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(54) **TANNING PROCESS WHICH COMPRISES OXIDATIVE LIMING STEP**

(57) The invention relates to a tanning process which comprises the following step: (a) an oxidative liming in base environment of a hide. The oxidative liming comprises a treatment of the hide with lime. The oxidative liming, i.e. step (a), comprises the following steps wherein the percentages are to be understood as percentages by weight with respect to the weight of the hide: (a1) immunizing the hair of said hide with 0.8 to 1.2%, preferably with about 1% of hydrated lime; (a2) thereafter, adding an unhairing solution of peroxide in a percentage of between 2 and 3% of hydrogen peroxide, at a pH of between 12.0 and 12.5, wherein the pH is preferably adjusted by alkalizing the mixture with caustic soda (NaOH); and (a3) thereafter, neutralizing the bath. The process allows recovering all the components of the liming, in particular also the protein part in the liming bath. The hide obtained with the liming is sulfide-free. The invention also relates to a complete tanning process, from brining up to dressing, which complies with the ISO 15987 standard.

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Description

Technical field of the invention

[0001] The invention relates to a tanning process which comprises an oxidative liming in base environment which allows reusing the liming waste until now intended for disposal, and which can be inserted in a full tanning process which prevents the use of heavy metals and reduces the emission of CO_2.

[0002] The invention also relates to a hide treated by the process according to the invention.

State of the art

[0003] The tanning process is the treatment to which hides are subjected in order to preserve and process them. Some steps of traditional tanning comprise the use of environmentally harmful materials, such as heavy metals or sulfides in the liming. Of course, there are already alternatives to the use of heavy metals, such as vegetable tanning, or to the use of sulfides, such as hydrogen peroxide liming (D. Castiello et al. in: "Sviluppo di un sistema di depilazione esente da solfuri", published at the URL: http://www.polotecnologico.com/file/ptnov06-gen07-sviluppodiunsistemadidepilazioneesentedasolfuri.pdf; consultation date: 20.01.2015) which does not use sulfides and which allows reusing by-products (not contaminated with sulfides) without having to carry out a necessary desulfurization.

[0004] The British patent GB 1 106 391 does not employ sulfides in the unhairing of hides but proposes the use of peroxide salts with hydroxides, such as sodium or calcium hydroxides, indicating the unsuitability of H_2O_2 in this process.

[0005] Document DD 284 695 indicates another unhairing process that prevents the use of sulfides, wherein a treatment with hydrogen peroxide is followed, after an intermediate washing, by treatment with hydroxides.

[0006] However, these substitutions are limited to single steps of the tanning process and often do not satisfactorily fit in the whole tanning process. In the prior art, countless innovation efforts have already been made to make the various steps of the tanning production process cleaner with the aim of obtaining nontoxic by-products and limiting pollutants. Each step, however, has always been designed and used as a stand-alone process; it has never been reported that a set of *"green"* steps were chained together in a single manufacturing process to obtain a biocompatible finished product free from potential metal chemical pollutants.

Disclosure of the invention

[0007] The object of the invention is to recover almost entirely the contents of the liming end exhaust bath.

[0008] Another object of the invention is to provide a liming step that does not use sulfides and that may be satisfactorily introduced throughout the tanning process.

[0009] A further object of the invention is to implement a tanning process that puts together a series of sequential steps in order to make the hide a finished product commercially adapted to meet the limits imposed by the regulations to be named *"metal-free"* hide without involving the production of problematic by-products difficult to be disposed of, which affect the current tanning industry.

[0010] Another object of the invention is to propose a tanning process that allows obtaining a finished product with physical properties equal to the similar products already on the market, but having chemical properties that make it biocompatible upon disposal, such as a total amount of the five metals chromium, aluminium, zirconium, titanium and iron of less than 1000 ppm, according to the ISO 15987 standard.

[0011] The above objects, other objects and advantages that will be better highlighted hereinafter are achieved by the object of the first claim, and precisely by a tanning process which comprises the following step:

(a) an oxidative liming in base environment of a hide wherein said oxidative liming comprises a treatment of said hide with lime, which is characterized in that said oxidative liming, i.e. step (a), comprises the following steps wherein the percentages are to be understood as percentages by weight with respect to the weight of the hide:

(a1) immunizing the hair of said hide with 0.8 to 1.2%, preferably with about 1% of hydrated lime;
(a2) thereafter, adding an unhairing solution of peroxide in a percentage of between 2 and 3% of hydrogen peroxide, at a pH of between 12.0 and 12.5, wherein the pH is preferably adjusted by alkalizing the mixture with caustic soda (NaOH); and
(a3) thereafter, neutralizing the bath.

[0012] The above objects were achieved only with a thorough study and research that led to the use of selected and low risk products. In this way, also the process by-products are completely biocompatible, as well as a potential source of income in the various branches of the primary sector.

[0013] The effort of this process invention was to make the whole set of steps integrable and in complete agreement with each other, in particular to make the liming insertable within an eco-friendly process. As is well known from the common experience of the industry, each step is inter-dependent with the others, so if they are not specifically structured, the quality of the finished product will be lower than in the standard processes used (creasing, blowing, etc.). To make an example: if we have a new liming step that makes use of biodegradable products where wastes that are also biodegradable and/or reusable are generated, it is not obvious that such a step is in perfect harmony with the downstream processes, such as tanning, dying, fattening, dressing, etc., even if these processes are those normally used and even more if they are innovative *eco-friendly* processes.

[0014] The task of the process developed therefore focused on the structuring of liming and of the other steps in such a way that it would allow chaining the various *"green"* steps already existing, modifying and improving them to make them in good agreement with each other, an issue that had never before been industrially addressed and resolved.

[0015] In the first place, it should be noted that the crucial and integral part of this patent application is the treatment and recovery of solids suspended in the exhaust liming bath normally disposed of as sludge, consisting of a mixture of residual hair, fat, proteins and lime, which have the landfill as final destination. In this step, with the use of lime and basic hydrogen peroxide (preferably alkalized with caustic soda), the hides undergo in the first place the complete unhairing and in the second place, the saponification and loss of the last residual fat.

[0016] This step, where in traditional processing sulfide is used, is the major source of water pollution and of production of by-products difficult to dispose of. For the intended purpose, it was then chosen to use hydrogen peroxide, a process known for decades but which always involved side effects in the subsequent steps and in the finished product such that its use never really took off use in industrial productions, because of incomplete unhairing, blows and nubucking of the grain and generally, inferior mechanical properties.

[0017] This very delicate step, compared to the prior art, has undergone major changes, both in itself and in the preceding and following steps.

[0018] As regards the "global warming" impact category, with the use of the oxidative liming according to the invention instead of the traditional one, it is possible to lower the emissions of CO_2 eq. by 3.3% (from 1.25 CO_2 eq. for the traditional liming to 1.21 CO_2 eq. for the oxidative liming).

[0019] In a preferred variant of the invention, the bath neutralization in step (a3) is carried out with the addition of an aliquot of calcium chloride of between 1 and 3%.

[0020] In another more preferred variant of the invention, the bath neutralization in step (a3) is carried out with the addition of an aliquot of calcium formate of between 1 and 3%.

[0021] The advantages of calcium formate are manifold: calcium formate is more soluble and better protects the grain compared to calcium chloride. With the addition of formate in place of chloride, a product is added that has no known peptizing effect on the hide grain but a product which is more delicate and less aggressive. Therefore, the hide quality is improved by this less strong action.

[0022] Another advantage is the reduced chloride content that is introduced in waste waters, knowing that treatment plants cannot be effective on chlorides unless with extremely expensive and virtually inapplicable treatments. The purification of formates is much less problematic.

[0023] In a further variant of the invention, the calcium chloride may also be replaced by hydrated lime.

[0024] Step (a1) may take place in the presence or, preferably, in the absence of sodium polyphosphate having a glassy structure. In case of presence, the preferred concentration of sodium polyphosphate having a glassy structure is about 0.5%.

[0025] Advantageously, the addition of an unhairing mixture of hydrogen peroxide in step (a2) follows after 20-40 minutes of immunization according to step (a1) in one or more aliquots depending on the amount and on the raw product in question.

[0026] Preferably, after steps (a1) and (a2), the hide is turned in a bath of lime/basic hydrogen peroxide, whose preferred duration is about three to four hours, preferably about 3 hours.

[0027] Advantageously, the unhairing solution of hydrogen peroxide is a 35% solution (w/w) and is added in a percentage of between 6 and 8%. Preferably, the caustic soda used is a 30% solution (w/w).

[0028] In a preferred variant, step (a1) is preceded by a treatment of said hide with α-amylase and hyaluronidase. The application of both enzymes occurs prior to liming, allowing the enzymes to attack the hair bulb with the effect that hairs come off better. The use of enzymes would also allow using less hydrogen peroxide and less soda, which have the negative effect of swelling the hide too much, thereby opening the fibers.

[0029] Tests carried out first in laboratory and then on semi-industrial scale showed that the combination of these two enzymes results in a benefit in unhairing, more rapid and efficient, as well as a qualitative improvement of the hides.

[0030] Advantageously, the hyaluronidase enzyme (such as DOX L pro B by Biodermol) is accompanied by the presence of microorganisms with a probiotic action.

[0031] This mixture between enzyme with hyaluronidase activity and microorganisms with probiotic action turns out to be more selective and specific than the enzyme system that will be described in table 2a, due to its high hyaluronidase

activity; moreover, due to its specificity against globular protein, it does not affect the grain which remains clean, firm and stretched. A reduction was also observed in the values of COD (Chemical Oxygen Demand) and of nitrogen present in the exhaust bath of the liming process, which is the significant consequence of a lower emptying of the hides, which are more respected in the loss of dermal substance.

[0032] The α-amylase enzyme (such as BIODERMOL WP by Biodermol) is a product that acts on chondroitin sulfate and on the aminoglycans of the dermis. Its presence facilitates the detachment of the hair from the bulb in a short time and is verifiable by the lower resistance the hair opposes to the detachment when subjected to manual check at the end of the soaking process. The introduction of this enzyme showed a better opening of the hides, highlighted by the fact that the same are more stretched and with a less attacked grain.

[0033] Also the microscopic analysis of the section of the hide showed that the α-amylase enzyme led to an improvement of the cleanliness in the follicular cavity that appears to be entirely free of hair bulbs.

[0034] In a preferred variant, during the liming, partially degraded hair is separated, preferably continuously. This separation can take place, for example, by means of a screening system or by decantation or centrifugation.

[0035] Preferably, after an automatic cycle of, for example 12 hours, the hides are completely unhaired, blubbered and cleaned, ready to be re-fleshed and, if required, split. The operation of adding hydrated lime is normally used in sulfide processes to immunize the hair shaft, but in the prior art it has always been avoided in hydrogen peroxide processes due to the fact that lime inhibits the oxidative activity of hydrogen peroxide. In fact, also the article by D. Castiello et al. mentioned above judges the use of calcium hydroxide disadvantageous and diverts from the invention. The inventor, contrary to what reported by D. Castiello et al., has observed that, in particular in the dilution ratios applied (as described in claim 2 and as described for example in the executive example), the initial addition of lime and the ionic interaction of calcium with the fibers subsequently allows a better control of the swelling: since in order to have certain values of alkalinity, hydrogen peroxide must be neutralized with a large amount of caustic soda, as the keratolytic oxidation takes place, the hydrogen peroxide would be consumed, and then the concentration of free soda (which previously acted as neutralizer) would increase over time, leading to a denaturing effect on collagen fibers, visible from the considerable degree of blowing and nubucking of the grain; with the introduction of a neutralizer, in particular calcium chloride, this negative result is inhibited.

[0036] The inventor has theorized that, in the presence of an excess of soda, the addition of calcium chloride would lead to its neutralization due to a precipitation reaction to calcium hydroxide, fulfilling the dual purpose of neutralization of caustic soda and calcification of the collagen fibers. It would be as if the process had been conducted in parallel only with lime and sodium chloride, a situation which is not sufficient to alkalize and activate hydrogen peroxide. In conventional sulfide processes, calcium chloride is sometimes used in a smaller amount (0.5 - 1%) but with a different purpose, namely to give a slight denaturing effect to protein fibers, which in the oxidative process herein is not found since it is added in the presence of the large excess of soda with which to react. All this is observable with the decrease of the pH checked at the end of the process: from 12.4-12.5 if lime was simply added, to 12 with the addition of calcium chloride, which as second result entails that the risk of carbonation is partially reduced, i.e. the development of calcium carbonate on the surface of the hides, by the reaction with carbon dioxide in the air, which is qualitatively harmful and irreversible.

[0037] This exothermic unhairing step is advantageously carried out on drums chemically resistant to the oxidizing agents used and provided with a cooling system.

[0038] With the process according to the invention, it is possible to entirely recover the contents of the exhaust bath at the end of liming, for example by decantation/centrifugation of the same in order to obtain the separation of suspended solids consisting of lime and residual hair and liquid component.

[0039] Advantageously, this liquid component is then treated with appropriate acid chemical reactions that allow the precipitation of the proteins extracted from the hides, as will be described later.

[0040] This precipitate was found to be reusable by chemical industries working for the production of fertilizers and the like.

[0041] As much interest has been shown towards the hair, previously obtained by filtration of the liming. Advantageously, keratins are obtained by hydrolysis from such hair. Keratins are very interesting for many purposes (such as shampoos and cosmetics).

[0042] With this method according to the invention, purifying and landfilling problematic waste material is prevented and a way is found to recover valuable organic substances.

[0043] In a preferred variant of the invention, before being subjected to the (a) liming step, the hide is subjected to a step of brining, subsequently to a hair stating step and then to a soaking step with the use of surfactants, and preferably enzymes. In this case, it preferably is the so-called fresh hide. The presence of enzymes is not essential but is useful to affect the layer of glycosaminoglycans present on the epidermal basal layer.

[0044] Advantageously, the process starts with a first step of brining, where fresh raw hides coming from slaughter undergo a first cleaning of the biological organic material by means of an aqueous solution having a high saline density.

[0045] Preferably, sea salt and an antibacterial product are used in brining. A preferred antibacterial product comprises polyvinylpyrrolidone-iodine.

[0046] Advantageously, it further comprises a C_{11}-C_{13} alcohol ethoxylate.

[0047] Advantageously, a first hair stating follows where the subcutaneous fatty part is eliminated. This allows a better chemical-physical action of the products used thereafter and thereby a saving on their use. In this step, the product obtained, or fleshing waste, essentially consisting of fatty material and proteins, will preferably constitute a secondary reuse material for other types of industries (for example as a basis for the extraction of the oil part contained therein which can find use as fuel in cogeneration units or saponifiers for detergent industries).

[0048] In an advantageous variant of the invention, the hides thus treated then enter into a third step called soaking. This part is preferably carried out with the use of water, surfactants, biocides, alkalizers and enzymatic products, all eco-friendly.

[0049] They are preferably selected in such a percentage as to facilitate the subsequent step as much as possible. Suitable percentages are given hereinafter in the description of preferred embodiments.

[0050] Advantageously, all the soaking steps are conducted at a temperature of about 25 °C, at about pH 7, so as to favor the enzymatic action. Preferably, the soaking ends with a basification, preferably with soda, where the system is cooled to 20 °C in preparation for the oxidative liming.

[0051] Advantageously, the enzymes comprise a protease enzyme.

[0052] The hides thus cleaned from any dirt and conditioned at the right pH value are ready to undergo liming, in its oxidative variant, in the fourth step.

[0053] In a preferred variant of the invention, the mixture obtained at the end of step (a) or (a3) is brought by acid treatment, preferably with phosphoric acid, to pH 3.5 - 4.5, resulting in the precipitation of a white substance primarily consisting of proteins extracted from the hide. Then, advantageously, the precipitated white substance is separated. Advantageously, instead, after appropriate neutralization, preferably with caustic soda, the acid bath is made available for reuse in a new liming bath.

[0054] Summarizing: the by-products resulting from the final discharge of the liming bath consist entirely of lime, protein and fatty residue. Upon the discharge of the oxidative liming process end bath, the same is advantageously recovered and treated as indicated above. In addition to recovery, first of lime and residual hair by decantation, filtration or centrifugation, the process advantageously continues to the next step, where by suitable acid treatment, at pH 3.5 - 4.5, the precipitation of a white substance is obtained, mainly consisting of proteins extracted from the hide, for example bovine. This precipitate is preferably separated by centrifugation/filtration and directed to the use, subject to the necessary treatments, for example in the fertilizer industry. The acid bath instead, after appropriate neutralization with, for example, caustic soda, is made available for reuse. This aqueous saline solution can be reused as brine required in the first process step, or very advantageously as a starting bath of a new liming, given the content of amines which in an interesting manner promote the reaction mechanism during the unhairing and liming.

[0055] This is an important and qualifying point in the process: it has always been thought of delegating the discharge treatment step to the purification step, generating large volumes of sludge intended for the landfill, and no one, at present, has ever dedicated to industrially recovering the organic materials present in the liming wastewater. In the past, only the recovery of sulfides and the hair recovery were addressed, methods that have both been abandoned at least by the applicant, but to the applicant's knowledge, no one has ventured on an industrial scale in the recovery of the protein material present; which has made oxidative liming all the more interesting because this protein material is not contaminated by sulfides. The hide obtained by liming is devoid of sulfides and mercaptans and this is an advantage too, because the hides may be subjected to a second fleshing, where a sulfide-free fleshing is obtained (present in the traditional process). Preferably, the deliming, retting and tanning operations are carried out in order to obtain *white* tanned hides, i.e. without metals. In particular, metals give a finished product of difficult disposal and result in the formation of by-products that are particularly problematic and difficult to be stored. In addition, at the end of the life cycle of tanned leather with chromium, the presence of the latter makes the incinerator disposal thereof problematic due to the development of hexavalent chromium at high combustion temperatures.

[0056] The name *white* of this type of tanning comes from the color that the leather acquires after the tanning treatment. These hides, in fact, have a pale cream or white color. *Wet white* tanning is a process that allows treating the hides without the use of harmful materials, but leaving the softness typical of chrome-tanning unchanged, in a fully eco-friendly manner. *Wet white* tanned leathers are also recyclable.

[0057] The main products used for white tanning proposed by the literature and by the market are vegetable and synthetic phenolic, disulfonic and naphthalene tannins, glutaraldhehydes, metals (zirconium, aluminum, etc.) and oils. Instead, the type of *white* tanning proposed by this application involves the use of a metal-free triazine tanning product.

[0058] Advantageously, the deliming operations involve the use of carbonate esters, mixtures of dicarboxylic acids and sulfate-free ammonium salts. Preferably, retting with enzymatic products is carried out, all structured so as to adapt the oxidative liming step to a *white* tanning system.

[0059] In a preferred embodiment of the invention, the process contemplates the following steps after the (a) liming step in the indicated order:

(b) a first deliming;
(c) a retting; and
(d) a second deliming.

[0060] The deliming is split into two deliming steps, carried out before and after the retting in order to minimize the calcium content, a cation which would interfere with the tanning agent, and in the case of oxidative liming, where the deamination action is more intense, the calcium content bound to the hide is higher than the conventional sulfide liming.

[0061] Advantageously, the first and the second deliming take place using sulfate-free ammonium salts, particularly ammonium chloride, wherein in the first deliming, surfactants and acids are also preferably used, in particular citric acid and formic acid, and in that in the second deliming, formic acid is preferably present. Preferably, the retting takes place using pancreatic enzymes.

[0062] In a preferred variant of the invention, the process according to the invention comprises, after step (d), a *white* tanning step (e) up to obtaining a contraction temperature equal to or higher than 72 °C. The contraction temperature is measured to evaluate whether tanning stabilized the hide.

[0063] Advantageously, tanning is carried out with triazine-derived products.

[0064] Advantageously, the pickel step is completely eliminated. Preferred tanning products also include synthetic tannins. Pickle is a process that usually completes the deliming and allows bringing the hide to a pH value suitable for the following tanning step. For the *white* tanning provided in a preferred variant of this patent application, the pickle step is preferably completely eliminated.

[0065] Therefore, a process is eliminated which would involve the use of sodium chloride, formic acid and sulfuric acid, tanning with triazine-derived products.

[0066] Also this step, normally known by the man skilled in the art, compared to the typical execution has undergone changes in the amount of use in order to better adapt to the preceding and following steps.

[0067] Advantageously, in the absence of the pickel process step and of possible consequent difficulties the tanning product may be subject to crossing the section of the hide, this process is carried out in cold, preferably at about 26 °C, and dry, i.e. without adding water except for that contained in the tanning product, and preferably with very long rotation times.

[0068] Advantageously, an ecological tanning of this type is also very accurate from the ecological point of view, in the use of special deliming agents that do not give a contribution of sulfates to the process. Therefore, it is preferable not to use a series of cheaper but more polluting deliming agents normally used in the tanning industry; this choice should be especially careful and accurate because, if not well executed, it would undermine the success of this particular tanning, even more sensitive than the traditional chromium tanning to the steps that precede it. At the end of said tanning, the hides have undergone a stabilization of the collagen fibers that allow obtaining a hide contraction temperature ≥ 72 °C.

[0069] The waste waters of these tanning processes are free of toxic substances, and free from problems related to their reuse; whereby this tanning end bath is advantageously centrifuged with separation of the unreacted solid and of the liquid which is then for example neutralized and re-used in the subsequent process. The solid centrifugation part can be admixed as bonding agent/additive to shaving which, as will be explained hereinafter, can be used as an important part of bonded leather.

[0070] Advantageously, at the end of the tanning, after pressing, the hides are shaved to the desired thickness and the operation results in a chromium-free byproduct called shaving, which due to this particular feature is useful for reuse especially in the field of bonded leather or in the production of biopolymers that can be reused as retanning agents for use also in the field of leather.

[0071] In a preferred variant of the invention, after the tanning step (e), the hide undergoes a retanning and fattening step (f). Retanning and fattening serve to strengthen the structure, previously weakened by the strong basic action of oxidative liming.

[0072] Advantageously, materials are used for fattening which are selected from natural and synthetic sulfited oils, synthetic emulsifying oils, a fattening based on oxidized sulfited fish oil, a fattening based on lecithin, a fattening based on neatsfoot oil. Preferably, the fattening is carried out in the presence of emulsifying and/or softening agents. A preferred retanning agent is a polymer based on condensed phenolsulfonic acid and a polymer based on condensed melamines. Both retanning and fattening were studied in the selection of products and percentages, in order to better meet the starting base, i.e. *metal-free* tanned hide from oxidative liming. The particular combination of steps and products for retanning depends on the articles targeted by the production, which may be the furniture, footwear, leather goods, clothing or the automotive industry. These articles can all be produced from *white* tanning. The choice of the type of fattening and/or retanning agent and their percentage amounts are determined precisely by the target articles. Roughly, the fattening percentages range from 6 to 14% and the percentages of retanning agent range from 5 to 10% (percentages referred to the weight of the hide being treated).

[0073] At the end of the wet steps and related processes, there are the final dressing steps, useful to cover any defects and make the hide suitable to become a finished product suitable for the applications required. Therefore, also these

processes are chosen selected according to the required specifications.

[0074] In a preferred variant of the invention, retanning and fattening use metal-free or low-metal chemicals in order to comply with the ISO 15987 standard. The final purpose of the hide affects the dressing type and the technical specifications required for that article.

[0075] For the dressing processes, especially for colors such as ochre and light brown, low-iron oxide pigments are advantageously selected. Herein, the presence of metal is justifiable as follows: the sum of the five metal Cr, Ti, Zr, Pb, Fe, in accordance with the abovementioned ISO standard, must be ≤1000 ppm. In the case of the invention, the measurements made meet and still maintain the *metal-free* leather characteristic and purpose.

[0076] Advantageously, in this last dressing step, the leather production principles complying with and approved by TUV are applied as corresponding to the provisions of the RAL VZ 140 and RAL GZ 430 regulations, normally known by the name BLAUER ENGEL.

[0077] Another aspect of the invention relates to a hide, particularly a calcined hide, which is free from sulfides and which comprises calcium. A sulfite-free calcined hide comprising calcium can be obtained by the process according to the invention. A calcined hide - which has therefore undergone a liming step - is also called "pelt" in technical jargon.

[0078] The hide from conventional liming contains sulfides and calcium while the hide from hydrogen peroxide liming according to the invention contains no sulfides but it does contain calcium. By calcium it is meant the calcium added to calcium naturally present in the hide. In the hide obtained after liming according to D. Castiello et al. above, the calcined hide contains neither sulfur nor calcium.

[0079] The objects and advantages mentioned will be further highlighted in the description of preferred embodiments of the invention given by way of a non-limiting example.

[0080] Variants of the invention are object of the dependent claims. The description of preferred exemplary embodiments of the process according to the invention is given by way of a non-limiting example.

Description of preferred exemplary embodiments

[0081] The following is the description of an exemplary embodiment of a tanning process according to the invention. The single products mentioned with a proper noun and the manufacturer may of course be replaced by similar products that comprise the same "active ingredient" or a product of the same chemical family having the same tanning effect. Of particular importance are the amounts of components (and correspondingly their mutual ratios), which may however vary with a tolerance of ± 3%. Rotation times, speeds and temperatures can vary with a tolerance of ± 5%.

[0082] All the steps which involve the use of chemical products are carried out in a drum, except for the dressing steps.

Part 1

[0083] 1500 kg of fresh raw cow hides are loaded in a polypropylene drum provided with a cooling system, following the first brining step, dung removal.

[0084] All product percentages below refer to the weight of the hides.

Table 1

Composition of the solution		Conditions
30%	water T = 20 °C	temperature in the drum = 20 °C
8%	sea salt	40 min rotation, 1 rpm speed
0.1%	Biodermol BTM OS	3 min rotation - 30 min stationary, 1 rpm speed for 12 hours

[0085] Biodermol BTM OS by Biodermol Ambiente Srl is an anti-bacterial product consisting of polyvinylpyrrolidone-iodine and C_{11}-C_{13} alcohol ethoxylate.

[0086] After the time indicated, the second step begins, where the drum is drained and the hides unloaded from drum undergo a first fleshing in order to eliminate most of the adipose layer (the residue left on the hide will be eliminated after liming).

[0087] The hides are loaded into the drum again where the third step begins, soaking. If the tables have empty lines, it means that the substances subsequently indicated are added to those already present in the bath.

[0088] Tables 2a and 2b show two alternatives of the soaking step, distinguished by the type of enzymes used.

Table 2a

Composition of the solution		Conditions
120%	water T = 28 °C	10 min rotation, 1 rpm speed
4%	sea salt	
0.15%	Biodermol BTM OS	
0.5%	Biodermol Rinverdente DOX L	60 min rotation, 1 rpm speed
0.5%	Biodermol Lipol DF	60 min rotation, 1 rpm speed
addition of		
0.15%	Biodermol Lipol DSX	60 min rotation, 1 rpm speed 3 min rotation - 12 min stationary, 1 rpm speed for 120 min
bath cooling start up to 20 °C		
addition of		
0.8%	Soda Solvay	120 min rotation, 1 rpm speed

Table 2b

Composition of the solution		Conditions
120%	water T = 28 °C	10 min rotation, 1 rpm speed
4%	sea salt	
0.15%	Biodermol BTM OS	
0.2%	Rinverdente DOX L pro B	60 min rotation, 1 rpm speed
0.5%	Biodermol Lipol DF	2 min, 20 min rotation,
0.15%	Biodermol Lipol DSX	9 hours stationary, pH = 7.5 $\pm$ 0.5
bath cooling start up to 20 °C		
0.8%	Soda Solvay	15 min rotation, 1 rpm speed, 2 min, 20 min rotation, 3 hours stationary
0.8%	Biodermol WP	90 min rotation, 1 rpm speed, pH = 9.0 $\pm$ 0.5

[0089] Biodermol products are from Biodermol Ambiente Srl.

Biodermol Rinverdente DOX L: protease enzyme.
Biodermol Lipol DF: polyenzyme (lipase).
Biodermol Lipol DSX: di-(2-ethylhexyl) sodium, anionic surfactant.
Biodermol DOX L pro B: enzyme with hyaluronidase activity and probiotic microorganisms.
Biodermol WP: α-amylase.

[0090] All steps are carried out at a temperature of 25 °C, pH 7, so as to promote the enzymatic action, except for the last basification step with soda, where the system is cooled to 20 °C in preparation for the oxidative liming.

[0091] Once this third step is completed, the bath is drained to begin the fourth step, the oxidative liming:

Table 3

Composition of the solution		Conditions
20%	water T = 16 °C	30 min rotation, 1 rpm speed
1%	hydrated lime	
0.5%	Coriagen® CR II NEW	
addition of		
17%	water T = 16 °C	diluted together before introduction in the drum 10 min rotation, 1 rpm speed
4.2%	30% caustic soda	
3.6%	hydrogen peroxide 130 volumes	
addition of		
17%	water T = 16 °C	diluted together before introduction in the drum, 60 minute rotation 1 rpm speed
4.2%	30% caustic soda	
3.6%	hydrogen peroxide 130 volumes	

[0092] The addition of hydrogen peroxide does not necessarily have to be carried out in two steps; the addition in one step as well as the addition in two steps are also contemplated.

[0093] Coriagen® CR II New by STAHL is a sodium polyphosphate having a vitreous structure.

[0094] These steps are conducted at 22 °C with cooling system switched on, in order to dispose of the heat produced by the oxidation of the keratinous material, the reaction being exothermic.

[0095] After one hour of rotation at 1 rpm speed of the combined mixture of all the steps in Table 3, the grilling system is switched on, consisting of a filter, where the hair is separated and removed from the bath. This step continues for two hours at the same rotational speed.

[0096] After the two hours, the grilling system is switched off and the process continues with the addition of:

Table 4

Composition of the solution		Conditions	
2%	Calcium chloride or, alternatively, calcium formate	30 min rotation, 1.1 rpm speed	temperature in the drum = 22 °C
		3 min rotation - 30 min stationary, 1 rpm speed for 8 hours	temperature in the drum = 24 °C (up to the unloading of the products)
bath drainage			
addition of			
200%	water T = 24 °C	5 min rotation, 1.5 rpm speed	
bath drainage			
addition of			
100%	water T = 24 °C	10 min rotation, 1 rpm speed	
0.15%	Coriagen® CR II NEW		
bath drainage			

[0097] When this operation is completed, the hides are unloaded, fleshed again, optionally split and then weighed again.

Part 2

[0098] After the first soaking-liming part, the deliming-tanning part follows.

[0099] The hides are loaded back into the drum, where they undergo deliming and retting. Deliming is carried out into two parts, before and after the retting, in order to minimize the calcium content. This is necessary in case of use of lime during the liming.

[0100] Reporting now the first washing and deliming part (hereafter, the percentages refer to the new post-fleshing weighing):

Table 5

Composition of the solution		Conditions
120%	water T = 30 °C	temperature in the drum = 30 °C (for the whole operation) 20 min rotation, 3 rpm speed
0.10%	Tergolix® SL 01	
0.2%	Dekalon CL-IT p	
bath drainage		
addition of		
150%	water T = 30 °C	10 min rotation, 3 rpm speed
addition of		
30%	water T = 30 °C	15 min rotation, 3 rpm speed
0.10%	Tergolix® SL 01	
0.5%	Dekalon® CL-IT p	
0.5%	Decalcian® N liq.	
addition of		
17%	water T = 30 °C	60 min rotation, 5.5 rpm speed
1.7%	Tergolix® SL 01	
0.05%	Dekalon® CL-IT p	
1%	Decalcian® N liq.	
bath drainage		
addition of		
100%	water T = 30 °C	30 °C temperature, 30 min rotation, 2.5 rpm speed
0.15%	Dekalon® CL-IT p	

Tergolix® SL 01 (Clariant): nonionic surfactant based on alcohol ethoxylates, fatty alcohol polyglycol ether and mono-undecylether polyethylene.
Dekalon® CL-IT p (Clariant): deliming product made from ammonium chloride and citric acid.
Decalcian® N liq. (Clariant): deliming product made from ammonium chloride and formic acid.

[0101] The last deliming bath is maintained in the following retting operation:

Table 6

Composition of the solution		Conditions
1.2%	Feliderm® bate PB1	30 °C temperature 30 min rotation, 2.5 rpm speed
addition of		
0.20%	Tergolix® SL 01	30 min rotation, 2.5 rpm speed
bath drainage		

Feliderm® bate PB1 (Clariant): pancreatic-derived enzyme mixture on a kaolin base.

[0102] With the last wash, the hides are cooled for the next and final deliming part:

Table 7

Composition of the solution		Conditions
250%	water T = 16 °C	18 °C temperature 5 min rotation, 3 rpm speed
addition of		
70%	water T = 16 °C	18 °C temperature 60 min rotation, 3 rpm speed
1%	Decalcian® N liq.	
bath drainage		
addition of		
300%	water T = 16 °C	5 min rotation, 3 rpm speed
bath drainage		

[0103] Having thus removed the lime and brought the pH to 8, in the order of weak alkalinity, the tanning operation follows:

Table 8

Composition of the solution		Conditions
10%	Granofin® F90	temperature in the drum = 26 °C 60 min rotation, 5.5 rpm speed
addition of		
0.2%	Acticide® WB300	180 min rotation, 5.5 rpm speed 8 hour rotation, 1.5 rpm speed
addition of		
30%	water T = 30 °C	temperature in the drum = 30 °C 60 min rotation, 5.5 rpm speed
1%	Catalix® L liq.	
addition of		
5%	Syncotan® MRL	240 minutes rotation 5.5 rpm speed temperature in the drum = 42 °C over 4 hours final pH around 4.8 ± 0.3
bath drainage		
addition of		
110%	water T = 16 °C	temperature in the drum = 28 °C
0.1%	Acticide® WB300	5 min rotation, 3 rpm speed

Granofin® F90 (Clariant): triazine-based tanning product.
Catalix® L. liq. (Clariant): cationic fattening, derived from imidazoline and ethoxylated fatty alcohols in aqueous solution.
Acticide® WB300 (Thor): Microbiocide based on 2-(thiocyanomethylthio)benzothiazole.
Syncotan® MRL (Clariant): synthetic substitution phenolic tannin.

[0104] The penetration of the triazine tanning agent is actually carried out in dry, and fixing is observed with the increasing acidification to average acid pH (4-5). The hide then undergoes a further retanning and fattening to strengthen

the structure, previously weakened by the strong basic action of oxidative liming. The temperature of contraction is then measured to assess whether the tanning stabilized the hide; this temperature must be above 72 °C. The hides are then unloaded, pressed and allowed to stand.

Part 3

[0105] In the third part, retanning, dying and fattening operations are carried out for a furnishing article. The hides, previously shaved to desired thickness, are again weighed and placed into suitable drums, such as steel (the percentages of products refer to the last weighing). Both retanning and fattening were studied in the selection of products and percentages, in order to better meet the starting base, i.e. *metal-free* tanned hide from oxidative liming.

[0106] A first washing, pre-fattening and acidification operation is then carried out:

Table 9

Composition of the solution		Conditions
250%	water T = 35 °C	temperature in the drum = 30 °C 60 min rotation, 2 rpm speed
1 %	Synthol CP 996	
0.3%	Rinverpal L27	
0.5%	oxalic acid	
bath drainage		

Synthol CP 996 (Smit & Zoon): pre-fattening, natural and synthetic sulfited oils.
Rinverpal L27 (Chemipal): anionic emulsifier to promote the degreasing and penetration, saponified fatty alcohols, alkyl ethoxy sulfate.

[0107] The retanning operation then follows:

Table 10

Composition of the solution		Conditions
300%	water T = 30 °C	temperature in the drum = 30 °C 20 min rotation, 5 rpm speed
3%	Synthol FL 327	
4%	Sulfhirol SQ 610	
3%	Synthol GS 606	
addition of		
16%	Syntan S liq.	30 min rotation, 5 rpm speed

Synthol FL 327 (Smit & Zoon): polymeric softening agent, emulsified synthetic oils.
Sulfhirol SQ 610 (Smit & Zoon): oxidized sulfited fish oil fattening.
Synthol GS 606 (Smit & Zoon): softening agent, natural and synthetic phosphate fatty polymer.

[0108] Syntan S liq. (Smit & Zoon): retanning agent, condensed phenolsulfonic acid-based polymer.

Table 11

Composition of the solution		Conditions
x+y+... %	mixture of dyes (percentages in the order of units)	20 min rotation, 5 rpm speed
addition of		
4%	Relugan® DLF liq.	120 min rotation, 5 rpm speed
6%	Syntan SF 156	

(continued)

Composition of the solution		Conditions
120 min rotation		
addition of		
150%	water T = 65 °C	temperature in the drum = 45 °C 20 min rotation, 5 rpm speed
addition of		
1%	formic acid	10 min rotation, 5 rpm speed
addition of		
1%	formic acid	10 min rotation, 5 rpm speed
bath drainage		

Dyes used: metal-free organic compounds.
Relugan® DLF liq. (BASF): retanning agent, condensed melamine-based polymer.
Syntan SF 156 (Smit & Zoon): retanning agent, condensed phenolsulfonic acid-based polymer.

[0109] Fixed to the hide by acidification of dyes and retanning agents, the fattening operation follows:

Table 12

Composition of the solution		Conditions
200%	water T = 50 °C	temperature in the drum = 45 °C 40 min rotation, 5 rpm speed
2%	Catalix 150	
bath drainage		
addition of		
200%	water T = 50 °C	temperature in the drum = 50 °C, 2 min rotation, 5 rpm speed
bath drainage		
addition of		
150%	water T = 55 °C	temperature in the drum = 50 °C 120 min rotation, 5 rpm speed
1.8%	Polyol HS 818	
3.6%	Synthol FL 327	
3.6%	Sulfhirol SQ 610	
3.6%	Synthol GS 606	
1%	Sorbolex SU	
0.3%	OPB - 10°	
0.3%	Omacal LS	
addition of		
0.3%	formic acid	15 min rotation, 5 rpm speed
addition of		
0.3%	formic acid	15 min rotation, 5 rpm speed
addition of		
0.3%	formic acid	60 min rotation, 5 rpm speed
bath drainage		

Catalix 150 (Stahl): polymeric fattening.
Polyol HS 818 (Smit & Zoon): lecithin-based fattening.
Sorbolex SU (Sacma): humidity adjuster, derived from catalytic hydrogenation of a glucose syrup.
OPB - 10° (Letex): neatsfoot oil-based fattening.
Omacal LS (Dermakim): anionic surfactant based on lauryl, sodium lauryl ether sulphate.

[0110] Lastly, if necessary, the dye is processed in order to correct and intensify the

Table 13

Composition of the solution		Conditions
200%	water T = 50 °C	10 min rotation, 5 rpm speed
x+y+... %	mixture of dyes (percentages in the order of tenths)	
addition of		
1%	formic acid	20 min rotation, 5 rpm speed
addition of		
200%	water T = 18 °C	10 min rotation, 5 rpm speed
0.2%	formic acid	
bath drainage		
addition of		
200%	water T = 18 °C	5 min rotation, 5 rpm speed
bath drainage		

[0111] The hides thus dyed, fattened and tanned can be unloaded and dried.
[0112] The series of parts regarding the aqueous phase operations on the drum therefore end.

Part 4

[0113] The dressing step is then carried out; in this case, for each operation, the products are mixed before use and subsequently, by means of a reverse cylinder machine by rollers distributed on the surface of the hide. The desired layer thickness is decided by the interchangeable type of roller, or based on the viscosity of the mixture of products.
[0114] As said, the mixtures are prepared in parts related to product unit (which may be grams or kilograms), where here in the recipe making are put without unit of measurement but only in relative amounts, for convenience.
[0115] The process involves the preparation of a first mixture of pre-priming cationic mixture:

Table 14

Composition of the solution	
600 parts	Soleda Roller 633/CT
400 parts	water
60 parts	BM 3085
x+y+z+... parts	coloring pigments Soleda (parts in the order of units or tenths)

Soleda Roller 633/CT (Sommer): cationic filler, filler based on inert charges and synthetic polymers.
BM 3085 (Sommer): aqueous dispersion of aliphatic polyurethane.
Coloring pigments Soleda (Sommer): aqueous dispersion with cation charge of inorganic and organic ground pigments.

[0116] Among the pigments, care is taken to select those free or low in metals.
[0117] The mixture thus prepared, by means of a reverse cylinder machine, is applied by rolling on the hide grain, in the order of grams per surface unit (ft^2).

[0118] A step with Emulsionante Opaco 9205 follows.

[0119] A mixture is then applied by spraying:

Table 15

Composition of the solution	
100 parts	Emulcell WD 9205
100 parts	water

Emulcell WD 9205 (Lmf Biokimica): nitrocellulose in water.

[0120] Subsequently, the hides undergo a pressing in order to put a desired natural grain in relief.

[0121] A dry drumming then follows, where via micro-cracks of the film just applied, the hides return to the initial softness; this is then emphasized by putting the hides in dry rotation on drum for 10 hours.

[0122] The hide is then stretched on a frame to eliminate any creases given by the dry drumming process.

[0123] The anionic/non-ionic covering operation then follows, carried out in the same manner as described above:

Table 16

Composition of the solution	
x+y+z+ ... parts	coloring pigments Contex (amounts in the order of units or tenths)
20 parts	Luron® lucido E
30 parts	Lepton® Filler H
20 parts	Lepton® Cera WN
600 parts	water
100 parts	Unires® BM-904-RU
100 parts	Regel 43
100 parts	Penetrating agent M
10 parts	Cross-linking agent 1360

Coloring pigments Contex (Samia): anionic aqueous dispersion of inorganic and organic pigments.
Luron® lucido E (BASF): thermosetting linker based on wax and caseins. Lepton® Filler H (BASF): filling wax emulsion.
Lepton® Cera WN (BASF): aqueous emulsion of siloxane.
Unires® BM-904-RU (Stahl): aqueous dispersion of aliphatic polyurethane. Regel 43 (Recalac): aqueous dispersion of aliphatic polyurethane.
Penetrating agent M (Bio-Finleather): wetting agent with anionic charge. Cross-linking agent 1360 (Samia): polyurea in aqueous dispersion.

[0124] Finally, in order to cross-link and bind everything together, a last fixative layer is applied that may be applied with a roller machine as indicated above, but also by spraying on a conventional sprinkle provided with automatic guns:

Table 17

Composition of the solution	
500 parts	Aquarius MW
250 parts	Aquarius SO
1000 parts	water
20 parts	MTW 4526
20 parts	Corial® Indurente AN
5 parts	AT 7612

Aquarius MW (Sommer): polyurethane in aqueous dispersion.
Aquarius SO (Sommer): polyurethane in aqueous dispersion.
MTW 4526 (Sommer): aqueous silicone emulsion.
Corial® Indurente AN (BASF): cross-linker of fixing agents.
AT 7612 (Recalac): preparation based on polysiloxanes in aqueous solution. All the previous mechanical stretching and drumming steps are then repeated, thereby obtaining the finished product.

[0125] In the execution step, further changes or variants not described may be made to the process object of the invention. Where such changes or such variants should fall within the scope of the following claims, they shall be understood as all protected by the present patent.

Claims

1. Tanning process comprising the following step:

(a) an oxidative liming in base environment of a hide wherein said oxidative liming comprises a treatment of said hide with lime, **characterized in that** said oxidative liming, i.e. step (a), comprises the following steps wherein the percentages are to be understood as percentages by weight with respect to the weight of the hide:

(a1) immunizing the hair of said hide with 0.8 to 1.2%, preferably with about 1% of hydrated lime;
(a2) thereafter, adding an unhairing solution of peroxide in a percentage of between 2 and 3% of hydrogen peroxide, at a pH of between 12.0 and 12.5, wherein the pH is preferably adjusted by alkalizing the mixture with caustic soda (NaOH); and
(a3) thereafter, neutralizing the bath.

2. Process according to claim 1, **characterized in that** the neutralization of the bath in step (a3) is carried out by adding an aliquot of calcium chloride of between 1 and 3%.

3. Process according to claim 1, **characterized in that** the neutralization of the bath in step (a3) is carried out by adding an aliquot of calcium formate of between 1 and 3%.

4. Process according to any one of the preceding claims, **characterized in that** during said liming, partially degraded hair is separated, preferably continuously.

5. Process according to any one of the preceding claims, **characterized in that** before passing by step (a), said hide is subjected to a brining step, then to a hair stating step, and then to a soaking step with the use of surfactants and preferably also enzymes.

6. Process according to any one of the preceding claims, **characterized in that** step (a1) is preceded by a treatment of said hide with α-amylase and hyaluronidase, preferably in combination with probiotic microorganisms.

7. Process according to any one of the preceding claims, **characterized in that** the solution obtained at the end of step (a) is brought with an acid treatment, preferably phosphoric acid, to pH 3.5-4.5 resulting in the precipitation of a white substance mainly consisting of proteins extracted from the hide and **in that** said white substance is separated.

8. Process according to any one of the preceding claims, **characterized in that** after step (a) the process involves the following steps in the indicated sequence:

(b) a first deliming;
(c) a retting; and
(d) a second deliming.

9. Process according to claim 8, **characterized in that** the first and the second deliming take place using sulfate-free ammonium salts, particularly ammonium chloride, wherein in the first deliming surfactants and acids are also used, in particular citric acid and formic acid, and wherein in the second deliming formic acid is preferably present, and **in that** the retting takes place by using pancreatic-derived enzymes and surfactants.

10. Process according to any one of claims 8 or 9, **characterized in that** after step (d), the process comprises a *white* tanning step (e) up to obtaining a contraction temperature equal to or higher than 72 °C.

11. Process according to claim 10, **characterized in that** after the tanning step (e), the hide undergoes a retanning and fattening step (f).

12. Process according to any one of the preceding claims, **characterized in that** the retanning and fattening step (e) uses metal-free or low-metal chemicals in order to comply with the ISO 15987 standard.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 16 8449

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	GB 1 106 391 A (DEGUSSA) 13 March 1968 (1968-03-13) * page 1, line 10 - page 2, line 18; examples 1-3,6 * -----	1-12	INV. C09D175/04 C14C11/00 C14C1/06 C14C1/04
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TECHNICAL FIELDS SEARCHED (IPC)

C14C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 August 2016	Neugebauer, Ute

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 16 16 8449

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24-08-2016

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REFERENCES CITED IN THE DESCRIPTION

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