

(19)



(11)

EP 3 798 325 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

31.03.2021 Bulletin 2021/13

(51) Int Cl.:

C14C 1/04 (2006.01)

C14C 3/08 (2006.01)

C14C 9/00 (2006.01)

C14C 3/22 (2006.01)

(21) Application number: **20020487.3**

(22) Date of filing: **21.10.2020**

(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

Designated Validation States:

KH MA MD TN

(71) Applicant: **Be Green Tannery Innovazione**

Conciaria Italiana

S.r.l.

83029 Solofra (AV) (IT)

(72) Inventors:

• **Felice, De Piano**

83029 Solofra (AV) (IT)

• **De Piano, Felice**

83029 Solofra (AV) (IT)

(54) **TANNING OF BOVINE, SHEEP AND GOAT SKINS WITH THE USE OF COMMERCIAL
SUBSTANCES, PROCESS AND OPERATING METHODS FOR FREE-METAL FINISHED
LEATHERS**

(57) Tanning with the use of commercial substances, for goat hides in pickel, process and operating methods for finished free-metal leathers

EP 3 798 325 A1

Description

DETAILED DESCRIPTION

[0001] This process, which is the subject of a patent filing, creates a tanning method for leather, which allows to obtain a metal free product, free of metals, obtaining the same characteristics in terms of quality as products containing chromium on the market.

[0002] As is well known in the tanning sector, leather processing is divided into various steps, first of all tanning, a fundamental and primary process for obtaining a good product during the subsequent stages of processing; this process, distinguished by type of raw material and use of the finished product, such as footwear or clothing, allows to optimize the production process and make the leather compliant with restrictive regulatory dictates on these substances (heavy metals), but is based above all on knowledge of chemicals used and huge water consumption.

[0003] The process prepared allows to improve two fundamental factors:

1. the consumption of water is reduced by about 30% compared to a chrome tanning;
2. the mixture used was made with a product easily available on the market.

[0004] The first point made it possible to have a reduction in the cost of natural resources (lower consumption) and to reduce the cost related to the purification of industrial waste water; while, the second, using commercial products, the cost of the blend used has a lower cost than products placed on the market with the "metal-free" specifications.

[0005] In any case, it should be noted that when chemical mixtures or products of the same intended use are referred to, we always refer to an industrial use for the tanning sector, marketed by operators in the sector.

[0006] After selecting the type of leather purchased in pickel, of sheep and goat origin, it is possible to perfect and implement the start-up and process phases; the same are selected by type and size, making a selection for the final requests, differentiating them from the first (best) to the fourth (worst) choice.

[0007] The tanning operation, which prepares the product to be considered "metal free", consists of 16 phases, divided by process and chemical composition used, so that each single step complies with the established standards.

[0008] For the descriptive phases that follow, a batch of sheep and goat pickel skin was considered, consisting of 1246 hides for an initial weight of about 1500 kg.

Phase 1

Bath preparation

[0009] The hides are loaded into drums, suitable for use in terms of size and weight, with a composite chemical mixture diluted in water, in order to favor the adsorption of substances (slow absorption) at a predetermined temperature.

[0010] The chemical composition is as follows:

- water weighing more than 20% of the initial weight of the entire lot;
- salt for a weight equal to 5% of the initial weight of the entire lot;
- sodium acetate trihydrate [CAS 6131-90-4] equal to 2% of the initial weight of the entire lot;
- alcohols, C11-13-branched, ethoxylated [CAS 68439-54-3] equal to 1% of the initial weight of the whole lot.

[0011] The chemical composition of the C11-13-branched, ethoxylated [CAS 68439-54-3] alcohols used has a concentration ($\geq 70 - < 90$)%.

[0012] The hides are rotated in the drum with the mixture for 2 hours.

[0013] At the end of this rotation phase, the hides have absorbed the substances present in the mixture, the entire content is discharged from the drum and left to soak inside containment trolleys for a time that can vary between 8 and 10 hours.

[0014] Once the initial preparation time has elapsed, the hides are removed from the bath, an operation typically called "trestle" and transferred to the operating machines, where they will be fleshing machine.

[0015] The leather retained about 20% of the mixture used, with a consequent weight increase of the entire batch, while maintaining the initial physical characteristics (thickness).

[0016] The fleshing operation allows to remove parts of the fleshings from the skin and remove part of the absorbed water, reducing the final weight by about 3% compared to the initial weight of the batch.

[0017] Following this preliminary step, preparation, bath and fleshing, the batch of hides is prepared for the subsequent phases, which will last 25 hours.

[0018] As for the previous phase and for all those to follow, the hides are loaded into drums, suitable for use by size and weight, with a composite chemical mixture diluted in water, in order to favor the adsorption of substances (slow absorption) at a preset temperature.

Phase 2

[0019] The chemical composition is as follows:

- water for a weight equal to 100% of the lot weight;
- sodium formate [CAS 141-53-7] for a weight equal

- to 2% of the lot weight;
- composite enzyme of alcohols, C9-11-iso-, C10-rich, ethoxylated [CAS 78330-20-8] and subtilisin [CAS 232-752-2] for a weight equal to 0.04% of the lot weight (this product can undergo a percentage variation according to specific needs);
- auxiliaries free of classified substances for a weight equal to 2% of the lot weight;
- sodium bicarbonate for a weight equal to 1.10% of the lot weight;
- mixture of solvents for a weight equal to 3% of the lot weight (this product can undergo a percentage variation according to specific needs).

[0020] The chemical composition of sodium formate [CAS 141-53-7] used has a concentration ($\geq 98.8 - < 99.7$)%.

[0021] The chemical composition of alcohols, C9-11-iso-, C10-rich, ethoxylated [CAS 78330-20-8] and subtilisin [CAS 232-752-2] used have the following concentrations: $\leq 10\%$ for the former, $\leq 0.3\%$ for the second.

[0022] The chemical composition of sodium bicarbonate is composed of two substances classified and having the following concentrations: sodium carbonate [CAS 497-19-8] concentration ($\geq 1 - < 3$)%, sodium hydrogen carbonate [CAS 144-55-8] concentration ($\geq 95 - < 99$)%.

[0023] The chemical composition of the solvent mixture consists of two substances classified and having the following concentrations: hydrocarbons, C9-C11, n-alkanes, isoalkanes, cyclics, $< 2\%$ aromatics [CE 918-481-9] concentration 90%, dichloropropane [CAS 78-87-5] concentration ($\geq 9 - < 10.5$)%.

[0024] The skins are rotated with the mixture for a time of 1.5 hours, with preset speed and controlled temperature settings.

[0025] After the set time has elapsed, the bathroom is drained, leaving the leather inside the drum.

Phase 3

[0026] The chemical composition is as follows:

- water for a weight equal to 50% of the lot weight;
- alcohols, C11-13-branched, ethoxylated [CAS 68439-54-3] equal to 1% of the lot weight;
- auxiliaries free of classified substances for a weight equal to 1% of the lot weight;
- carboxylic acids, di-, C4-6 [CAS 68603-87-2] equal to 1% of the lot weight.

[0027] The chemical composition of the C11-13-branched, ethoxylated [CAS 68439-54-3] alcohols used has a concentration ($\geq 70 - < 90$)%.

[0028] The chemical composition of carboxylic acids, di-, C4-6 [CAS 68603-87-2] used has a concentration ($\geq 60 - < 90$)%.

[0029] The hides are rotated with the mixture for a time of 1 hour, with preset speed and controlled temperature

settings.

[0030] After the set time has elapsed, the bathroom is drained, leaving the leather inside the drum.

5 Phase 4

Wash

[0031] At the end of the first stages of preparation, the hides contained in the drum are washed, using a mixture of water and salt.

[0032] The quantity of water used is equal to 100% of the weight of the lot, while for the salt a percentage equal to 1% of the weight of the lot is used.

[0033] The washing is carried out in 3 sequences, for a duration of 45 minutes each, the hides are immersed in water and the predetermined amount of salt is added. The rotation takes place for the preset time and then the toilet drains, this operation is repeated 3 times.

[0034] After the predetermined time and after having carried out the third and last wash, it is possible to move on to the following phases, keeping the hides inside the drum.

25 Phase 5

[0035] The chemical composition is as follows:

- water for a weight equal to 100% of the lot weight;
- 30** - salt for a weight equal to 8% of the lot weight;
- formic acid [CAS 64-18-6] for a weight equal to 1% of the lot weight.

[0036] The chemical composition of formic acid [CAS 64-18-6] used has a concentration of $< 85\%$.

[0037] The mixture with the hides is kept in the drum for a time of 4 hours, according to the preset speed and controlled temperature settings.

40 Phase 6

[0038] After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- 45** - 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl) triethanol [CAS 4719-04-4] for a weight equal to 3% of the lot weight.

50 **[0039]** The chemical composition of 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl) triethanol [CAS 4719-04-4] used has a concentration ($\geq 25 - < 50$)%.

[0040] The mixture with the hides is kept in the drum for a time of 1.5 hours, according to the preset speed and controlled temperature settings.

55

Phase 7

[0041] After the time of the previous phase, during the rotation of the drum bath, the same chemical composition of Phase 6 is added.

[0042] The mixture with the hides is kept in the drum for a time of 1.5 hours, according to the preset speed and controlled temperature settings.

Phase 8

[0043] After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- auxiliary for a weight equal to 1.5% of the lot weight.

[0044] The chemical composition of the auxiliary mixture is composed of two substances classified and having the following concentrations: phenol [CAS 108-95-2] concentration ($\geq 0.1 - < 0.25$)%, formaldehyde [CAS 50-00-0] concentration ($\geq 0 - < 0.01$)%.

[0045] The mixture with the hides is kept in the drum for a time of 30 minutes, according to the preset speed and controlled temperature settings.

Phase 9

[0046] After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- polymer free of classified substances for a weight equal to 20% of the lot weight.

[0047] The mixture with the hides is kept in the drum for a time of 30 minutes, according to the preset speed and controlled temperature settings.

Phase 10

[0048] After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- fattening for a weight equal to 3% of the lot weight.

[0049] The chemical composition of the fattening consists of 4 classified substances: alkenes, C11-14, hydroformylation products, distn. residues, reaction products with maleic anhydride and sodium bisulfite, sodium salts [CE 938-654-2] ($\geq 10.5 - < 12$)%, 2-butoxyethanol [CAS 111-76-2] ($\geq 2.5 - < 3$)%, chloride of 2-(8-heptadecenes)-4,5-didro-1,3-bis(2-hydroxyethyl)-1H-imidazolium [CAS 67846-04-2] ($\geq 2 - < 2.5$)%, 2-(2-butoxyethoxy)ethanol [CAS 112-34-5] ($\geq 1 - < 1.5$)%.

[0050] The mixture with the hides is kept in the drum for a time of 30 minutes, according to the preset speed

and controlled temperature settings.

Phase 11

5 **[0051]** After the time of the previous phase, during the rotation of the drum bath, the addition of the same chemical composition of Phase 9 takes place.

10 **[0052]** The mixture with the hides is kept in the drum for a time of 30 minutes, according to the preset speed and controlled temperature settings.

Phase 12

15 **[0053]** After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- auxiliary for a weight equal to 2% of the lot weight.

20 **[0054]** The chemical composition of the auxiliary mixture is composed of two substances classified and having the following concentrations: phenol [CAS 108-95-2] ($\geq 0.5 - < 1$)%, formaldehyde [CAS 50-00-0] ($\geq 0 - < 0.01$)%.

25 **[0055]** The mixture with the hides is kept in the drum for a period of 5 hours, according to the preset speed and controlled temperature settings.

Phase 13

30 **[0056]** At the end of the previous phase, the hides in drum with the bath of the composite mixtures added in the various phases, are left in rotation for a time of 8 hours, so that the absorption of the substances penetrates further into the hides and guarantees the final result.

35 **[0057]** The rest of the hides in the bath takes place at room temperature, allowing the bath to cool to the external climatic conditions; this procedure does not alter what has been prepared in the phases described up to now.

40

Phase 14

45 **[0058]** After the previous phase, the drum resumes rotation according to the preset parameters, activating the bath temperature control again.

[0059] A chemical composition is added as follows:

- water for a weight equal to 50% of the lot weight;
- formic acid [CAS 64-18-6] for a weight equal to 0.5% of the lot weight.

50

[0060] The chemical composition of formic acid [CAS 64-18-6] used has a concentration of $< 85\%$.

55 **[0061]** The mixture with the hides is kept in the drum for a time of 25 minutes, according to the preset speed and controlled temperature settings.

Phase 15

[0062] After the time of the previous phase, during the rotation of the drum bath, the following chemical composition is added:

- oxalic acid [CAS 6153-56-6] for a weight equal to 1% of the lot weight.

[0063] The mixture with the hides is kept in the drum for 1 hour, according to the preset speed and controlled temperature settings.

Phase 16

[0064] Bath unloading and drum unloading.

[0065] In this phase, the last of the tanning sequence, the bath and the hides are unloaded into special trolleys, to then be placed on a "trestle".

[0066] The hides will be transferred to the mechanical pressing operations, carried out with felt holding and drying machines, with an unheated ironing roller, which allows the leather to be stretched and at the same time wrung out the load of water and chemical mixtures contained in the same.

[0067] After this operation, it is possible to move on to the drying phase at a controlled temperature, before moving on to the following phases.

whatever the origin of the pickel hides is, it can be applied to any origin of the product, obtaining a leather ready to be defined as metal-free.

- 5 **3.** Tanning process **consisting of** standard chemical substances and easily replicable process for the corresponding weight of the hides to be processed.
- 10 **4.** Tanning process **characterized by the fact that** water consumption is reduced by 30% compared to chrome tanning.
- 15 **5.** Production process **characterized by the fact that** it improves the production process, containing costs and reducing the polluting load generated by the production process.
- 20 **6.** Production process **characterized by the fact that** it reduces production times by about 16% compared to standardized production processes on the chrome tanning cycle, with a consequent reduction in the company's energy expenditure and consumption.
- 25
- 30

Claims

1. Tanning process **characterized by the fact that** standard products and substances easily available on the market are used, consisting of: 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol [CAS 4719-04-4], 2-butoxyethanol [CAS 111-76-2], 2-(2-butoxyethoxy)ethanol [CAS 112-34-5], carboxylic acids, di-, C4-6 [CAS 68603-87-2], formic acid [CAS 64-18-6], alcohols, C9-11-iso-, C10-rich, ethoxylated [CAS 78330-20-8], alcohols, C11-13-branched, ethoxylated [CAS 68439-54-3], alkenes, C11-14, hydroformylation products, distn. residues, reaction products with maleic anhydride and sodium bisulfite, sodium salts [CE 938-654-2], sodium bicarbonate, sodium carbonate [CAS 497-19-8], 2-(8-heptadecene)-4chloride,5-didro-1,3-bis(2-hydroxyethyl)-1H-imidazolium [CAS 67846-04-2], dichloropropane [CAS 78-87-5], alcohols composite enzyme, C9-11-iso-, C10-rich, ethoxylated [CAS 78330-20-8], phenol [CAS 108-95-2], formaldehyde [CAS 50-00-0], sodium acetate trihydrate [CAS 6131-90-4], sodium formate [CAS 141-53-7], subtilisin [CAS 232-752-2], hydrocarbons, C9-C11, n-alkanes, isoalkanes, cyclics, <2% aromatics [EC 918-481-9], sodium hydrogen carbonate [CAS 144- 55-8].
- 35
- 40
- 45
- 50
- 55

2. Tanning process **characterized by the fact that**



EUROPEAN SEARCH REPORT

Application Number
EP 20 02 0487

5

10

15

20

25

30

35

40

45

50

55

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	US 2013/239340 A1 (REINEKING CLAUS [DE] ET AL) 19 September 2013 (2013-09-19) * paragraphs [0007] - [0017] * * examples A-D *	1-6	INV. C14C1/04 C14C9/00 C14C3/08 C14C3/22
X	US 2019/078169 A1 (COLOMER DURAN RAMON [ES]) 14 March 2019 (2019-03-14) * paragraphs [0001] - [0006], [0010] - [0019], [0038], [0053], [0054], [0065] * * page 1 * * claims 1,6,10 *	1-6	
X	WO 2014/091341 A1 (COLORTEX S P A [IT]) 19 June 2014 (2014-06-19) * page 4, line 30 - page 6 * * example 1 *	1-6	
			TECHNICAL FIELDS SEARCHED (IPC)
			C14C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 February 2021	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	

 1
EPO FORM 1503 03.82 (P04C01)

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

EP 20 02 0487

5

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-02-2021

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013239340 A1	19-09-2013	AR 084137 A1	24-04-2013
		AU 2011328554 A1	04-04-2013
		BR 112013011268 A2	01-11-2016
		CN 103210096 A	17-07-2013
		EP 2638180 A1	18-09-2013
		ES 2526524 T3	13-01-2015
		HK 1187080 A1	28-03-2014
		KR 20140010366 A	24-01-2014
		MX 338051 B	31-03-2016
		TW 201233806 A	16-08-2012
		US 2013239340 A1	19-09-2013
US 2019078169 A1	14-03-2019	UY 33718 A	29-06-2012
		WO 2012062411 A1	18-05-2012

		AU 2016294578 A1	18-01-2018
		BR 112017028229 A2	28-08-2018
		CA 2990936 A1	19-01-2017
		CN 107835860 A	23-03-2018
		DK 3322827 T3	07-10-2019
		EP 3322827 A1	23-05-2018
		ES 2749674 T3	23-03-2020
		HK 1250248 A1	07-12-2018
WO 2014091341 A1	19-06-2014	JP 6812407 B2	13-01-2021
		JP 2018520253 A	26-07-2018
		KR 20180030052 A	21-03-2018
		PT 3322827 T	25-10-2019
		RU 2018103258 A	15-08-2019
		US 2019078169 A1	14-03-2019
		WO 2017009786 A1	19-01-2017

		EP 2929060 A1	14-10-2015
		ES 2610465 T3	27-04-2017
		PT 2929060 T	30-12-2016
		WO 2014091341 A1	19-06-2014
