



(11)

EP 2 862 944 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.04.2015 Bulletin 2015/17

(51) Int Cl.:
C14C 3/10 (2006.01) **C14C 3/14** (2006.01)
C14C 3/28 (2006.01) **D06P 3/32** (2006.01)
D06P 1/34 (2006.01) **C14C 3/08** (2006.01)

(21) Application number: **13188958.6**

(22) Date of filing: **16.10.2013**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME

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

(57) An ecological tanning and dyeing process of leather, skins, hide or pelts which is chrome-free and combines vegetable or oil tanning, said ecological tanning process is based on a composition comprising :

- a tanning composition comprising

- 10 to 20% of glucose
- 10 to 30% of a mix of oils
- 2 to 15% of vegetable tannins

- and water

and said ecological dyeing process is based on a combination of :

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

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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 process is based on a biodegradable composition comprising :

- a tanning composition comprising
 - 10 to 20% of glucose
 - 10 to 30% of a mix of oils
 - 2 to 15% of vegetable tannins
- and water and said ecological dyeing process is based on a combination of :
 - 1 to 10% of natural rubber
 - 1 to 10% of originally natural pigments
 - water

[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 :

- 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 :

- 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 process is based on a biodegradable composition comprising :

- a tanning composition comprising

- 10 to 20% of glucose
- 10 to 30% of a mix of oils
- 2 to 15% of vegetable tannins

- and water

and said ecological dyeing process is based on a combination of :

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

2. An ecological tanning and dyeing process of leather, skins, hide or pelts wherein oils are from animals.
3. An ecological tanning and dyeing process of leather, skins, hide or pelts wherein oils are vegetal oils.
4. An ecological tanning and dyeing process of leather, skins, hide or pelts 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 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 :
 - 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 :
 - 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.

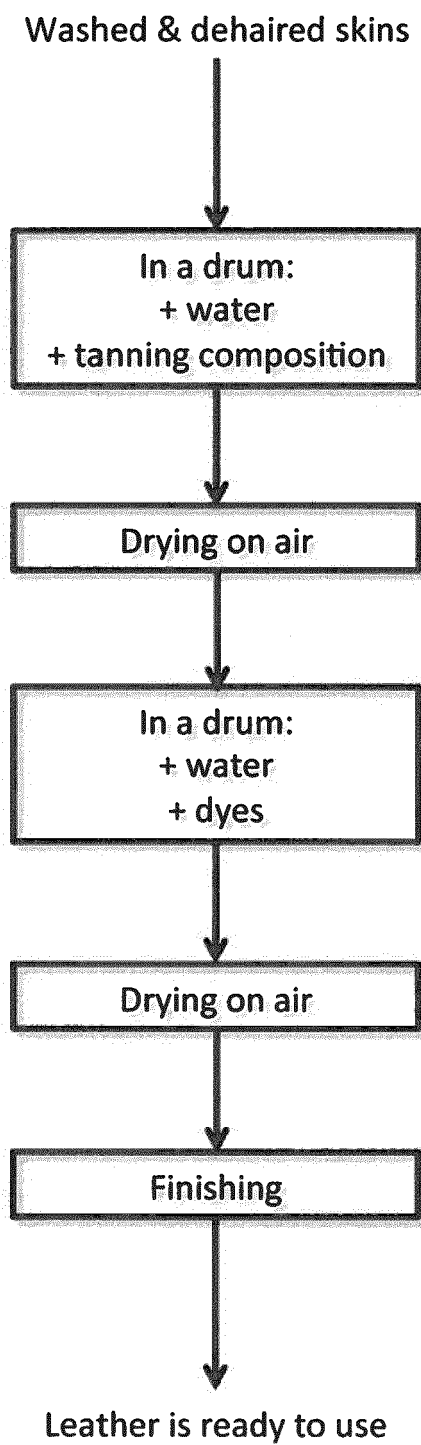


Fig 1



EUROPEAN SEARCH REPORT

Application Number
EP 13 18 8958

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	DE 39 29 366 A1 (SIMONTORNYAI BOERGYAR [HU]) 22 March 1990 (1990-03-22) * page 2, line 45 - page 3, line 22 * * page 4, lines 35-60; examples 1,3 *	1-6,8	INV. C14C3/10 C14C3/14 C14C3/28 D06P3/32 D06P1/34 C14C3/08
X	US 196 339 A (DE CORDOVA G. ET AL.) 23 October 1877 (1877-10-23) * the whole document *	4,5,8	
X	US 4 784 664 A (SIEGLER MARCEL [US] ET AL) 15 November 1988 (1988-11-15) * column 3, lines 4-5 * * examples 1,6,7 *	4,5,8	
X	GB 405 315 A (ICI LTD; LESLIE PAIGE RENDELL; GODFREY EDWARD SCHARFF) 2 February 1934 (1934-02-02) * page 1, line 41 - page 2, line 20 * * page 2, lines 23-47 *	7	
			TECHNICAL FIELDS SEARCHED (IPC)
			C14C D06P
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 9 July 2014	Examiner Neugebauer, Ute
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)



Application Number

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 13 18 8958

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-5, 8

tanning and dyeing process combining vegetable and oil
tanning involving a composition comprising glucose, mixture
of oils and vegetable tannins.

2. claim: 6

Composition comprising glucose, animal or vegetal oils,
vegetable tannins and water;

3. claim: 7

Biodegradable and environment-friendly composition
comprising natural rubber, natural pigments and water.

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

EP 13 18 8958

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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09-07-2014

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2006067801 A **[0010]**
- EP 0849365 A **[0011]**
- WO 2010130311 A **[0012]**
- WO 2005038124 A **[0014]**
- NZ 193940 **[0016]**
- EP 0543689 A **[0017]**