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(54) **Ecological tanning and dyeing process and product obtained**

Ökologisches Gerb- und Färbeverfahren sowie erhaltenes Produkt

Procédé de teinture et de tannage écologique et produit obtenu

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Description

Field of the invention

[0001] The invention relates to an ecological tanning and dyeing process of leather, hide, skins or pelts.

[0002] The methods used in tanneries comprise the steps of:

- « working as river » which is a phase of cleaning the skin in an aqueous medium and / or via mechanical means to remove salts conservation, hair, flesh, fats, keratin, soluble proteins, bacteria and the superficial dirt. The skins are washed scraped and shaved if necessary, and called "Pelts"
- the "pickle" that reduce the pH of the skin to improve the preservation of skins by acid treatment aims,
- the "tanning" in which the collagen fibres are stabilized by the tanning agents so that the skin becomes rot, the "currying" which includes the following: neutralization and washing, followed by a re-tanning, of drying and a hot food, which are mostly conducted in a single treatment tank. At this stage, the leather is called "Crust" and "finishing" which includes several mechanical treatments, as well as the application of a surface layer to improve the appearance and feel of leather.

[0003] The tanning step is considered the most important in the chain of processing raw hides that are stiff and after storage putrescible and are thus transformed into a soft rot and what the leather material. Systems most commonly used tanning are:

- mineral tanning which uses trivalent chromium salts,
- vegetable tanning based on tanning power plant extracts wood or bark of certain trees and
- tanning made via synthetic.

[0004] The existing mineral tanning processes are implemented in an aqueous medium. The tanning chromium chloride or chromium sulfate is the most common. The tanning with chromium is often preceded by acid treatment in a step known as "pickling".

[0005] Pickling keeps the gut and skin reactivity to decrease the reaction sites, vis-à-vis the chromium, so as not to interfere with its diffusion into the collagen. Indeed, in the tanning step, trivalent chromium is inserted between the collagen fibres and the reticle by forming complexes with the anionic sites of the polypeptide chains. Tanning with chromium salts leads to a leather with excellent physicochemical properties, including flexibility, tear resistance and high thermal resistance.

[0006] However, it proves harmful to the environment due to the use of recycled or easily removable as chromium metal. Thus, tanning baths are never completely depleted chromium, which leads to the release of baths containing significant amounts of chromium (about 25 to

30% compared to the quantities introduced). However, chromium is a toxic pollutant releases and agent must undergo treatments statutorily disposal of chromium which are very expensive and do not allow direct recovery of chromium. In addition, we observe during finishing operations after the tanning (especially during dyeing) of salting-chromium polluting the bathroom and require removal treatments as for tanning baths. In addition, the use of metals such as chromium sometimes leads, due to the action of these allergenic, skin reactions in the user. It should be noted that, given a limited amount of chromium is attached to the skin to treat in a single tanning, it can undergo a new stage of tanning with chromium salts so that larger amount of chromium may be secured by the thus treated skin. This step retannage aims to ensure better penetration of dyes, improve the general feel, thickness, toughness, chemical resistance and heat resistance.

Background and drawbacks of the previous art

[0007] Tanning is the process to make hide or skins non putrescible. Many tanning processes are known in the art. Among them, chrome-based tanning or vegetable tanning are widely used. However, chrome-based tanning are dangerous for human health and environment.

[0008] Vegetable tanning is known since a long time and is considered as one of the best process to obtain a good quality and suppleness leather. But it is long and expensive. This process uses tannins from wood, bark, fruit, leaf, gall or natural polymers. The main used species are oak, chestnut, sumac, myrobollan or mimosa. Vegetable tanning consists in mixing skins or leather in water with an homogenate or extract of one or some of this species. It takes several months to tan a hide. So, this ancestral tanning process is not really adapted to industry. Moreover, natural dyes are not as efficient as synthetic dyes with fading problems during the life of the leather.

[0009] New processes have been developed. Among them, chrome-based is the quicker and the cheaper way to tan hide or skins. But, leather obtained by this process cannot be used for every application. The obtained leather is not suppleness and could generate allergies. Because of the toxicity of the sludge generated by this process, new technics need to be developed to protect the environment.

[0010] For example, the international patent application WO2006/067801 deals with a bio-tanning process for leather making. Conventionally skins/hides are tanned with metal-ions and vegetable tannins. Environmental constraints on the discharge of toxic metal-ions and poor biodegradable vegetable tannins in the wastewater have become serious issue. In this invention, the pelts are tanned using eco-benign bio-molecules other than vegetable tannins to reduce the pollution loads. Performance of the leathers is on par with conventionally processed leathers.

[0011] The European patent EP0849365 is about a composition for preparing leather or hides comprises a retanning agent, a dubbing agent and optionally adjuvants, which when added to an at least 8-fold amount of water at 10-60 degrees C forms a homogeneous mixture.

[0012] Some solutions of the previous art deal with new kind of molecules, design to be as efficient as chrome but less polluting. The patent application WO2010/130311 describes a tanned leather, skin or pelt which is produced by non-metal tanning, comprising the step of tanning with a non metallic tanning agent in a tanning bath, the tanning bath having a pH of from 6 to 10 at the beginning of tanning step. The invention relates to the defined tanning process, particular tanning agent compositions, the use of the tanned leather, skins or pelts for further processing and the produced tanned and optionally further processed leather, skins or pelts.

[0013] An other challenge of eco-friendly tanning processes is pigments. Usually, tanning and dyeing skins, pelts or leather are two different steps. The well known natural pigments to dye hides are campeach wood extracts (red to black), chestnut (greenish-brown), yellow wood (yellow to orange), indigo (blue), cochineal (red), tara. There are also synthetic colours based on basic dyes, acid dyes, direct dyes and sulphur dyes.

[0014] The patent application WO2005/038124 deals with a process for the production of pigment-dyed leather wherein a tanned leather is retanned at a pH GBP 4.5 with a combined retanning agent, which is a combination of a syntan or syntan precursor with a basic metal tanning agent, and is pigment-dyed in an aqueous dye bath with at least one pigment in the form of an aqueous dispersion of a colour pigment, in which the average particle size of the dispersed particles is < 5 microm, in the presence of a surface active aliphatic mono-, di- or triamine containing a C12-30-hydrocarbon radical and at least one polyethyleneglycolether chain, or an amphoteric derivative thereof, at a pH GBP 4.5, provides pigment-dyeings of outstanding colour yield, levelness and reproducibility of the pigment-dyeing, with satisfactory surface penetration, and also of satisfactory hiding properties with respect of any irregular previous dyeings of the substrate, while the typical leather structure is substantially maintained and visible, suitable compositions therefor, and the pigment-dyed substrates.

[0015] Some news technics emerged combining tanning and dyeing in the same bath.

[0016] For example, the patent application NZ193940 presents a process for dyeing and tanning pelts in a single bath, wherein these materials, which can be fat-liquored before-hand, are (a) dyed with at least one anionic dye and simultaneously pickled, and (b) tanned with at least one tannin, at a temperature in the range from 158 to 458C and in an aqueous liquor which has been adjusted to a pH value of 1 to 4.

[0017] The patent application EP0543689 describes compositions to simultaneously tan and dye hides, characterized by the fact that they contain at least one tanning

compound able to form chromophore groups and at least one coupler able to develop with the chromophore groups of the compound tanning the final colour.

[0018] But this combination technics are not necessary environment friendly by mixing natural and synthetic products.

Solution proposed by the invention

[0019] The purpose of the present invention is to provide a new process to tan leather, skins, hide or pelts to preclude the above drawbacks. Indeed, the invention concerns an ecological tanning and dyeing process of leather, skins, hide or pelts which is chrome-free and combines vegetable and oil tanning, said ecological tanning and dyeing process comprising the following steps :

- pre-tanning the skins
- placing pre-tanned skins in a drum with a totally biodegradable and environment-friendly tanning composition comprising in percentage of weight of skins to be tanned
 - 10 to 20% of glucose
 - 10 to 30% of a mix of animal or vegetal oils
 - 2 to 15% of vegetable tannins
 - and water
- drying on air the skins
- dyeing the skins in a drum with a totally biodegradable and environment-friendly dyeing composition comprising in percentage of weight of skins to be tanned:
 - 1 to 10% of natural rubber
 - 1 to 10% of originally natural pigments
 - water

- drying on air the skins.

[0020] Percentages are essentially related to weight of skins to be tanned.

[0021] Different types of skins can be tanned and dyed by this process but it is particularly adapted to sheep.

[0022] Advantageously oils are from animals.

[0023] Advantageously oils are vegetal oils.

[0024] Advantageously vegetable tanning uses vegetable tanning agents from wood, bark, fruit, leaf, gall or natural polymers.

[0025] In a preferred embodiment originally natural pigments are non synthetic and do not contain any metal complexes.

[0026] An other purpose of the invention is a composition for ecological tanning process of leather, skins, hide or pelts, which comprises in percentage of weight of skins to be tanned:

- 10 to 20% of glucose

- 10 to 30% of animal or vegetal oils
- 2 to 15% of vegetable tannins
- 50 to 70% of water

said composition is totally biodegradable and environment-friendly.

[0027] An other purpose of the invention is a composition for ecological dyeing process of leather, skins, hide or pelts which comprises in percentage of weight of skins to be tanned:

- 1 to 10% of natural rubber
- 1 to 10% of originally natural pigments
- water

said composition is totally biodegradable and environment-friendly.

[0028] An other purpose of the invention is a product obtained by said ecological tanning and dyeing process.

Description of the best embodiment of the invention

[0029] The invention will be better understood with the description of the best embodiment.

[0030] The ecological tanning and dyeing process disclosed by the invention comprises several steps.

[0031] The figure 1 describes the process steps according to the invention.

[0032] The skins are pre-tanned as usually done in that technical field. Dehaired sheep skins are placed in a wood or polycarbon drum with a tanning mix comprising 10 to 20% of glucose, 10 to 30% of a mix of several natural oils, 2 to 15% of vegetable tannins and 50 to 70% of water. The mix of oils is composed by animals and vegetables oils but each proportion depends on the nature of the skins and the desired colour. Indeed, oil combination influences the result of the tanned skin. The tanning step is between 2 and 3 days long at ambient temperature.

[0033] At the end of this step, the tanned skins are hanged and dried by air for several hours or days.

[0034] Then, skins can be dye with non synthetic and originally natural pigments which are not containing any metal complexes. They are obtained from wood extracts for brown colours, mineral extracts for grey colours or vegetable extracts for brown, yellow and light colours. Skins are placed for 24 to 48 hours at 35 to 50°C in a dedicated drum with a mix of pigments to obtain desired colour and rubber to fix the colour. This dyeing process gives a specific colour and texture effect to the leather which cannot be obtained by other process, in particular with traditional vegetable tanning. Indeed, it allows to have light colours and more brilliant and more shiny colours.

[0035] Leathers are then dried on air as previously.

[0036] Some additional steps can be done as softening the leather by leaving leather in a drum for several hours or as fixing the colours. Leathers are then ready to be

used for many different applications.

Claims

1. An ecological tanning and dyeing process of leather, skins, hide or pelts which is chrome-free and combines vegetable and oil tanning, said ecological tanning and dyeing process comprising the following steps:

- pre-tanning the skins
- placing pre-tanned skins in a drum with a totally biodegradable and environment-friendly tanning composition comprising in percentage of weight of skins to be tanned :

- 10 to 20% of glucose
- 10 to 30% of a mix of animal or vegetal oils
- 2 to 15% of vegetable tannins
- and water

- drying on air the skins
- dyeing the skins in a drum with a totally biodegradable and environment-friendly dyeing composition comprising in percentage of weight of skins to be tanned :

- 1 to 10% of natural rubber
- 1 to 10% of originally natural pigments
- water

- drying on air the skins

2. An ecological tanning and dyeing process of leather, skins, hide or pelts according to claim 1 wherein oils are from animals.

3. An ecological tanning and dyeing process of leather, skins, hide or pelts according to claim 1 wherein oils are vegetal oils.

4. An ecological tanning and dyeing process of leather, skins, hide or pelts according to anyone of claims 1 to 3 wherein vegetable tanning uses vegetable tanning agents from wood, bark, fruit, leaf, gall or natural polymers.

5. An ecological tanning and dyeing process of leather, skins, hide or pelts according to anyone of claims 1 to 4 wherein originally natural pigments are non synthetic and do not contain any metal complexes.

6. A composition for ecological tanning process of leather, skins, hide or pelts, which comprises in percentage of weight of skins to be tanned :

- 10 to 20% of glucose

- 10 to 30% of animal or vegetal oils
- 2 to 15% of vegetable tannins
- 50 to 70% of water

said composition is totally biodegradable and environment-friendly.

7. A composition for ecological dyeing process of leather, skins, hide or pelts which comprises in percentage of weight of skins to be tanned :

- 1 to 10% of natural rubber
- 1 to 10% of originally natural pigments
- water

said composition is totally biodegradable and environment-friendly.

8. Product obtained by said ecological tanning and dyeing process according to claim 1 to 5.

Patentansprüche

1. Ökologischer Gerbe- und Färbeprozess von Leder, Häuten, Balg oder Fellen, der chromfrei ist und pflanzliches und Ölgerben kombiniert, wobei der genannte ökologische Gerbe- und Färbeprozess die folgenden Schritte umfasst:

- Vorgerben der Häute
- Platzieren der vorgegerbten Häute in ein Fass mit einer komplett biologisch abbaubaren und umweltfreundlichen Gerbezusammensetzung, umfassend in Gewichtsprozent von zu gerbenden Häuten:

- 10 bis 20 % Glukose
- 10 bis 30 % einer Mischung aus tierischen oder pflanzlichen Ölen
- 2 bis 15 % pflanzliche Gerbstoffe
- und Wasser

- Trocknen der Häute an der Luft
- Färben der Häute in einem Fass mit einer komplett biologisch abbaubaren und umweltfreundlichen Färbezusammensetzung, umfassend in Gewichtsprozent von zu gerbenden Häuten:

- 1 bis 10 % natürliches Gummi
- 1 bis 10 % ursprünglich natürliche Pigmente
- Wasser

- Trocknen der Häute an der Luft.

2. Ökologischer Gerbe- und Färbeprozess von Leder, Häuten, Balg oder Fellen gemäß Anspruch 1, wobei

die Öle von Tieren stammen.

3. Ökologischer Gerbe- und Färbeprozess von Leder, Häuten, Balg oder Fellen gemäß Anspruch 1, wobei die Öle pflanzliche Öle sind.

4. Ökologischer Gerbe- und Färbeprozess von Leder, Häuten, Balg oder Fellen, gemäß irgendeinem der Ansprüche 1 bis 3, wobei das pflanzliche Gerben pflanzliche Gerbstoffe aus Holz, Rinde, Früchten, Blättern, Galle oder natürlichen Polymeren verwendet.

5. Ökologischer Gerbe- und Färbeprozess von Leder, Häuten, Balg oder Fellen gemäß irgendeinem der Ansprüche 1 bis 4, wobei die ursprünglich natürlichen Pigmente nicht synthetisch sind und keinerlei Metallkomplexe enthalten.

6. Zusammensetzung für einen ökologischen Gerbeprozess von Leder, Häuten, Balg oder Fellen, der in Gewichtsprozent von zu gerbenden Häuten umfasst:

- 10 bis 20 % Glukose
- 10 bis 30 % tierisches und pflanzliches Öl
- 2 bis 15 % pflanzliche Gerbstoffe
- 50 bis 70 % Wasser

die genannte Zusammensetzung ist komplett biologisch abbaubar und umweltfreundlich.

7. Zusammensetzung für einen ökologischen Färbeprozess von Leder, Häuten, Balg oder Fellen, der in Gewichtsprozent von zu gerbenden Häuten umfasst:

- 1 bis 10 % natürliches Gummi
- 1 bis 10 % ursprünglich natürliche Pigmente
- Wasser

die genannte Zusammensetzung ist komplett biologisch abbaubar und umweltfreundlich.

8. Durch den genannten ökologischen Gerbe- und Färbeprozess gemäß Anspruch 1 bis 5 erhaltenes Produkt.

Revendications

1. Procédé de tannage et de teinture écologique de cuir, peaux ou fourrures, sans chrome, qui combine un tannage végétal et à base d'huile, ledit procédé de tannage et de teinture écologique comprenant les étapes suivantes :

- pré-tannage des peaux

- mise en place des peaux pré-tannées dans un tambour avec une composition de tannage respectueuse de l'environnement et totalement biodégradable, comprenant, en pourcentage de poids de peaux à tanner :
- 10 à 20 % de glucose
 - 10 à 30 % d'un mélange d'huiles animales ou végétales
 - 2 à 15 % de tannins végétaux
 - et de l'eau
- séchage à l'air des peaux
- teinture des peaux dans un tambour avec une composition de teinture respectueuse de l'environnement et totalement biodégradable, comprenant, en pourcentage de poids de peaux à tanner :
- 1 à 10 % de caoutchouc naturel
 - 1 à 10 % de pigments d'origine naturelle
 - et de l'eau
- séchage à l'air des peaux
2. Procédé de tannage et de teinture écologique de cuir, peaux ou fourrures selon la revendication 1, dans lequel les huiles sont d'origine animale.
3. Procédé de tannage et de teinture écologique de cuir, peaux ou fourrures selon la revendication 1, dans lequel les huiles sont d'origine végétale.
4. Procédé de tannage et de teinture écologique de cuir, peaux ou fourrures selon l'une quelconque des revendications 1 à 3, dans lequel le tannage végétal utilise des agents de tannage végétaux provenant du bois, de l'écorce, de fruits, de feuilles, de la galle ou de polymères naturels.
5. Procédé de tannage et de teinture écologique de cuir, peaux ou fourrures selon l'une quelconque des revendications 1 à 4, dans lequel les pigments d'origine naturelle ne sont pas synthétiques et ne contiennent pas de complexes de métaux.
6. Composition pour un procédé de tannage écologique de cuir, peaux ou fourrures, comprenant, en pourcentage de poids de peaux à tanner :
- 10 à 20 % de glucose
 - 10 à 30 % d'huiles animales ou végétales
 - 2 à 15 % de tannins végétaux
 - 50 à 70 % d'eau
- ladite composition étant respectueuse de l'environnement et totalement biodégradable.
7. Composition pour un procédé de teinture écologique de cuir, peaux ou fourrures, comprenant, en pourcentage de poids de peaux à tanner :
- 1 à 10 % de caoutchouc naturel
 - 1 à 10 % de pigments d'origine naturelle
 - et de l'eau
- ladite composition étant respectueuse de l'environnement et totalement biodégradable.
8. Produit obtenu par ledit procédé de tannage et de teinture écologique, selon les revendications 1 à 5.

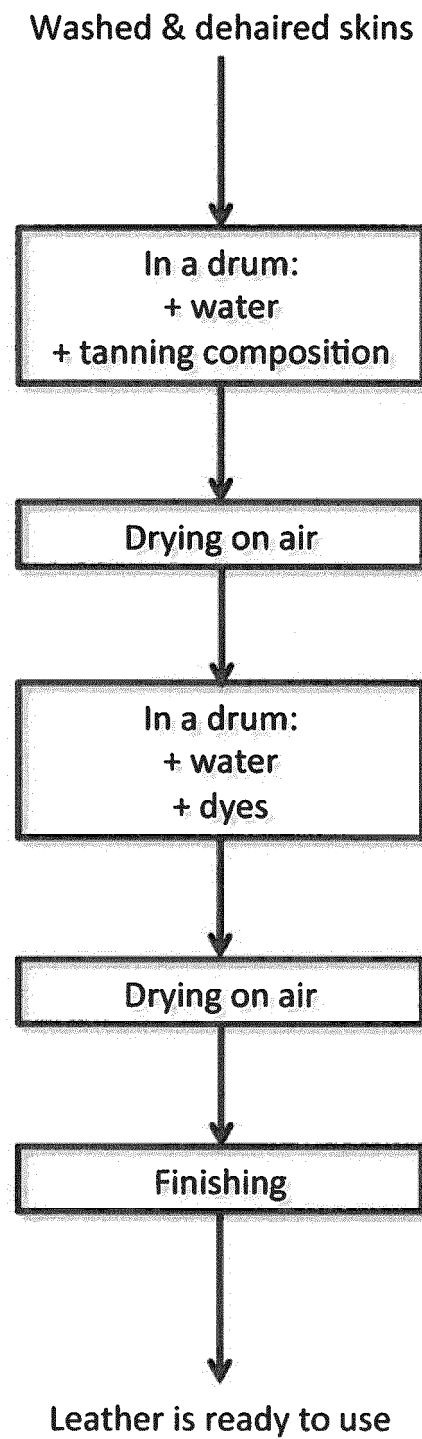


Fig 1

REFERENCES CITED IN THE DESCRIPTION

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