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(54) **METHOD FOR OBTAINING A TANNED PRODUCT**

(57) Method for obtaining a tanned product, comprising at least one pretanning step, comprising at least one calcination operation, executed in a drum, in order to depilate the raw hide, a subsequent decalcination operation, executed in a drum, in order to remove at least lime residues from the depilated raw hide, and a subsequent pickling operation, executed in a drum, in order to obtain the pretanned hide. The method also comprises at least one tanning step, in which the pretanned hide is treated in a drum, and such tanning step comprises a first tannin treatment, executed by a temperature comprised be-

tween 15 and 30°C, with at least one first tanning product comprising tannins, and a second tannin treatment, executed by a temperature comprised between 20 and 35°C, with at least one second tanning product comprising tannins, in order to obtain a tanned hide.

The method also comprises at least one retanning step, in which the tanned hide is treated by means of at least one first retanning product, comprising tannins and such retanning step being executed within 168 hours from the start of said pretanning step.

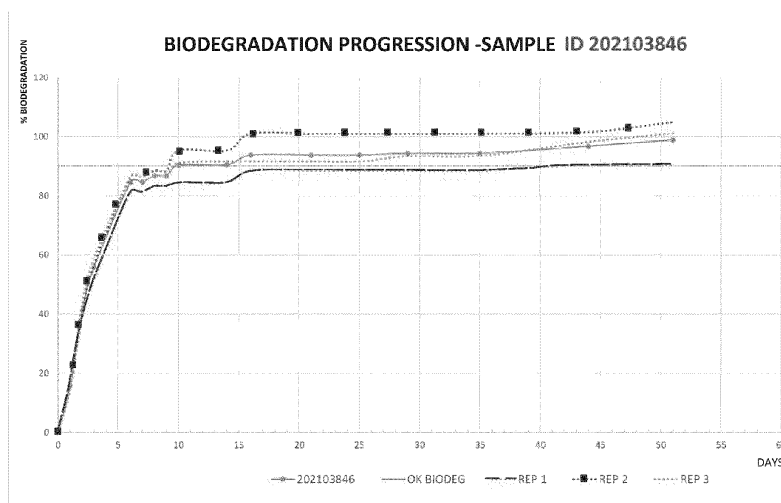


Fig. - 1 Progression of the biodegradation of the sample 202103846

DescriptionField of application

5 **[0001]** The present invention regards a method for obtaining a tanned product according to the preamble of the independent claim 1.

[0002] The present method for obtaining a tanned product is intended to be advantageously employed in tanneries, in the field of production of tanned products, such as for example hides, leather or other finished products deriving from a raw hide.

10 **[0003]** In particular, the method for obtaining tanned products, object of the present invention, is advantageously employable for producing a semifinished tanned product, therefore intended to sustain subsequent transformations in order to obtain a tanned product which is for example employable as a semifinished product for the clothing industry and fashion industry in general, or also for the furniture/interior design industry.

[0004] The method, object of the present invention, advantageously allows obtaining a biodegradable tanned product, hence susceptible of being autonomously degraded over time following the disposal thereof.

15 **[0005]** The invention is therefore inserted in the industrial field of production of tanned products, or more generally in the field of production of semifinished products for the clothing industry and fashion in general, or also for the furniture/interior design industry.

20 State of the art

[0006] Known in the field of production of tanned products are methods aimed for treating raw hides in multiple steps, so as to obtain a tanned hide, in which therefore the process of biodegradation is stopped and which is therefore suitable for sustaining successive working operations aimed for transforming the aforesaid tanned hide into a finished product, for example as a clothing article.

25 **[0007]** The methods for obtaining a tanned product usually provide for a pretanning step, which comprises a calcination operation, executed in a drum, in order to depilate the raw hide, a subsequent decalcination operation, executed in a drum in order to remove the lime residues of the calcination operation from the depilated raw hide and a subsequent pickling operation, executed in a drum, in order to obtain a complete lime-removal of the hide and thus obtain a hide ready to be tanned.

30 **[0008]** The aforesaid methods also provide for a tanning step, usually chrome tanning, in which the pretanned hide is treated in a drum, by means of trivalent chromium salts or compounds, in order to obtain a tanned hide.

[0009] Usually, the tanning step is followed by a subsequent retanning step, which has the object of substantially entirely stopping the degradation processes of the hide, in fact rendering it a stabilized hide that is suitable to be employed as semifinished product in the various fields in which hides are used. The tanned hide by means of chrome tanning is capable of being stored for a long time, usually even 9 months, before sustaining a retanning working.

35 **[0010]** The method for obtaining a tanned product of known type, described in brief up to now, has in practice shown that it does not lack drawbacks.

[0011] The main drawback lies in the fact that such tanning is polluting and potentially dangerous for the environment, due to the heavy metals employed which are inevitably released into the environment following tanning.

40 **[0012]** A further drawback lies in the fact that the chrome tanning is unable to ensure a completely natural aspect for the tanned hide and moreover the latter, if chrome-tanned, has an altered odor, of chemical type, which confers a not very nice appearance to the tanned hide for the final user.

[0013] In order to at least partly remedy the aforesaid drawbacks of the aforesaid method, a further method was developed in which the tanning step is completely natural, and is known in fact as vegetable tanning, and is therefore free of chrome.

45 **[0014]** Also such method has nevertheless shown in practice that it does not lack drawbacks. A first drawback lies in the fact that the aforesaid method comprising a step of vegetable tanning and retanning resulted unsuitable for being industrialized and employed large scale on a high number of hides, and has only found use for small productions of hides. This is due to the fact that such hides have a considerable degradation caused by the lack of stabilization of the hide, due to the lack of chrome.

50 **[0015]** A further drawback lies in the fact that the tanned hides obtained with the aforesaid method have revealed themselves to be not very nice to the touch, and in particular they have proven themselves to be provided with poor softness, lacking the properties necessary for their commercialization, in particular in the field of fashion and of clothing in general.

55 **[0016]** A further drawback lies in the fact that the tanned hides obtained with the aforesaid method have proven hard to dye and generally complicated to be worked in the subsequent finishing steps aimed to confer to the hide the aesthetic characteristics necessary for its use, in particular in the fashion and clothing field.

[0017] A further drawback lies in the fact that the tanned hides obtained with the aforesaid method have demonstrated that they are not completely biodegradable, and therefore not classifiable as biodegradable product.

[0018] Also known from the document EP 2110446 A1 is a tanning method which provides for employing vegetable tannins, such as in particular 10% Quebracho ATO, 5% Mimosa and 5% Chestnut, and for employing, in a final retanning step, tannins deriving from an apple extract.

[0019] In addition, the document WO 2018025210 A1 describes the use, in a process of tanning the hides, of olive mill wastewater as tanning product, in a quantity greater than 50%. The document EP 2862944 A1 describes a method of known type for the treatment of the sheep hide, which comprises a tanning step, during which a product based on vegetable tannins is employed for a duration of 2-3 days.

[0020] Also the latter methods of known type are unable to resolve the abovementioned drawbacks in an entirely efficient manner.

Presentation of the invention

[0021] In this situation, the problem underlying the present invention is therefore that of overcoming the drawbacks manifested by the methods in order to obtain a tanned product of known type, by providing a method for obtaining a tanned product, which allows obtaining a tanned product that is stabilized and substantially lacking degradations.

[0022] A further object of the present invention is to provide a method for obtaining a tanned product, which allows obtaining a biodegradable tanned product.

[0023] A further object of the present invention is to provide a method for obtaining a tanned product, which allows obtaining a tanned product provided with high tactile properties and in particular is provided with a high softness.

[0024] A further object of the present invention is to provide a method for obtaining a tanned product, which allows obtaining a tanned product provided with high mechanical properties.

[0025] A further object of the present invention is to provide a method for obtaining a tanned product, which allows obtaining a tanned product which is easily workable in the subsequent finishing operations and which is in particular easily dyeable.

[0026] A further object of the present invention is to provide a method for obtaining a tanned product, which allows reducing the environmental impact of one's working operations.

Brief description of the drawings

[0027] The technical characteristics of the invention, according to the aforesaid objects, are clearly seen in the contents of the below-reported claims and the advantages thereof will be more evident in the following detailed description, made with reference to the enclosed drawings, which represent a merely exemplifying and non-limiting embodiment of the invention, in which:

- figure 1 shows a graph of a biodegradability test executed on a preferred embodiment of the method, object of the present invention.

Detailed description of a preferred embodiment

[0028] With reference to the enclosed drawings, reference number 1 overall indicates a method for obtaining a tanned product, according to the present invention.

[0029] This is advantageously intended to be employed for the production of a tanned product, which can be for example a tanned product made of hide or a tanned product made of leather, which is advantageously intended to sustain subsequent working operations so as to obtain a product made of semifinished hide or leather employable in variable commodity fields, such as for example in the field of clothing or of fashion in general. The method for obtaining a tanned product, in accordance with the invention comprises at least one step for arranging raw hide.

[0030] Advantageously the aforesaid step for arranging the raw hide provides for placing at least one raw hide within a container, usually made of wood, known in the technical jargon with the term drum and which can be actuated in rotation in order to allow the treatment of the raw hide contained at its interior.

[0031] Of course, as a function of the dimensions of the drum the latter is susceptible of containing a different number of raw hides. In particular, the drum employed for the aforesaid method is configured for containing, at its interior, about five hundred raw hides.

[0032] Advantageously, the raw hide is a hide which has not been previously subjected to salt treatments, which are usually aimed to increase the preservation times of the raw hide but have negatively affected the biodegradability results of the raw hide. Therefore, for the purpose of optimally preserving the raw hide notwithstanding the absence of a salt treatment, the raw hides are transported to the destination site by means of refrigerated vehicles, so as to sufficiently

slow the degradation process before the treatment of the raw hides.

[0033] The method also comprises at least one pretanning step, in which the raw hide is worked so as to obtain a pretanned hide, and such pretanning step comprises at least one calcination operation, executed in a drum, in order to depilate the raw hide.

[0034] More in detail, such calcination operation is executed in a tank or alternatively in a suitable barrel for depilation, well-known to the man skilled in the art and therefore not described in detail hereinbelow.

[0035] The pretanning step also comprises a subsequent decalcination operation, executed in a drum, in order to remove at least lime residues from the depilated raw hide.

[0036] Advantageously the aforesaid decalcination operation comprises a first decalcination operation, in which the raw hide is placed within the drum together with a first solution comprising water, preferably in a quantity comprised between 80% and 120% with respect to the weight of the raw hide in the drum and still more preferably in a quantity substantially equal to the weight of the raw hide.

[0037] Advantageously the first solution of the first decalcination operation also comprises metabisulfite, which is added in the drum in a quantity comprised between 0.1% and 1% with respect to the weight of the raw hide in the drum.

[0038] Advantageously the aforesaid first decalcination operation is executed at a temperature comprised between 20°C and 30°C, preferably for a time comprised between 20 and 60 minutes. At the end of the first decalcination operation the drum is advantageously drained in order to remove the first solution.

[0039] Advantageously, in the following present description, the duration times of the single operations will be indicated, or the times of the entire steps of the method, object of the present invention, which will be intended as the time for which the drum is actuated in rotation with the hides and with the different components added within the drum.

[0040] Of course, it is possible that between two distinct operations, a step of stopping the drum takes place, in which the latter is not actuated in movement. Such stopping step will be advantageously to be intended as not affecting for the purpose of the determination of the duration of the preceding and/or successive operation.

[0041] Advantageously the decalcination step comprises a second decalcination operation, preferably following the first decalcination operation, in which the raw hide is treated by means of a second solution.

[0042] Advantageously the second solution comprises water, ammonium sulfate and lactic acid. Preferably the second solution comprises a quantity of water comprised between 10% and 30% with respect to the weight of the raw hide, preferably moreover the quantity of ammonium sulfate is comprised between 0.2% and 1% with respect to the weight of the raw hide and preferably the quantity of lactic acid is comprised between 0.5% and 1.5% with respect to the weight of the raw hide.

[0043] Advantageously the aforesaid second decalcination operation is executed at a temperature comprised between 20°C and 30°C, preferably for a time comprised between 30 and 120 minutes. Advantageously during the second decalcination operation, the admixing is executed of further lactic acid, preferably in a quantity close to 0.3% with respect to the weight of the raw hide. Preferably the aforesaid admixing of lactic acid is executed at about 30 minutes from the end of the second decalcination operation.

[0044] The pretanning step also comprises a subsequent pickling operation, executed in a drum, in order to obtain the pretanned hide, ready to be subsequently tanned.

[0045] Advantageously, before the aforesaid pickling operation, at least one washing operation is executed, which provides for introducing within the drum water, preferably an ambient temperature and preferably in a quantity close to 100% by weight with respect to the weight of the raw hide, and during such washing operation the drum is actuated for at least 5 minutes, and preferably for a time less than 20 minutes.

[0046] Advantageously the water of the washing operation is subsequently drained from the drum.

[0047] Advantageously the pickling operation provides for a first pickling operation, in which formic acid is added into the drum, preferably at a temperature comprised between 20°C and 30°C, and such first pickling operation is executed for a duration comprised between 15 and 45 minutes. Preferably the formic acid is added in a quantity comprised between 0.5 and 1.5 % with respect to the weight of the raw hide in the drum.

[0048] Preferably, together with the formic acid in the first pickling step, also a fungicide additive is added, in particular the product known in the market with the name "PREVENTOL WB PLUS-L" provided by the company LANXESS Deutschland GmbH. Advantageously the pickling operation provides for a second pickling operation, in which sulfuric acid is added in the drum, preferably at a temperature comprised between 20°C and 30°C, and such second pickling operation is executed for a duration comprised between 150 and 270 minutes.

[0049] Advantageously the sulfuric acid is added without having executed any operation of removal of the formic acid, and of possible other additives, previously inserted in the pickling operation.

[0050] Preferably the sulfuric acid is added in a quantity comprised between 0.2 and 1.6% with respect to the weight of the raw hide in the drum.

[0051] Advantageously the aforesaid quantity of sulfuric acid is added in two doses introduced in two different moments of the second pickling operation and in particular at the start of the second pickling operation and after a first time interval comprised between 20 and 60 minutes. Preferably, the two doses of sulfuric acid are substantially equal to each other

such to equally divide the total introduced quantity of sulfuric acid.

[0052] Advantageously, at the end of the pickling operation, which preferably determines the end of the pretanning step, the drum is drained of the solutions introduced during the different operations of the pretanning step.

[0053] The set of operations executed in the pretanning step are usually known in the technical jargon of the field with the expression "beamhouse operations" and group together the set of operations adapted to prepare the raw hide to receive the subsequent tanning treatments.

[0054] Advantageously the pretanning step comprises at least one soaking operation, executed in a drum and preferably preceding the calcination. The aforesaid soaking operation is advantageously adapted to restore to the raw hide the water that it had lost in the preservation process, and to clean the raw hide, eliminating the dirt and in particular the blood.

[0055] Advantageously the pretanning step comprises at least one stripping operation, which is a mechanical operation executed preferably before the calcination and with which the residue subcutaneous tissues of the connection tissues of the raw hide are eliminated at the animal carcass.

[0056] Advantageously the pretanning step comprises at least one maceration operation, which is an enzymatic operation preferably executed after the decalcination in order to complete the latter operation, eliminating residues of other non-useful interfibrillar substances and at the same time loosening the fibrous structure of the hide. Such maceration operation also advantageously allows obtaining a softer and more flexible pretanned hide. Advantageously during the aforesaid maceration operation, a macerating solution is inserted in the drum, preferably at a temperature comprised between 20°C and 35°C, and such macerating solution is maintained within the drum for a time comprised between 20 and 60 minutes.

[0057] Advantageously the aforesaid macerating solution comprises a first degreasing component, in particular the product known in the market with the name "Eusapon OC" provided by the company BASF SE, and a second macerating component, in particular the product known in the market with the name "Oropon On 2" provided by the company TFL.

[0058] The method also provides for at least one tanning step, in which the pretanned hide is treated in a drum and such tanning step comprises a first tannin treatment, executed by a temperature comprised between 15 and 30°C. The first tannin treatment is executed with at least one first tanning product comprising tannins, in particular synthetic tannins. Advantageously the first tanning product is added in a percentage comprised between 5 and 15% with respect to the weight of the raw hide in the drum.

[0059] For example, the first tannin treatment provides for employing, as first tanning product, the product known in the market with the name "SUSTAN PRE" provided by the company "GSC Group Spa", preferably added in a quantity of about 10% with respect to the total weight of the raw hide in the drum.

[0060] Preferably, during the first tannin treatment the first tanning product is admixed with a degreasing product, in particular the product known in the market with the name "G-SOFT O" provided by the company "GSC Group Spa", in a quantity advantageously comprised between 0.5 and 1.5% with respect to the weight of the pretanned hide in the drum.

[0061] Advantageously the first tannin treatment of the tanning step is executed for a time interval comprised between 60 and 120 minutes and still more preferably for about 90 minutes.

[0062] The tanning step also comprises a second tannin treatment, executed by a temperature comprised between 20 and 35°C, with at least one second tanning product, so as to obtain a tanned hide. Advantageously the second tanning product is added in a percentage comprised between 2 and 10% with respect to the weight of the raw hide in the drum. The aforesaid second tanning product comprises tannins deriving from olive mill wastewater, preferably from a condensate of olive mill wastewater. In particular, as is known, the olive mill wastewater are aqueous substances deriving from olive oil working processes.

[0063] For example, the second tanning product comprises the product known in the market with the name "SUSTAN FP" and the product known in the market with the name "AMINEX PF" both provided by the company "GSC Group Spa".

[0064] Advantageously the second treatment of said tanning step is executed for a time interval comprised between 150 and 330 minutes and still more preferably for about 240 minutes. Advantageously, according to a preferred embodiment, the first tannin treatment is executed before the second tannin treatment. In accordance with a different embodiment, such tannin treatments can be executed in reverse order.

[0065] The method also provides for at least one retanning step, in which the tanned hide is treated by means of at least one first retanning product, comprising tannins.

[0066] The retanning step is executed within 168 hours from the start of the pretanning step and preferably within 72 hours from the start of the same pretanning step.

[0067] Advantageously between the tanning step and the retanning step, a pressing and a subsequent shaving operation are executed, which are aimed to remove the excess liquids that are present from the hide, before the subsequent retanning step.

[0068] Advantageously the retanning step comprises at least one third tannin treatment, in which the first retanning product is employed, which comprises advantageously synthetic tannins, in a quantity comprised between 10% and 16% with respect to the weight of the hide in the drum.

[0069] Advantageously the retanning step comprises at least one fourth tannin treatment, in which a second retanning product comprising synthetic tannins is employed, in a quantity comprised between 7% and 13% with respect to the weight of the hide in the drum. Advantageously, in the third tannin treatment, two first retanning products are employed, comprising synthetic tannins, preferably different from each other.

[0070] For example the third tannin treatment provides for employing, as first retanning products, the product known in the market with the name "G-TAN RB" and the product "G-TAN PQ", both provided by the company "GSC Group Spa", preferably both added in a quantity close to 7% with respect to the total weight of the hides in the drum. Advantageously, in the fourth tannin treatment, two second retanning products are employed, comprising synthetic tannins, preferably different from each other.

[0071] For example the fourth tannin treatment provides for employing, as second retanning products, the product known in the market with the name "G-TAN RB" and the product "G-TAN SL POLV.", both provided by the company "GSC Group Spa", preferably both added in a quantity close to 5% with respect to the total weight of the hides in the drum. Advantageously the third tannin treatment is executed for a duration comprised between 10 and 50 minutes and still more preferably for about 30 minutes.

[0072] Advantageously the fourth tannin treatment is executed for a duration comprised between 30 and 150 minutes and still more preferably for about 90 minutes.

[0073] Preferably, during the fourth tannin treatment, in addition to the second retanning product, also a resin-based additive is added into the drum, in particular the product known in the market with the name "G-PLAST FM" provided by the company "GSC Group Spa" and still more preferably in a quantity comprised between 2 and 10% with respect to the weight of the hide in the drum.

[0074] Advantageously the third tannin treatment and/or the fourth thermal treatment are executed at a temperature comprised between 20°C and 45°C.

[0075] Advantageously the tanning step also provides a stabilization operation, preceding the first tannin treatment, which provides for the addition in the drum of a saline solution of water and salt, preferably at a temperature of about 20°C.

[0076] Advantageously the aforesaid solution comprises water, preferably in a quantity comprised between 50 and 70% with respect to the weight of the raw hide in the drum, and salt, preferably in a quantity comprised between 2 and 10% with respect to the weight of the raw hide in the drum.

[0077] Advantageously the aforesaid saline solution is provided with a density, measured in Baumé, which is comprised between 6 and 9 Bé.

[0078] Advantageously the tanning step provides for a treatment aimed to increase the tanning power of the second tannin treatment, which is attained between the first and the second tannin treatment, preferably by means of addition of sodium formate within the drum. Advantageously the aforesaid treatment with sodium formate is executed for a time interval comprised between 30 and 90 minutes and preferably the sodium formate is added into two separate doses and in particular, in accordance with the preferred embodiment, the second dose of sodium formate is added after a time from the first dose comprised between 15 and 45 minutes.

[0079] Advantageously the entire tanning step is executed for a time interval comprised between 300 and 500 minutes and preferably the entire tanning step is executed without ever draining the drum of the various products and additives added during the tanning step and therefore the various products and additives are added on each other.

[0080] Of course therefore each product is susceptible of coming into contact and in some cases also act on the hide, even after the step in which it is employed. Nevertheless, the above-indicated time intervals refer to the single operation and not to the time that the product or products employed in such operation remain in contact with the hide. Advantageously the retanning step provides for a soaking operation, preceding the third tannin treatment, which provides for the addition in the drum of a soaking solution of water and of a soaking additive, adapted to increase the absorption of water by the hide, and in particular the product known in the market with the name "NEOFAT AM/C" provided by the company "GSC Group Spa", preferably at a temperature of about 30°C. Advantageously the aforesaid soaking solution comprises water, preferably in a quantity comprised between 200 and 300% with respect to the weight of the raw hide in the drum, and the aforesaid soaking additive is preferably added in a quantity comprised between 0.5 and 3% with respect to the weight of the raw hide in the drum.

[0081] Advantageously the aforesaid soaking operation is executed for a time interval comprised between 30 and 90 minutes and preferably subsequently such soaking solution is drained from the drum.

[0082] Advantageously the retanning step provides for a first degreasing operation, executed between the soaking operation and the third tannin treatment, which provides for the addition of a degreasing solution of water and of at least one degreasing additive in the drum, preferably two degreasing additives and in particular the products known in the market with the name "G-SOFT STH 73" and "G-SOFT CLP" both provided by the company "GSC Group Spa". The aforesaid degreasing operation is advantageously attained at a temperature of about 30°C, preferably for a time interval comprised between 10 and 30 minutes.

[0083] Advantageously the aforesaid degreasing solution comprises water, preferably in a quantity comprised between 50 and 110% with respect to the weight of the raw hide in the drum, and the degreasing additives are preferably added

in a quantity comprised between 1 and 3% with respect to the weight of the raw hide in the drum.

[0084] Advantageously, the retanning step also provides for the addition, preferably executed between the degreasing operation and the third tannin treatment, of at least one resin, and preferably two resins, in particular "G-PLAST CSS" and "G-PLAST J 8". The aforesaid addition of resins is advantageously attained at two different moments, at a time interval preferably comprised between 10 and 40 minutes from each other.

[0085] Advantageously the first resin is added in a quantity comprised between 3 and 9% with respect to the weight of the raw hide in the drum, while the second resin is added in a quantity comprised between 2 and 6% with respect to the weight of the raw hide in the drum.

[0086] Advantageously, the retanning step provides for a second degreasing operation, executed between the third tannin treatment and the fourth tannin treatment, which preferably has the same dosage described above for the first degreasing operation.

[0087] Preferably the second degreasing operation is executed for a time interval comprised between 5 and 15 minutes.

[0088] Advantageously, the retanning step provides for a third degreasing operation, executed after the fourth tannin treatment, which is preferably executed at a temperature comprised between 30°C and 60°C.

[0089] Advantageously the third degreasing operation is executed by means of the same degreasing additives employed in the first and in the second degreasing operation, but preferably employed in a greater quantity and in particular in a quantity comprised between 4% and 12% (the two degreasing additives summed together).

[0090] The aforesaid third degreasing operation is advantageously attained for a time interval comprised between 30 and 90 minutes.

[0091] Advantageously during the aforesaid retanning step, preferably after the aforesaid third degreasing operation, formic acid is added within the drum, preferably in a quantity of about 1.5% with respect to the total weight of the hides within the drum, so as to improve the action of the abovementioned degreasing additives.

[0092] Advantageously the formic acid is also added before the third degreasing operation, preferably in a quantity of about 1.5% with respect to the total weight of the hides within the drum.

[0093] Advantageously the entire retanning step is executed for a time interval comprised between 250 and 450 minutes and preferably the third and the fourth tannin treatment of the retanning step are executed without ever draining the drum of the various retanning products and additives added during the retanning step.

[0094] Of course therefore each product is susceptible of coming into contact with and in some cases also acting against the hide, even after the step in which it is employed. Nevertheless, the above-reported time intervals refer to the single treatment and not to the time that the product or products employed in such operation remain in contact with the hide.

[0095] Advantageously, after the retanning step, the hides are discharged from the drum within a tank, preferably made of steel or plastic material, and within such tank the tanned hides are rewashed, preferably with water, in order to then be extended in order to drain the excess water deriving from the aforesaid washing.

[0096] Advantageously, in addition, following the aforesaid washing, the hides undergo an operation of pressing and softening, which is a mechanical operation in which, by means of a machinery provided with rotating cylinders, the hides are subjected to a pressing force preferably variable between 7 and 25 tons.

[0097] Advantageously, subsequently, a drying step is attained, in which the excess liquids are moved from the hides. Preferably the drying step comprises a vacuum drying operation, still more preferably at a temperature comprised between 30°C and 50°C. Advantageously the drying step is executed for a duration comprised between 250 and 600 seconds.

[0098] Advantageously the drying step also comprises a drying operation.

[0099] Advantageously, finally, a staking step is executed, well-known to the man skilled in the art and therefore not described in detail hereinbelow.

[0100] Of course, the tanned hides thus obtained can be subsequently subjected to operations of finishing and/or dyeing aimed to confer to the hide the desired final appearance as a function of their use.

[0101] Advantageously the treated hide by means of the method, object of the present invention, is biodegradable.

[0102] More in detail, with the term "biodegradable" it will be intended hereinbelow a hide capable of being converted in CO₂ and H₂O by means of the action of microorganisms and in which in particular the level of biodegradation is greater than 90% in a time of less than six months.

[0103] Hereinbelow, a preferred embodiment of the method, object of the present invention, will be schematically illustrated.

EP 4 180 541 A1

Step of the method	Product added in a drum	Quantity of product added in a drum [% with respect to the weight of the hide in a drum]	Time Interval [min]	Temperature [°C]	Operation at end of time interval
Decalcination	Water	100.00	30	25	Draining
	Metabisulfite	0.30			
	Water	80.00	30	25	Draining
	Water	20.00	60	25	
	Ammonium sulfate	0.50			
	Lactic acid	1.00			
	Lactic acid	0.30	30	25	
Maceration	Eusapon OC	0.15	40	25	Draining and discharging
	Oropon On 2	0.08			
Pickling	Water	100.00	10	20	Draining
	Water	50.00	5	20	Draining
	Water	40.00	30	25	
	Salt (NaCl)	9.00			
	PREVENTOL WB PLUS-L	0.20	30	25	
	Formic acid	1.00			
	Sulfuric acid	0.40	30	25	
	Sulfuric acid	0.40	180	25	Draining upon reaching the correct PH
Tanning	Water	60.00	10	20	
	Salt (NaCl)	5.00			
	SUSTAN PRE	10.00	90	20	
	G-SOFT O	1.00			
	Sodium formate	1.50	30	30	
	Sodium formate	1.00	30	30	
	AMINEX PF/ SUSTAN FP	5.00	240	30	Draining, washing and discharging

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(continued)

Step of the method	Product added in a drum	Quantity of product added in a drum [% with respect to the weight of the hide in a drum]	Time Interval [min]	Temperature [°C]	Operation at end of time interval
Retanning	Water	250.00	60	25	Draining
	NEOFAT AM/C	1.00			
	Water	80.00	15	30	
	G-SOFT STH 73	1.00			
	G-SOFT CLP	1.00			
	G-PLAST CSS	6.00	30	30	
	G-PLAST J 8	4.00	30	30	
	G-TAN RB	7.00	30	30	
	G-TAN PQ	7.00			
	G-SOFT STH 73	1.00	10	30	
	G-SOFT CLP	1.00			
	G-PLAST FM	6.00	90	30	
	G-TAN RB	5.00			
	G-TAN SL POLV.	5.00			
	Water	200.00	10	25	
	Formic acid	1.50			
	Formic acid	1.50	30	30	Controlling and draining
	Water	150.00	60	30	
	G-SOFT CLP	4.00			
	G-SOFT STH 73	4.00			
	Formic acid	1.50	30	30	Controlling and draining

[0104] The hide obtained by means of the preferred embodiment of the method, described above in the table, was tested so as to evaluate the level of biodegradability of the hide itself. More in detail, the hide was tested in accordance with the norm UNI EN 13432:2002, using the test method provided by this norm: UNI EN ISO 14855-1:2003.

[0105] The compound used as inoculation advantageously derives from a composting plant that treats the organic fraction of solid urban waste. The age of the compost in question is about 3 months. The material, once it reached the laboratory, was sieved between 0.5 and 1 cm, in a manner such to eliminate possible rough materials and subsequently expanded clay was added with the function of inert structuring material, so as to improve the pores of the compost and hence ensure optimal aerobic conditions for the entire duration of the test.

[0106] The hide specimen was instead ground and reduced to a grain size of about 1 mm.

[0107] The aforesaid test was executed for a duration of 51 days, in accordance with the aforesaid norm in fact the test can be stopped when a percentage biodegradability value is reached $D_t > 90\%$.

[0108] As set forth above, the percentage biodegradability represents the quantity of CO₂ developed by the specimen, removed from the value of the blank (C of the inoculation compound), in relation to the maximum theoretical CO₂ that

can be developed by the specimen based on the content of organic carbon (TOC). The theoretical quantity of CO₂ that can be developed (ThCO₂) is calculated from the following equation (§ 9.1, UNI EN ISO 14855-1:2013):

$$\text{ThCO}_2 = \text{MTOT} \times \text{CTOT} \times \frac{44}{12}$$

[0109] Where MTOT are the grams of dry substance of the specimen being tested placed in the reactor at the start of the test, CTOT is the proportion of the total organic carbon (TOC) present in MTOT in grams per gram, and 44 and 12 are respectively the molecular weight of the carbon dioxide and the atomic weight of the carbon.

[0110] The total percentage biodegradability is calculated from the following equation (§ 9.2, UNI EN ISO 14855-1:2013):

$$\text{Dt} = \frac{[(\text{CO}_2)\text{T} - (\text{CO}_2)\text{B}]}{\text{ThCO}_2} \times 100$$

[0111] Where (CO₂)T is the cumulative quantity of carbon dioxide developed by each composting reactor containing the specimen being tested, in grams per reactor, (CO₂)B is the cumulative quantity of carbon dioxide developed by each composting reaching containing the blank in grams per reactor, ThCO₂ is the theoretical quantity of carbon dioxide that can be produced by the specimen being tested, in grams per reactor.

[0112] In the following table, the results are reported of the biodegradability test executed in accordance with the norm and with the above-described specifications, in which it is inferred that at 51 days from the start of the test, the specimen has a percentage of degradation of 98.8%.

[0113] Such results are also visible from the graph enclosed in figure 1.

Parameters Test Method	Measurement unit	Values encountered $\pm$ uncertainty
Biodegradability (Dt) ID 202103846 Rep.. 1/3 Maximum value at plateau	%	90.5 $\pm$ --
Biodegradability (Dt) ID 202103846 Rep.. 2/3 Maximum value at plateau	%	104.8 $\pm$ --
Biodegradability (Dt) ID 202103846 Rep.. 3/3 Maximum value at plateau	%	101.1 $\pm$ --
Biodegradability (Dt) ID 202103846 Average maximum value at plateau	%	98.8 $\pm$ --

[0114] The invention thus conceived therefore attains the pre-established objects.

[0115] The commercial names of the products indicated in the present description are intended to be relative to the products provided by the corresponding manufacturing companies at the date of the first filing of the present patent.

Claims

1. Method for obtaining a tanned product, **characterized in that** it comprises:

- at least one step for arranging raw hide;
- at least one pretanning step, in which said raw hide is worked so as to obtain a pretanned hide, said pretanning step comprising at least:
 - a calcination operation, executed in a drum, in order to depilate said raw hide;
 - a subsequent decalcination operation, executed in a drum, in order to remove at least lime residues from said depilated raw hide, and
 - a subsequent pickling operation, executed in a drum, in order to obtain said pretanned hide;
- at least one tanning step, in which said pretanned hide is treated in a drum and said tanning step comprises:

- a first tannin treatment, executed at a temperature comprised between 15 and 30°C, with at least one first tanning product comprising tannins;
- a second tannin treatment, executed at a temperature comprised between 20 and 35°C, with at least one second tanning product, which comprises tannins deriving from olive mill wastewater, in order to obtain a tanned hide;

- at least one retanning step, in which said tanned hide is treated by means of at least one first retanning product, comprising tannins;

said retanning step being executed within 168 hours from the start of said pretanning step.

2. Method according to claim 1, **characterized in that** said retanning step is executed within 72 hours from the start of said pretanning step.

3. Method according to claim 1 or 2, **characterized in that** said first tanning product is used in a drum in a percentage comprised between 5 and 15% with respect to the weight of said raw hide in said drum.

4. Method according to any one of the preceding claims, **characterized in that** said second tanning product is used in a drum in a percentage comprised between 2 and 10% with respect to the weight of said raw hide in said drum.

5. Method according to any one of the preceding claims, **characterized in that** the first treatment of said tanning step is executed for a time interval comprised between 60 and 120 minutes.

6. Method according to any one of the preceding claims, **characterized in that** the second treatment of said tanning step is executed for a time interval comprised between 150 and 330 minutes.

7. Method according to any one of the preceding claims, **characterized in that** said retanning step comprises:

- at least one third tannin treatment, in which a first retanning product is employed which comprises synthetic tannins, in a quantity comprised between 10% and 16% with respect to the weight of the hide in said drum, and
- at least one fourth tannin treatment, in which a second retanning product is employed which comprises synthetic tannins, in a quantity comprised between 7% and 13% with respect to the weight of the hide in said drum.

8. Method according to claim 7, **characterized in that** said third tannin treatment is executed for a duration comprised between 10 and 50 minutes.

9. Method according to claim 7 or 8, **characterized in that** said fourth tannin treatment is executed for a duration comprised between 30 and 150 minutes.

10. Method according to any one of the preceding claims from 7 to 9, **characterized in that** said third tannin treatment and/or said fourth tannic treatment are executed at a temperature comprised between 20°C and 45°C.

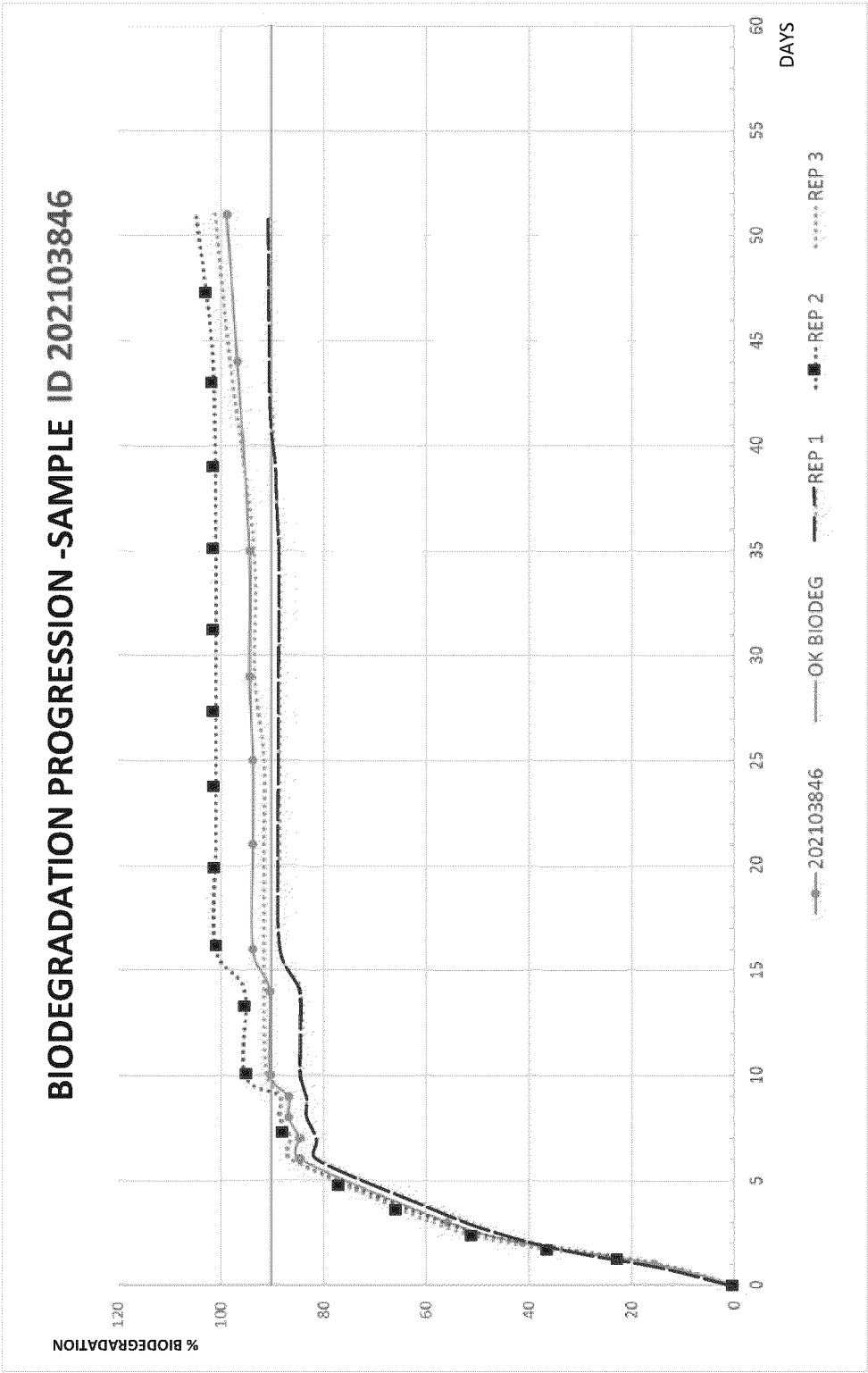


Fig. - 1 Progression of the biodegradation of the sample 202103846



EUROPEAN SEARCH REPORT

Application Number

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EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	WO 2018/025210 A1 (TANNOV S R L [IT]) 8 February 2018 (2018-02-08) * examples 2-4 * * page 1, line 5 - page 9, paragraph 3 * -----	1-10	INV. C14C1/06 C14C1/08 C14C3/10 C14C3/28
A,D	EP 2 110 446 A1 (CLARK C & J INT LTD [GB]) 21 October 2009 (2009-10-21) * paragraphs [0001] - [0015], [0017] - [0031], [0033] - [0050]; table 1 * -----	1-10	
A,D	EP 2 862 944 A1 (BALENCIAGA [FR]) 22 April 2015 (2015-04-22) * paragraphs [0001] - [0006], [0019] - [0036] * * example 1 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)
			C14C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 3 March 2023	Examiner Neugebauer, Ute
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 2018025210 A1		08-02-2018	CN	109952384 A		28-06-2019
			EP	3494237 A1		12-06-2019
			ES	2880083 T3		23-11-2021
			PL	3494237 T3		13-12-2021
			PT	3494237 T		14-07-2021
			WO	2018025210 A1		08-02-2018

EP 2110446 A1		21-10-2009	EP	2110446 A1		21-10-2009
			ES	2453945 T3		09-04-2014

EP 2862944 A1		22-04-2015	EP	2862944 A1		22-04-2015
			ES	2625320 T3		19-07-2017

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 2110446 A1 [0018]
- WO 2018025210 A1 [0019]
- EP 2862944 A1 [0019]