ratio that is due to the high proportion of constituent atoms residing at the grain boundaries.

Methods for producing nanofluids are state of the art. Two techniques are frequently used to make nanofluids: the single-step direct vaporation method, which simultaneously makes and disperses the nanoparticles directly into the base fluids, and the two-step method which first makes nanoparticles and then disperses them into the base fluids. For nanofluids prepared by the two-step method, dispersion techniques such as high shear and ultrasound can be used to create various particle/fluid combinations.

In general, the nanoparticles are dispersed in the base fluid in a concentration less than 20 % by weight, preferably less than 15 % by weight, more preferred less than 10 % by weight.

Preferably, the base fluid of the nanofluid is water.

For stabilizing the dispersion, the nanofluid may contain the stabilizers and/or surfactants for dispersions known in the art.

Such stabilizers and/or surfactants may be selected from monomers, oligomers and polymers of anhydrides, such as maleic anhydride and esters thereof, glycols, such as ethylene glycol and polyethylene glycols, polyvinyl compounds, such as polyvinyl alcohol, polyvinyl acetate and polyvinyl pyrrolidone, modified celluloses, such as methyl cellulose and hydroxyethyl cellulose, phenols, such as nonyl phenol, carboxylates, such as sodium octyl succinate, dimethylformamide, N-methyl-pyrrolidone, and the like.

Alcohols such as short chain alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohols and butyl alcohols, and long-chain alcohols, such as dodecyl alcohol and tridecyl alcohol, may also be added.
The term "treating" means that said nanofluid soaks said wood sheet, that is the nanofluid is allowed to penetrate through the front surface via the thickness dimension through the back surface, or vice versa, or through the front and back surface throughout the thickness dimension of the sheet, thereby completely wetting the wood sheet.

The nanofluid can be applied either on one surface of the wood sheet or on both surfaces provided that the nanofluid soaks the sheet in order allow the nanofluid to penetrate the sheet throughout the thickness dimension.

The presence of the nanoparticles on the front and back surface and throughout the thickness can basically be evidenced by methods such as Scanning Electron Microscopy (SEM) having a resolution from about 1 - 3 nm, Energy Dispersive X-Ray Spectroscopy in combination with SEM (SEM-EDX) having a resolution from about 2 - 3 nm, Environmental Scanning Electron Microscopy (ESEM) having a resolution from about 20 - 50 nm, Transmission Electron Microscopy (TEM) having a resolution from about 0.25 - 2 nm, Scanning Tunneling Microscopy (STM) and/or Atomic Force Microscopy (AFM). These methods are well known in the art.

The treating by soaking can be achieved by processes that are known in the art, for example by application of the nanofluid by a spraying process, by the application of the nanofluid by means of a brush, by dunking the wood veneer into the nanofluid, by applying the nanofluid by means of rollers. In each case, the soaking can be enhanced by means of pressure, such as incubation.

The nanofluid can be applied either on one surface of the wood sheet or on both surfaces provided that the nanofluid soaks the sheet.

Wood comprises wood fibers. The term "wood fibers" as used herein means cellulose elements and/or lignocellulose-origin material or the like of trees. Then, both the wood fibers of the front and back surfaces and throughout the thickness are soaked in the process of the invention. Without wishing to be bound to a theory, it is believed, if nanoparticles comprising amino-group-containing silane is used, said amino group-containing silane reacts via its amino group with hydroxyl groups of the lignocellulose-
origin material, thus producing a covalent bond between the nanoparticle and the wood fiber of the wood sheet to result in the wood product having enhanced properties. However, it is also possible that the nanoparticles are bound via non-covalent interaction, e.g. via van-der-Waals interaction.

The wood sheet produced in the process of the invention is very stable with regard to thickness, length and width dimensions, i.e. the dimensions will in general not be altered or only negligibly altered during the manufacturing process.

If necessary, the wood sheet can be cut to size to produce e.g. a veneer. In a subsequent step, the sheets or sheets of veneer which were cut to size, can be joined by an adhesive. Suitable adhesives are two-component polyurethane adhesives or adhesives based on polyurea.

It is also possible to join wood sheets by means of the above adhesives prior to the treating with a nanofluid. In general, the already joined sheets will resist the treatment duration and the treatment temperature.

For example, a surface having a width and length of approximately 50 cm and a thickness of 1 mm can be soaked by the nanofluid within a process time between 10 to 300 minutes.

The soaking temperature in general is between 20 °C and 60 °C, preferably 30 °C to 50 °C.

However, the skilled person will readily appreciate that different process times and soaking temperatures will be necessary depending on the type of wood, the thickness dimension, the type of nanofluid and/or type of nanoparticle used.

If necessary, the soaked wood sheet can be dried in order to obtain a dry sheet which can be sold or which can be further processed. The drying methods known in the common manufacturing processes for veneers may be applied.
Further process steps may include the sanding of the back and/or the front surfaces or the polishing of said surfaces.

If the one or both surfaces of the wood sheet are further processed by sanding or polishing, the properties imparted by the nanoparticles are not affected but, to the contrary, are maintained. This advantageously distinguishes the wood sheet from wood products of the prior art where only the surface but not the thickness dimension has been treated with nanofluids. Here, sanding and polishing may result in a loss of the properties imparted by the nanofluids due to the removal of the part of the wood surface where the nanoparticles were present.

If desired, it is also possible to apply a varnish onto the surface of the sheets having nanoparticles. For example, an epoxy-based varnish can be applied to further improve e.g. the mechanical resistance such as the scratch resistance. However, in general, this will not be necessary due to the advantageous properties imparted by the nanoparticles. A protecting step as necessary for the wood surfaces of the prior art by application of a varnish or coating can be omitted.

If the surface of the sheet is not further treated with a coating, such as a varnish, the surface feel of the new wood surface will remain warm and soft with tactile surface structure. Advantageously, the natural appearance of wood can be maintained with such a sheet, further distinguishing the new wood surface from wood surfaces of the prior art that have been treated with a coating.

It has been proven that the moisture content of a wood sheet prior to the treating with a nanofluid may affect the quality of the resulting wood sheet.

In general, the quality is enhanced, if the moisture content of said wood sheet prior to the treating with a nanofluid is below the fiber saturation point (f.s.p.). Said fiber saturation point defines the point in a drying process of wood where said wood predominantly contains no "free" water, however, only "bonded" water. "Free" water is in the cell cavities of the wood and "bonded" water is in the cell walls of the wood. The moisture content is determined according to DIN 52183. Other determination methods may also be used,
such as electrical methods (measurement of the Ohmic resistance) or the determination via reflection of infrared radiation. However, it is advisable to use the above DIN-method as a calibration method in order to obtain comparable values.

Accordingly, in a preferred embodiment of the process of the invention, the moisture content of said wood sheet prior to the treating with a nanofluid is below the fiber saturation point.

In general, the fiber saturation point is below 40%, preferably below 35%, more preferred below 32%.

As used herein, a "treated sheet" is a sheet that has been treated according to the process of the invention so as to confer enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances, to said wood sheet compared to an otherwise similar wood sheet that has not been treated with said nanofluid.

In one embodiment the invention pertains to a wood sheet having a front surface and a back surface and a thickness comprising nanoparticles, wherein said nanoparticles are present on said front surface, said back surface and throughout the thickness, preparable by a process, the process comprising: treating said front and back surfaces and the thickness of a wood sheet with a nanofluid comprising nanoparticles, wherein said nanofluid soaks said wood sheet.

The invention also pertains to a wood product, the wood product comprising a wood sheet having a front surface, a back surface and a thickness comprising nanoparticles, wherein said nanoparticles are present on said front surface, said back surface and throughout the thickness, and a substrate.

Substrates may be selected from the group consisting of wood, plywood, laminated fiber sheet, plastic, metal, such as aluminum, or stone.
Thus, it is possible to provide a wood product, wherein the substrate can be selected from a relatively cheap material, which is improved or ennobled with the high-grade wood sheet of the invention.

Such a wood product is manufactured by a process wherein the wood sheet of the invention is fixed onto said substrate. Preferably, it is glued onto said substrate by means of an adhesive.

Preferably, two component polyurethane systems can be applied as adhesive.

The invention also pertains to the use of the sheet and of the wood product comprising said sheet and said substrate.

Said sheet and said wood product comprising said sheet and a substrate may be used in all applications, where enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances, are required. Such applications comprise both outdoor and indoor applications, where a wood surface is subjected to humidity, moisture, oil, dirt, bacteria, UV radiation, microorganisms, mechanical stress, and the like.

The wood sheet comprising nanoparticles based on amino group-containing silanes has excellent repellent properties. Dirt, bacteria, fungi, and water as well as liquids based on oil are prevented from penetrating into said surface. Therefore, the surface of the sheet will maintain a clean appearance.

In particular, the wood sheet having a front surface, a back surface and a thickness comprising nanoparticles, characterized in that said nanoparticles are present on said front surface, said back surface and throughout the thickness, wherein the nanoparticles are based on amino group-containing silanes, has an enhanced hydrophobicity and olio-phobicity as compared to an otherwise similar wood sheet that has not been treated with a nanofluid comprising said amino group-containing silane.
The sheets comprising nanoparticles in general have an excellent stability against UV radiation, i.e. surface structure and color of the sheet will be maintained over a period of many years.

Preferably, the wood sheet and the wood product comprising said sheet and a substrate can be used for the equipment of bathrooms, wellness installations, clinical practice equipments, equipment in yachting, equipment for restaurants.

Said equipment of bathrooms preferably is selected from the group consisting of walls, floors, wash basins, showers, bath tubs.

Said wellness installations preferably are selected from the group consisting of swimming pools and saunas.

Said clinical practice equipments preferably are selected from all surfaces to be easily and hygienically cleaned.

Said equipment in yachting preferably is selected from the group consisting of decks and body fairing.

Said equipment of restaurants preferably is selected from the group consisting of tables and bars.

The present invention, for the first time, achieves the optimization of a wooden material at the raw material production level, as opposed to the finished product level as disclosed in the prior art. The present invention, for the first time, allows the raw material consumer to choose the wooden specie that best suits the demands of the product's manufacture and end use, while simultaneously allowing the supplementing of a choice of one or many desirable wood characteristics of different wood species. The present invention therefore, increases opportunities for wooden applications, for species applications, and natural resource optimisation. The compositional change of the wooden material as achieved by the present invention allows almost all manners of further processing (i.e. sanding, cutting, joining) without changing either the enhanced or the natural proper-
ties of the wooden material. Selective characteristic combinations also permit further treatments such as varnishing or staining according to the consumer's plan for further manufacturing.

In a particularly preferred embodiment of the invention, the veneer employed in the process of the invention is manufactured according to the process as described in EP 1 688 228 B1. Such veneers are commercially available and are sold under the trademark Vinterio® such as Vinterio Stratus® and Vinterio Nimbus®. The use of such veneers as the starting material in the process of the invention allows the manufacture of particularly advantageous wood veneers comprising nanoparticles. Since, contrary to the other known methods of the prior art for producing veneers, the process for the manufacture of Vinterio® veneers maintains the natural appearance of the thus produced veneers, the process of the present invention preserves this natural appearance. Said natural appearance, depending on the used nanofluid and the type of nanoparticles dispersed therein, is also preserved under exposure to environmental impacts, such as mechanical stress; influence of water, oils and fats, dust and dirt; influence of acids, bases, oxygen, particularly oxygen in combination with heat, radiation, in particular UV radiation; influence of microorganisms and creatures which digest wood, i.e. which can destroy wood surfaces and/or which may cause fouling of wood, for example microorganisms such as bacteria and fungi, or termites.

EP 1 688 228 claims a process for the manufacture of a veneer in the form of a sheet which is composed of slices from board-like, plane pieces of wood wherein said slices are jointly adhered by means of an adhesive, the process comprising steps (i) to (iv):

(i) gluing board-like, plane pieces of wood holohedrally by means of an adhesive to a beam-like block of wood,

(ii) watering said beam-like block of wood obtained in step (i),

(iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain said veneer,

(iv) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point.
Accordingly, in a particularly preferred embodiment, the wood sheet comprising nanoparticles of the present invention is obtainable by a process comprising steps (i) to (v):

(i) gluing board-like, plane pieces of wood holohedrally by means of an adhesive to a beam-like block of wood,

(ii) watering said beam-like block of wood obtained in step (i),

(iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain a veneer in the form of a sheet,

(iv) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point to obtain a veneer which is composed of slices from board-like, plane pieces of wood wherein said slices are jointly adhered by means of said adhesive,

(v) treating the front and back surfaces and the thickness of said veneer of step (iv) with a fluid comprising nanoparticles, wherein said fluid soaks said wood sheet.

It is also conceivable to employ in the process of the invention also wooden material having a greater thickness dimension than the wood sheet or the veneer according to the invention. Thus, it is conceivable that also lumber, i.e. pieces or boards of wood, having a thickness of more than 10 mm, can be treated according to the process of the invention with the result of lumber having a front and a back surface and a thickness comprising nanoparticles, wherein said nanoparticles are present on said front and back surfaces and throughout the thickness.

It is also conceivable that still thicker lumber, e.g. pieces or boards of wood having a thickness of e.g. 40 or 50 mm or more, may also be treated according to the process of the invention. Herein, it is conceivable that it is not necessary that nanoparticles are present throughout the whole thickness dimension, but only in a portion of the thickness. It is conceivable that a depth of penetration from both the front and the back surface into the thickness dimension of e.g. 10 mm or 15 mm, respectively, is sufficient to impart the advantageous addressed characteristics to said lumber.
The person skilled in the art will readily appreciate that the characteristics of a wood sheet having a front surface, a back surface and a thickness comprising nanoparticles, characterized in that said nanoparticles are present on said front surface, said back surface and throughout the thickness, so as to confer enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances, to said wood sheet compared to an otherwise similar wood sheet that has no nanoparticles on its front and back surfaces and throughout its thickness, can be determined by sensoric means, in particular by optic and haptic inspection.

Water repellence can also be ascertained by the measurement of the wood moisture content or by the measurement of a water’s drop contact angle on the wooden surface. These methods are well known in the art.

Second embodiment

The second embodiment relates to a composite and an improved process for applying nanoparticles to a porous material to form a composite, said composite comprising said porous material and said nanoparticles.

The problem was solved by

a composite material comprising a porous material and nanoparticles, wherein said nanoparticles comprise a derivative of silica selected from the group consisting of alkoxysilanes and polyalkoxysilanes, wherein said alkoxy-silanes and polyalkoxysilanes comprise at least one amino group and
a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:

(i) soaking said porous material with a composition comprising a metal oxide precursor.

Preferably, the composition comprises water or an alcohol, or water and an alcohol.

Contrary to the processes of the prior art that require the generation and isolation of nanoparticles and application of these isolated nanoparticles to a porous material, the
metal oxide-comprising particles generated in the process of the present invention are not isolated but generated in situ, i.e. inside the substrate to be provided with said metal oxide-comprising particles. Contrary to the processes of the prior art, it is not necessary to isolate said metal oxide-comprising particles, so that a complex reaction step can be omitted. Therefore, the process of the present invention is advantageous over the processes of the prior art with regard to economic aspects, thus particularly advantageous for the industrial applicability.

Furthermore, it has been discussed that nanoparticles in isolated form are potentially harmful substances, since they may penetrate the human skin, respiratory tracts and gastrointestinal tract due to their small sizes. The process of the invention favorably avoids the exposure of humans to isolated nanoparticles since the particles are generated and processed in situ.

The process of the invention does not only allow for an improved penetration, but also for an improved attachment of the particles to the porous material. Since in the process of the present invention, the formation of the metal oxide-comprising particles from the metal oxide-precursor may proceed via hydroxyl or alkoxy group-containing intermediates as explained below, these intermediates may react with functional groups of the porous material. This allows an improved binding of the metal oxide particles by means of covalent bonds resulting in a permanent or substantially permanent bonding of said particles to the surface and/or throughout the thickness, either partially or completely of said porous material. This enhances the advantageous characteristics imparted by said metal oxide-comprising particles to the porous material.

The present invention, for the first time, achieves the optimization of a wooden material as the porous material at the raw material production level, as opposed to the finished product level as disclosed in the prior art. The present invention, for the first time, allows the raw material consumer to choose the wooden specie that best suits the demands of the product's manufacture and end use, while simultaneously allowing the supplementing of a choice of one or many desirable wood characteristics of different wood species. It also allows to create characteristics that wood does not have at all. The present invention therefore, increases opportunities for wooden applications, for species applications,
and natural resource optimisation. The compositional change of the wooden material as achieved by the present invention allows almost all manners of further processing (i.e. sanding, cutting, joining) without changing either the enhanced or the natural properties of the wooden material. Selective characteristic combinations also permit further treatments such as varnishing or staining according to the consumer’s plan for further manufacturing. The same is true for other porous materials such as leather, textiles, paper, biological tissue and plastics.

Accordingly, the invention also pertains to a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:

(i) soaking said porous material with a composition comprising a metal oxide-precursor and water to generate said metal oxide-comprising particles \textit{in situ}.

Preferably, the metal oxide-comprising particles are nanoparticles. Such preferred metal oxide-comprising particles generated \textit{in situ} in the process of the invention preferably have at least one dimension less than 500 nm, preferably less than 400 nm, more preferred less than 300 nm, still more preferred less than 200 nm.

Particularly preferred are particles having at least one dimension less than 100 nm, preferably below 50 nm, more preferred below 30 nm. The size of said particles relates to the average size, which can be determined according to methods known in the art. For example, the determination by light scattering is mentioned.

Preferred metals of the metal oxide-comprising particles are metals selected from the group consisting of boron, silicon, aluminum, titanium, zirconium, cerium.

The term “metal oxide-precursor” means any compound that may be converted into the respective metal oxide, preferably into said metal oxides of boron, silicon, aluminum, titanium, zirconium. Said metal oxide-precursors can also be present in the form of mixtures.
In principle, besides the above defined metal oxide-precursors, also oxide precursors of the elements from groups III, IV and IVb of the Periodic Table can be present in the composition of (i).

Preferably, the metal oxide-precursor is a metal alkoxide or a metal chloride or a metal hydroxide. In a preferred embodiment, the metal oxide-precursor is an alkoxide or a chloride, preferably an alkoxide or chloride of boron, silicon, aluminum, titanium, zirconium, cerium.

In a particularly preferred embodiment, the metal oxide-precursor is an alkoxide of silicon, preferably a tetraalkoxysilane. Preferably, said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane.

The metal oxide-precursor is slowly hydrolyzed by water to generate the desired metal oxide-comprising particles. In order to accelerate said hydrolysis reaction, a base or an acid may be added to the composition of (i). Said base or acid functions as catalyst and causes the desired acceleration.

Preferred bases are sodium hydroxide, ammonia, primary, secondary and tertiary amines. In one embodiment, salts of ammonia, primary, secondary and tertiary amines are employed.

Preferably, the base is ammonia.

Preferred acids are hydrochloric acid, phosphoric acid, sulfuric acid, acetic acid.

Acetic acid is preferred.

It is also possible to add an alcohol to the composition of (i). Preferred is a water soluble alcohol such as methanol or ethanol. Isopropyl alcohol may also be employed. Such an alcohol may improve the solubility of the employed alkoxide in water and may also stabilize the generated metal oxide-comprising particles.
In a particularly preferred embodiment, the composition of (i) comprises a tetraalkoxysilane, water and a base.

Particularly preferred is a composition comprising tetraethoxysilane (TEOS), water and ammonia.

Still more preferred is a composition comprising tetraethoxysilane, water, ammonia and ethanol or methanol.

A composition comprising tetraethoxysilane, water, ammonia and ethanol for generating silica-comprising particles has been the object of intensive investigation. The process is also known as Stöber process and the thus produced particles are known as Stöber particles. Reference is made to the above document of the prior art WO 03/074420 A1 and the literature cited therein, and whose content is fully incorporated herein by reference.

Due to the available comprehensive research and publication regarding the Stöber process, it is not necessary to explain said process herein in detail. Therefore, the Stöber process is only briefly discussed herein.

The formation of Stöber particles proceeds in a sol-gel process. The size of said particles can be exactly regulated via the concentration of ethanol, water, ammonia, TEOS and reaction temperature within a range of preferably from 50-500 nm. Thus, the Stöber particles may be regarded to be nano-sized. It is within routine experimentation of the person skilled in the art to find a composition and reaction conditions, which will match the aspired characteristics of said particles, in particular with regard to the size thereof.

The fundamental reactions of the Stöber process can be described by hydrolysis and condensation reactions. Said process proceeds via hydrolysis of a Si-OC₂H₅ moiety to a Si-OH moiety and liberation of ethanol, the condensation of a Si-OC₂H₅ moiety and a Si-OH moiety, wherein a Si-O-Si moiety and ethanol are formed, the condensation between two Si-OH moieties, wherein Si-O-Si moiety and water are formed. The overall reaction consists in the hydrolysis of Si(OC₂H₅)₄ to SiO₂ and ethanol.
In the Stöber process, in general, alcohol, water and ammonia are firstly provided. Then, TEOS is added. The alcohol serves as a co-solvent for the water-insoluble TEOS. Ammonia catalyses both the hydrolysis and the condensation reaction.

Due to said preparation of the metal oxide-comprising particles, said particles are free from disturbing surfactants, stabilizers and the like. Additionally, the particles have a multi-functional surface that can be modified. In particular, said surface can be modified made-to-measure depending on the aspired characteristics and desired application of the metal oxide-comprising particles. For example, the silanol groups in the intermediates of the Stöber process allow a functionalisation of the particle surface. Respective embodiments are disclosed below.

The term "soaking" as used in the present application, in its broadest meaning also encompasses the covering/impregnating of surfaces. It, however, also includes the application of the composition such that the same migrates into or through the porous material with the result that said porous material is saturated with said metal oxide-precursor and water. Soaking can be achieved by processes that are known in the art. Such processes comprise spraying the composition of (i) onto the porous material, the application by means of a brush, dunking, dipping, injecting, fluid-flow. The composition of (i) may also be applied onto said porous material by means of rollers. In each case, the soaking can be enhanced by application of pressure and/or heat, such as incubation.

In a preferred embodiment, soaking is performed by applying the composition of (i) from the vapor phase to the porous material.

In one embodiment of the process, the substrate is soaked with a composition comprising the metal oxide-precursor, water, ammonia or an acid, and alcohol, wherein the ingredients of said composition are simultaneously added to the substrate.

Accordingly, said embodiment relates to a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:
soaking said porous material with a composition comprising a metal oxide-precursor, water, ammonia or an acid, and alcohol, wherein metal oxide-precursor, water, ammonia or acid, and alcohol are simultaneously added to the substrate.

However, it is also possible to add the metal oxide-precursor, water, ammonia and alcohol in an arbitrary sequence to the substrate.

In one embodiment, it is possible to firstly soak the porous material with water and ammonia and then to soak the thus pre-treated porous material with the metal oxide-precursor.

Accordingly, said embodiment relates to a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:

(i) soaking said porous material with a composition comprising water and ammonia or acid,

(1) soaking the product from (0) with a metal oxide-precursor and water.

Alcohol, preferably methanol or ethanol or isopropanol, may be present in (0) and/or (i).

In a particularly preferred embodiment, it is possible to firstly soak the substrate with the metal oxide-precursor. Preferably, said metal oxide-precursor is applied to the substrate in the form of a suspension or dispersion in water, which optionally also contains an alcohol. Afterwards, the thus soaked substrate is soaked with an aqueous ammonia solution or an acid in order to convert the metal oxide-precursor into the metal oxide-comprising particles in situ. The thus metal oxide-comprising particles are generated within the pores and capillaries of said substrate.

Accordingly, said embodiment relates to a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:
(i) soaking said porous material with a composition comprising a metal oxide-precursor and water,
(ii) soaking the soaked porous material from (i) with ammonia or an acid.

Alcohol, preferably methanol or ethanol or isopropyl alcohol, may be present in (i) and/or (ii).

In still another embodiment, it is possible to firstly soak the porous material with a solution of the metal oxide-precursor in alcohol, preferably methanol or ethanol or isopropyl alcohol, and then to add water and ammonia. Then, step (i) may be divided in substeps (i.1) and (i.2):

Accordingly, said embodiment relates to a process for producing a composite, the composite comprising a porous material and metal oxide-comprising particles, the process comprising:

(U) soaking said porous material with a composition comprising a metal oxide-precursor and alcohol,
(i.2) soaking the soaked porous material from (i.1) with water and ammonia or an acid.

At any stage of the disclosed processes, further metal oxide-precursor can be added.

In one embodiment, the process comprises:

(i) soaking said porous material with a composition comprising a metal oxide-precursor such that said porous material is saturated with said composition, and subsequent to the soaking reacting said composition such that said nanoparticles are generated in situ within and throughout said porous material.

In a preferred embodiment, the porous material is a wood sheet, preferably a veneer.
In another preferred embodiment, the metal oxide-precursor comprises a silicon alkylalkoxy compound. Preferably, alkyl residue of said silicon alkylalkoxy compound bears a functional group.

Preferred functional groups are selected from amino, carboxyl, halide, epoxy, hydroxyl, thiol, aldehyde, cyanate, vinyl.

A preferred amino group-containing silane has the formula $\text{H}_2\text{N-Y-Si(OR)}_3$, wherein $Y$ defines a branched or unbranched $\text{C}_1$-$\text{C}_2$ chain, and $R$ is a $\text{C}_1$-$\text{C}_4$ alkyl residue.

Non-limiting examples of suitable silicon alkylalkoxy compounds are compounds such as octly(triethoxy)silane, aminoethyl(triethoxy)silane, 3-(triethoxysilyl)propylsuccinic anhydride, 3,3,3-trifluoropropyltrimethoxysilane.

Since such silicon alkylalkoxy compound may be also hydrolyzed under the conditions of the Stöber process or Stöber-like processes, such a compound can be incorporated into the metal oxide-comprising particles via condensation reactions. Thereby, the particle surface can be functionalized. If the functional group is suitable to react with functional groups contained in the polymers of the porous material, the metal oxide-comprising particle can be covalently linked to said polymer, or to an article comprising said polymer, or to an article of manufacture comprising said article comprising said polymer, or to an article of manufacture comprising said polymer, such as wood, textiles, leather, paper or biological tissue, or articles of manufacture comprising wood, textiles, leather, paper or biological tissue.

It is possible to add said alkylalkoxy compound at any stage of the disclosed processes. However, it is preferred to employ said silicon alkylalkoxy compound after said porous material has been soaked with said metal oxide-precursor or to employ said silicon alkylalkoxy compound together with said metal oxide-precursor.

Particularly preferred derivatives of alkylalkoxy compounds comprise one or more amino groups. Such compounds are known from the prior art, for example from US 6,916,507.
The thus resulting metal oxide-comprising particles comprising amino groups are particularly preferred in the process of the invention.

In another preferred embodiment, the metal oxide-precursor comprises a silicon alkoxy-halide, such as triethoxyfluorosilane.

In another preferred embodiment, it is possible to soak the porous material such as the wood sheet with the metal oxide-precursor, preferably from the vapor phase, and to use the water already contained in said porous material for carrying out the Stöber or the Stöber-like process in the process according to the invention.

The base, such as ammonia, or the acid, such as acetic acid, may be employed in liquid form, e.g. dissolved in water, or in gaseous form, i.e. from the vapor phase.

In one embodiment, at first the porous material is soaked with the metal oxide-precursor from the vapor phase. Subsequent to said soaking, the soaked porous material sheet is soaked with said base or acid.

In another embodiment, both the metal oxide-precursor and the base, such as ammonia, or the acid, such as acetic acid, may be employed from the vapor phase.

In one embodiment, it is possible to firstly soak the porous material with the metal oxide-precursor from the vapor phase, and to subject the soaked porous material to the base or the acid from the vapor phase.

In another embodiment, it is possible to firstly soak the porous material with the base or the acid from the vapor phase, and then to subject the porous material to the metal oxide-precursor from the vapor phase.

Accordingly, in one embodiment, the process comprises:
(i) soaking said porous material with a composition comprising a metal oxide-precursor, wherein soaking is performed by applying said composition from the vapor phase to said porous material.

In another embodiment, the process comprises:

(i) soaking said porous material with a composition comprising a metal oxide-precursor, wherein soaking is performed by applying said composition from the vapor phase to said porous material; and prior or subsequent to said soaking with said metal oxide-precursor soaking said porous material with a base or an acid, wherein said base or said acid is applied in liquid form or is applied from the vapor phase.

By means of the modification of the surface by incorporating suitable substances into the condensation process of the Stöber particles, it is possible to confer to and enhance specific resistances of the composite with regard to mechanical, physical, chemical and/or biological resistances.

The term "enhanced mechanical resistance" comprises an enhanced stiffness or enhanced flexibility, rigidity and scratch resistance.

The term "enhanced physical resistance" comprises enhanced repelling properties against water, oils and fats, dust and dirt. In particular, said physical resistance is an enhanced hydrophobicity and oliophobicity.

The term "enhanced chemical resistance" comprises an enhanced resistance against all solids, fluids, gases and radiation which may cause a damage or an adverse alteration of the substrate, e.g. an alteration caused by acids; bases; oxygen, particularly oxygen in combination with heat; radiation, in particular UV radiation. In particular, said enhanced resistance is an enhanced acid and base resistance, an enhanced fire resistance, and an enhanced radiation resistance.
The term "enhanced biological resistance" comprises an enhanced resistance against microorganisms and creatures which digest said substrate, i.e. which can destroy the surface of the substrate and/or which may cause a fouling of the substrate, for example microorganisms such as bacteria and fungi, or termites.

For example, metal oxide-comprising particles comprising amino groups and fluoro groups are particularly preferred, if hydrophobicity and/or oleophobicity are to be enhanced.

Said composition of (i) may also comprise modifying compounds that are applicable to the surface of the metal oxide-comprising particles. By means of said modifying compounds, it is possible to confer to and enhance specific resistances of the composite with regard to mechanical, physical, chemical and/or biological resistances.

Accordingly, the composition in (i) comprises modifying compounds selected from the group consisting of metals, metal oxides, bioactive agents, anti-microbial/fungal agents, drugs, pharmaceuticals, sunblock agents, dyes, pigments, scents, fragrances, insect repellents, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, reflective particles, thermochromic materials, heat-absorbing or heat-releasing phase change agents, fabric softeners, zeolites, activated carbon, electrographic agents, luminescent agents such as fluorescent and phosphorescent agents.

Preferred metals are cerium, iron, copper, silver, gold, platinum, palladium, rubidium, vanadium.

Preferred metal oxides are the oxides of cerium, iron, copper, silver, gold, platinum, palladium, rubidium, vanadium.

It is further possible to adsorb polymers on the surface of the metal oxide-comprising particles. Polymers are polymers such as acrylates, styrene-based polymers, polybutadiene-based polymers, polyesters, polyurethanes, polyamides, and the like.
Also fluorocarbons or fluoropolymers may be applied. These fluoro compounds typically comprise one or more fluorochemical radicals that contain a perfluorinated carbon chain having from 3 to about 20 carbon atoms, more preferably from about 6 to about 14 carbon atoms. These fluorochemical radicals can contain straight chain, branched chain, or cyclic fluorinated carbon, or any combination thereof. The fluorochemical radicals can optionally contain heteroatoms such as oxygen, sulfur, or nitrogen. Fully fluorinated radicals are preferred, but hydrogen or chlorine atoms may also be present as substituents. It is additionally preferred that any fluorochemical radical contain from about 40% to about 80% fluorine by weight, and more preferably, from about 50% to about 78% fluorine by weight.

The modifying agent can be added at any stage of the process of the invention. Such modifying agent may be added prior to the addition of the metal oxide-precursor, together with the metal oxide-precursor or subsequent to the metal oxide-precursor.

The process is stopped by removing the volatile components by application of heat or in vacuum. Volatile compounds may be water, ammonia and alcohol.

The term "porous material" means any substrate that can be soaked with the composition of (i), e.g. through capillaries that might be present in the substrate and in which the metal oxide-precursor and water are transported into the interior of the porous material by means of capillary force.

Preferably, said porous material is a natural or synthetic polymer and/or is an article comprising said natural or synthetic polymers, or is an article of manufacture produced from said natural or synthetic polymers.

Preferably, such a natural or synthetic polymer is selected from the group of polymers containing moieties of cellulose such as cellulose as such or lignocellulose peptide, lignin, polyester, polyamide, polyurethane, polystyrene, polyethylene, polypropylene, polysilane, polysiloxane, polysilicate. Bioactive polymers such as proteins, glycoproteins, nucleic acids, peptidic nucleic acids, saccharides, hormones, haptenes, vitamins can also be employed.
Articles and/or articles of manufacture comprising said polymers or articles of manufacture produced from said natural or synthetic polymers are preferably selected from the group preferably consisting of wood, leather, textiles, paper, biological tissue and/or plastics.

In a particularly preferred embodiment, the porous material is wood or comprises wood.

Composites comprising wood or a wooden surface as the porous material, the composites being produced according to the process of the invention, maintain the addressed improved characteristics even during the further processing. For example, a mechanical treatment by sanding a wooden surface, which is equipped with a lacquer or a varnish in order to protect the surface against water, reduces the protection characteristics, whereas sanding a wooden surface produced according to the process of the invention maintains the addressed characteristics. In general, lacquers and varnishes are also unstable against UV radiation or against weather and/or atmospheric conditions, whereas a wooden surface produced according to the process of the invention has an excellent resistance against UV radiation and weather and/or atmospheric conditions. Thus, advantageously, a wooden surface produced according to the invention has an extended durability over the wooden surfaces of the prior art. A particular advantage of a wooden surface produced according to the invention is that said wooden surface still maintains the natural optical and tactile characteristics of the employed wood. By contrast, the treatment of wooden surfaces using the methods of the prior art results in a disadvantageous change of the natural appearance, or the optical and tactile characteristics of the employed wood. The addressed advantages of a wooden surface produced according to the process of the invention over the wooden surfaces produced to processes of the prior art were neither foreseeable nor could be expected.

In one preferred embodiment, said wood is veneer or lumber.

The term "veneer" means a ply of natural wood obtained from a log or other unit of natural lumber by any suitable means. These means include slicing or peeling a log or another unit of natural lumber. The term "slicing" includes means such as flat cut, true quarter, bastard quarter, flat quarter and rift cut. The term "peeling" includes stay log-half,
peeled and peeled-out of center. These processes are known in the art. Veneers that can be applied for the invention can be manufactured according to processes which are disclosed and referenced, for example, in EP 1 688 228. There are no limits to the tree's pieces from which the veneer is obtained. Non-limiting examples of wood comprise hard wood, such as oak, walnut, beech, and soft wood, such as spruce, fir and pine.

As can be readily appreciated, a veneer or a wood sheet has a front and a back surface, that is the observed and reverse surface. The area of these surfaces is defined by the length and width dimensions of the veneer or sheet. The thickness dimension extends between the perpendicular to the front and back surface.

The permissible thickness range of a veneer or a sheet can vary depending upon the species of tree from which it was obtained, the intended use of the sheet, and other factors. In general, the thickness can vary between 0.1 mm and some centimeters, e.g. up to 5 cm.

Veneers can be very thin, such as 0.5 mm or less, and can approach, in certain instances, about 2.5 cm in thickness. Generally, however, a veneer tends to be thin in the thickness dimension relative to one or both the length and width dimensions. From a practical standpoint, most veneers tend to have a thickness of 6 mm or less. In general, thinner veneers (such as 6 mm or less) are more practical within most species of wood.

Preferably, the thickness of the wood sheet or wood veneer is from 0.1 mm to 10 mm, more preferred from 0.2 mm to 6 mm, still more preferred from 0.5 mm to 3 mm.

In a particularly preferred embodiment of the invention, the veneer employed as the porous material in the process of the invention is manufactured according to a process as described in EP 1 688 228 B1. Such veneers are commercially available and are sold under the trademark Vinterio® such as Vinterio Stratus® and Vinterio Nimbus®. The use of such veneers as the starting material in the process of the invention allows the manufacture of particularly advantageous wood veneers comprising nano-scaled metal oxide-comprising particles. Since, contrary to the other known methods of the prior art for producing veneers and spliced faces, the process for producing of Vinterio® veneers maint-
tains the natural appearance of the thus produced veneers, the process of the present invention preserves this natural appearance. Said natural appearance, depending on the used metal oxide-comprising particles, is also preserved under exposure to environmental impacts, such as mechanical stress; influence of water, oils and fats, dust and dirt; influence of acids, bases, oxygen, particularly oxygen in combination with heat, radiation, in particular UV radiation; influence of microorganisms and creatures which digest wood, i.e. which can destroy wood surfaces and/or which may cause fouling of wood, for example microorganisms such as bacteria and fungi, or termites.

EP 1 688 228 claims a process for producing a veneer in the form of a sheet which is composed of slices from board-like, plane pieces of wood wherein said slices are jointly adhered by means of an adhesive, the process comprising steps (i) to (iv):

(i) gluing board-like, plane pieces of wood holohedrally by means of an adhesive to a beam-like block of wood,
(ii) watering said beam-like block of wood obtained in step (i),
(iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain said veneer,
(iv) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point.

Accordingly, in a particularly preferred embodiment the invention pertains to a process for producing a composite, the composite comprising a veneer in the form of a sheet and comprising metal oxide-comprising particles, the process comprising:

(i) gluing board-like, plane pieces of wood holohedrally by means of an adhesive to a beam-like block of wood,
(ii) watering said beam-like block of wood obtained in step (i),
(iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain said veneer,
(iv) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point,
(v) soaking said veneer obtained in (iv) with a composition comprising a metal oxide-precursor and water.

Preferably, said metal oxide-precursor is TEOS. Preferably, said composition of (i) comprises ammonia or an acid, and an alcohol, preferably methanol, ethanol, or isopropanol.

The term "soaking" means that said metal oxide-precursor and water soaks said wood sheet, that is the metal oxide-precursor and water are allowed to penetrate through the front surface via the thickness dimension through the back surface, or vice versa, or through the front and back surface throughout the thickness dimension of the sheet, thereby completely wetting the wood sheet.

The metal oxide-precursor and water can be applied either on one surface of the wood sheet or on both surfaces provided that the metal oxide-precursor soaks the sheet in order to allow the metal oxide-precursor to penetrate the sheet throughout the thickness dimension.

It is also possible to employ in the process of the invention also wooden material having a greater thickness dimension than a veneer. Thus, lumber, i.e. pieces or boards of wood, having a thickness of more than 10 mm, can be soaked according to the process of the invention with the result of lumber having a front and a back surface and a thickness comprising nano-scaled metal oxide-comprising particles, wherein said metal oxide-precursor and water are present on said front and back surfaces and throughout the thickness. Consequently, if said metal oxide-precursor is converted into said metal oxide-comprising particles, said particles are also present on said front and back surfaces and throughout the thickness.

It is also possible to soak thicker lumber, e.g. pieces or boards of wood having a thickness of e.g. 40 or 50 mm or more, according to the process of the invention. Herein, it is not necessary that nano-scaled metal oxide-comprising particles are present throughout the whole thickness dimension, but only in a portion of the thickness. It is possible that a
depth of penetration from both the front and the back surface into the thickness dimension of e.g. 10 mm or 15 mm, respectively, is sufficient to impart the advantageous characteristics to said lumber.

The term "lumber" means any piece of wood that is sawn from a log. In general, the thickness of such wood is more than 10 mm.

In a preferred embodiment, it is possible to soak wood only with the metal oxide-precursor and to use the water already contained in said wood for carrying out the Stöber or the Stöber-like process in the process according to the invention.

Wood comprises wood fibers. The term "wood fibers" as used herein means cellulose elements and/or lignocellulose-origin material or the like of trees. Without wishing to be bound to a theory, it is believed that metal oxide-comprising particles comprising amino groups may react via its amino group with functional groups of the lignocellulose-origin material, thus producing a covalent bond between the particle and the wood fiber of the wood to result in a wood product having enhanced properties. However, it is also possible that the nanoparticles are bound via non-covalent interaction, e.g. via van-der-Waals interaction.

A composite comprising wood as such or a wooden surface produced according to the process of the invention is very stable with regard to thickness, length and width dimensions, i.e. the dimensions will in general not be altered or only negligibly altered during the manufacturing process.

If necessary, said composite can be cut to size to produce a sheet, e.g. a veneer. In a subsequent step, the sheets or sheets of veneer which were cut to size, can be joined by an adhesive. Suitable adhesives are e.g. two-component polyurethane adhesives or adhesives based on polyurea.

It is also possible to join wood sheets by means of the above adhesives prior to the soaking with the composition of (i). In general, the already joined sheets will resist the treatment duration and the treatment temperature.
For example, a surface having a width and length of approximately 50 cm and a thickness of 1 mm can be soaked in the process of the invention within a process time between 5 to 300 minutes.

The soaking temperature in general is between 0 °C and 80 °C, preferably 5 °C to 50 °C, more preferred 5 - 40 °C.

However, the skilled person will readily appreciate that different process times and soaking temperatures will be necessary depending on the type of wood, the thickness dimension, and the type of metal oxide-comprising particle used. The finding of the optimal reaction conditions belongs to routine experiments of the person skilled in the art.

If necessary, the soaked wooden surface can be dried in order to obtain a dry surface which can be sold or which can be further processed. The drying methods known in the common manufacturing processes for veneers may be applied.

Further process steps may include the sanding of the back and/or the front surfaces or the polishing of said surfaces.

If the one or both surfaces of the wood sheet are further processed by sanding or polishing, the properties imparted by the metal oxide-comprising particles are not affected but, to the contrary, are maintained. This advantageously distinguishes the wood sheet from wood products of the prior art where only the surface but not the thickness dimension has been treated with nanoparticles, and where sanding and polishing may result in a loss of the properties imparted by the nanoparticles due to the removal of the part of the wood surface where the nanoparticles were present.

If desired, it is also possible to apply a varnish onto the surface of the sheets having nanoparticles. For example, an epoxy-based varnish can be applied to further improve e.g. the mechanical resistance such as the scratch resistance. However, in general, this will not be necessary due to the advantageous properties imparted by the metal oxide-comprising particles. A protecting step as necessary for the wood surfaces of the prior art by application of a varnish or coating can be omitted.
If the surface of the sheet is not further treated with a coating, such as a varnish, the surface feel of the new wood surface will remain warm and soft with tactile surface structure. Advantageously, the natural appearance of wood can be maintained with such a sheet, further distinguishing the new wood surface from wood surfaces of the prior art that have been treated with a coating.

In one embodiment, the porous material of the composite is a wood sheet having a front surface and a back surface and a thickness comprising metal oxide-comprising particles, wherein said metal oxide-comprising particles are present on said front surface, said back surface and throughout the thickness. Preferably, said wood sheet is preparable by a process, the process comprising: soaking said front and back surfaces and the thickness of a wood sheet with a composition comprising a metal oxide-precursor and water.

The invention also pertains to a composite, the composite comprising a porous material, wherein the porous material is a wood product, the wood product comprising a wood sheet having a front surface, a back surface and a thickness comprising metal oxide-comprising particles, wherein said metal oxide-comprising particles are present on said front surface, said back surface and throughout the thickness, and a substrate.

Substrates may be selected from the group consisting of wood, plywood, laminated fiber sheet, plastic, metal, such as aluminum, or stone.

Thus, it is possible to provide a wood product, wherein the substrate can be selected from a relatively cheap material, which is improved or ennobled with the high-grade wood sheet produced according to the process of the invention.

Such a wood product is manufactured by a process wherein the wood sheet produced according to the process of the invention is fixed onto said substrate. Preferably, it is glued onto said substrate by means of an adhesive, or by ultrasonic welding.

Preferably, two component polyurethane systems can be applied as adhesive.
The invention also pertains to the use of the sheet and of the wood product comprising said sheet and said substrate.

Said sheet and said wood product comprising said sheet and a substrate may be used in all applications, where enhanced mechanical or physical or chemical or biological resistance, or combinations of said resistances, are required. Such applications comprise both outdoor and indoor applications, where a wood surface is subjected to humidity, moisture, oil, dirt, bacteria, UV radiation, microorganisms, mechanical stress, and the like.

The wood sheet comprising nanoparticles based on fluoro group-containing silanes has excellent repellent properties. Dirt, bacteria, fungi, and water as well as liquids based on oil are prevented from penetrating into said surface. Therefore, the surface of the sheet will maintain a clean appearance.

According to the process of the invention, the metal oxide particles are not only present on the front and back surface of the wood sheet, but also throughout the thickness or the thickness dimension, i.e. throughout the dimension which extends perpendicular between the front and back surface of the sheet, in particular of the veneer.

The sheets comprising metal oxide-comprising particles in general have an excellent stability against UV radiation, i.e. surface structure and color of the sheet will be maintained over a period of many years.

Preferably, the wood sheet and the wood product comprising said sheet and a substrate can be used for the equipment of bathrooms, wellness installations, clinical practice equipment, equipment in yachting, equipment for restaurants.

Said equipment of bathrooms preferably is selected from the group consisting of walls, floors, wash basins, showers, bath tubs.
Said wellness installations preferably are selected from the group consisting of swimming pools and saunas. Said clinical practice equipment preferably are selected from all surfaces to be easily and hygienically cleaned.

Said equipment in yachting preferably is selected from the group consisting of decks and body fairing.

Said equipment of restaurants preferably is selected from the group consisting of tables and bars.

The characteristics of a composite prepared according to the invention can be determined by sensoric means, in particular by optic and haptic inspection.

Water repellence can also be ascertained by the measurement of the moisture content or by the measurement of a water's drop contact angle on the composite's surface. These methods are well known in the art.

The quantity of said nanoparticles being present on the front and the back surfaces and throughout the thickness of said wood sheet preferably is from 0.5 g nanoparticles/m² wood sheet to 20 g nanoparticles/m² wood sheet, preferably from 1 g/m² to 15 g/m², more preferred from 2 g/m² to 10 g/m².

The term "wood" also encompasses wood-like porous materials such as bamboo, straw, rattan, sisal and hemp.

In another preferred embodiment, the porous material is a textile.

The term "textile" encompasses fibers, garments, yarns, fabrics, or any other web. Thus, the term "textile" also encompasses woven, knitted, stitch-bonded, and non-woven fabrics derived from natural, man made, and/or synthetic fibers and blends of such fibers; cellulose-based papers; and the like. They can comprise fibers in the form of continuous or discontinuous monofilaments, multifilaments, fibrils, fibrillated tapes or films, staple fibers, and yarns containing such filaments and/or fibers, and the like, which fibers can
be of any desired composition. The fibers can be of natural, man-made, or synthetic origin. Mixtures of natural fibers, man-made fibers, and synthetic fibers can also be used. Included with the fibers can be non-fibrous elements, such as particulate fillers, flock, binders, sizes and the like. The textiles and webs are intended to include fabrics and textiles, and may be a sheet-like structure [woven (including jacquard woven for home furnishings fabrics) or non-woven, knitted (including weft inserted warp knits), tufted, or stitch bonded] and may be comprised of any of a variety of fibers or structural elements. The nonwovens may be stitch bonded, ultrasonic bonded, wet laid, dry laid, solvent extruded, air or gas blown, jet interlaced, hydroentangled, and the like, and may have a broad variety of properties including stretch, air permeability, or water vapor breathability. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of manmade fibers derived primarily from natural sources include regenerated cellulose rayon, Tencel® and Lyocell®, cellulose esters such as cellulose acetate, cellulose triacetate, and regenerated proteins. Examples of synthetic fibers or structural elements include: polyesters (including polyethylene glycol terephthalate), wholly synthetic polyesters, polyesters derived from natural or biological materials such as corn, polyamides (e.g. nylon), acrylics, olefins such as polyethylene or polypropylene, aramids, azlons, modacrylics, novoloids, nitrils, aramids, spandex, vinyl polymers and copolymers, vinal, vinyon, and hybrids of such fibers and polymers.

Articles such as wound wipe pads, napkins, tissue paper, towels, carpets, fabrics for upholstery, curtains, are also comprised by the term "textiles".

It is possible to employ the process of the invention in the textiles in the form of fibers, webs or articles of manufacture produced from said fibers and/or webs. Said articles of manufacture are for example coats, jackets, hats and caps. By treatment according to the process of the invention, said articles of manufacture can be provided with enhanced water resistance or fire resistance. The such treated cloths are e.g. useful as rain jackets or as clothes for fire fighters.

In another preferred embodiment, the porous material is leather.
The term "leather" means a material created through the tanning of hides and skins of animals, primarily cattlehide. The tanning process converts the putrescible skin into a durable, long-lasting and versatile natural material. Leather may be applied for the manufacture of seats for cars and boats, furniture, shoes, boots.

It is possible to treat raw leather according to the process of the invention, or to treat articles of manufacture produced from raw leather, such as leather jackets, shoes, or soles of a shoe, purses, bags, or leather furniture.

In another preferred embodiment, the porous material is paper.

The term "paper" means a material mainly used for writing upon, printing upon or packaging. It is produced by pressing together wet fibers, typically vegetable fibers composed of cellulose. Said term also encompasses paperboards, wallpapers, archive papers, technical papers such as filters, cardboards.

Preferably, the metal oxide-precursors according to the invention are applied to said vegetable fibers as long as said fibers are in a wet state.

In another preferred embodiment, the porous material is a biological tissue. The term "biological tissue" encompasses human and animal tissues as well as plant tissues. Examples of human and animal tissues are epithelium tissue, connective tissue, muscle tissue, nervous tissue and liquid tissue such as blood and lymph. These tissues are contained in skin, organs, bones, cartilage, fat, muscles, nerves. Examples of plant tissue are epidermis, exodermis and cork, i.e. cells forming the outer surface of leaves and of plant bodies; vascular tissue such as xylem and phloem; and ground tissue.

In a particular embodiment of the invention, the process according to the invention allows to conserve said biological tissue.

If leather and/or biological tissue is employed as porous substrate, the metal oxide-precursor preferably is applied from the vapor phase in order achieve a sufficient soaking
of the porous material. For the same reason, water and the base preferably are also applied from the vapor phase.

In another embodiment of the invention, the porous material is plastics. The term "plastics" means synthetic fibers in the form of a web, such as a sponge.

If textiles, leather, paper, biological tissue and/or plastics are applied as porous materials in the process according to the invention, basically the soaking steps as disclosed in detail in connection with wood also apply to said porous materials.

Basically, also stones, such as bricks or sculptures, and metals, such as a metal web, can be employed as porous material in the reaction according to the invention.

Therefore, in one embodiment of the invention, the porous material is selected from the group consisting of wood, textiles, leather, paper, biological tissue, plastics, stone, metal.

In another embodiment, the porous material is selected from the group consisting of wood, textiles, leather, paper, biological tissue.

In still another embodiment, the porous material is selected from the group consisting of wood, textiles, paper.

The presence of the nanoparticles can basically be evidenced by methods such as Scanning Electron Microscopy (SEM) having a resolution from about 1 - 3 nm, Energy Dispersive X-Ray Spectroscopy in combination with SEM (SEM-EDX) having a resolution from about 2 - 3 nm, Environmental Scanning Electron Microscopy (ESEM) having a resolution from about 20 - 50 nm, Transmission Electron Microscopy (TEM) having a resolution from about 0.25 - 2 nm, Scanning Tunneling Microscopy (STM) and/or Atomic Force Microscopy (AFM). These methods are well known in the art.

The invention also pertains to a composite, the composite comprising a porous material, a metal oxide-precursor and water.
In a preferred embodiment, the invention pertains to a composite comprising a porous material selected from the group consisting of wood, leather, textiles, paper, biological tissue, plastics, stone and/or metal; an alkoxide of a metal selected from the group consisting of boron, silicon, aluminum, titanium, zirconium, cerium; and water.

In another preferred embodiment, the invention pertains to a composite comprising a porous material selected from the group consisting of wood, leather, textiles, paper, biological tissue, stone and/or metal; a tetraalkoxysilane; water, and ammonia.

In another preferred embodiment, the invention pertains to a composite comprising a porous material selected from the group consisting of wood, leather, textiles, paper, biological tissue, plastics, stone and/or metal; a tetraalkoxysilane; water; ammonia; and an alcohol. Preferably, the alcohol is ethanol or isopropanol.

In another embodiment, the invention pertains to a composite, said composite comprising a porous material and metal oxide-comprising particles, said composite being obtainable by a process comprising:

(i) soaking said porous material with a composition comprising a metal oxide-precursor and water.

In particular, the invention also pertains to a composite, said composite comprising a porous material and metal oxide-comprising particles, said composite being obtainable by a process comprising:

(i) soaking said porous material with a composition comprising a metal oxide-precursor and water to generate said metal oxide-comprising particles in situ.

Disclosed is also a process for producing a wood sheet, preferably a veneer, the process comprising:
providing a composition comprising metal oxide-comprising particles obtainable by converting a metal oxide-precursor into said metal oxide-comprising particles,

soaking the front and back surfaces and the thickness of said wood sheet with the metal oxide-comprising particles obtained in (j).

Preferably, (j) is carried out in the presence of an alcohol and a base or an acid. Preferably, the alcohol is ethanol or isopropanol and the base is ammonia.

In another embodiment, an alkylalkoxy silane and/or a modifying agent is is added in (j) and/or Qj), preferably in (j). Said alkylalkoxy silane and the modifying agent have the meaning as defined above.

Examples

Example 1: Preparation of a nanofluid in a two-step process using commercially available starting materials

Step 1: Preparation of nanoparticles

200 g nanosized silica powder. 20 g fluorocarbon surfactant and 50 g 3-aminopropytriethoxysilane are mixed in 200 toluene and are stirred for 5 h at room temperature. Subsequently, toluene is removed by evaporation. The resulting product is dried at 120 °C for 2 h and subsequently dispersed with air-flow crusher to obtain white powdered modified material.

Step 2: Preparation of a nanofluid

100 g of the nanoparticles of step 1 are dispersed in a mixture of 860 g distilled water, 20 g polyvinylalcohol and 20 g n-butanol using Ultra Turrax® equipment to obtain a nanofluid having the above produced nanoparticles dispersed therein.
Example 2: Soaking a wood veneer with the nanofluid of Example 1

A veneer made from sapele wood and having a length and a width of approximately 50 cm and a thickness of 1 mm is completely dunked into the nanofluid of Example 1. After 30 min, the veneer is removed and is dried at 100 °C for 5 min.

The veneer has the same appearance and feel of the otherwise similar wood sheet that has no nanoparticles on its front and back surfaces and throughout its thickness.

Example 3: Comparison of the water repellence of the veneer soaked with the nanofluid according to Example 2 with the corresponding veneer that is not soaked with the nanofluid

The veneer of Example 2 and the corresponding veneer that is not soaked with the nanofluid are dunked into water. After 30 seconds, the veneers are removed from the water. The water repellence is compared by sensoric methods, i.e. by optic and haptic inspection. The surface of the veneer according to the invention is still dry as can be seen and felt; water drops roll off the surfaces of said veneer. The veneer not being treated with the nanofluid is wet throughout the whole thickness due to absorbed water.

Example 4: Applying nanoparticles produced in a Stöber process to a veneer

A veneer was soaked with a solution of isopropanol containing 10 % by weight of ethoxy(triethyl)silane and 5 % by weight of tetraethoxysilane. The soaked veneer was dried in air. Subsequent to the drying, the veneer was soaked with an aqueous solution containing 1 % by weight of ammonia and 0.5 % by weight of ammonium fluoride. Afterwards, the thus treated veneer was dried for 60 minutes at a temperature of 40 °C. Water drops applied to said veneer had a contact angle of approximately ≥ 120 °, thus evidencing the hydrophobic characteristics of said veneer.
Example 5  Applying modified nanoparticles produced in a Stöber process to a veneer

Example 4 was repeated with the difference that the isopropanol solution additionally contained 0.05% by weight of triethoxyfluorosilane. The measured contact angle of water drops was $\geq 120^\circ$. Compared to a veneer that had not been treated, the veneer according to this Example also exhibited oliophobicity, which could be evidenced by optic inspection when applying oil to the treated and non-treated veneer.

Example 6  Applying modified nanoparticles produced in a Stöber process to a cotton gauze

Example 4 was repeated with the difference that instead a veneer a cotton gauze was employed. The measured contact angle of water drops was $\geq 120^\circ$.

Example 7  Applying ammonia from the vapor phase (gas phase)

Example 4 was repeated with the difference that the dried veneer obtained after the soaking with the isopropanol solution was treated with gaseous ammonia for one hour in an autoclave. The veneer exhibited a contact angle of $\geq 120^\circ$ against water.
Claims

1. Composite material comprising a porous material and nanoparticles, characterized in that said nanoparticles comprise a derivative of silica selected from the group consisting of alkoxy silanes and polyalkoxysilanes, wherein said alkoxy silanes and polyalkoxysilanes comprise at least one amino group.

2. Composite material of claim 1, wherein said porous material is selected from the group consisting of wood, textile, leather, paper, biological tissue.

3. Composite material of claim 1 or 2, wherein said porous material has a front surface, a back surface and a thickness, and wherein said nanoparticles are present on said front surface, said back surface and throughout the thickness.

4. Composite material of claim 3, wherein said porous material is a wood sheet.

5. Composite material of claim 4, wherein said wood sheet is a veneer.

6. Composite material of claim 4 or 5, said wood sheet being obtainable by a process comprising steps (i) to (v):

   (i) gluing board-like, plane pieces of wood hoiohedraiyy by means of an adhesive to a beam-like block of wood,

   (ii) watering said beam-like block of wood obtained in step (i),

   (iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain a veneer in the form of a sheet,

   (iv) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point to obtain a veneer which is composed of slices from board-like, plane pieces of wood wherein said slices are jointly adhered by means of said adhesive,
(v) treating the front and back surfaces and the thickness of said veneer of step (iv) with a fluid comprising nanoparticles, wherein said fluid soaks said wood sheet; or soaking said veneer of step (iv) with a composition comprising a metal oxide-precursor and water.

7. Composite material of any one of the preceding claims, wherein the nanoparticles are metal oxide-comprising particles.

8. Composite material of any one of the preceding claims, wherein the nanoparticles comprise a modifying compound selected from the group consisting of metals, metal oxides, bioactive agents, anti-microbial/fungal agents, drugs, pharmaceuticals, sunblock agents, dyes, pigments, scents, fragrances, insect repellents, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, reflective particles, thermochromic materials, heat-absorbing or heat-releasing phase change agents, fabric softeners, zeolites, activated carbon, electrographic agents, luminescent agents such as fluorescent and phosphorescent agents.

9. Process for the manufacture of a composite material comprising a porous material and nanoparticles, comprising: soaking said porous material with a fluid comprising nanoparticles, characterized in that said nanoparticles comprise a derivative of silica selected from the group consisting of alkoxysilanes and polyalkoxysilanes, wherein said alkoxysilanes and polyalkoxysilanes comprise at least one amino group.

10. Process of claim 9, wherein said porous material is selected from the group consisting of wood, textile, leather, paper, biological tissue.

11. Process of claim 9 or 10, comprising

(i) soaking said porous material with a composition comprising a metal oxide-precursor.
12. Process of claim 11, wherein said composition comprises water or an alcohol, or water and an alcohol

13. Process of claim 11 or 12, wherein said soaking is performed by applying the composition of (i) from the vapor phase to said porous material.

14. Process of any one of claims 11 to 13, wherein the metal oxide-precursor is a metal alkoxide, a metal chloride, or a metal hydroxide.

15. Process of any one of claims 11 to 14, wherein the metal is selected from the group consisting of boron, silicon, aluminum, titanium, zirconium, cerium.

16. Process of any one of claims 14 or 15, wherein the metal alkoxide is a tetraalkoxysilane.

17. Process of any one of claims 11 to 16, comprising:

(i) soaking said porous material with a composition comprising a metal oxide-precursor such that said porous material is saturated with said composition, and subsequent to the soaking reacting said composition such that said nanoparticles are generated in situ within and throughout said porous material.

18. Process of any one of claims 11 to 17, comprising:

(0) soaking said porous material with a composition comprising water and ammonia or an acid,

(1) soaking the soaked porous material from (0) with a metal oxide-precursor and water; or

(i) soaking said porous material with a composition comprising a metal oxide-precursor and water,
(ii) soaking the soaked porous material from (i) with ammonia or an acid; or

(i.1) soaking said porous material with a composition comprising a metal oxide-precursor and alcohol,

(i.2) soaking the soaked porous material from (i.2) with water and ammonia or an acid.

19. Process of any one of claims 9 to 18, wherein the nanoparticles or the composition in (i) further comprise modifying compounds selected from the group consisting of metals, metal oxides, bioactive agents, anti-microbial/fungal agents, drugs, pharmaceuticals, sunblock agents, dyes, pigments, scents, fragrances, insect repellents, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, reflective particles, thermochromic materials, heat-absorbing or heat-releasing phase change agents, fabric softeners, zeolites, activated carbon, electrographic agents, luminescent agents such as fluorescent and phosphorescent agents.

20. Process of any one of claims 9 to 19, wherein the porous material is a wood sheet.

21. Process of claim 20, wherein said wood sheet is a veneer.

22. Process of claim 20 or 21, comprising: treating the front and back surfaces and the thickness of said wood sheet with a fluid comprising nanoparticles, wherein said fluid soaks said wood sheet.

23. Process of any one of claims 20 to 22, further comprising prior to the soaking:

(i) gluing board-like, plane pieces of wood holohedrally by means of an adhesive to a beam-like block of wood,

(ii) watering said beam-like block of wood obtained in step (i),
(iii) cutting said beam-like block of wood obtained in step (ii) such that the section plane is transversely arranged to the plane which is defined by the adhesion layers in said block to obtain a veneer in the form of a sheet,

(iii) drying said veneer obtained in step (iii) until the moisture content is below the fiber saturation point to obtain a veneer which is composed of slices from board-like, plane pieces of wood wherein said slices are jointly adhered by means of said adhesive.
INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/004796

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) and to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B27K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<td>A</td>
<td>WO 01/91925 A (UNIV MICHIGAN TECH [US])</td>
<td>2-8,10, 11,14,15</td>
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<td>6 December 2001 (2001-12-06)</td>
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<td>- (0225); claim 1</td>
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<td>A</td>
<td>EP 1 762 352 A (TNO [NL])</td>
<td>1-3,8-11</td>
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<td>14 March 2007 (2007-03-14)</td>
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<td>paragraphs [0035], [0036]; claims 1-10,12-15; examples 1,2</td>
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Further documents are listed in the continuation of Box C

X See patent family annex

* Special categories of cited documents

**A** document defining the general state of the art which is not considered to be of particular relevance

**E** earlier document but published on or after the international filing date

**L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

**O** document referring to an oral disclosure, use, exhibition or other means

**P** document published prior to the International filing date but later than the priority date claimed

**T** later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

**Y** document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

**A** document member of the same patent family

Date of the actual completion of the international search

19 August 2009

Date of mailing of the international search report

03/09/2009

Name and mailing address of the ISA/
European Patent Office, P B 5818, Patentaan 2
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Fax (+31-70) 340-3016

Authorized officer

Derz, Thomas
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<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 2006/235145 A1 (POON HO C [HK] ET AL) 19 October 2006 (2006-10-19) cited in the application paragraphs [0050], [0083]; claim 1; examples 5,8</td>
<td>1,9-11</td>
</tr>
<tr>
<td>Y</td>
<td>EP 1 688 228 A (HD WOOD TECHNOLOGIES LTD [MT]) 9 August 2006 (2006-08-09) paragraphs [0022], [0047], [0072], [0084], [0118]</td>
<td>6,23</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 882 555 A (SHINETSU CHEMICAL CO [JP]) 9 December 1998 (1998-12-09) cited in the application page 4, lines 40-42,54 - page 7, lines 4,12,34-36,56; claims 1,5; examples 7,11 page 8, lines 1-4,36-42,49 - page 3, lines 46-54</td>
<td>1-5,7-22</td>
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<tr>
<td>Y</td>
<td>US 6 607 994 B2 (SOANE DAVID S [US] ET AL) SOANE DAVID S [US] ET AL) 19 August 2003 (2003-08-19) claims 1,5,8,12; examples III-2,V-1</td>
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<td>US 2005/208087 A1 (KUERZINGER KONRAD [DE] ET AL) 22 September 2005 (2005-09-22) paragraphs [0012], [0014], [0021], [0023], [0055], [0075], [0082], [0169]</td>
<td>1-3,8</td>
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<td>Publication date</td>
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<tr>
<td>WO 0191925</td>
<td>06-12-2001</td>
<td>AU 6522901 A</td>
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