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(54) An environmental low-impact and low-toxicity procedure to realize an ecological leather and the leather obtained with the same

(57) The present invention concerns a low environmental impact and low toxicity process to realize an ecological hide completely free of undesired negative effects (such as allergic reactions, irritations, skin inflammations, and so on), both in the workers at the productive process and in the users of the finished product.

The present invention concerns also said hide realized with said process.

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Description

Technical field

[0001] The present invention concerns a low environmental impact and low toxicity process (therefore, compatible from the ecological point of view and with relation to health) to realize an *"ecological"* hide, that is a hide completely free of undesired toxic effects (such as, just as a way of non-limiting example, allergic reactions, inflammations, skin irritations, and so on), both on the workers at the productive process and on the consumers, that is the purchasers/users of the finished product.

[0002] The present invention concerns also the hide realized with said process.

Background art

[0003] In the tanning industry, it is known that the realization of hides (in particular, of quality hides) implies the application of a very long and complex series of manufacturing passages during which the hides undergo treatments that require the use of significant amounts of highly toxic and highly polluting materials.

[0004] In particular, the traditional tanning processes commonly applied in the sector comprise, among others, three indispensable/necessary manufacturing phases (in the present document briefly indicated with the term "*steps*") that are distinguished by their hazardousness, toxicity and polluting action also in the long term. We refer to the steps commonly known in the field as "Pickle", "Tanning", and "Re-tanning".

[0005] The **first** of these steps (designated in the sector as Pickle [or "*Pickling*"]) consists of the preparation of the hides for the subsequent phase of effective tanning by means of the treatment of the same with a robust mixture of **salts** (for example, sodium chloride and sulfate), of **strong acids** (such as organic acids, for example, formic acid, and inorganic acids, for example sulfuric acid) at rather low pH values (of about 2,5), and of the **so-called *pickling* agents,** such as, for example, naphthalenesulfonic acid (employed to reduce a part of HCOOH and of H_2SO_4).

[0006] The **second** of these steps (designated in the sector as Tanning) consists of the treatment of hides, pretreated in the above-mentioned Pickle phase, with **heavy metals mixtures** (in particular, **chromium salts,** aluminum, iron, zirconium and titanium, among the most common ones); aldehydes, for example, formaldehyde, glutaric dialdehyde; syntans, that can contain very high formaldehyde values, vegetable tannins (that carry the C.O.D. [*Chemical Oxygen Demand*], index of the amount of organic pollutants present in the water] of the baths and the wastewaters at very high values and that do not have much resistance to light, degrading themselves in toxic and/or polluting substances); sulphur chlorides or sulphur chlorinated paraffins.

[0007] The **third** of these steps (designated in the sector as Re-tanning), basically consists of a first further treatment, for a whole night, of the hides, obtained from the preceding step of Tanning, with **heavy metals** (in particular **Chromium** salts), **aldehydes**, various additives, followed by, the next day, a second further treatment, the so-called anionic re-tannings, in the presence of rather toxic synthetic resins and/or anionic synthetic tannins.

[0008] From the rough description of the reactants above, it results evident that these three steps are very hazardous since they are toxic (in particular, in an immediate way, for the workers at the productive cycle) and highly polluting (for example, the heavy metals used in the tanning can pollute easily and in a permanent way the surrounding environment and also the aquifers). Moreover, their execution requires at least three, but also more, working days, with a rather high relative water and electric energy consumption, affecting unfavorably the overall production costs.

[0009] The last aspect, but not for this less important: the hides obtained at the end of a traditional tanning process (as commonly applied in the sector) that comprises the indispensable passages of Pickle, Tanning and Re-Tanning as commonly known in the sector and as described above, still contain quantitatively and qualitatively significant residues of the toxic pollutants described above (in particular, the heavy metals), thus provoking a series of toxic effects (allergic reactions, skin irritations, inflammations and so on), both on the workers at the productive process, and on the users of the finished product.

[0010] Various trials have been done in the last years to reduce both the negative environmental impact and the toxicity at least of the above-mentioned manufacturing phases.

[0011] For example, WO 2012/062413 describes a tanning process without metals and without the pickle phase based on halogenated sulfonated organic compounds.

[0012] EP 2 415 879 A1 describes a tanning process without metals and without the Pickle phase based on aqueous compositions of compounds containing carbamoyl-sulfonate groups.

[0013] Neither of the two, however, is capable of providing a completely satisfying solution to all the inconveniences highlighted before. Therefore, so far, the desired solution has not been acceptably found.

Technical problem

[0014] The need to have a low environmental impact and low toxicity productive process remains alive in the sector to realize a hide that is completely *"ecological",* that is free of undesired toxic effects (allergic reactions, irritations, inflammations, and so on) described before.

[0015] The aim of the present invention is that of giving an adequate answer to the need mentioned above.

Disclosure of invention

[0016] The Applicant has studied diligently the problem previously described, taking into account both the Italian and Community laws concerning environmental anti-pollution and those laws relative to the low toxicity of the intermediate reactants and of the final products (that is, the hides) obtained and put in commerce.

[0017] As a result of its own studies, the Applicant has now found out that, by selecting and combining in an adequate manner a series of completely non-toxic products, or, at least, notoriously less toxic and/or less polluting (with respect to those traditionally used), it has been unexpectedly possible, on the one hand, to reduce the environmental impact and the toxicity of the overall process and, on the other hand, to eliminate completely the two necessary steps (hazardous, toxic and polluting) of Pickle and Tanning of the known art and to modify completely the step of Re-tanning of the traditional process, by simplifying and detoxifying it, thus providing an adequate answer to the technical problem previously described.

[0018] It is, therefore, object of the present invention a productive process, of low environmental impact and low toxicity, to realize an ecological hide, that is without undesired toxic effects on the organism, free of the traditional steps of Pickle and Tanning, as indicated in the independent claim attached.

[0019] It is also another object of the present invention the ecological hide obtained by means of this process, as indicated in the independent claim attached.

[0020] Other objects of the present invention are described in the dependent claims attached.

Detailed description of the invention

[0021] The present invention refers to a process, of low toxicity and low environmental impact (both at short and long term), for the industrial preparation of ecological hide (that is, presenting the characteristics of complete non-toxicity, both for the manufacturing workers and for the final users), wherein said process is substantially characterized in that it is free of the two indispensable manufacturing steps of the known art (highly toxic and polluting) called Pickle and Tanning, as previously described, wherein said two steps are substituted by a single step (non-toxic or polluting), conventionally/for simplicity reasons designated by the Applicant in the present document as Pre-tanning.

[0022] In other words, the process in accordance with the present invention is characterized in that it comprises one step, conventionally designated by the Applicant as Pre-tanning, and is also characterized by the absence of the indispensable standard steps of the known art commonly called Pickle and Tanning, described before.

[0023] Moreover, the process in accordance with the present invention is **further characterized** by the presence of one step, conventionally/for simplicity reasons designated by the Applicant in the present document as Re-tanning, wherein, unlike what is taught and applied in the known art, said step of Re-tanning of the present invention is made **without employing the heavy metals** and/or the other toxic substances commonly employed in the known art, but using an adequate selection of re-tannings based on known non-toxic natural products, as described below in the present description.

[0024] In a preferred embodiment, the process in accordance with the present invention comprises or consists of, schematically, at least the following manufacturing phases:

a) a PHASE I (preliminary), comprising the manufacturing steps designated as: (i) Soaking, (ii) Liming, (iii) De-liming, (iv) Bating;
b) a PHASE II (intermediate), comprising the manufacturing steps designated as: (v) Re-tanning, (vi) Fatting, (vii) Dyeing;
c) a PHASE III (final), comprising the manufacturing step designated as: (viii) Finishing;

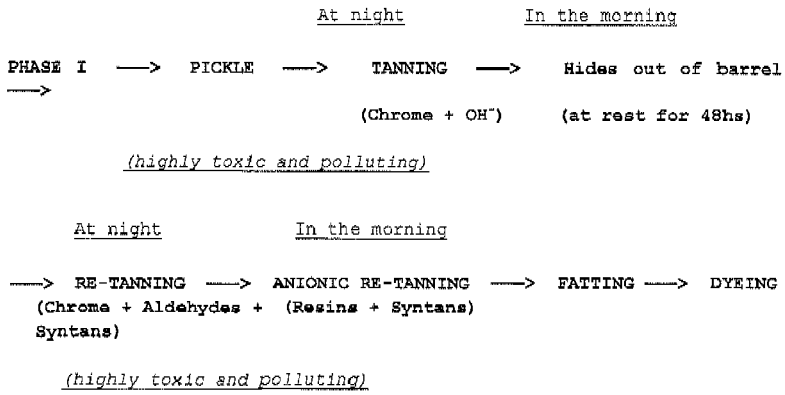
characterized in that, in said process, between the PHASE I and the PHASE II said manufacturing step (non-toxic or polluting) conventionally designated by the Applicant as Pre-tanning is carried out; and further characterized in that, in said process, the necessary standard steps (highly toxic and polluting) of the known art, described before, called Pickle and Tanning, are not carried out.

[0025] Said process is further characterized in that the step designated as Re-tanning of the present invention is carried out **without employing the heavy metals** and/or the other very toxic substances commonly employed in the

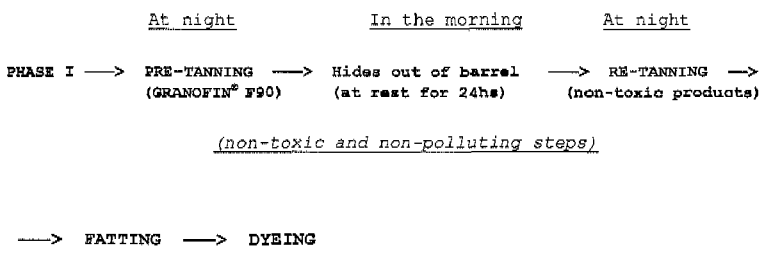
known art, but using known tannings based on known non-toxic natural products, as described below in the present description.

[0026] For more clarity, the aspects that characterize a standard process for the realization of a marketable hide in accordance with the technology commonly employed in the known art (Scheme 1) are here compared, schematically, with the aspects that characterize the process in accordance with the present invention (Scheme 2).

SCHEME 1



SCHEME 2



[0027] It results evident that there is an improvement in terms of toxicity and pollution thanks to the process in accordance with the present invention, as highlighted in the Scheme 2, with respect to the standard process in accordance with the technology commonly employed in the known art, as highlighted in Scheme 1.

[0028] Moreover, it is important to add that, while, for example, the operation of the step of Re-tanning of the state of the art (Scheme 1) requires on the whole a period of time comprised between 26 and 28 hours, the operation of the so-called step of Re-tanning of the present invention (Scheme 2) requires on the whole a period of time comprised between 18 and 20 hours, with an average saving of 8 hours.

[0029] Moreover, it has been calculated that the process of Scheme 2 (invention) has allowed to realize a water saving comprised between the 15 and the 45% in volume, with respect to the process of Scheme 1 (state of the art).

[0030] Moreover, it has also been calculated that the process of Scheme 2 (invention) has allowed to realize an electric energy consumption saving comprised between the 20 and the 30%, with respect to the process of Scheme 1 (state of the art).

[0031] Before going on with the detailed description of the invention, it is necessary to premise that, before starting the process of the present invention, the hides, as received from the provider (that is, conserved in sodium chloride sprinkled on the skin side and on the flesh side), are weighed and introduced into wooden *"barrels",* or made of inox steel, or of polypropylene, or of wood internally covered with polypropylene, of cylindrical shape. For the purposes of the present invention, said barrels are preferably in polypropylene, or internally covered with polypropylene (the polypropylene does not absorb or release contaminant substances, unlike wooden and steel barrels). Into these barrels will be introduced then, in due time and in sequence, the chemical products/reactants and the amounts of solvent (substantially water) necessary to make the single steps of the process. Each step consists of appropriate barrel rotation times with introduction and emptying (into and from the same) of the products/reactants necessary to realize the step itself.

[0032] It is premised also, for simplicity purposes to read the data presented from now onwards in the present document, that, initially, the percentages of the products used are expressed as percentages by weight with reference to the initial weight of the hides as received by the provider. Subsequently, after the so-called *"fleshing"* treatment (that will be

described below), the hides will be re-weighed and, from this point onwards, the percentages of the products used will be expressed as percentages by weight with reference to the new weight, for simplicity purposes defined "fleshed" weight.

[0033] Last, it is premised also that in all the steps of the process of the present invention (also in those commonly known and applied) the maximum care has been placed, in any case, in the selection of the most appropriate reactants, privileging, at equal efficiency, those less toxic and polluting.

[0034] This is valid, in particular, also for the step of Finishing of the PHASE III of the process of the invention, which differs from the corresponding step of Finishing of the standard process of the state of the art precisely in the accurate selection of the reactants and of the toxicologically and ecologically most compatible products.

[0035] Consequently, also said step of Finishing of the process of the invention, considered together with the others, results to be a characterizing element of the process of the invention on the whole.

[0036] From the whole of all this accurate selection, have emerged, unexpectedly, the overall advantages of the process of the present invention (for example, low toxicity, low pollution levels, reduced manufacturing times, substantial savings in terms of reactants, of water, of electric energy, and so on).

[0037] In the PHASE I (commonly called Riviera), the step (i) (Soaking) has the aim of re-giving the hides the water lost during the conservation (re-hydration); of cleaning the hide; and of removing the salt of conservation.

[0038] In said step (i), it is normally made use of: various antibacterial agents, commonly known in the art, preferably, those based on organic sulfur compounds, with a pH of about 10 (for example, the product commercially available in Italy with the commercial name TRUPOSEPT® BA; product of: Trumpler Italia S.P.A, IT, in a total concentration of about 0,6%); soaking enzymes commonly known in the art (for example, the product commercially available in Italy with the commercial name FORTRAN® K-225; product of: KEMIA TAU s.a.s La Cassa TORINO, in a total concentration of about 1%); salts with alkaline reaction, such as hydroxides, bicarbonates or carbonates (for example, sodium carbonates in an overall concentration of about 0,9% and sodium hydroxide in an overall concentration of about 0,3%); detergents commonly known in the art (for example, the product commercially available in Italy as ALYSOL LDG; product of: POLYCOLOR s.r.l. Santa Croce Sull'Arno PISA, in an overall concentration of about 0,6%) and/or wettings commonly known in the art (for example, the product commercially available in Italy with the commercial name IDROTEX® WS Spec; product of: KEMIA TAU s.a.s. La Cassa TORINO, in a total concentration of about 1,3%). The step (i) comprises one or more barrel rotation periods and terminates with a phase that, in technical terms, is conventionally defined as "Automatic by Night", during which the hides, into the barrel, suffers rotation periods followed by rest periods. In general, the barrel makes some minutes of rotation followed by sixty minutes of rest; all this is automatized for a working cycle of about twelve hours, preferably carried out during the night (hence the name).

[0039] After the Automatic by Night, the following morning the hides are dissolved, relaxed and cleaned and are ready to undergo the step (ii).

[0040] In the PHASE I, the step (ii) (Liming) has the purpose of solubilizing the globular proteins, of saponifying the natural fats, of destroying the skin, of making the hide re-inflate in such a way as to obtain spaces between the fibers, which will be important for the subsequent fixation of the non-toxic tannings of the present invention.

[0041] In said step (ii), use of the following is made: hydrated lime, known commercial anti-wrinkle agents (containing a part of organically-bound sulfur), reducing products such as commercial sodium sulphide (Na_2S), at the 60/62%, with a content of S around the 24,6%, and the commercial sodium hydrogen sulphate (NaHS), at the 70/72%, with a content of S around the 40%.

[0042] The chemical products/reactants mentioned above are appropriately balanced, according to the type of hide to be treated, in the light of the common technical knowledge of the sector, in such a way as to obtain the desired re-inflating degree, cleaning of the hair bulb and drawing up of the natural wrinkles of the hide. Also this step (ii) terminates with the phase called Automatic by Night, as described before.

[0043] In the morning the hides are taken out from the barrel and, before going on with the process of the invention, it generally undergoes two external mechanical treatments, known and commonly applied in the sector: the Fleshing and the Splitting (the fleshing serves to eliminate the flesh and adipose tissue residues from the flesh layer, while the splitting sections the *"grain"* side from the "*flesh*" side, defined also *"crust"*).

[0044] After these two operations, conducted with traditional methods and apparatus, the hides (fleshed and split) are again weighed (*fleshed weight*) and introduced into the barrel to undergo the subsequent steps of de-liming and bating. From here onwards, as already anticipated, the percentages of the products/reactants used will be referred to the weight of the hides after the fleshing (*fleshed weight,* as defined above).

[0045] In the PHASE I, the step (iii) (De-liming) and the step (iv) (Bating) have, respectively, the aim of eliminating the lime used in the preceding step (ii) (making thus lower the pH of the hide from about 12,5 of final Liming to 7,5-8,5), and of completing the opening of the hide (already initiated in step (ii)), eliminating the elastic proteins that keep the fibers tight.

[0046] In said step (iii), in order to take out the lime use is made of mild delimings, which are preferably constituted of organic salts based on buffered dicarboxylic acids, for a period of time comprised between about 40 min and 60 min, preferably, of 50 min.

[0047] In the subsequent step (iv), use is made of bates based on proteolytic enzymes of pancreatic origin for a period

of time comprised between about 50 min and 70 min, preferably, of 60 min. At the end, it is treated/rinsed with current water to lower the temperature of the bath and the pH (at about 7-7,5) in such a way as to inhibit the further enzymatic action.

[0048] The PHASE I above is executed following substantially the process and the modalities of the standard tanning cycle, optimizing, according to the type of hide, the times, the selection and the amounts of the reactants (privileging those that are less toxic) and using the machinery known and commonly employed in the sector.

[0049] At the end of the PHASE I above and before the PHASE II, which will be described below, the process of the present invention foresees an intermediate step conventionally designated by the Applicant in the present document as Pre-tanning. Said step, so-called Pre-tanning, is used in substitution of the necessary standard steps (highly toxic and polluting) of the state of the known art, commonly known as Pickle and Tanning.

[0050] Substantially, said step of Pre-tanning, as described below, has the aim of preparing the hides for the subsequent operations, in the first place, for the mechanical operations of the "Pressing" and of the "'Shaving". Moreover, it has also allowed to increase advantageously the affinity of the hides and the chemical reactants selected for the manufacturing steps of the PHASE II (Re-tanning, Fatting and Dyeing), with respect to what has been obtained with the phases of Pickle and Tanning of the known art. Following this, it has been advantageously possible to reduce the manufacturing times and the amounts of the reactants of the subsequent steps, obtaining an unexpectedly saving also in terms of water and electric energy used, as already explained.

[0051] The so-called step of Pre-tanning, as used in the process of the present invention, comprises the following manufacturing. After finishing with the washing of the step (iv) (Bating) of the PHASE I and making all the residue of the washing bath exit and drain from inside the barrel, an appropriate non-toxic amphoteric heterocyclic aromatic organic tanning agent is introduced into said barrel, having a pH similar to 6,5, free of metals, aldehydes, phenols (for example, the product commercially available in Italy as GRANOFIN® F90; product patented by Clariant, based on a non-toxic halogenated heterocyclic aromatic derivative; product of CLARIANT Prodotti - ITALY, S.p.A) in an amount comprised between 5% and 20% by weight, with respect to the weight of the fleshed hides; preferably, between 8% and 12%, more preferably of about the 10%, applying a continuous barrel rotation for the whole night (about 12 hours). In the morning, from 70% to 120% is added, preferably about the 100%, of water at a temperature comprised between 35°C and 45°C, preferably of about 40°C and then between 1% and 5%, preferably about the 3%, of a synthetic tannic product (synthetic tanning), substitutive of the phenol, preferably based on a phenol-based synthetic tanning, but without formaldehyde and free phenol (for example, the product available commercially in Italy as CLARIANT Prodotti - ITALY, S.p.A.), applying a barrel rotation comprised between 50 min and 70 min, preferably of 60 min. Then the bath is emptied and, after the drainage, water from 100% to 300% is introduced, preferably about the 200%, at a temperature comprised between 25°C and 35°C, preferably of 30°C, making the barrel rotate from 5 min to 15 min, preferably 10 min; after which the bath and the hides are discharged.

[0052] At this point, preferably, the hides are piled and left at rest for about 24 hours; then, they preferably undergo three external mechanical treatments, well known and commonly applied in the sector, which are: the pressing, the shaving and the trimming (the pressing compresses the wet hide, stretching it appropriately; the shaving, made from 1 mm to 1,3 mm, preferably, from 1,1 mm to 1,2 mm, renders the thickness of the hide itself homogeneous; the trimming, last, eliminates a series of residues of shavings and of preceding manufacturing works). The operations above are carried out with modalities and apparatus well known an commonly used in the sector. It is worth it to highlight that, in the standard process of the known art (exemplified in Scheme 1 before), between the pressing and the shaving a further mechanical treatment is introduced, the so-called splitting. Thanks to the so-called step of Pre-tanning of the present invention, described above, it has been advantageously possible to avoid this operation, with benefits in terms of yield and of quality of the hide obtained.

[0053] At the end of these mechanical operations above, the beginning of the PHASE II of the process of the present invention is preferably preceded by a brief phase of soaking or re-conditioning of the hides. Said brief phase of soaking/re-conditioning consists of putting the hides in water from 200% to 400%, preferably about the 300%, at a temperature comprised between 30°C and 40°C, preferably of 35°C, applying a barrel rotation time from 20 min to 40 min, preferably of 30 min; after which the barrel is emptied of the water.

[0054] As already highlighted, thanks to the adoption of the non-toxic and non polluting step designated by the Applicant as Pre-tanning, as described above, it has been unexpectedly and advantageously possible to eliminate completely both the steps (highly toxic and polluting, apart from expensive in terms of consumption of water, electric energy and time) of Pickle and Tanning necessarily employed in the common standard practice, though obtaining at least the same effects (on average better) on the finished hide. This fact has also allowed to make a further advantageous thorough selection of more delicate chemical, less toxic agents, also with a great binding capacity on the hide, which, as a consequence, have contributed to improve the environmental compatibility and the non toxicity also of the subsequent steps of the process of the present invention.

[0055] In the PHASE II, the step (v) of the present invention, conventionally designated as Re-tanning by the Applicant, has unexpectedly resulted sufficient to substitute the traditional necessary steps of Tanning and Re-tanning of the known art (Scheme 1 above), advantageously completing the tanning process of the hides initiated in the preceding step, the

so-called Pre-tanning, and, as it will result clear from the description below, is preferably made in conjunction with the step (vi) (Fatting).

[0056] After the elimination of the water of the treatment of re-conditioning above, water is introduced into the barrel from 50% to 150% by weight, preferably about the 100%, at a temperature comprised between 30°C and 40°C, preferably of about 35°C; then a mixture is added comprising; from 1% to 6%, preferably from 2% to 4%, more preferably the 3%, of at least a dispersion of an appropriate known non-ionic non-toxic re-tanning co-polymer with fatting action, at pH = 6,0-7,5, (for example, the product commercially available in Italy with the commercial name TERGOTAN® PO 62 emuls. 1:3; fatting polymer at about the 50% of active substance; product of CLARIANT Prodotti S.p.A., ITALY; it creates greater connections with the subsequent re-tannings); and from 1% to 5%, preferably from 1% to 3%, more preferably about the 2%, of a further lubricating agent at ionic charge, preferably based on sulphated vegetable oils and lecithin, at the 90% of active substance and at pH = 6-7,5 (for example, the product commercially available in Italy with the commercial name DERMINOL® NLM emuls. 1:5; product of CLARIANT Prodotti S.p.A., ITALY; it improves the lubrication); and applying a barrel rotation from 50 min to 70 min, preferably of 60 min. After that, in the same bath, a synthetic tanning is added, from 5% to 12%, preferably from 7% to 9%, more preferably the 8%, preferably a condensed naphthalene anion with modifiers of the pH, at the 92-98% of active substance, pH = 2,5-3,5 in solution at the 5% (for example, the product commercially available in Italy with the commercial name TANICOR® VTN emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY; it disperses better the tannings added subsequently); and applying a barrel rotation from 55 min to 65 min, preferably 60 min. At this point the pH of the bath results to be of about 3,6. The process goes on by further adding, in the same bath, a mixture of: a) from 15% to 25%, preferably the 20%, of a pyrogallolic tanning, preferably based on pyrogallolic tannings, on tare, at the 67% of active substance, at pH 3,5 (for example, the product commercially available in Italy with the commercial name TRUPOTAN® TR emuls. 1:1; product of TRUMPLER S.p.A., ITALY); b) from 2% to 8%, preferably from 4% to 6%, more preferably about the 5%, of a filling agent, preferably a proteic filler derived from the proteins of milk, at the 90%-95% of active substance (for example, the product commercially available in Italy with the commercial name MARACRYL® SD emuls. 1:1; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); c) from 5% to 12%, preferably from 7% to 9%, more preferably about the 8%, of a polypeptide re-activating the tanner bindings, preferably a proteinaceous product based on solubilized polypeptides from poultry feathers (for example, the product commercially available in Italy with the commercial name CROMOPLEN® PRT emuls. 1:5; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI; it re-activates the tanner bindings); and applying a barrel rotation from 55 min to 65 min, preferably of 60 min. After this operation, it is further added, in the same bath, the same amount of the same mixture of the preceding products a), b) and c), applying then a barrel rotation for a period comprised from 5 hours and 30 min to 6 hours and 30 min, preferably of 6hs, and terminating this phase in "Automatic by Night" (as already explained before in the PHASE I).

[0057] The following morning the barrel is made to rotate for other 10 min approximately; at this point the pH of the bath results to be of about 4-4,1. The process goes on by adding, in the same bath, from 80% to 120%, preferably the 100%, of water at a temperature comprised between 40°C and 50°C, preferably of 45°C, and a mixture constituted of: a minimum amount, from 0,4% to 0,6%, preferably of 0,5%, of a metal sequestering agent, preferably an appropriate mixture of polyphosphates and of alkali metal salts, at the 96% of active substance (for example, the product commercially available in Italy with the commercial name UTANIT® AF emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY; and a minimum amount, from 0,4% to 0,6%, preferably of 0,5%, of a chelating for the same, preferably a dicarboxylic acid such as the oxalic acid (for example, the product commercially available in Italy with the commercial name Acido Ossalico emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY); and applying a barrel rotation for a period of time comprised between 25 min and 35 min, preferably 30 min. At the end of this rotation period, the bath is emptied.

[0058] After the rinse, the draining of the hide is carried out, introducing into the barrel water from 100% to 300%, preferably 200%, at a temperature comprised between 45°C and 55°C, preferably 50°C, and applying a barrel rotation from 5 min to 15 min, preferably 10 min; after which the bath is emptied.

[0059] After the draining, the following are introduced into the barrel, in sequence:

i) from 50% to 150%, preferably the 100%, of water at a temperature comprised between 45°C and 55°C, preferably 50°;

ii) from 1% to 3%, preferably the 2%, of a methacrylic polymer (for example, the one commercially available in Italy as TRUPOTAN® RS emuls. 1:3, described before; product of TRUMPLER S.p.A., ITALY; it serves to strengthen the fibers), and applying a barrel rotation from 30 min to 50 min, preferably of 40 min;

iii) from 3% to 5%, preferably the 4%, of a fattener (for example, the product DERMINOL® NLM emuls. 1:5, described before (based on sulfated vegetable oils and lecithin, at the 90% of active substance; product of CLARIANT Prodotti S.p.A., ITALY)); and

iv) a mixture consisting of: from 5% to 7%, preferably the 6%, of a fattener, for example the one commercially available with the commercial name of DERMINOL® RF emuls. 1:5, described before (based on synthetic alkylated alcohols derivative of mineral oils and of ethoxylated lanolin, at the 60% of active substance; product of CLARIANT

Prodotti S.p.A., ITALY); from 0,3% to 0,7%, preferably the 0,5%, of sodium lauryl sulfate in aqueous solution (for example, commercially available in Italy with the commercial name RESOPAN MN emuls. 1:5; product of CLARIANT Prodotti S.p.A., ITALY), and applying a barrel rotation from 50 min to 70 min, preferably of 60 min;
v) from 0,3% to 0,7%, preferably the 0,5%, of a sequestering agent (for example, the product commercially available in Italy with the commercial name UTANIT® AF emuls. 1:1, described before (it has the purpose, in particular, of sequestering eventual traces of metals, for example iron)); applying a barrel rotation from 20 min to 40 min, preferably of 30 min.

[0060] In the process described above the assembly of said components iii) and iv) constitutes the fattening component and gives softness to the touch to the final hide.

[0061] At the end of this complex process, the bath is emptied.

[0062] After the draining, water is introduced again into the barrel from 100% to 300%, preferably the 200%, at a temperature comprised between 25°C and 35°C, preferably of 30°C, and it is added, in the same bath, from 1% to 2%, preferably the 1,5%, of a complex of phosphonates and polyacrylates (for example, commercially available in Italy as CHELENE® DSE emuls. 1:3; product of CLARIANT Prodotti S.p.A., ITALY; it serves to sequester the iron ions and the heavy ions, eventually still present, and to fix in the best way the preceding stage); and applying a rotation from 10 min and 30 min, preferably of 20 min; after which, the barrel is emptied and drained. As it can be clearly noted, in the step (v) (of Re-tanning of the present invention) of the PHASE II, described above in detail, modest amounts of poorly toxic and poorly polluting reactants have been employed (significantly inferior to those used normally in the known art), thus contributing significantly to reduce advantageously the possible negative environmental impact of the process itself on the whole.

[0063] In fact, at the end of the various treatments, the discharge baths have resulted particularly exhausted, that is, very scarce in the content of residue substances, above all those polluting and toxic, with respect to what can be found in the corresponding discharge baths of the traditional tanning processes. Some significant examples, though non-exhaustive, of the favorable values of residue polluters found in the discharge baths of the process of the present invention are shown in the following Chart 1.

Chart 1: Analysis of the residue waters of the baths of Tanning, Pre-tanning and Re-tanning of the standard processes of the state of the art and of the invention

	Bath A)	**Bath B)**	**Bath C)**	**Bath D)**	**Bath E) ***
Residue	**Value found (Internal method) [mg/L]**				
Chromium	3.243,67	2.688,46	116	0,023	0,28
Cadmium	≤ 0,01	≤ 0,01	≤ 0,01	0,0007	0,0030
Zirconium	1,0	≤ 0,01	1,53	0,011	0,048
Manganese	2,26	1,25	1,24	0,19	--
Copper	0,12	0,09	0,85	0,029	0,26
Pond	1,58	4, 96	3,60	≤ 0,0001	≤ 0,0001

A): from the step of Tanning of the state of the art (Scheme 1)
B): from the step of Re-tanning (night) of the state of the art (Scheme 1)
C): from step of Re-tanning (morning) of the state of the art (Scheme 1)
D): from the step of Pre-tanning of the invention (Scheme 2)
E): from the step of Re-tanning of the invention (Scheme 2)
* : the modest increases registered are due to the employ of a steel barrel that has released traces of metals, though in such an amount that it has not altered the efficiency of the method.

[0064] After the step (v) (Re-tanning) above, the PHASE II of the process of the present invention foresees the realization of the phase (vii) (Dyeing) of the hides. Also in this step (vii) (Dyeing) the maximum care has been placed in the selection of the more natural and less toxic dyes in order to improve the environmental impact and the toxicity of the process of the invention.

[0065] Obviously, the color and/or the mixture of the colors are modulated, in the concentration and in the variety of the colors themselves, according to the final color that wants to be given to the hide and to the technical knowledge of the manufacturing worker. In said step (vii) (Dyeing), after the draining above, into the barrel water is introduced from 40% to 60%, preferably the 50%, at a temperature comprised between 25°C and 35°C, preferably of 30°C, with a barrel

rotation from 5 min to 15 mien, preferably of 10 min; after which, the desired mixture of dyes is added (preferably synthesis acid dyes that bind on the hides, derivatives of food dyes and substantially free of metals), appropriately dosed and in the necessary concentration to obtain the tone of color that wants to be reached, applying a barrel rotation from 50 min to 70 min, preferably of 60 min. After this phase of dyeing it is added, in the same bath, from 150% to 250%, preferably the 200%, of water at a temperature comprised between 45°C and 55°C, preferably of 50°C, with a barrel rotation from 5 min to 15 min, preferably of 10 min; then formic acid diluted 1:10 is added slowly (generally in a period of time that goes from 15 min to 25 min) up to reaching a value of pH comprised between 3,7 and 4, preferably of 3,8-3,9, applying then a barrel rotation from 50 min to 70 min, preferably of 60 min. At this point, the bath is drained, then water is re-introduced from 100% to 300%, preferably the 200%, at a temperature comprised between 25°C and 35°C, preferably of 30°C, and from 0,8% to 1,2%, preferably the 1%, of sodium formate in powder to remove the residue acidity, and applying a barrel rotation from 15 min to 25 min, preferably of 20 min. Once this operation is terminated, the bath is drained, after which water is still introduced into the barrel from 100% to 300%, preferably the 200%, between 25°C and 35°C, preferably at 30°C, and then from 0,8% to 1,2%, preferably the 1%, of the product CHELENE DSE dil. 1:3 (already mentioned before) to eliminate the residue acidity and to sequester the last residues of the metallic ions (for example, the iron), and applying a barrel rotation from 15 min to 25 min, preferably of 20 min. once this last passage of purification is terminated, the bath is completely drained and then the hides are taken out from the barrel, piling them and leaving them to rest all night.

[0066] The following day, the hides are dried using traditional techniques and machineries commonly used in the sector.

[0067] At this point, the following is the PHASE III of the process of the invention, which substantially comprises the step (viii) (Finishing).

[0068] Said step (viii) (Finishing) is executed on the dried hides and has the aim of improving and also of giving a particular protection to the grain side of the hide (sometimes also to the flesh side), through applications of substances (appropriately selected among those known provided with low or no toxicity), which determine the realization of a surface film, thus giving a particular aesthetic aspect apart from the desired softness features.

[0069] Said step of Finishing consists of a series of operations (mechanical and not) known and commonly applied in the sector. Preferably, said phases are selected from the following:

- Shaving: it has the aim of rendering homogeneous the thickness of the hide. For example, using a traditional machine, the thickness is brought to a value comprised between 1,4 mm and 1,7 mm, preferably, comprised between 1,5 mm and 1,6 mzn.
- Stocking: it has the aim of softening the hide. It is realized through the shaking of the hide in drum-tumblers with adjustment of the speed and the humidity for a period of time on average comprised between 3 and 6 hours, preferably of 3-4 hours.
- Nailing: it has the aim of stretching the hide, increasing and blocking the dimensions thereof, on specific frames of variable sizes.
- Application of a so-called "Undercoat"; it has the aim of giving the hide the desired final aspect and consists of the application (preferably, repeated) under the form of spray on the same of a series of products suitable for the desired aim. The products applied are well known in the sector and, in accordance with the aim of the present invention, are selected among those less toxic and provided with high adhesive capacity and high penetration capacity with relation to the hide.

[0070] Just as a way of example, absolutely non-limiting, in a preferred embodiment, the undercoat consists of a mixture constituted of: from 40 pp to 80 pp, preferably from 50 to 70 pp, of organic and/or inorganic-based pigments in water with solids at the 35% (for example, the products commercially available in Italy as PIGMENTI TELAFIN; products of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 80 pp to 100 pp, preferably 90 pp, of a casein binder and polyamide in water with solids at the 14% (for example, the product commercially available in Italy with the commercial name PROTAN® LP 3150; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 10 pp to 30 pp, preferably 20 pp, of condensed starch with fat acids, with solids at the 19% (for example, the product commercially available in Italy with the commercial name GW® 5; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 60 pp to 80 pp, preferably 70 pp, of a formulation of waxes, acrylic emulsions and polyurethane dispersions, with solids at the 18% (for example, the product commercially available in Italy with the commercial name BIOFLEX® CR 5146; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 300 pp to 500 pp, preferably 450 pp, of water at a temperature between 30° and 40°, preferably at 35°; from 80 pp to 120 pp, preferably 100 pp, of an emulsion of acrylic resin, with solids at the 20% (for example, the product commercially available in Italy as BIOFLEX'" GR 5204; product of LMF BIOKIMICA S.p.A., Santa Croce SuII'Arno, PI); from 50 pp to 70 pp, preferably 60 pp, of a polyurethane dispersion, with solids at the 24% (for example, the product commercially available as BIOTHANE® UW 6014; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 10 pp to 30 pp, preferably 20 pp, of a dispersion of fluorine carbon resin in water, with solids at the 18% (for example, the product commercially available as MODIFIER® MW 7514; product of LMF

BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI); from 30 pp to 50 pp, preferably 40 pp, of a penetrating agent in hydro-alcoholic phase, with active matters at the 100% (for example, the product commercially available as PENETRATOR® PT 7300; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI).

[0071] In the composition described above, as a way of example, the amounts indicated as pp represent amounts in grams of each single component with respect to the total amount of mixture to prepare (for example, pp = g/Kg, that is grams of each single component per kilogram of total mixture to prepare, under the form of water solution, wherein, usually, water represents from the 50 to the 60%). In the light of the above, as a way of example, but not limiting, it results clear that the prudent and appropriate selection made between the less toxic and polluting products has rendered possible significant advantages in terms of toxicity and pollution also to said step of Finishing of the process of the invention, characterizing it with respect to the corresponding step of Finishing of the standard process of the known art.

[0072] As a consequence, also the step of Finishing of the process of the present invention, taken into consideration together with the other steps of said process, represents a **further characterizing aspect** of the process itself, with respect to the standard processes commonly applied in the tanning art.

[0073] The application of the undercoat described above is then followed by other operations known and commonly applied, such as, the Print, the Staining, the Bicolor Effect, the Fixing, the Ironing, the Stocking, the Knifing, the Final Tact. All these operations are executed using traditional apparatus, technologies and knowledge that are commonly employed in the sector.

[0074] The hides obtained with the process according to the invention, as described before, have shown to present characteristics that can be absolutely compared (and are also often better) to those of analogous hides realized with the standard processes commonly employed in the sector. Moreover, they have shown to contain only minimum amounts (on the whole non toxic or polluting) of residue products deriving from the manufacturing, as illustrated in the examples, though not-limiting, of the following Chart 2.

Chart 2: Analysis of the content of the residues of manufacturing in hides obtained through the standard processes of the state of the art and that of the invention

	Hide F)	**Hide G)**
Residue	**Value found (*) [mg/Kg]**	
Formaldehyde	43,9 - 140	< 5
Chromium (total content)	13.000 - 17.000	2-10
Cadmium (total content)	17 - 35	N.D.
Lead (total content)	8 - 12	≤ 2
Nickel (total content)	10 - 15	≤ 5
11): obtained through the process of the state of the art (Chart 1) **G):** obtained through the process of the invention (Chart 2) **(*)** methods of analysis: formaldehyde - UNI EN ISO 17226-1:2008; Metals - UNI EN ISO 170'72-2:2011 N.D.: not detectable		

[0075] Said amounts/traces of residue substances are not significant from the point of view of the toxicity and of the eco-compatibility, thus giving origin to a product of low environmental impact as well and, above all, absolutely non-toxic or allergenic.

[0076] To prove this, a *patch Test,* executed at the Analysis Laboratory of the S. Raffaele University of Milan (ABICH) on twenty sane human volunteers, has shown that the hide of the invention is not irritating.

[0077] It results, therefore, a further object of the present invention also the hide obtained through the process described in the present description and in the attached claims.

[0078] Last, preliminary studies and in-depth analysis on the degree of biodegradability and of composting of the hides realized with the process in accordance with the present invention make one think that the same present an advantageous applicative potential also from this point of view.

Conclusions

[0079] The process of the present invention has revealed of low environmental impact and substantially free of toxicity.

[0080] Further, said process has unexpectedly allowed to obtain a final hide having optimal characteristics with regard to aesthetics, softness, brightness, homogeneity of the dye and elasticity, absolutely not inferior to those of the hides

obtained with the traditional tanning processes.

[0081] Moreover, the hide realized with the process of the present invention can, eventually, contain only traces of chromium and/or of other metals (substantially deriving from the machineries of metal with which the hides are manufactured), of formaldehyde, of phenols, of phthalates, in a not significant amount from the point of view of the toxicity and of the eco-compatibility, thus resulting a low environmental impact product as well and, above all, absolutely non toxic or allergenic.

[0082] In addition, the hide realized with the process of the present invention seems to be potentially very interesting also from the point of view of the properties of biodegradability and of composting.

Claims

1. A process for the industrial preparation of an ecological hide at least comprising a manufacturing step, which increases/improves the hide affinity for the reactants used in the next manufacturing *steps,* wherein said step comprises:

   - introducing into the working barrel a tanning agent based on an amphoteric halogenated heterocyclic aromatic organic compound, having a pH around 6.5, free of metals, aldehydes, phenols [commercially available in Italy as GRANOFIN® F90; product of CLARIANT Prodotti S.p.A, ITALY] in an amount of 5% to 20% by weight, in comparison with the *fleshed weight,* of the fleshed hides, and applying a continuous barrel rotation for the whole night (around 12 hrs);
   - adding, the next morning, 70% to 120% by weight of water at a temperature of 35°C to 45°C and then 1% to 5% by weight of a syntan product, based on phenol-based synthetic tannins, but without formaldehyde and free phenol [commercially available in Italy as SYNCOTAN^3 MRL Liq; product of CLARIANT Prodotti S.p.A., ITALY], and applying a barrel rotation of 50 min to 70 min;
   - emptying the bath and, after draining, introducing 100% to 300% by weight of water at a temperature of 25°C to 35°C and applying a barrel rotation of 5 min to 15 min;
   - emptying the bath and taking out the hides;

   and wherein, in said process, the necessary standard *steps* of the known art called Pickle and Tanning are not carried out.

2. The process according to claim 1, further comprising a manufacturing step, which is carried out without using the heavy metals and the other toxic substances that are used in the known art, but using non-toxic natural product-based re-tannings, in which said *step* at least comprises:

   - introducing into the working barrel 50% to 150% by weight of water at a temperature of 30°C to 40°C;
   - adding a mixture comprising: 1% to 6% by weight of a dispersion of a lubricating non-ionic non-toxic co-polymer having pH = 6.0-7.5 [commercially available in Italy as TERGOTAN® PO 62 emuls. 1:3; product of CLARIANT Prodotti S.p.A., ITALY], and 1% to 5% by weight of an additional lubricating agent at ionic charge, based on sulphated vegetable oils and lecithin, at 90% of active substance and having pH = 6-7.5 [commercially available in Italy as DERMINOL® NLM emuls. 1:5; product of CLARIANT Prodotti S.p.A., ITALY], and applying a barrel rotation of 50 min to 70 min;
   - adding, into the same bath, 5% to 12% by weight of a synthetic tanner, an anionic naphthalenesulphonate condensed with pH modifiers, at 92-98% of active substance, having pH = 2.5-3.5 in 5% solution [commercially available in Italy as TANICOR® VTN emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY], and applying a barrel rotation of 55 min to 65 min;
   - adding, into the same bath, a mixture of:

     a) 15% to 25% by weight of a pyrogallolic tanner, based on pyrogallolic tannins, on tare, at 67% of active substance, having pH = 3,5 [commercially available in Italy as TRUFOTAN® TR emuls. 1:1; product of TRUMPLER S.p.A., ITALY];
     b) 2% to 8% by weight of a filling agent, a proteic filler derived from milk proteins, at 90-95% of active substance [commercially available in Italy as MARACRYL® SD emuls. 1:1; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI);
     c) 5% to 12% by weight of a polypeptide reactivating the tanner bindings, a proteinaceous product based on solubilized polypeptides from poultry feathers [commercially available in Italy as CROMOPLEN® PRT emuls. 1:5; product of LMF BIOKIMICA S.p.A., Santa Croce Sull'Arno, PI]; and applying a barrel rotation

of 55 min to 65 min;

- adding, into the same bath, the same amount of the same mixture of the previous a), b) and c) products; applying a barrel rotation of 5 hrs and 30 min to 6 hrs and 30 min and finishing this phase in "*Automatic by Night*" working, for about 12 hours, during the night;
- rotating the barrel, the next morning, for about 10 additional minutes; then adding, into the same bath, 80% to 120% by weight of water at a temperature of 40°C to 50°C and then a mixture consisting of: 0,4% to 0,6% by weight of a metal sequestering agent, preferably a mixture of polyphosphates and of alkali metal salts, at 96% of active substance [commercially available in Italy as UTANIT® AF emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY] and 0,4% to 0,6% by weight of a chelant for the same metals, preferably a bi-carboxylic acid such as oxalic acid [commercially available in Italy as Oxalic acid emuls. 1:1; product of CLARIANT Prodotti S.p.A., ITALY] ; and applying a barrel rotation of 25 min to 35 mini
- emptying the bath.

3. The process according to anyone of the preceding claims, at least comprising the following manufacturing phases:

a) one PHASE I, comprising the following manufacturing *steps:* (i) *Staking,* (ii) *Liming,* (iii) *De-liming,* (iv) *Bating;*
b) one PHASE II, comprising the following manufacturing *steps:* (v) *Re-tanning,* according to claim 2, (vi) *Fatting,* (vii) *Dyeing;*
c) one PHASE III, comprising the manufacturing *step:* (viii) *Finishing;* in which between PHASE I and PHASE II the *step* according to claim 1 (so called *Pre-tanning)* is carried out; with the proviso that, in said process, the necessary standard *steps* of the known art called *Pickle* and *Tanning* are not carried out.

4. An ecological and non-toxic hide, obtained by the process according to anyone of claims from 1 to 3.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 16 3245

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 June 2014	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 14 16 3245

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