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(54) **Tanning of hides and skins**

(57) Methods of tanning hides or skins are disclosed, the methods comprising a fruit tanning step of contacting, for a predetermined time and at a predetermined temperature, a hide or skin with a tanning liquor comprising a fruit tanning extract. The preferred fruit is of the family

Maloideae, preferably apple. Also disclosed are leathers obtainable by the methods, products comprising the leathers and methods for producing fruit tanning extracts.

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Description**Field of the Invention**

5 **[0001]** The present invention relates to methods of tanning hides or skins, to leathers obtained by the methods and to methods of extracting tanning extracts from fruit.

Background of the Invention

10 **[0002]** Tanning of hides or skins to produce leather is an ancient process that takes advantage of the property of hides or skins that they absorb tanning chemicals that prevent putrefaction, increase resistance to moisture and promote suppleness.

15 **[0003]** The tanning process involves the reaction of the tanning chemicals with collagen fibres present in the hide or skin. The most common tanning chemicals are chromium based compounds (e.g. chromium sulfate), synthetic tanning chemicals, alum, aldehydes (e.g. formaldehyde) and vegetable tanning compositions.

20 **[0004]** Vegetable tanning compositions are composed of polyphenolic compounds, with the tanning properties related to the size of the molecule and the number of phenolic -OH groups. Vegetable tanning compositions are sometimes referred to as "tannins". Although the term "tannin" refers to the ancient use of some tannins in the tanning process, the term is now widely applied to any plant-derived large polyphenolic compound containing sufficient hydroxyls and other suitable groups (e.g. carboxyl groups) to form strong complexes with macromolecules whether or not such compounds have previously been used to tan hides or skins.

25 **[0005]** Vegetable tannins used in tanning are derived from tree bark, in particular, the bark of oak, chestnut, quebracho and mimosa.

30 **[0006]** There is a need for improved tanning processes that have a lesser environmental impact and yet still provide leather of good quality.

35 **[0007]** It is an object of the present invention to address this need.

Summary of the Invention

40 **[0008]** The present invention accordingly provides, in a first aspect, a method of tanning hides or skins, the method comprising a fruit tanning step of contacting for a predetermined time and at a predetermined temperature, a hide or skin with a tanning liquor comprising a fruit tanning extract.

45 **[0009]** The advantage of using a fruit tanning extract is that it is possible to use fruits which are readily available and do not involve the felling, for example, of trees but are an annually renewable resource.

50 **[0010]** Preferably, the fruit is an edible fruit. This is advantageous because edible fruits are produced in large quantities and a large amount of edible fruit waste is available.

55 **[0011]** Generally, the fruit will be a fleshy fruit.

60 **[0012]** The most preferred fruits are of the family Rosaceae, in particular subfamily Maloideae (also known as Pomoidae).

65 **[0013]** Maloideae fruits are produced in large quantities throughout the world and typically contain relatively large quantities of polyphenolic compounds. The most preferred fruit is, therefore, a pome, even more preferably an apple. Apples are known to contain polyphenolic compounds, including quercetin, catechin, gallic acid, phloretin and chlorogenic acid. Surprisingly, it has been discovered that these compounds have properties that make them suitable for use in tanning of hides or skins. Apples are particularly advantageous because the apple, apple juice and cider industries (cider being an alcoholic beverage produced from apples) produce large quantities of apples and waste products, much of which will contain these polyphenolic compounds.

70 **[0014]** The content of polyphenolic compounds in apples depends very much on the variety of the apple, as well as climate and other growing conditions. Typically, apples grown under low nitrogen regimes or adverse weather conditions tend to contain more polyphenolic compounds. These compounds are also increased in amount if nutrients are restricted during the growing season of the apple. There is also a possibility of using unripe apples which typically contain higher quantities of the polyphenolic compounds.

75 **[0015]** The preferred type of apple is a cider apple. The use of cider apples is advantageous because many cider apples contain high quantities of polyphenolic compounds and also because, typically, the flesh of the apple has a fibrous texture making it easier to extract the juice.

80 **[0016]** There are a large number of traditional cider apple varieties grown in, for example, England. Of these varieties, the preferred varieties for use in the method of the present invention are bittersweet and bittersharp cider apples. Bittersweet apples impart the characteristic flavour of English West Country ciders and are typically low in acid and high

in polyphenolic compounds (the "tannin" component of the cider). Bittersweet apples are relatively high both in acid and polyphenolic compounds. Examples of varieties of bittersweet or bittersweet apples include Michelin or Dabinett.

[0017] Preferably, the method of the present invention further comprises one or more further tanning steps. These tanning steps may be vegetable or synthetic tanning steps and may take place either before or after the fruit tanning step.

[0018] The method may also further comprise one or more of the following steps after the fruit tanning step: neutralisation, fatliquoring, fixation and finishing. Similarly, the method may comprise one or more of the following steps before the fruit tanning step: soaking, liming and/or dehairing, fleshing, splitting, pickling, salting and shaving.

[0019] In a preferred embodiment of the present invention, the fruit tanning step is a fruit retanning step. In this embodiment, the fruit tanning step takes place after a first tanning step which, as discussed above, may involve a vegetable (e.g. chestnut, oak, mimosa or other tree bark or wood extract) or synthetic tanning agent.

[0020] There may be one or more tanning steps before the fruit retanning step.

[0021] The tanning liquor also, preferably, comprises one or more vegetable or synthetic tanning agents in addition to the fruit tanning extract. Typically, the fruit tanning extract would be between 20 and 60% of the tanning liquor usually by weight, occasionally by volume. Preferably, the fruit tanning extract would be between 25 and 50%, more preferably between 25 and 40% of the tanning liquor. If dried fruit tanning extract were to be used then the dried (e.g. spray dried) fruit tanning extract would be between 5 and 25% preferably 5 and 20% and most preferably 5 and 15% of the tanning liquor by weight.

[0022] It is advantageous if the predetermined time involved in the fruit tanning step is from 6 hours to 48 hours, preferably from 6 to 36 and more preferably from 12 to 24 hours. The predetermined temperature is preferably from 25 to 85°C, more preferably from 25 to 50°C, most preferably from 25 to 40°C.

[0023] In the method according to the invention, the fruit tanning extract is preferably obtainable by aqueous extraction of pulped fruit at elevated temperature. Alternative extraction methods which may be used include solvent extraction or aqueous extraction by boiling under pressure.

[0024] The benefit of aqueous extraction at elevated temperature not under pressure is primarily one of cost but it also reduces the likelihood of degradation of the polyphenolic compound in the fruit extract.

[0025] The elevated temperature is preferably between 40 and 100°C, more preferably between 50 and 80°C and most preferably between 50 and 75°C.

[0026] The pulped fruit from which the fruit tanning extract is obtained in the most preferred embodiment is apple pomace either before or after pressing of the juice for cider. The apple pomace may be either wet pomace or dried pomace (e.g. spray dried pomace) or a mixture of the two.

[0027] In a second aspect of the present invention, there is provided leather obtainable by a method as discussed in relation to the first aspect.

[0028] Products produced using the leather obtainable by the methods of the present invention find use in many applications including in footwear (e.g. shoes and boots), other articles of clothing, upholstery, luggage or item holders or other uses of leather products.

[0029] In a third aspect of the present invention, there is provided a method for producing a fruit tanning extract, the method comprising:

providing fruit,
pulp the fruit,
contacting the fruit with water at an elevated temperature for a predetermined extraction time,
adding a preservative,
optionally, filtering and/or sieving, and
optionally, drying the fruit tanning extract.

[0030] The elevated temperature is as discussed in relation to the first aspect of the present invention and will generally be between about 40 and 100°C. The predetermined extraction time is typically 1 to 4 hours, preferably 2 to 3.5 hours, most preferably 2 to 3 hours. On completion of the extraction, preservative (usually less than 0.5% by weight, more preferably less than 0.1% by weight) is added to the extract to reduce the potential for putrefaction. The preservative may include one or more biocides (for example, Myacid AS) or fungicides.

[0031] Optionally, the fruit tanning extract may be filtered and/or sieved after extraction. Optionally, the fruit tanning extract may be dried after the optional filtering or sieving process. Methods of drying include those known to the skilled person and include spray drying or other methods of evaporative drying or freeze drying, the most preferred drying method is spray drying.

Detailed description of the invention

[0032] The invention will now be further illustrated by a detailed description of a method of tanning bovine hides using

fruit tanning extracts derived from apples.

[0033] In cider production, apples are washed prior to milling (comminution) so that leaves, twigs, silt etc. are removed. The wet pomace waste after pressing is unstable and susceptible to microbiological attack, and so it is usually spray dried within minutes of pressing to prolong storage time. The waste requires dry storage in a darkened room/area to avoid oxidation by light.

[0034] Trials were carried out using simple aqueous extraction of wet or dry apple waste by heating in water at 70°C, aqueous extraction under pressure and solvent extraction. The tannin content was measured using the Official SLTC method and the Lowenthal Permanganate Titration method (as used in the cider industry). There is a difference in the tannin content between the wet and dry apple wastes. The results showed that for the dry apple waste (using the Lowenthal Permanganate Titration) the tannin content is about 0.06% by weight compared to about 0.04% by weight for the wet apple waste.

[0035] There was no advantage in using the more expensive routes of extraction by aqueous boiling under pressure or solvent extraction (using e.g. toluene) so simple heated water extraction (70°C) was chosen. This aqueous system gives several environmental advantages including avoiding the need to remove the solvent by distillation and keeping the COD lower.

Method for tannin extraction

[0036] The spray dried apple waste is weighed and introduced into a tanning processing drum. 700% of water (relative to the weight of apple waste) is added at 74°C and the drum is run to obtain a homogenous mix. After 5 min the temperature is checked and a further 120% of water at 80°C is added. At this stage the extract is a viscous slurry at temperature of 60°C. The process is run for a further 2.5 hours with continuous monitoring of temperature and appearance.

[0037] On completion of the extraction, 0.08% of biocide (Myacid AS) is added to reduce the potential for putrefaction. The process is run for a further 10 min and left overnight to cool.

[0038] The following day, the drum is run for 10 min to re-mix the extract which is then filtered using either an Archimedeian screw technique or filter press. To avoid putrefaction, a further 0.04% of biocide and 0.04% of fungicide are added to the final extracted liquid. In total 80 kg of dried pomace results in about 220 kg of liquid tannin extract being obtained with a moisture content of 96% by weight and 4% unfiltered solids. Analysis (of the liquid phase) indicated a tannin content of 1-2 weight %.

Tanning Process

[0039] The liquid tannin extract obtained from the apple extraction is used in combination with vegetable tannins and syntans to tan bovine hides to produce leather.

1. Preparation

[0040] The hides are prepared for tanning using the conventional beamhouse process of soaking, liming, fleshing, splitting, and pickling. They are then sammed and shaved to 1.1 - 1.2 mm substance and placed into a drum containing 150% water and 0.5% oxalic acid to minimise the iron staining. They are washed with water at 20°C and are ready for tanning.

2. Tannage

[0041] During the tanning process the collagen fibre is stabilized and converted to leather by the cross-linking action of the tanning agents rendering the hide no longer susceptible to putrefaction. Tanning also increases the tensile strength and heat resistance.

[0042] Following the washing process, the hides are pretanned using 70% water, 2% Paralene PGS and 2% Sellasol SL. These syntans assist penetration of the vegetable tanning chemicals. This is followed by the main vegetable tannins using 10% Quebracho ATO, 5% Mimosa and 5% Chestnut. This process lasts for 60 min at 20°C.

3. Apple re-tannage

[0043] Following this main tannage, the apple retanning is carried out in a separate process using 100% water, 45% liquid apple tanning extract, 5% Chestnut, 5% Fitapor GT, 1.5% of Manacryl SRG and 1% of Dermadol ID. Thus a blend of apple tannin and conventional vegetable retanning agents and a resin retannage are used. This process takes place at 30°C for 6 hours and is then run intermittently overnight (5min/hour). The retanning process improves the feel and handle of the leather, fills the looser parts of the leather, improves the resistance to alkali, perspiration and general wear

characteristics.

4. Neutralisation

- 5 **[0044]** Following retannage, a light oxalic acid wash is given again to minimise the risk of iron staining, using 100% water at 30°C and 0.5% oxalic acid for 30 min. This is followed by neutralisation with 50% water at 40°C, 2% sodium formate and 4% Dermaflex FR/C to obtain pH 4.5-4.8. This assists penetration of the subsequent fatliquoring.

5. Fatliquoring

- 10 **[0045]** The fatliquoring is a combination of 8% Dermadol BK, 3.5% Dermadol MC, 1.5% Dermadol ID and 5% Tresin ML Liq for 60 min. Leathers are fatliquored to lubricate the fibres and achieve product-specific characteristics of softness and drape.

15 6. Fixation

[0046] At the end of the process, the leathers are given a last oxalic acid wash and a little syntan to dry the surface. The final treatment is fixation of the chemicals with 1% Remsol ALM and 1% formic acid.

- 20 **[0047]** The process of steps 1 to 6 is further described in Table 1.

7. Finishing

- 25 **[0048]** To enhance the appearance of the leather and provide the performance characteristics expected, finishing operations are carried out. A range of mechanical finishing operations such as buffing/dedusting, dry milling (mechanical softening) and polishing are carried out. A surface coat is also applied to provide protection, hand feel, colour and gloss and to meet the customer requirements.

8. Leather produced by the process

- 30 **[0049]** Leather produced by the method according to the invention is of excellent quality with very similar properties of suppleness and other properties to leather produced using a conventional process.

Spray drying of liquid tanning extract

- 35 **[0050]** Trials were conducted using liquid tanning extract which had been spray dried. A sample of 5 kg of apple liquid tanning extract was spray dried producing approximately 50 g of spray dried extract. The spray dried extract may be used in the tanning process in place of the liquid tanning extract, with important advantages in reducing dilution and hence allowing an increased fruit tannin content in the tanning process.

Table 1: Tanning process

Step n° Operation	chemical	%	Time min	T (°C)	pH	Comments
	Water	150		20		
	Oxalic acid	0.5	20			
45 Drain and wash						
	Water	70		20		
	Paralene PGS	2				
50	Sellazol SL	2	30			
tannage						
	Quebracho ATO	10				
	Mimosa	5				
55	Chestnut Bark	5	60	20		

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(continued)

	tannage					
5	Drain					
	Retan					
	Water	100				
	Apple Extract	45				
10	Chestnut Bark	5				
	Fitapor GT	5				
	Manacryl SRG	1.5				
15	Dermadol ID	1	6 hours + 5 min/hour	30		Run automatically overnight
	Drain					
20	Water	100		30		
	Oxalic acid	0.50				
	Drain and wash					
	Neutralise					
25	Water	50		40		
	Sodium formate	2				
	Dermaflex FR/C	4	15			pH 4.5 - 4.8
30	Fatliquor					
	Dermadol BK	8				
	Dermadol MC	4				
	Dermadol ID	2				
35	Tresin MG Liq	5	60			
	Oxalic acid	0.3				
40	Retan					
	Remsol ALM	1	15			
	Fixation					
45	Formic acid	1	20			

Claims

- 50 1. A method of tanning hides or skins, the method comprising,
a fruit tanning step of contacting, for a predetermined time and at a predetermined temperature, a hide or skin with
a tanning liquor comprising a fruit tanning extract.
2. A method as claimed in claim 1, wherein the fruit is an apple.
- 55 3. A method as claimed in claim 2, wherein the fruit is a cider apple.
4. A method as claimed in any one of the preceding claims further comprising one or more further tannage steps.

5. A method as claimed in any one of the preceding claims, further comprising one or more of the following steps after the fruit tanning step: neutralisation, fatliquoring, fixation and finishing.

6. A method as claimed in any one of the preceding claims further comprising one or more of the following steps before the fruit tanning step: soaking, liming and/or dehairing, fleshing, splitting, pickling, samming and shaving.

7. A method as claimed in any one of the preceding claims, wherein the fruit tanning is a fruit re-tannage step.

8. A method as claimed in claim 7, further comprising one or more tannage steps before the fruit re-tannage step.

9. A method as claimed in any one of the preceding claims, wherein the tanning liquor also comprises one or more vegetable or synthetic tanning agents.

10. A method as claimed in any one of the preceding claims, wherein the predetermined time is from 6 hours to 48 hours.

11. A method as claimed in any one of the preceding claims, wherein the predetermined temperature is from 25 to 85°C.

12. A method as claimed in any one of the preceding claims, wherein the fruit tanning extract is obtainable by aqueous extraction of pulped fruit at elevated temperature.

13. Leather obtainable by a method as claimed in any one of claims 1 to 12.

14. A product comprising leather as claimed in claim 13.

15. A method for producing a fruit tanning extract, the method comprising:

providing fruit

pulping the fruit,

contacting the fruit with water at an elevated temperature for a predetermined extraction time,

adding a preservative,

optionally, filtering and/or sieving, and

optionally, drying the fruit tanning extract.



EUROPEAN SEARCH REPORT

Application Number
EP 08 15 4833

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	FR 926 892 A (PERFECTIONNEMENTS IND SOC ET) 14 October 1947 (1947-10-14) * page 1, line 43 - page 2, line 47 * * page 2, line 87 - page 3, line 17 * -----	1,4-6, 10-14	INV. C14C3/10
X	DE 905 054 C (C F ROSER G M B H) 25 February 1954 (1954-02-25)	1,5,6, 10,11, 13,14	
A	* page 1, line 1 - page 2, line 47 * -----	3,4,7,8	
X	DATABASE WPI Week 200275 Thomson Scientific, London, GB; AN 2002-693877 XP002496059 & JP 2002 180099 A (TEIKOKU KASEI KOGYO KK) 26 June 2002 (2002-06-26) * abstract * -----	1,5,6, 9-14	
			TECHNICAL FIELDS SEARCHED (IPC)
			C14C
3 The present search report has been drawn up for all claims Place of search Munich Date of completion of the search 17 September 2008 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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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:

1-14

☐ 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 08 15 4833

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: 1-14

Method of tanning hides or skins comprising contacting a hide or skin with tanning liquor comprising a fruit tanning extract (claim 1); Leather obtainable by said method (claim 13); a product comprising said leather (claim 14).

2. claim: 15

Method for producing a fruit tanning extract.

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

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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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17-09-2008

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 926892	A	14-10-1947	NONE	
DE 905054	C	25-02-1954	NONE	
JP 2002180099	A	26-06-2002	NONE	