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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C14C 1/08	A1	(11) International Publication Number: WO 91/05877
		(43) International Publication Date: 2 May 1991 (02.05.91)

(21) International Application Number: PCT/SE90/00652

(22) International Filing Date: 11 October 1990 (11.10.90)

(30) Priority data:
8903378-1 13 October 1989 (13.10.89) SE

(71) Applicant *(for all designated States except US):* AGA AKTIEBOLAG [SE/SE]; S-181 81 Lidingö (SE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only) :* TUOHIMAA, Timo [FI/FI]; Korkeavuoremlati 17 A 9, SF-00130 Helsinki (FI). UKKONEN, Aila [FI/FI]; Yliskylänkoori 5 Al, SF-00840 Helsinki (FI).

(74) Agent: WIEDEMANN, Bernd; Aga Aktiebolag, S-181 81 Lidingö (SE).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.

Published
With international search report.

(54) Title: A METHOD OF TREATING HIDES

(57) Abstract

There is described a method for treating delimed and bated hides, i.e. pelts. According to the inventive method, the pelts are brought to a suitable mineral tanning state and then tanned with mineral salts. The inventive treatment process corresponds to the conventional processes of pickling, tanning and basifying. The inventive method includes the treatment of pelts with weakly acid treatment liquids while supplying carbon dioxide and additions of tanning mineral substances subsequent to pretreatment, without or with the addition of solely a small amount of liquid, wherein the quantity of treatment liquid is supplemented after a predetermined treatment time.

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A Method of Treating Hides

The present invention relates to a method of pretreating and mineral-tanning hides which have been delimed and steeped in bate, i.e. have been bated. This method is intended to obviate the pickling and basifying steps (German: "Abstumpfen") which respectively precede and follow the conventional mineral tanning process.

Because of a greater awareness of present day environmental problems, the method is intended to reduce effluent emissions which contain contaminating mineral salts, acids and mineral tanning substances irreversibly bound to the hides.

By pickling is meant the treatment of organic products with salts, often in weak acid solutions. In the production of leather, the object of the pickling process is to bring the prepared hides and skins to a slightly acid state, suitable for mineral-tanning purposes.

The hide-substance can be brought to the desired degree of acidity, by treating the hide material with a strong acid in salt solution. Subsequent to being bated, the pelts, i.e. the hides stripped from hair, softened and delimed or decalcinated, will contain varying quantities of alkali.

Another object of the pickling process is to stabilize reaction of the pelts on the acid side, so as to create favorable conditions in the initial stages of the mineral-tanning process.

Hides or pelts to which acids are chemically bound have a lower affinity to tanning mineral salts than hides which are chemically neutral. Tanning is rendered more gentle by proceeding in the aforesaid manner and "drawing of the grain" and other leather defects are eliminated. The salt contained in the pickled pelts also has the same effect.

Strong mineral acid solutions result in pronounced swelling of the hides. This swelling can be reduced by adding a neutral salt, e.g. sodium chloride, which functions to dehydrate the functional hide-groups ionized by the acid.

It is necessary to adapt the amount of acid used in the

pickling process to the nature of the pretreatment to which the hide or pelt has been subjected, and also to the type of leather to be produced and to the subsequent tanning process. Mineral acid, for instance sulfuric acid, is used in quantities which range from 0.5-2 percent, based on the weight of the pelt. The amount of salt required is normally about 10 percent calculated on the weight of the pelt. The salt-concentration should not be less than 5 percent, since a weaker salt solution than 5 percent is unable to prevent acid-swelling totally.

By basifying ("Abstumpfung") is meant increasing the acid pH-value, necessary in the initial stage of a mineral-tanning process, to a weaker acid range.

Furthermore, it is desired to convert to tanning-active carboxyl anions those carboxylic groups which are responsible for binding the mineral-tanning substances to the fibers of the hide. At the same time, the anions present in the mineral-tanning substance complex shall be exchanged for hydroxyl ions ("masking"), thereby resulting in a condensation reaction between the complex mineral-tanning substance bound to the fibers of the hide ("Verolung").

This condensation reaction results in cross-linking within the hide and therewith in stabilization of the hide fibre-network (tanning).

Basification is achieved either by adding more or less strongly basic reacting salts (e.g. $NaHCO_3$, HCOONa, MgO) or not-readily dissolved but acid-soluble salts (e.g. MgO, $MgCO_3$) already present in the mineral tanning substance.

An object of the present invention is to provide a method in which hides can be tanned with mineral tanning substances in the absence of pickling and basifying ("Abstumpfen") processes.

Another object of the invention is to reduce the quantities of salt, acid and non-bound mineral tanning substances contained in the waste water discharged from tanneries to the recipient.

Another object is to provide a method of treating hides with which tanning can be effected satisfactorily with smal-

ler quantities of mineral tanning substances, by more efficient use of said substances.

These objects are achieved in accordance with the invention with a method of treating delimed and bated hides which replaces pickling and renders basification ("Abstumpfung") unnecessary in the subsequent mineral tanning process. The method is characterized by washing the bated hides once or a number of times with a slightly acid washing liquid which contains carbon dioxide, and subsequently treating the drained washing liquid with (powderous mineral tanning substance) in or without liquid, optionally while adding carbon dioxide and/or small quantities of acid. The amount of liquid present can be increased during the tanning process. Preferred embodiments of the invention are defined in the Claims dependent on the independent Claim.

Normally, deliming and subsequent bating of the hides is effected in horizontal rotating drums. Upon completion of the bating process, the treatment liquid is allowed to drain-off the pelts, i.e. the dehaired, softened, delimed and bated hides.

The pelts are then washed once or a few times at room temperature with 50-200 percent, wherein 0.2 to 0.5 percent of an acid, preferably formic acid, diluted with water to a ratio of 1:10 is added in order to avoid the risk of the pelts swelling.

Because the alkali present in the hides quickly neutralizes the acid added to the system, and in order to bind residual quantities of calcium or magnesium compounds present in the hides or in the treatment liquid, either a carbon-dioxide generating substance or a gas which contains carbon dioxide, preferably pure carbon dioxide, is added to the rotating drum when commencing the washing process. The gas can be introduced directly into in the liquid and dissolved therein or delivered over the liquid surface (for instance through a hollow drum axis), said gas being dissolved in the liquid as a result of drum rotation.

The carbon dioxide is added in an amount of 0.5 to 5 percent by weight of the weight of the pelt. The washing time

may vary from 15 to 60 minutes, although shorter or longer periods are not excluded at times. The washing process can be carried out once or a number of times, although the pH of the washing liquid shall lie between 4.0 and 6.0, normally between 4.3 and 5.3, and particularly between 4.6 and 4.8, upon completion of the wash.

The washing liquid is drained-off and the pelts therewith dewatered after each washing stage.

0 to 30 percent water, normally 10 percent, is charged to the drum containing the dewatered pelts; when the pH value of the latest washing liquid that has drained off is above 5, it is suitable to add 0.1 to 0.3 percent acid, normally 0.2 percent formic acid, to the treatment liquid. The treatment liquid may contain additions of water-soluble fats or water-emulsifiable fats (German: "Lickeröle") in a quantity of up to 4 percent of the weight of the pelts.

At the same time, tanning salts of low basicity are added to the treatment liquid in an amount of 0.5 to 2 percent, preferably 1 percent, said salts normally being alum compounds or commercially available sulphate-masked mineral tanning substances having a basicity of at most 33 percent. As the drum containing the pelts, the addition chemicals and possibly also the treatment liquid rotates, a gas containing carbon dioxide, for instance gaseous carbon dioxide, is charged to the drum. The carbon dioxide can be introduced, for instance, directly into the treatment liquid or over the surface thereof, said gas dissolving in the liquid as a result of drum rotation. The carbon dioxide is added in an amount corresponding to 0.5 to 5 percent by weight of the weight of the pelts. The treatment time is 0.5 to 3 hours, but may be longer or shorter in certain cases.

A sufficiently large quantity of treatment liquid is obtained even when using small quantities of treatment liquid, as a result of the liquid that is given up by the water-sodden delimed pelts.

When the drum containing the pelts and the treatment liquid has rotated for a time period of from 30 to 60 minutes, a commercially available sulphate-masked mineral-tan-

ning substance having a basicity of 0 to 50 percent is introduced into the drum in an amount of 10 percent. When the amount of treatment liquid produced in the drum is very small, 10 to 30 percent treatment liquid can be added to the drum, together with the tanning substance, said additional treatment liquid optionally containing an acid in an amount of 0.1 to 0.5 percent by weight.

The drum is allowed to rotate while continuing the supply of carbon dioxide, until the tanning substance has completely penetrated the hides present in the drum. This normally takes from 1 to 4 hours.

The supply of carbon dioxide to the drum is interrupted, when the tanning substance has soaked through the hides ("durchgegerbt"). At the same time, the amount of treatment liquid present is increased, by adding water, in an amount of 20 to 100 percent, calculated on the weight of the hides corresponding to the conventional tanning method. The temperature of the treatment liquid can be increased from 30° to 40°C, by supplying energy to the system or through the heat generated by friction.

The tanning drum is then allowed to rotate for at least a further hour. It is preferred, however, to continue the method for a longer period of time, normally from 4 to 8 hours, preferably over night, so as to improve the take-up of tanning substances. The drum is preferably rotated discontinuously and, for instance, at most for 5 minutes in each hour.

Upon completion of the treatment process, the thus treated ("tanned") pelts can be further processed in a conventional manner.

Example

Subsequent to bating hides, the bating liquid was emptied from the treatment drum and 100 percent water, calculated on the weight of the pelts, was added to the hides, or rather the pelts, present in the drum. The water contained 0.2% formic acid (HCOOH). The drum was then rotated for 30 minutes. At the same time, carbon dioxide was introduced through the hollow shaft of the drum at a flow rate of 5

liters per minutes.

At the end of this drum-rotation period, the washing liquid was allowed to drain-off and the washing stage described in the previous paragraph was repeated. The liquid was found to have a pH = about 4.8 upon termination of the 30-minute long rotation period in the second stage. This washing liquid was also allowed to drain-off.

10 percent water, 0.2 percent formic acid and 2 percent technical chromium alum [$KCr(SO_4)_2:xH_2O$] in powder form. The treatment drum was then rotated for 30 minutes, during which time carbon dioxide was introduced to the drum through the hollow shaft at a flow rate of 5 liters per minute.

3 percent of a commercially available sulphate-mask chromium tanning substance having a basicity of 33 percent was then introduced into the drum, in powder form. This chromium preparation is retailed, for instance, under the designations CHROMOSAL B, CUTRICHROM, BASOCHROM. The treatment drum was then rotated for a further 60 minutes, while introducing gaseous carbon dioxide to the drum. The treatment liquid had a pH = 3.9 upon completion of this treatment process. The tanning substance was found to have completely penetrated the pelts present in the tank in the drum.

50 percent water (calculated on the weight of the hides) having a temperature of 30°C was then introduced into the drum and the supply of carbon dioxide was interrupted and the drum rotated for a further 60 minutes. The pelts were left in the drum over night, in order to improve the take-up of tanning substance, the treatment drum being rotated each hour over a total time of 60 minutes.

The wet blue produced in this way could then be further treated in a conventional manner to produce leather of a quality comparable with the quality of leather produced by conventional processes.

Upon completion of the inventive treatment process, the chromium content of the treatment liquid was found to be less than 0.5 g Cr_2O_3 per liter. The residual chromium in solution in the treatment liquid could be precipitated substantially quantitatively, by simple alkalization of the treatment

liquid to a pH = 8.5, without adding flocculation agents.

Leather analyses were carried out on crusts obtained with the present inventive method and these analyses were compared with the analyses of industrially produced crusts.

To this end, wet blues obtained in accordance with the present inventive method were transported to a tannery and there further treated together with wet blues produced conventionally in said tannery.

The tannery produces upper leather for shoes. Deliming was carried out in a conventional manner, with ammonium sulphate, and 5 percent BAYCHROM-tanning substances were used in the tanning process. The analysis results are set forth in the following Table.

Table

	Aga-crust	Convent. crust
Ash content in percent	2.99-3.15	3.91-4.19
Cr_2O_3-content in percent	2.59-2.83	3.16-3.27
pH-value	3.96	3.95
Thickness in mm	1.58-1.85	1.69-1.94
Tensile strength in daN/cm^2	110-133	102-141
Elongation in percent	72-80	70-78

CLAIMS

1. A method of treating delimed and bated hides or pelts in a manner to bring said pelts to a state suitable for mineral tanning, and for tanning said pelts with a mineral tanning substance, **characterized** by treating the pelts in a treatment vessel, for instance a drum, with a wash liquid containing a small quantity of acid; by supplying carbon dioxide to said liquid during the treatment process; draining the washing liquid from said pelts; optionally repeating the treatment with washing liquid once or a number of times; finally draining washing liquid from the pelts and tanning said pelts with a mineral tanning substance.

2. A method according to Claim 1, **characterized** by repeating the treatment with washing liquid from 1 to 3 times.

3. A method according to Claim 1 or 2, **characterized** in that the washing liquid constitutes 50-200 percent of the weight of the pelts.

4. A method according to one or more of Claims 1-3, **characterized** in that the washing liquid is water and that said water contains 0.2-0.5 percent acid, preferably formic acid.

5. A method according to one or more of Claims 1-4, **characterized** by adding to each washing step carbon dioxide in an amount corresponding to 0.5-5 percent of the weight of the pelts.

6. A method according to one or more of Claims 1-5, **characterized** in that the washing time is 15-60 minutes.

7. A method according to one or more of Claims 1-6, **characterized** by adding tanning salts to the pelts subsequent to the last washing-liquid draining step.

8. A method according to Claim 7, **characterized** in that the tanning salts are in powder form.

9. A method according to Claim 7 or 8, **characterized** in that the tanning salts are slightly basic or non-basic sulphate-masked salts which have a slight basicity or no basicity at all.

10. A method according to one or more of Claims 7-9, **characterized** in that the tanning salts are added in a quantity of

between 0.5-2 percent by weight, preferably between 0.8-1.2 percent by weight calculated on the weight of the pelts.

11. A method according to one or more of Claims 7-10, **characterized** in that together with the tanning salts, treatment liquid is added in an amount corresponding to 0-30 percent by weight, preferably 10 percent by weight calculated on the weight of the pelts.

12. A method according to Claim 11, **characterized** by adding acid to the treatment liquid in an amount corresponding to 0.1-0.3 percent by weight, preferably 0.2 percent by weight, calculated on the weight of the hides.

13. A method according to Claim 11 or 12, **characterized** by adding to the treatment liquid carbon dioxide in the form of a carbon-dioxide-containing gas or a carbon-dioxide-producing substance.

14. A method according to Claim 12 or 13, **characterized** by rotating the treatment vessel subsequent to adding the tanning salts and while adding said carbon dioxide, such as to bring the pelts in rotation in said vessel, and maintaining said rotation for a period of from 0.5 to 2 hours, preferably for 1 hour.

15. A method according to Claim 14, **characterized** in that further tanning salts are added in an amount of 1-4 percent upon completion of said rotation time, whereafter the supply of carbon dioxide and rotation of the vessel is continued for 1-4 hours.

16. A method according to Claim 15, **characterized** by thereafter interrupting the supply of carbon dioxide and adding water in an amount of 20-100 percent, preferably 40-50 percent calculated on the weight of the pelts, under continued rotation of said vessel for at least 1 hour.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00652

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 14 C 1/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 14 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	WO, A1, 8810317 (AGA AKTIEBOLAG ET AL) 29 December 1988, see page 3, line 1 - line 9; page 4, line 2 - line 5; page 6, line 10; page 7, line 15 - line 27; claims 1,7,8,11	1,2,5,6, 13,14
A		3,4,7-12,15, 16
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A	DE, C1, 3827382 (MESSER GRIESHEIM GMBH) 24 May 1989, see claim 1	1-16
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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21st December 1990	1991 -01- 15
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Inga-Karin Petersson Inga-Karin Petersson

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 90/00652

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 90-11-28
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		EP-A-	0357682	90-03-14
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