

DESCRIPTION

TITLE: Method for preparing leather comprising the use of a silylated compound and leather obtained by this method

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The present invention relates to a finished leather having at least one ennobling property provided by a silylated treatment agent as well as to methods for preparing such a finished leather, comprising the use of a silylated compound during the tanning step and/or during an ennobling step subsequent to tanning.

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The transformation of a hide into finished leather includes many steps. All of these steps can be classified into three main groups, which can be defined as follows: A) the steps of preparing the hides, B) the steps of operations of tanning, and C) the ennobling steps.

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During the steps of preparing the hides, the raw hides of animals are received. These hides can be sorted according to the presence of faults, their quality, their size, their weight, etc. During these preparation steps, the parts of the hides which are not desired to be kept, such as for example the legs, are cut out and removed. The hides are then cleaned. To do this, the hides are soaked in a large volume of water, for example in a fuller (rotating barrel) or in a sewing machine (stationary vessel with moving blades). An antiseptic can be added. Once cleaned, the hides are shaved to remove hair, for example by chemical means. The hides also undergo a fleshing step which consists of removing the subcutaneous tissues. These steps are called river steps.

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At the end of the steps of preparing the hides, hides which can be so-called "pickled" hides or so-called "delimed" hides are obtained. The "pickled" hides are hides with high salinity and a low pH, generally less than 3.0. The "delimed" hides are hides coming out of the river steps with a pH generally comprised between 7.5 and 9.0.

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During tanning operations, the hides prepared as indicated above, for example the "pickled" hides and the "delimed" hides, are degreased. If necessary, these hides are rehydrated. At this stage, the hides are putrescible and ready to be tanned. The tanning step itself consists of a chemical treatment allowing to transform these putrescible hides into non-putrescible and resistant leathers. The chemical treatment implements tanning agents. Indeed, the hides are made up of collagen fibers. During tanning, the tanning agents form bonds between the collagen fibers of the hides, allowing these hides to be stabilized and transforming them into resistant and non-putrescible leather.

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Different tanning agents can be used to tan hides.

In the leather industry, the most widely used tanning agent is chromium at oxidation state 3 (Cr^{3+}). Indeed, the Cr^{3+} chrome tanning method is easy to implement, efficient and makes it possible to obtain leathers with properties that meet market expectations.

5 Other metals may be used as tanning agents, such as aluminum, iron, titanium or zirconium. Silicic acid ($\text{Si}(\text{OH})_4$) can also be used as a tanning agent.

It is also possible to use glutaraldehyde as a tanning agent, or even vegetable tannins or synthetic organic compounds.

10 At the end of the tanning step, the obtained leathers can be drained, rinsed and optionally spun.

The ennobling steps are the steps which make it possible to make the leathers obtained at the end of the tanning operations usable for the manufacture of leather objects, in other words, these are the steps that make it possible to obtain a finished leather. The ennobling steps comprise the grinding steps and the finishing steps.

15 The grinding steps can be carried out in a wet or dry environment. These steps can comprise, in particular, steps of retanning, dyeing, fatliquoring, spinning, staking and thicknessing. Retanning consists of giving the leather a certain hardness. In the field of the leather industry, we also talk about “garnishing” the leather, or giving the leather “roundness”. This retanning is generally carried out using treatment agents, which can be chemical compounds, such as polyphenols, resins or even metals, which are added to the leather, for example by mixing these treatment agents with the leather in an aqueous solution in a fuller under conditions of temperature, agitation, duration and pH that the person skilled in the art determines according to the result he wishes to obtain. Dyeing consists of adding color to the leather. This step is also carried out using treatment agents, which, in the case of dyeing, can be in particular coloring agents. As with retanning, the dyeing step is carried out in an aqueous medium in a fuller, by mixing the leather and the coloring agent(s) according to a method and conditions of temperature, agitation, duration and pH determined by the person skilled in the art. The fatliquoring step consists of fatliquoring the leather in order to make it supple. The fatliquoring step is carried out by means of treatment agents, such as fatliquoring agents which may, for example, be chemical compounds comprising in their formula one or several fatty chains, in other words one or several fatty acids. The fatliquoring step is also generally carried out in an aqueous medium, for example in a fuller, in which the leather and the chemical compounds with fatty chains are mixed according to a method defined by the person skilled in the art according to the result he wishes to obtain. Stacking consists of stretching the tanned hides, for example to make them more supple. Stacking is carried out mechanically. Thicknessing consists of adjusting the thickness of the tanned hides according to the desired thickness for

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the finished leather. This thickening is carried out mechanically by means of a machine provided for this purpose.

The finishing steps are generally carried out outside the fuller, in other words rather in an ambient environment, and consist of giving the leather a surface finish.

5 The finishing steps are generally carried out by combining a mechanical action (for example smoothing, printing, etc.) with a treatment agent, which can for example be a film-forming chemical compound, which will help to obtain the desired effect. The finishing steps can thus for example give the leather aesthetic properties: these aesthetic properties can for example be a color, which is then produced by printing a coloring agent on the leather. These aesthetic properties can also be a shiny, velvety, matt, satiny or grained, etc. appearance, which is obtained by mechanically working the leather, for example by means of a smooth plate (smoothing), a rotopress, a satinizing machine, a graining machine, etc. with film-forming chemical agents capable of imparting shine, velvety, mattness, etc. The finishing steps can also impart protective properties to the leather in order to give the leather a longer lifespan: these protective properties can, for example, be resistance to stains, abrasion, water, in particular salt water, resistance to light, in particular the sun, etc. Here too, these protective properties are obtained by mechanically working the leather as seen above with treatment agents, which can, for example, be film-forming chemical compounds, capable of giving the leather resistance to stains, abrasion, water, light, etc.

Thus, the ennobling steps, such as for example the grinding and finishing steps, are used to give the leather one or several properties, generally using treatment agents which, as described above but without being exhaustive, may be retanning agents, such as for example polyphenols and metals, dyeing agents, such as coloring agents, fatliquoring agents, such as chemical compounds comprising in their formula one or several fatty acids, aestheticizing agents, such as chemical agents capable of imparting shine, velvetiness, mattness, satin, grain, protective agents, such as chemical agents capable of imparting resistance to stains, abrasion, water, light, etc. to the leather.

30 However, it has been observed in the existing finished leather preparation methods that the leather objects made from these finished leathers could see some of their properties, provided during the ennobling steps, degraded during use, during the lifespan of the objects, or when these objects are used in certain specific circumstances. Color bleeding phenomena have thus been observed: such bleeding can occur in a humid or dry environment and results in part of the coloring agent used to give the leather a color bleeding onto another surface, for example the skin of a user. Migration phenomena, known in the leather industry as "PVC (polyvinyl chloride) migration" have also been observed: when a colored finished leather is used in a

product in combination with another material, part of the coloring agent used to color the leather can migrate to this other material, thus deteriorating the initial aesthetic appearance of the product. Poor lightfastness of certain coloring agents has also been observed. We also sometimes observe unwanted yellowing of the finished leather when it has been fatliquored with agents containing fatty acids: the destruction of these fatty acids over time causes this yellowing which is damaging to the initial aesthetic appearance of the product.

Thus, it appears that with the conventional leather preparation methods, at least part of the treatment agents added to the leather during the ennobling steps may be caused to be separated from the finished leather during the lifespan of a leather object made with such finished leather. This phenomenon is not desirable.

Document CN 111 500 799 A1 describes a method for tanning and retanning buffalo hides using a macromolecule which is a silane coupling agent.

There therefore remains a need for a method for preparing finished leather which would make it possible to provide the leather with one or several ennobling properties by means of one or several treatment agents, such that this or these treatment agent(s) would remain fixed to the leather in an optimal manner during the lifespan of the finished leather and independently of the circumstances in which this finished leather is used.

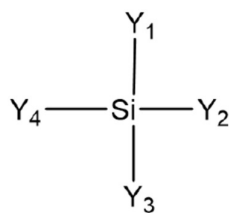
The applicant has developed a new method for preparing a finished leather making it possible to fix one or several treatment agents on the leather in an optimal and durable manner. For this, the preparation method according to the invention comprises the use of at least one silylated treatment agent during the tanning step and/or during a subsequent ennobling step, the tanning step comprising the use of a silicic acid precursor of $(\text{Si}(\text{OH})_4)$.

An object of the present invention relates to a finished leather comprising at least one ennobling property provided by at least one silylated treatment agent, said silylated treatment agent being fixed to a three-dimensional Si-O-Si network by a covalent bond, said three-dimensional Si-O-Si network being linked by hydrogen, ionic or covalent bonds to the collagen constituting the finished leather.

Another object of the present invention relates to a method for preparing a finished leather according to the invention, from raw hides, said method comprising at least the following steps of:

- i) preparing raw hides in order to obtain hides ready for tanning,
- ii) tanning the hides from step i) by means of a tanning composition comprising at least one tanning agent of formula (I):

[Chem 1]



(I)

in which Y^1 , Y^2 , Y^3 and Y^4 , which may be identical or different, are selected independently of each other as a halogen atom, a $-[OSiO_uR^{1_{3-u}}]_v$ group, a $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ group or a $-OR^2$ group, two or more of the $-[OSiO_uR^{1_{3-u}}]_v$, $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ and $-OR^2$ groups which can be connected to each other by a covalent bond, in which:

- u is an integer ranging from 0 to 3, v is an integer greater than or equal to one, and R^1 is selected as a hydrogen atom, a C_1-C_{10} alkyl group, an aryl group, a C_2-C_{10} alkenyl group, a C_2-C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^1 including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioethers groups,

- R^2 is selected as a hydrogen atom, a C_1-C_{10} alkyl group, an aryl group, a C_2-C_{10} alkenyl group, a C_2-C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^2 including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

said method being characterized in that said at least one silylated treatment agent is implemented during the tanning step ii) and/or during an ennobling step iii) subsequent to the tanning step ii).

Preferably, Y^1 , Y^2 , Y^3 and Y^4 , which may be identical or different, are selected independently of each other as a halogen atom, a $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ group or a $-OR^2$ group. Preferably, Y^1 , Y^2 , Y^3 and Y^4 , which may be identical or different, are selected independently of each other as a halogen atom, or a $-OR^2$ group.

Another object of the present invention relates to a method for preparing a finished leather according to the invention, from raw hides, said method comprising at least the following steps of:

- a) preparing raw hides in order to obtain hides ready for tanning,
- b) tanning and ennobling the hides from step a) by means of a treating composition comprising at least said silylated treatment agent.

The present invention also relates to a finished leather having at least one ennobling property, likely to be obtained by these methods.

The present invention also relates to a method for disenobling a finished leather obtained by the methods according to the invention comprising at least one

step during which said finished leather is soaked in a basic solution in order to bring the pH of the leather to a value greater than or equal to 10.5, preferably to a value ranging from 11.5 to 13.0.

5 The methods according to the invention make it possible to obtain finished leathers having ennobling properties that are particularly stable over time and during use. Indeed, the hides ready to be tanned comprise collagen fibers. The compounds used during step ii) or step a) of tanning of the methods according to the invention are precursors of $\text{Si}(\text{OH})_4$. The polymerization of the $\text{Si}(\text{OH})_4$ during the tanning step will create a three-dimensional Si-O-Si network linked to the collagen constituting the
10 hides. This three-dimensional network will make it possible to stabilize the hides and thus tan them. The advantage of these methods is that, during the tanning step, part of the silicon of the $\text{Si}(\text{OH})_4$ does not react and remains present in this three-dimensional network. The three-dimensional network thus formed has a residue of groups, in the form of silanol functions (Si-OH) on the surface. These groups will allow
15 a modification of the leather in a covalent and controlled manner.

Thus, the use of a silylated treatment agent during the tanning step and/or during a subsequent ennobling step will make it possible to fix the silyl group of the treatment agent to the three-dimensional Si-O-Si network created during the tanning step, by creating a new Si-O-Si bond resulting from the condensation reaction of at
20 least one silanol group of this three-dimensional network and of at least one silanol group of the silylated treatment agent. This Si-O-Si siloxane bond, covalent in nature, is particularly stable and durable over time. Thus, the silyl group of the treatment agent will find itself nested within the three-dimensional Si-O-Si network formed during the tanning step and thus strongly fixed to the collagen of the hide, and therefore to the
25 finished leather. Due to the nesting of the silyl group of the silylated treatment agent within the three-dimensional Si-O-Si network linked to the collagen of the hides, the property provided to the finished leather by the silylated treatment agent is particularly stable: in fact, according to the methods according to the invention, the silylated treatment agent is linked to the three-dimensional Si-O-Si network by means of its silyl
30 functional group which is covalently linked to the three-dimensional Si-O-Si network, itself linked by hydrogen, ionic or covalent bonds to the collagen constituting the hides and therefore the finished leather.

Definitions

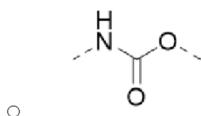
In the present application, the following terms:

35 - "raw hides" means synthetic hides or hides of animal origin containing collagen, but which have not yet undergone the hide preparation steps described above, making these hides ready to be tanned;

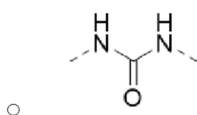
- "hides ready for tanning" means hides resulting from the hide preparation operations as described above, for example pickled or delimed hides, which have also been degreased;
- "tanned hides" or "leather", means hides which have undergone at least one tanning step;
- "finished leather", means tanned hides having undergone at least one ennobling step;
- "alkoxysilane group": means the Si-OR⁵ group, in which R⁵ is selected as a hydrogen atom, a C₁-C₁₀ alkyl group, an aryl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a polyalkylene oxide group or its derivatives, R⁵ optionally including one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,
- "silanol group": means the Si-OH group, which may result from the hydrolysis of alkoxysilane groups,
- "silyl group": means a group selected from the alkoxysilane group, the silanol group, a halosilane, a silicon polymer, where:
 - halosilane is Si-X, where X is a halogen atom, and
 - the silicon polymer is Si-K, where K is a $-\text{[OSiO}_s\text{R}^6_{3-s}]_t$ group where s is an integer ranging from 0 to 3, t is an integer greater than or equal to one, and R⁶ is selected as a hydrogen atom, a C₁-C₁₀ alkyl group, an aryl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a polyalkylene oxide group or its derivatives, R⁶ optionally including one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,
 - "silylation": means a grafting reaction between a silylating molecule, that is to say including on one side an alkoxysilane group and on the other side a reactive organic group such as for example an isocyanate group, an epoxy group, an amine group, and a silylable molecule, that is to say a molecule or a polymer having a silylable group, in other words a group reactive to the silylating molecule. As silylating molecules, we can cite 3-isocyanatopropyl triethoxysilane (ICPTES), 3-glycidoxypropyl trimethoxysilane (GPTMS), 3-aminopropyl triethoxysilane (APTES), triethoxysilane, 3-mercaptopropyl trimethoxysilane (MPTES). As silylable group, we can cite the amine group (-NH₂), the hydroxyl group (-OH), the carboxyl group (-COOH), the isocyanate group (NCO) and the vinyl group (-CH=CH₂).
 - "silylated treatment agent": means any treatment agent having at least one silyl group;
 - "treatment agent": any compound capable of providing one or several ennobling properties to a tanned hide or to a hide ready to be tanned. Advantageously, the compound may be in any form capable of receiving by silylation a silylating molecule including one or several silyl groups, for example a molecule, a polymer, a

material, and preferably comprises at least one silylable group. Advantageously, the treatment agent may thus be defined as a compound comprising two complementary parts, a part T on the one hand and a part A on the other hand, together forming a compound of formula T-A, where the part T corresponds to the compound providing the treatment functionality (for example molecule, polymer, material, nanoparticle) without its silylable group and which will be called the treating group of the treatment agent, and where the part A corresponds to the silylable group of the treatment agent (for example amine, hydroxyl, carboxyl, vinyl group). Once the treatment agent has undergone silylation, the group A is transformed into a linking group W between the treating group T and the silyl group of the silylated treatment agent. The linking group W may for example be selected from:

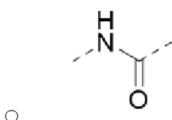
[Chem 2]



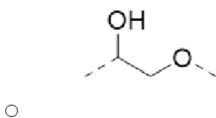
[Chem 3]



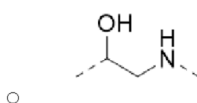
[Chem 4]



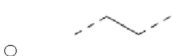
[Chem 5]



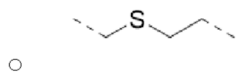
[Chem 6]



[Chem 7]



[Chem 8]



- “ennobling property”: means any property that one may wish to bring to a tanned or ready-to-be-tanned hide in order to obtain a finished leather usable in the possible applications of leathers. As ennobling properties, we can cite, in a non-exhaustive manner, the properties providing the following effects: compostable, gas absorber (Ex CO₂), degradable, ephemeral leather, edible, antibacterial, self-hydrating, antiseptic, anti-wave, anti-sweating, with shape memory, fungicide, cooling effect, thermoregulating, foam effect (plush), anti-dirt, fatty proof, resistant to fresh water, resistant to salt water, fire retardant, abrasion resistant, protection against chemicals, protection against Hv, flexibility, elasticity, fatliquoring, hardeners, filling, anti-friction, antistatic, anti-wave, anti-infrared, non-slip, touch modifier, photochromic, thermochromic, odorous, luminescent, phosphorescent, colors, fluorescent, reflective, wet effect, matte effect, shiny effect, metallic effect, chemoChromic, transparent leather, slate effect, medical indicators, release active ingredient, rebound effect, sound insulation, thermal storage and inertia, thixotropic character, thermal insulation, electrical storage, automatic graining, surface loss, Nubuck effect without sanding, quantum dot (semiconductor particles, emitting a color depending on the size and frequency received), traceability marker, extensible, mycosable, reconstitutable, sticky effect, thermoformable, humidity sensor, magnetic, tactile, polymerization precursor, leather with a taste, self-healing, sound effect, data storage, GPS (Global Positioning System) location, electrical conductor.

Advantageously, the treatment agent contributing to providing flexibility, elasticity, a fatliquoring effect, can be selected from the following compounds:

- fatty acids such as aliphatic or branched carboxylic acids, made of chains of at least 4 carbons, more or less unsaturated, that is to say having one or several double bonds, preferably from 4 to 36 carbon atoms; by way of example, we can cite butyric acid, palmitic acid, arachidic acid;

- polyethylene glycols with molar masses ranging from 62 to 20000 g/mol.

Advantageously, the treatment agent contributing to providing an aesthetic effect such as color, luminescence, phosphorescence, fluorescence, a matte effect, a shiny effect, a metallic effect, a slate effect, a transparent effect, can be selected from the following compounds:

- coloring agents;

- fluorescein.

Advantageously, the treatment agent contributing to providing a hardening and/or filling effect can be selected from the following compounds:

- metals;
- polyphenols;
- cellulose derivatives, such as hydroxypropyl methyl cellulose.

5 Detailed description

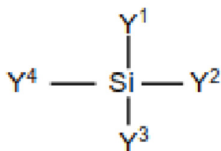
The hides concerned by the methods according to the invention can be any hides containing collagen, whether these hides are synthetic or of animal origin. These hides can for example come from animals whose hide contains collagen, such as for example bovine, sheep, goats, reptiles (snakes, lizards, crocodilians, alligatoridae),
10 fish, birds, amphibians, pigs.

In a first step of the methods according to the invention, step i) or step a), raw hides are prepared in order to obtain hides ready to be tanned.

The rehydration and degreasing operations are well known to the person skilled in the art. For example, to rehydrate and degrease pickled hides, the hides can be placed in a fuller, water, salt and a degreaser can be added. The fuller is a rotating
15 drum well known to the person skilled in the art. The degreaser can, in a known manner, be selected from surfactants, for example nonionic and anionic surfactants. For example, the fuller can be rotated without heat for a duration ranging from 15 min to 10 hours, the fuller can be drained and then the hides can be rinsed with salt water
20 at room temperature. Hides ready to be tanned are thus obtained.

In a first method according to the invention, according to a step ii), the hides ready to be tanned are tanned with a tanning composition comprising at least one tanning agent of the following formula (I):

[Chem 1]



(I)

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in which Y^1 , Y^2 , Y^3 and Y^4 , which may be identical or different, are selected independently of each other as a halogen atom, a $-[OSiO_uR^{1_{3-u}}]_v$ group, a $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ group or a $-OR^2$ group, two or more of the $-[OSiO_uR^{1_{3-u}}]_v$, $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ and $-OR^2$ groups which can be connected to each other by a covalent bond, in
30 which:

- u is an integer ranging from 0 to 3, v is an integer greater than or equal to one, and R^1 is selected as a hydrogen atom, a C_1-C_{10} alkyl group, an aryl group, a

C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a polyalkylene oxide group or its derivatives, R¹ including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioethers group,

- R² is selected as a hydrogen atom, a C₁-C₁₀ alkyl group, an aryl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a polyalkylene oxide group or its derivatives, R² including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

Preferably, Y¹, Y², Y³ and Y⁴, which may be identical or different, are selected independently of each other as a halogen atom, a -O-[SiO_uH_{u-1}R¹_{3-u}]_v-H group or a -OR² group. Preferably, Y¹, Y², Y³ and Y⁴, which may be identical or different, are selected independently of each other as a halogen atom, or a -OR² group.

For the purposes of the present invention:

- "C₁-C₁₀ alkyl" group means a saturated, linear or branched, hydrocarbon chain including from 1 to 10 carbon atoms, such as for example a methyl, ethyl, isopropyl, tert-butyl, pentyl, etc. group.

- aryl group means an aromatic group, preferably including from 5 to 10 carbon atoms, comprising one or several rings and eventually comprising a heteroatom, in particular an oxygen, a nitrogen or a sulfur, such as for example a phenyl, furan, indole, pyridine, naphthalene, etc. group.

- "C₂-C₁₀ alkenyl" group means a linear or branched, hydrocarbon chain including at least one unsaturation and including from 2 to 10 carbon atoms, such as for example an ethenyl (vinyl), propenyl, 2,4-hexadienyl, etc. group.

- "C₂-C₁₀ alkynyl" group means a linear or branched, hydrocarbon chain including at least one double unsaturation and including from 2 to 10 carbon atoms, such as for example an acetylene, propyne, butyne, etc. group.

- "polyalkylene oxide" group means polymers of ethylene oxide units, the number of ethylene oxide units is an integer greater than or equal to 1,

- Derivatives of polyalkylene oxides mean one or several synthetic polymers selected from copolymers of carboxylic acids and carboxylic esters of poly(alkylene glycol), copolymers of carboxylic acids and poly(alkylene amide glycol), copolymers of carboxylic acids and poly(alkylene glycol) imide, copolymers of carboxylic acids and poly(alkylene glycol) vinyl ethers, neutralized or non-neutralized, and mixtures thereof.

In one embodiment, Y¹, Y², Y³ and Y⁴ are selected independently of each other as a chlorine atom, an -OH group or an -OCH₂CH₃ group.

The compound of formula (I) may be a precursor of Si(OH)₄ or directly Si(OH)₄. Thus, in one embodiment, the compound of formula (I) is Si(OH)₄. In another embodiment, the compound of formula (I) is Si(OCH₂CH₃)₄.

During the tanning step, a three-dimensional Si-O-Si network is created by polymerization of $\text{Si}(\text{OH})_4$. This three-dimensional network bounds to the collagen constituting the hides and stabilizes the latter. Tanned hides are obtained.

In addition to the compound of formula (I), the tanning composition generally
5 comprises at least water.

The tanning composition may also include a salt, such as sodium chloride.

The salt optionally present in the tanning composition has the function of preventing the hides from swelling in water. For the purposes of the present application, salt means an ionic compound of cations and anions forming a neutral product and
10 without a net electrical charge. The salt may, for example, be selected from potassium chloride, sodium chloride and mixtures thereof. The need for the presence of a salt in the tanning composition is determined by the person skilled in the art. This need will generally depend on the pH selected for the tanning composition. For example, if the pH of the aqueous solution is less than 5.0, the tanning composition will preferably
15 comprise a salt. The preparation of such a salt solution is within the ability of the person skilled in the art. Determining the amount of salt, for example sodium chloride, necessary to prevent the hides from swelling is within the ability of the person skilled in the art.

The tanning composition may also comprise any tanning agent other than the
20 compound of formula (I). For example, the tanning composition may comprise an additional tanning agent selected from the following compounds: chromium, glutaraldehyde, triazines, vegetable tannins such as mimosa, chestnut, quebracho, and mixtures thereof.

Advantageously, the compound of formula (I) is present in the tanning
25 composition, by mass relative to the mass of the hides ready to be tanned, in a content ranging from 0.1 to 100%, preferably ranging from 5% to 60%, more preferably ranging from 5% to 30%.

The contact of the hides ready to be tanned and of the tanning composition is generally done in a fuller. The pH of the tanning composition is brought to the desired
30 value, for example to a value ranging from 1.5 to 10.5, by adding acid or base to the composition.

The fuller is then left to rotate for a duration allowing the silicic acid to penetrate the hides. This duration can thus vary depending on the thickness of the hides and the nature of the hides. The duration of this step can be easily determined by the person
35 skilled in the art depending on the hide to be tanned. The fuller is preferably rotated at room temperature, in other words a temperature less than or equal to 30°C , preferably a temperature ranging from 20 to 25°C . Once the silicic acid has penetrated the hides, a step of neutralizing the composition can be carried out, for example by bringing the

pH of the tanning composition and of the hides to a value ranging from 2.1 to 10.5, preferably to a value ranging from 4.0 to 8.0.

At the end of the tanning stage, we obtain stabilized hides, which are tanned hides, also called leathers.

5 The method comprises the use of at least one silylated treatment agent in order to provide the leather with one or several ennobling properties.

According to this first method according to the invention, the silylated treatment agent can be implemented during the tanning step ii) and/or during an ennobling step iii) subsequent to the tanning step ii).

10 In one embodiment, the silylated treatment agent is at least implemented during the tanning step ii). In such a case, the silylated treatment agent is generally added to the tanning composition.

Advantageously, the tanning composition further comprises said at least one silylated treatment agent, said silylated treatment agent being present in the tanning composition in a content ranging from 0.1 to 50%, preferably from 0.1 to 35%, preferably from 0.1 to 25%, more preferably from 0.1 to 10%, by mass relative to the mass of the compound of formula (I).

During the tanning step, the silyl group of the silylated treatment agent will bond to the three-dimensional Si-O-Si network created by the polymerization of $\text{Si}(\text{OH})_4$, by condensation reaction of at least one silanol group of this three-dimensional network and of at least one silanol group of the silylated treatment agent. The silylated treatment agent will thus be strongly bonded to this three-dimensional network. It should be noted that in this first method according to the invention, during this tanning step ii), the silylated treatment agent preferably does not constitute a tanning aid, the tanning being performed mainly by the polymerization of the silicic acid $\text{Si}(\text{OH})_4$.

During the tanning step, several different silylated treatment agents can be used to give the leather one or several ennobling properties.

Alternatively or in combination, the silylated treatment agent may at least be implemented during an ennobling step, step iii), subsequent to the tanning step ii).

30 During the ennobling step, the silyl group of the silylated treatment agent will be bound to the three-dimensional Si-O-Si network created during tanning with $\text{Si}(\text{OH})_4$, by condensation reaction of at least one silanol group of this three-dimensional network and of at least one silanol group of the silylated treatment agent. The silylated treatment agent will thus be strongly bound to this three-dimensional network, thus ensuring a particularly strong fixing of the silyl group inside or on the surface of the tanned hides. The property/properties provided to the finished leather by the silylated treatment agent will thus be particularly stable.

The ennobling step can be carried out in a dry, ambient or humid environment. For example, an aqueous solution of the silylated treatment agent can be prepared. The tanned hides can be placed in an acidic or basic aqueous solution, preferably acidic, for example having a pH ranging from 1.5 to 2.0, in a fuller, to which the aqueous solution of the silylated treatment agent is added. The fuller can be rotated under stirring and duration conditions determined by the person skilled in the art. The pH of the solution comprising the hides and the silylated treatment agent is then adjusted to a value ranging from 3.0 to 10.5, preferably ranging from 3.5 to 7.0, more preferably ranging from 4.0 to 5.0. At the end of this treatment, the fuller is emptied and the treated hides can be rinsed.

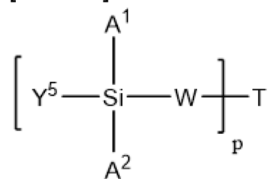
Alternatively, this aqueous solution of the silylated treatment agent can be deposited on the surface of the tanned hides. The polymerization of the silylated treatment agent can, for example, be carried out by simply drying the tanned hides thus treated.

During the ennobling stage, several different silylated treatment agents can be used simultaneously or successively in order to give the leather one or several ennobling properties.

The method according to the invention can thus comprise several ennobling steps.

Advantageously, the silylated treatment agent is selected from the compounds of the following formula (II):

[Chem 9]



(II)

in which

- A^1 and A^2 , which are identical or different, are selected independently of each other as Y^5 or $W-T$,

- Y^5 is selected as a halogen atom, a $-[OSiO_qR^{3-q}]_r$ group, a $-O-[SiO_qH_{q-1}R^{3-q}]_r-H$ group or a $-OR^4$ group, two or more of the $-[OSiO_qR^{3-q}]_r$, $-O-[SiO_qH_{q-1}R^{3-q}]_r-H$ or $-OR^4$ groups optionally being connected to each other by a covalent bond, wherein:

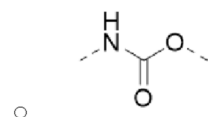
- q is an integer ranging from 0 to 3, r is an integer greater than or equal to one, and R^3 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives,

R^3 being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

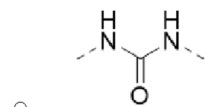
- R^4 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^4 being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

- p is an integer greater than or equal to 1,

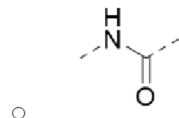
- W is selected as a linking group selected from:
[Chem 2]



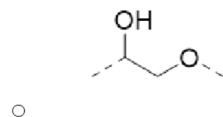
[Chem 3]



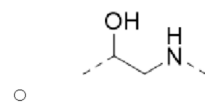
[Chem 4]



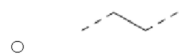
[Chem 5]



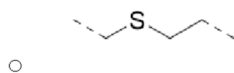
[Chem 6]



[Chem 7]



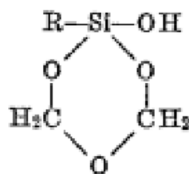
[Chem 8]



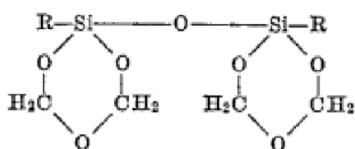
- T is the treating group of a treatment agent.

Preferably, Y^5 is selected as a halogen atom, a $-O-[SiO_qH_{q-1}R^{3-4}]_r-H$ group or a $-OR^4$ group. Preferably, Y^5 is selected as a halogen atom or a $-OR^4$ group.

Preferably, the compounds of formula (II) above do not correspond to the following formulas (III) and (IV):



(III)



(IV)

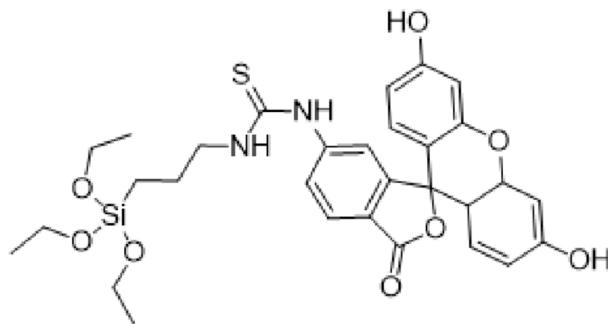
in which R is a hydrocarbon group.

“hydrocarbon group” means an organic compound consisting exclusively of carbon and hydrogen atoms.

Advantageously, the silylated treatment agent is selected from:

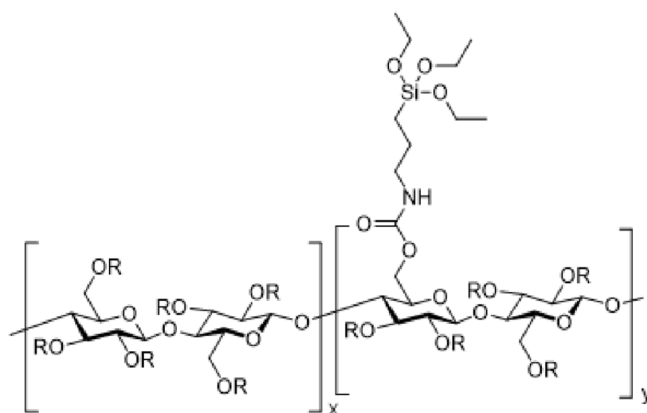
- silylated fluorescein of the following formula:

[Chem 10]



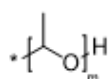
- silylated hydroxypropyl methylcellulose of the following formula:

[Chem 11]



in which x is an integer greater than or equal to 1, y is equal to $(1-x)$, and R is selected from $-H$, $-CH_3$ or the following formula:

[Chem 12]

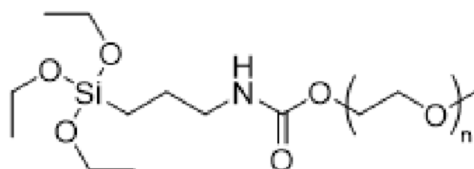


5

in which m is an integer greater than or equal to 1,

- the silylated polyethylene glycol of the following formula:

[Chem 13]



in which n is an integer greater than or equal to 1,

and mixtures thereof.

10

In a second method according to the invention, according to step a), tanning and ennobling of the hides ready to be tanned are carried out using a treating composition comprising at least said silylated treatment agent. For the purposes of the present application, the term "treating composition" means a composition capable of

15 tanning and ennobling hides in a single step. Thus, according to this second method, the tanning and ennobling can be carried out in a single step using a single compound, the silylated treatment agent. Thus, the treating composition can be free of the compound of formula (I).

During step b) of tanning and ennobling, a three-dimensional Si-O-Si network is

20 created by polymerization of the silylated treatment agent. This three-dimensional network bounds to the collagen constituting the hides and stabilizes the latter. Furthermore, the treating group of the silylated treatment agent is also covalently

bonded to this three-dimensional Si-O-Si network. This produces tanned and ennobled hides, in other words, finished leathers.

In addition to the silylated treatment agent, the treating composition generally comprises at least water.

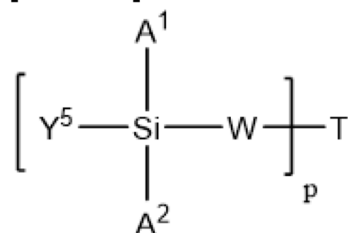
The treating composition may also comprise a salt to prevent the hides from swelling in water, as seen previously. The treating composition may also comprise any tanning agent, such as, for example, a tanning agent selected from the following compounds: chromium, glutaraldehyde, triazines, vegetable tannins such as mimosa, chestnut, quebracho, and mixtures thereof.

Advantageously, the treating composition is brought to a pH ranging from 1.0 to 10, preferably ranging from 1.5 to 4.0, preferably ranging from 1.6 to 2.0.

Advantageously, the silylated treatment agent is present in the treating composition, by mass relative to the mass of the hides ready to be tanned, in a content ranging from 1 to 100%, preferably ranging from 1 to 50%, preferably ranging from 1 to 20%.

Advantageously, the silylated treatment agent is selected from the compounds of formula (II) below:

[Chem 9]



(II)

in which

- A^1 and A^2 , which are identical or different, are selected independently of each other as Y^5 or W-T,

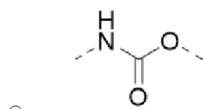
- Y^5 is selected as a halogen atom, a $-[OSiO_qR^{3-q}]_r$ group, a $-O-[SiO_qH_{q-1}R^{3-q}]_r-H$ group or a $-OR^4$ group, two or more of the $-[OSiO_qR^{3-q}]_r$, $-O-[SiO_qH_{q-1}R^{3-q}]_r-H$ or $-OR^4$ groups optionally being connected to each other by a covalent bond, wherein:

- q is an integer ranging from 0 to 3, r is an integer greater than or equal to one, and R^3 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^3 being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

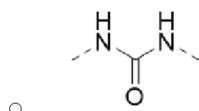
- R^4 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^4 being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

5

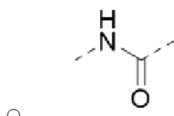
- p is an integer greater than or equal to 1,
- W is selected as a linking group selected from:
[Chem 2]



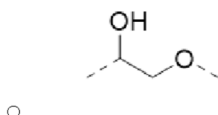
[Chem 3]



[Chem 4]

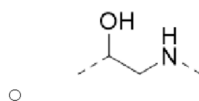


[Chem 5]

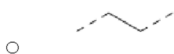


[Chem 6]

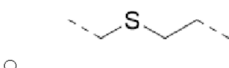
10



[Chem 7]



[Chem 8]

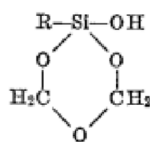


- T is the treating group of a treatment agent.

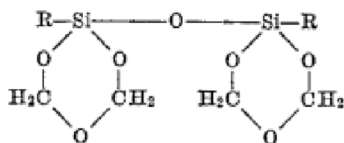
15

Preferably, Y^5 is selected as a halogen atom, an $-O-[SiO_qH_{q-1}R^{3-q}]_r-H$ group, or an $-OR^4$ group. Preferably, Y^5 is selected as a halogen atom or an $-OR^4$ group.

Preferably, the compounds of formula (II) above do not correspond to the following formulas (III) and (IV):



(III)



(IV)

5

in which R is a hydrocarbon group.

The term «hydrocarbon group» means an organic compound consisting exclusively of carbon and hydrogen atoms.

According to this second method according to the invention, the finished leather
 10 obtained at the end of step b) of tanning and ennobling may be subjected to other ennobling steps subsequent to step b). These subsequent ennobling steps may use a silylated treatment agent, which may be the same as the one used in step b) of tanning and ennobling, or another silylated treatment agent.

The methods according to the invention are particularly simple to implement and
 15 make it possible to provide one or more ennobling properties to sustainably tanned hides. Moreover, according to the methods according to the invention, it is possible to provide several ennobling properties to the leather in a single ennobling step and/or in a single tanning/ennobling step.

The present invention also relates to a method for disenobling a finished
 20 leather according to the invention, comprising at least one step during which said finished leather is soaked in a basic solution in order to raise the pH of the leather to a value greater than or equal to 10.5, preferably to a value ranging from 11.5 to 13.0.

For example, to carry out the disenobling, the finished leathers may be soaked
 in an aqueous solution, for example in a fuller. The aqueous solution may comprise a
 25 degreaser. The degreaser may be selected from surfactants, for example nonionic and anionic surfactants. The purpose of such a step is to degrease and rehydrate the leathers. The fuller may then be drained and the leathers may be rinsed in the fuller at room temperature.

The leathers are soaked in an aqueous solution comprising a basifying agent to raise the pH of the hides and/or leathers to a value greater than or equal to 10.5, preferably to a value ranging from 11.5 to 13.0.

The basifying agent may, for example, be selected from sodium bicarbonate, sodium carbonate, ammonia, sodium hydroxide, and mixtures thereof.

Bringing the finished leathers to a pH greater than or equal to 10.5, preferably ranging from 11.5 to 13.0, results in the three-dimensional Si-O-Si network bonded to the hide collagen breaking down. The silylated treatment agent is therefore detached from the leathers, which therefore no longer include the properties previously provided by the silylated treatment agent.

The invention will be better understood in light of the experimental section below and the attached figures, in which:

- [Fig. 1] is the fluorescent microscope photograph of the samples from tests B0, B1 and B2 of Example 1,
- [Fig. 2] is a graph showing the release of fluorescein as a function of time for Example 1 (according to the invention and comparative),
- [Fig. 3] is a photograph taken under UV lamp of the samples E1 and E0 of Example 2,
- [Fig. 4] is a photograph showing the resistance of fluorescein as a function of time for Example 2 (according to the invention and comparative).

EXPERIMENTAL PART

Example 1

Preparation of a finished leather with fluorescent properties by implementing a silylated treatment agent during the tanning step

a) Preparation of $\text{Si}(\text{OH})_4$ from $\text{Si}(\text{OCH}_2\text{CH}_3)_4$

1 L of $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ and 1 L of water are mixed.

The pH of this mixture is adjusted to a value ranging from 1.5 to 2.0 using a strong acid, such as hydrochloric acid or sulfuric acid, this list not being exhaustive.

The hydrolysis reaction of $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ to $\text{Si}(\text{OH})_4$ is exothermic. Therefore, the mixture is preferably maintained at the desired temperature, for example, around 30°C, using a cooling bath. The mixture is preferably stirred vigorously for 15 to 120 minutes. The hydrolysis reaction can take from 20 minutes to 2 hours. At the end of this reaction, a clear silicic acid solution with the chemical formula $\text{Si}(\text{OH})_4$ is obtained.

10% sodium chloride by mass is added, based on the total mass of the previously prepared silicic acid solution.

b) Preparation of the finished leather

Test B1: Addition of 0.25 mol% of silylated fluorescein relative to the number of moles of $\text{Si}(\text{OH})_4$

i) *Preparation of the hides ready to be tanned*

Lamb hides are available, either pickled hides from a storage pickle or delimed hides. These hides are degreased and rehydrated according to the expertise of those skilled in the art to obtain hides ready for tanning. The hides are weighed.

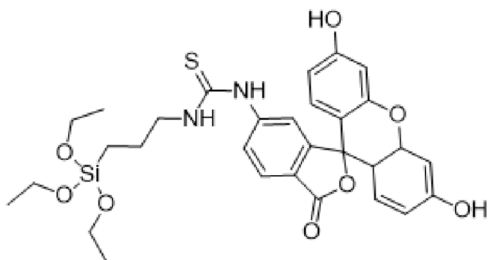
5 ii) *Tanning*

The hides are placed in a fuller in a salt solution. The pH of the hides and the salt solution is brought to a value ranging from 1.5 to 2.0.

A silylated fluorescein solution is prepared by dissolving silylated fluorescein powder (prepared in the laboratory) in an acidic water solution (pH comprised between
10 1.5 and 2.0) to obtain a mass concentration of 25 g/L.

The used silylated fluorescein has the following formula:

[Chem 10]



The following are added to the fuller, by mass relative to the mass of the hides:

- 15
- 50% cold water at 25°C,
 - 5% sodium chloride,
 - 13% Si(OH)_4 hydrolyzed from $\text{Si(OCH}_2\text{CH}_3)_4$ as described in point a).

1.56% of silylated fluorescein is also added, by mass relative to the mass of Si(OH)_4 . This amount represents 0.25% by mole relative to the number of moles of
20 Si(OH)_4 ; or 0.20% by mass relative to the mass of the hides.

The fuller is rotated for 4 hours at room temperature, namely 25°C.

Then, 5% by mass relative to the mass of the hides of sodium formate is added to the fuller at 25°C. The fuller is rotated for 1 hour. The final pH of the solution is approximately 3.8-4.0.

25 Then, 5% by mass relative to the mass of the hides of sodium formate is added to the fuller at 25°C. The fuller is rotated overnight. The final pH of the solution is approximately 4.0-4.5.

The fuller is then drained and the hides are rinsed. Tanned hides with fluorescent properties are obtained.

30 Test B2: Addition of 0.03 mol% of silylated fluorescein relative to the number of moles of Si(OH)_4

This test is carried out using the same procedure as that used for Test B1, but by replacing the 0.25 mol% of silylated fluorescein relative to $\text{Si}(\text{OH})_4$ with 0.03 mol% of silylated fluorescein relative to $\text{Si}(\text{OH})_4$.

Test B0: No addition of silylated fluorescein

This test is performed using the same procedure as that used for test B1, but without the addition of silylated fluorescein.

Test B1bis: Addition of 0.25% mol of unsilylated fluorescein relative to the number of moles of $\text{Si}(\text{OH})_4$: this test constitutes a negative control with the aim of demonstrating that silylated fluorescein binds covalently to the Si-O-Si network.

This test is performed using the same procedure as that used for test B1, but by replacing the 0.25% mol of silylated fluorescein relative to $\text{Si}(\text{OH})_4$ with 0.25% mol of unsilylated fluorescein relative to $\text{Si}(\text{OH})_4$.

c) Controlling the fluorescent properties of the finished leather obtained in point b)

For each test B0, B1, and B2, once the hides have been tanned, rinsed, and still wet, a sample of tanned hide measuring approximately 2 cm by 1 cm is cut at the neck.

The samples are analyzed using a Leica thunder imager (model Organism) fluorescent microscope.

The obtained results are shown in Figure 1: trace referenced B1 shows the fluorescence obtained for Test B1. Trace referenced B2 shows the fluorescence obtained for Test B2. Trace referenced B0 shows the fluorescence obtained for Test B0.

d) Demonstration of the stability of the provided property

For each test B1, B1bis, once the hides are tanned, rinsed, and still wet, a sample of tanned hide (1.76 g) measuring approximately 2 cm by 0.5 cm is cut at the neck. The samples are placed in two separate tubes and 10 mL of a brine solution (10% NaCl by mass relative to water) are added, then the tubes are stirred circularly. At various times, the 10 mL solution was collected for analysis using a UV spectrometer (Agilent Technologies Carry 60 UV-Vis) at a wavelength of 495 nm, and the leather sample was placed in a new brine bath. This operation was repeated until the fluorescein release stabilized.

The obtained results are shown in Figure 2: Using a calibration curve relating the fluorescein molar concentration to its UV absorbance at 495 nm, the amounts of silylated fluorescein (B1) and unsilylated fluorescein (B1bis) present in the samples can be calculated. In other words, the release of fluorescein from the leathers can be monitored over time. The curves show that a large amount of unsilylated fluorescein (B1bis), which is not bound to the tanning Si-O-Si network, is released over time. In

contrast, very little silylated fluorescein (B1), which is covalently bound to the Si-O-Si network, is released over the same period.

Thus, in this example, a finished leather with the property of being fluorescent was obtained by using a silylated treatment agent during the tanning step. In this example, the compound of formula (I) is $\text{Si}(\text{OH})_4$ and the compound of formula (II) is silylated fluorescein. The compounds of formulas (I) and (II) are thus added during the tanning step. Tanning and ennobling are therefore carried out simultaneously. The method is therefore quick and easy to implement.

10 **Example 2**

Preparation of a finished leather with fluorescent properties by implementing a silylated treatment agent during an ennobling step after tanning

a) Preparation of the finished leather

In this example, $\text{Si}(\text{OH})_4$ is prepared in the same way as in point a) of Example 1.

i) *Preparation of the hides ready to be tanned*

Lamb hides are available, either pickled hides from a storage pickle or delimed hides. These hides are degreased and rehydrated according to the expertise of those skilled in the art to obtain hides ready for tanning. The hides are weighed.

ii) *Tanning*

The hides are placed in a fuller in a salt solution. The pH of the hides and the salt solution is brought to a value ranging from 1.5 to 2.0.

The following are added to the fuller, by mass relative to the mass of the hides:

- 50% cold water at 25°C,
- 5% sodium chloride,
- 13% $\text{Si}(\text{OH})_4$ hydrolyzed from $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ as described in point a) of Example 1.

The fuller is rotated for 4 hours at room temperature (25°C).

Then, 5% sodium formate by mass relative to the mass of the hides is added to the fuller at 25°C. The fuller is rotated for 1 hour. The final pH of the solution is approximately 3.8-4.0.

Then, 5% sodium formate by mass relative to the mass of the hides is added to the fuller at 25°C. The fuller is rotated overnight. The final pH of the solution is approximately 4.0-4.5.

The fuller is then drained, and the tanned hides are rinsed, then dried.

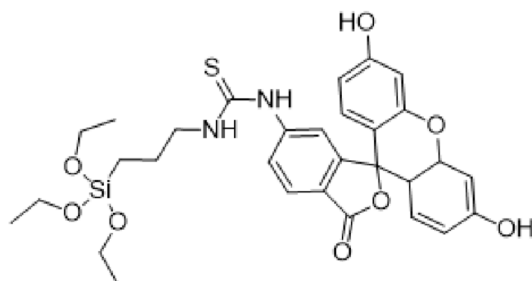
iii) *Ennobling Step*

A silylated fluorescein solution is prepared by dissolving silylated fluorescein powder (prepared in the laboratory) in an acidic water solution (pH comprised between 1.5 and 2.0) in order to obtain a mass concentration of 1.5 g/L.

The used silylated fluorescein has the following formula:

5

[Chem 10]



The silylated fluorescein solution is withdrawn with a syringe and deposited on the surface of the tanned hides from step ii) in the form of drops. The grafting reaction of silylated fluorescein to the three-dimensional Si-O-Si network created in step ii) of tanning with $\text{Si}(\text{OH})_4$ is carried out by drying.

10

The finished leather is left to air dry for 2 hours. This produces a finished leather with fluorescent properties.

b) Controlling the resistance to water washing of the property provided to the leather

15

The areas where the drops of silylated fluorescein solution were deposited are identifiable on the finished leather by yellow marks.

In order to demonstrate the stability of the provided fluorescence property, two samples of finished leather are prepared, from the finished leather from step iii), one sample to be tested, hereinafter referred to as E1, and a control sample, hereinafter referred to as E0.

20

The sample E1 is placed in a water solution (pH 7) for 2 weeks. The control sample E0 is kept as a non-immersed control.

After two weeks, the samples E1 and E0 are analyzed under an ultraviolet (UV) lamp at 366 nm. Figure 3 is a photograph of what is observed under this lamp.

25

The part labeled E1 corresponds to the tested sample E1, and the part labeled E0 corresponds to the control sample E0. No difference is observed between the sample E1 that was immersed and the sample E0 that was not immersed. This test shows that the property provided by leather ennobling, namely fluorescence, withstands washing in water for at least two weeks. The ennobling property provided to leather by silylated fluorescein is therefore stable over time.

30

c) Demonstration of the stability of the conferred property

Test E1bis: Ennobling with unsilylated fluorescein

The test E1bis is a negative control designed to demonstrate that the silylated fluorescein binds covalently to the Si-O-Si network.

The test E1bis is performed using the same procedure as that used for the test E1 above, but by replacing the silylated fluorescein with unsilylated fluorescein during the ennobling step.

More specifically, at the end of tanning step ii) above, a tanned hide sample P is selected.

During the ennobling step, the silylated fluorescein and unsilylated fluorescein solutions are successively withdrawn with a syringe and deposited on the surface of the tanned hide sample P in the form of drops: the letter C is formed by deposition, where the upper half of the letter C is made with unsilylated fluorescein (Test E1bis), and the lower half of the letter C is made with silylated fluorescein (Test E1). The grafting reaction of silylated fluorescein to the three-dimensional Si-O-Si network created in step ii) of tanning by $\text{Si}(\text{OH})_4$ is carried out by drying. There is no grafting reaction of unsilylated fluorescein, which dries only on the surface of the leathers.

The leather ennobled with unsilylated fluorescein (Test E1bis) and the leather ennobled with silylated fluorescein (Test E1) are left to dry in the open air for 2 hours.

The locations where the drops of silylated and unsilylated fluorescein solution were deposited are identifiable on the finished leather by yellow marks.

In order to demonstrate the covalent grafting of silylated fluorescein, and conversely the non-grafting of unsilylated fluorescein, the tanned hide sample P is immersed in a brine solution (10% NaCl by mass relative to water). At different times, the tanned hide sample P was analyzed under an ultraviolet (UV) lamp at 366 nm.

Figure 4 shows the images of what was observed under this lamp at different times, in other words $t=0$ h, $t=7$ h, $t=24$ h, and $t=120$ h. The part labeled E1 corresponds to the silylated fluorescein, and the part labeled E1bis corresponds to the unsilylated fluorescein. It can be seen that the trace corresponding to the unsilylated fluorescein disappears over time, no longer being visible after 120 h. In contrast, the trace corresponding to the silylated fluorescein does not fade and is stable over time.

This test demonstrates the benefits of working with silylated fluorescein, which is covalently grafted to the leather. This covalent grafting allows the ennobling properties, namely fluorescence, to be preserved much longer than with unsilylated fluorescein, which is not covalently grafted to the leather. The ennobling properties provided to the leather by silylated fluorescein are therefore stable over time.

Example 3

Preparation of a finished leather nourished by the use of the silylated treatment agent during the tanning step

In this example, Si(OH)_4 is prepared in the same way as in point a) of Example 1.

i) *Preparation of hides ready to be tanned*

Lamb hides are available, either pickled hides from a storage pickle or delimed hides. These hides are degreased and rehydrated according to the expertise of those skilled in the art to obtain hides ready for tanning. The hides are weighed.

ii) *Tanning*

The hides are placed in a fuller in a salt solution. The pH of the hides and the salt solution is adjusted to a value ranging from 1.5 to 2.0.

A monosilylated PEG solution is prepared by dissolving monosilylated PEG powder (prepared in the laboratory) in an acidic water solution (pH comprised between 1.5 and 2.0) to obtain a mass concentration of 25 g/L.

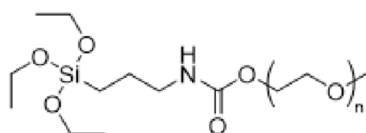
The following are added to the fuller, by mass relative to the mass of the hides:

- 50% cold water at 25°C,
- 5% sodium chloride,
- 13% Si(OH)_4 hydrolyzed from $\text{Si(OCH}_2\text{CH}_3)_4$ as described in point a) of Example 1.

10% monosilylated poly(ethylene glycol) (PEG) is also added, by mass relative to the mass of Si(OH)_4 . This amount represents 0.18 mol% relative to the number of moles of Si(OH)_4 ; or 1.3% by mass relative to the mass of the hides.

The used monosilylated PEG has the following formula:

[Chem 13]



where n is an integer greater than or equal to 1.

The fuller is rotated for 4 hours at room temperature, namely 25°C.

Then, 5% sodium formate by mass, relative to the mass of the hides, is added to the fuller at 25°C. The fuller is rotated for 1 hour. The final pH of the solution is approximately 3.8-4.0.

Then, 5% sodium formate by mass, relative to the mass of the hides, is added to the fuller at 25°C. The fuller is rotated overnight. The final pH of the solution is approximately 4.0-4.5.

The fuller is then drained and the hides are rinsed.

A fatliquored finished leather is obtained.

Example 4

Preparation of a finished leather trimmed by implementing a silylated treatment agent during an ennobling step after tanning

5 In this example, Si(OH)_4 is prepared in the same way as in point a) of Example 1.

i) Preparation of hides ready to be tanned

Lamb hides are available, either pickled hides from a storage pickle or delimed hides. These hides are degreased and rehydrated according to the expertise of those skilled in the art to obtain hides ready for tanning. The hides are weighed.

ii) Tanning the hides

The hides are placed in a fuller in a salt solution. The pH of the hides and the salt solution is brought to a value ranging from 1.5 to 2.0.

The following are added to the fuller, by mass relative to the mass of the hides:

- 15 - 50% cold water at 25°C,
- 5% sodium chloride,
- 13% Si(OH)_4 hydrolyzed from $\text{Si(OCH}_2\text{CH}_3)_4$ as described in point a) of Example 1.

The fuller is rotated for 4 hours at room temperature, namely 25°C.

20 Then, 5% sodium formate by mass relative to the mass of the hides is added to the fuller at 25°C. The fuller is rotated for 1 hour. The final pH of the solution is approximately 3.8-4.0.

Then, 5% sodium formate by mass relative to the mass of the hides is added to the fuller at 25°C. The fuller is rotated overnight. The final pH of the solution is approximately 4.0-4.5.

25 The fuller is then drained and the tanned hides are rinsed.

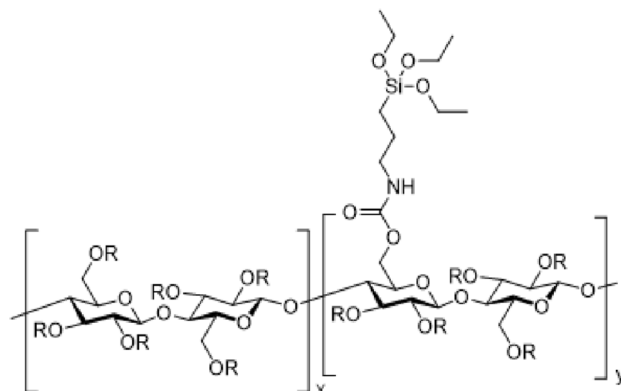
iii) Ennobling step

The tanned hides from step ii) are placed in a fuller. 500% water, by mass relative to the hides, is added. 2% sodium bicarbonate, by mass relative to the hides, is added to homogenize the pH of the hides to a value ranging from 5.0 to 8.0, preferably 6.0 to 7.5.

The fuller is rotated for approximately 40 minutes. The fuller is then emptied.

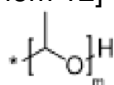
A silylated hydroxypropyl methyl cellulose (HPMC) solution is prepared by dissolving silylated HPMC powder (prepared in the laboratory) in a water solution (pH comprised between 6.0 and 8.0) in order to obtain a mass concentration of 12.5 g/L.

35 The silylated hydroxypropyl methyl cellulose has the following chemical formula:
[Chem 11]



where x is an integer greater than or equal to 1, y is equal to $(1-x)$, and R is selected from $-H$, $-CH_3$, or the following formula:

[Chem 12]



5

where m is an integer greater than or equal to 1.

After dissolution, the mixture is added to the fuller containing the tanned hides. The fuller is rotated, and the temperature is set at 50°C . Stirring is carried out for 2 hours, then formic acid (3% by mass relative to the mass of the hides) is added to fix the HPMC (hydrolysis and condensation of the siloxane group at an acidic pH). A pH comprised between 3.0 and 4.5 is obtained. The fuller is stirred for 1 hour, then emptied, and the tanned and fatliquored hides are rinsed.

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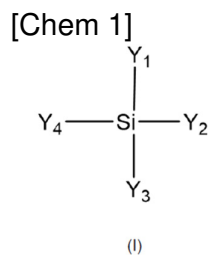
This produces a finished, trimmed leather.

CLAIMS

1. A finished leather comprising at least one ennobling property provided by at least one silylated treatment agent, said silylated treatment agent being fixed to a three-dimensional Si-O-Si network by a covalent bond, said three-dimensional Si-O-Si network being linked by hydrogen, ionic, or covalent bonds to the collagen constituting the finished leather.

2. A method for preparing a finished leather according to claim 1, from raw hides, said method comprising at least the following steps:

- i) preparing raw hides in order to obtain hides ready for tanning,
- ii) tanning the hides from step i) using a tanning composition comprising at least one tanning agent of formula (I):



in which Y^1 , Y^2 , Y^3 and Y^4 , identical or different, are selected independently of one another as being a halogen atom, a $-[OSiO_uR^{1_{3-u}}]_v$ group, a $-O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ group or a $-OR^2$ group, two or more of the $-[OSiO_uR^{1_{3-u}}]_v$, $O-[SiO_uH_{u-1}R^{1_{3-u}}]_v-H$ and $-OR^2$ groups being able to be connected to each other by a covalent bond, in which:

- u is an integer ranging from 0 to 3, v is an integer greater than or equal to one, and R^1 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^1 including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioethers groups,

- R^2 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^2 including optionally one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

said method being characterized in that said at least one silylated treatment agent is implemented during the tanning step ii) and/or during an ennobling step iii) subsequent to the tanning step ii).

3. The method according to claim 2, characterized in that said at least one silylated treatment agent is used at least during the tanning step ii).

4. The method according to claim 3, characterized in that the tanning composition further comprises said at least one silylated treatment agent, said silylated

treatment agent being present in the tanning composition in a content ranging from 0.1 to 50%, preferably from 0.1 to 35%, preferably from 0.1 to 25%, more preferably from 0.1 to 10%, by mass relative to the mass of the compound of formula (I).

5. The method according to any one of claims 2 to 4, characterized in that said at least one silylated treatment agent is at least implemented during an ennobling step iii) subsequent to tanning.

6. The method for preparing a finished leather according to any one of claims 2 to 5, characterized in that Y^1 , Y^2 , Y^3 and Y^4 are independently selected from each other as being a chlorine atom, an -OH group or an -OCH₂CH₃ group.

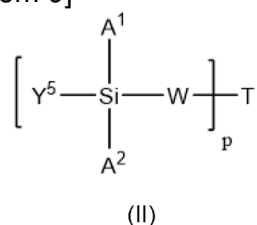
7. The method according to claim 6, characterized in that the compound of formula (I) is Si(OH)₄.

8. The method according to claim 6, characterized in that the compound of formula (I) is Si(OCH₂CH₃)₄.

9. The method according to any one of claims 2 to 8, characterized in that the compound of formula (I) is present in the tanning composition, by mass relative to the mass of the hides ready to be tanned, in a content ranging from 0.1 to 100%, preferably from 5% to 60%, more preferably from 5% to 30%.

10. The method according to any one of claims 2 to 9, characterized in that said at least one silylated treatment agent is selected from the compounds of following formula (II):

[Chem 9]



in which

- A^1 and A^2 , identical or different, are independently selected from each other as Y^5 or W-T,

- Y^5 is selected as an halogen atom, an -[OSiO_qR³_{3-q}]_r group, an -O-[SiO_qH_{q-1}R³_{3-q}]_r-H group or an -OR⁴ group, two or more of the groups -[OSiO_qR³_{3-q}]_r, an -O-[SiO_qH_{q-1}R³_{3-q}]_r-H and -OR⁴ being able to be connected together by a covalent bond, in which:

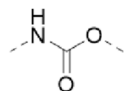
- q is an integer ranging from 0 to 3, r is an integer greater than or equal to one, and R³ is selected as a hydrogen atom, a C₁-C₁₀ alkyl group, an aryl group, a C₂-C₁₀ alkenyl group, a C₂-C₁₀ alkynyl group, a polyalkylene oxide group or its derivatives, R³ being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

- R^4 is selected as a hydrogen atom, a C_1 - C_{10} alkyl group, an aryl group, a C_2 - C_{10} alkenyl group, a C_2 - C_{10} alkynyl group, a polyalkylene oxide group or its derivatives, R^4 being optionally substituted by one or several amine, ammonium, amide, ketone, ester, aldehyde, thiol or thioether groups,

5 - p is an integer ranging from 0 to 2, and B is selected as a heteroatom or R^5 greater than or equal to 1,

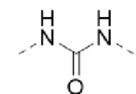
- W is selected as a linking group selected from:

[Chem 2]

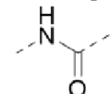


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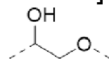
[Chem 3]



[Chem 4]

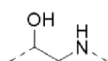


[Chem 5]

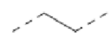


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[Chem 6]

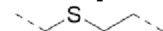


[Chem 7]



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[Chem 8]

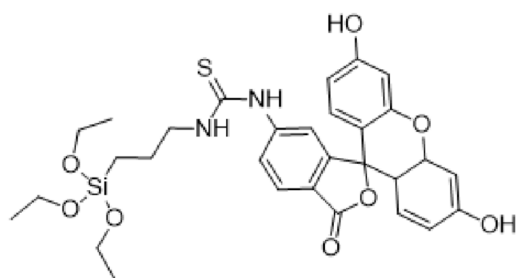


- T is the treating group of a treatment agent.

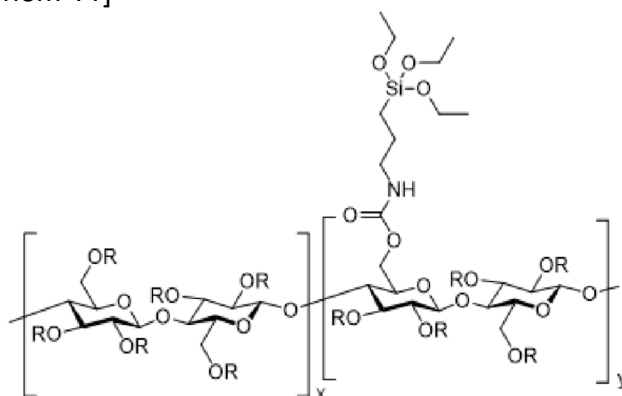
11. The method according to any one of claims 2 to 9, characterized in that the silylated treatment agent is selected from:

25 - the silylated fluorescein of the following formula:

[Chem 10]

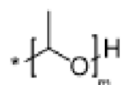


- the silylated hydroxypropyl methylcellulose of the following formula:
[Chem 11]



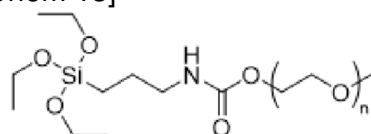
- 5 wherein x is an integer greater than or equal to 1, y is equal to (1-x), and R is selected from -H, -CH₃ or the following formula:

[Chem 12]



wherein m is an integer greater than or equal to 1.

- 10 - the silylated polyethyleneglycol of the following formula:
[Chem 13]

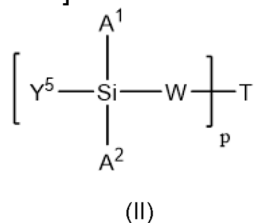


wherein n is an integer greater than or equal to 1.
and mixtures thereof.

- 15 12. A method for preparing a finished leather according to claim 1, from raw hides, said method comprising at least the following steps:
- a) preparing the raw hides in order to obtain hides ready for tanning,
 - b) tanning and ennobling the hides resulting from step a) using a treatment composition comprising at least said silylated treatment agent.

13. The method of claim 12, characterized in that said silylated treatment agent is selected from the compounds of formula (II) below:

[Chem 9]



5 in which

- A^1 and A^2 , identical or different, are selected independently of each other as being Y^5 or W-T ,

- Y^5 is selected as a halogen atom, an $-\text{[OSiO}_q\text{R}^{3-q}]_r$ group, an $-\text{O-[SiO}_q\text{H}_{q-1}\text{R}^{3-q}]_r\text{-H}$ group or an $-\text{OR}^4$ group, two or more of the groups $-\text{[OSiO}_q\text{R}^{3-q}]_r$, an $-\text{O-[SiO}_q\text{H}_{q-1}\text{R}^{3-q}]_r\text{-H}$ and $-\text{OR}^4$ being able to be connected together by a covalent bond,

10 in which

- q is an integer ranging from 0 to 3, r is an integer greater than or equal to one, and R^3 is selected as being a hydrogen atom, a group $\text{C}_1\text{-C}_{10}$ alkyl, an aryl group, a $\text{C}_2\text{-C}_{10}$ alkenyl group, a $\text{C}_2\text{-C}_{10}$ alkynyl group, a polyalkylene oxide group or its derivatives, R^3 being optionally substituted by one or more amine, ammonium, amide,

15 ketone, ester, aldehyde, thiol or thioether groups,

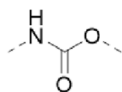
- R^4 is selected as a hydrogen atom, a $\text{C}_1\text{-C}_{10}$ alkyl group, an aryl group, a $\text{C}_2\text{-C}_{10}$ alkenyl group, a $\text{C}_2\text{-C}_{10}$ alkynyl group, a polyalkylene oxide group or its derivatives, R^4 being optionally substituted by one or more amine, ammonium, amide,

20 ketone, ester, aldehyde, thiol or thioether groups,

- p is an integer greater than or equal to 1,

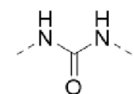
- W is selected from a linking group selected from:

[Chem 2]

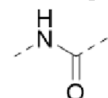


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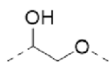
[Chem 3]



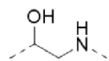
[Chem 4]



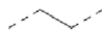
[Chem 5]



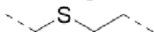
[Chem 6]



[Chem 7]



[Chem 8]



5

- T is the treating group of a treating agent.

10 14. A finished leather having at least one ennobling property, capable of being obtained by the method according to any one of claims 2 to 11 or the method according to any one of claims 12 to 13.

15 15. A method for disenobling a finished leather according to claim 1 or 14, or obtained by the method according to any one of claims 2 to 11 or by the method according to any one of claims 12 to 13, comprising at least one step during which said finished leather is soaked in a basic solution in order to bring the pH of the leather to a value greater than or equal to 10.5, preferably to a value ranging from 11.5 to 13.0.