

(19)



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(11)

EP 1 520 911 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

06.04.2005 Bulletin 2005/14

(51) Int Cl.7: **C14C 9/02**, C14C 13/00

(21) Application number: **03425647.9**

(22) Date of filing: **03.10.2003**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**

Designated Extension States:

AL LT LV MK

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(54) **Method for manufacturing leather**

(57) The present invention relates to a method for manufacturing leather starting from natural raw hides, preferably of bovine and ovogoaty origin, the leather obtained from this method having an improved combination of characteristics of softness, waterproofing, elasticity, fulness to touch, colour solidity and fastness,

washability, fastness to light and to fading. This leather can advantageously be used in the manufacturing of clothing items, footwear, leather goods and furnishing without requiring further specific finishing interventions.

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Description

Field of Application

[0001] In its more general aspect, the present invention relates to the treatment of raw hides for manufacturing leather destined to be used in clothing items, footwear, leather goods, etc.

[0002] In particular, the present invention relates to a method for manufacturing a leather having an improved combination of characteristics that make it particularly suitable for the above uses.

Prior Art

[0003] Several methods for manufacturing leather from raw animal hides are known in the art. As a general rule, these methods comprise three manufacturing steps.

[0004] In the first manufacturing step, the raw hides undergo a series of treatments having the aim of smoothing and cleaning them so as to make them suitable for being tanned.

[0005] The treatments of this first manufacturing step generally include:

- soaking the preserved hides in water in order to recover the umidity lost during their conservation and to remove water-soluble materials such as salts, blood, etc..
- dehairing and liming by treating the hides in suitable dressings with calcium hydroxide and sodium sulphide,
- deliming, i.e. treating the hides with weak acid solutions or salts thereof in order to remove the residual calcium hydroxide,
- treating the hides with enzymatic products (so called "bating") with the aim of removing residual parts (residual hairs and relevant roots) thus smoothing and cleaning the hides and making them suitable for being tanned.

[0006] In the second manufacturing step, the cleaned hides are tanned according to any of a variety of conventional methods. Typically the hides are tanned by using a tanning agent of the mineral or vegetal type. In the tanning with a mineral agent, the hides are first treated with a saline and acid solution (so called pickling) and then with a solution of the tanning agent (e.g. chromium sulphate) containing additives facilitating the fixing of the tanning agent to the hide.

[0007] Instead, in the tanning with a vegetal agent (typically tannin), the hides are generally first treated with a solution containing tannin and suitable additives and then with an acid solution facilitating the fixing of

the tannin to the hide and the removal of the residual tannin.

[0008] At this stage the third manufacturing step begins, wherein the tanned hide may undergo a variety of treatments according to the final destination of use and to the desired characteristics to be conferred to the hide itself. For example the hide can be lubricated with a suitable mixture of fats and oils to improve for instance its characteristics of softness, and it can be dyed by using any of the conventional methods known to the skilled in the art.

[0009] According to the used dyeing method, also washing characteristics can be conferred to the hides, these characteristics giving the possibility of subjecting the hide to a washing treatment with common household means without incurring in dye release for example on possible fibres coupled with the hide itself.

[0010] In some cases, the hides also undergo a retanning treatment for introducing further additives able to confer to the hide additional characteristics, e.g. waterproofing, fulness to the touch, etc. and/or to enhance the previously conferred characteristics.

[0011] Although a great deal of methods for treating raw hides for obtaining a leather having one or more characteristics chosen for example among softness, fulness to the touch, waterproofing, washability, elasticity, colour fastness, etc. are thus available to the skilled in the art, it is anyway difficult at present to manufacture a leather having a suitable combination of these characteristics.

[0012] In fact, the suitable conferment of these characteristics to the final leather is reached only by accurately controlling a complex series of variables involved by the manufacturing method among which the nature of the additives and solutions used in the various manufacturing steps, pH of the treatment solutions, treatment times, etc..

[0013] There is thus the need of providing a method for manufacturing leather allowing to confer to the finished product improved characteristics with respect to those conferred by state-of-the-art methods. In particular, there exist the need of providing a washable dyed leather having at the same time good characteristics of softness, fulness to the touch, fastness of the colour, waterproofing and elasticity.

[0014] The problem underlying the present invention is that of providing a method for manufacturing leather satisfying all the above needs.

Summary of the invention

[0015] Such a problem is solved, according to the invention, by a method for manufacturing washable leather comprising the preparation, in a conventional way, of tanned hides starting from raw hides and characterised in that it comprises the following additional steps of:

- a) subjecting the tanned hides to retanning,

b) subjecting said retanned hides to at least a lubrication treatment with an emulsion obtained by mixing 70-90 parts by weight of an organic phase constituted of synthetic hydrophobic oils and 10-30 parts by weight of a watery phase constituted of an emulsion of silicone compounds.

c) subjecting said retanned and lubricated hides to dyeing with a dyeing agent possibly in association with cationic acrylic resins,

d) subjecting the dyed hides obtained by step c) to a fixing treatment with a watery emulsion comprising silicone compounds and with metallic salts.

[0016] According to an embodiment of the invention, the method further comprises, before step b), at least one of the following steps:

- treating said retanned hides with a pH regulating agent so as to enhance the pH to a value of around 6-7,
- treating said retanned hides possibly after having enhanced their pH to 6-7 with a watery solution or watery suspension of acrylic resins.

[0017] In the method according to the invention, the preparation of tanned hides starting from raw hides includes the normal operations of cleaning the raw hides so as to get them ready for the tanning and the tanning treatment itself.

[0018] The operations of cleaning the raw hides can be carried out in a conventional way by following the above described procedures, which render the hides smooth, clean and hides ready for being tanned.

[0019] Preferably, the tanning is carried out by means of a chromium tanning agent so as to obtain hides of the type known as Wet Blue. Such hides can be subjected, before retanning, to a bleaching treatment with sodium hydrosulphite and oxalic acid, the latter as a reducing agent. Such bleaching treatment results being efficient to get rid of superficial dirt and thus it is preferable especially if, in the following manufacturing steps, a light dye is to be given to the hides.

[0020] In the method according to the invention, the bleaching treatment is preferably carried out by placing the hides in a conventional apparatus known as tumbler and thus by adding in sequence, the percentages by weight on the weights of the hides to be treated, 100-300% of water, preferably around 200%, 1-3%, preferably 2% by weight of anhydrous sodium hydrosulphate and 0,3-1%, preferably 0,5% of a conventional dislubricating agent chosen among fatty acids and soaps.

[0021] The tumbler is then placed in rotation for a period of around 30-90 minutes, preferably 60 minutes and, at the end of the rotation 0,7-1,5% by weight of

oxalic acid are added, preferably 1%. After having placed the tumbler again in rotation for around 30-60 minutes, preferably 40 minutes, an abundant washing with running water is then carried out.

[0022] In the method according to the invention, the retanning treatment of the hides, possibly having already been subjected to the above described bleaching treatment, is carried out in a conventional way, preferably by using a chromium tanning agent, e.g. powder oxide chromium.

[0023] Preferably, the retanning treatment is carried out by adding to the tumbler containing the hides to be treated, in percentages by weight on the weight of the hides, 50-200% of water, preferably around 100%, 5-6% of chromium oxide and 0,5-0,6% of sodium bicarbonate. Then the tumbler is placed in rotation for a period of 2-4 hours, preferably 3 hours and at the end of the rotation an abundant washing with running water is carried out.

[0024] In the method according to the invention, the enhancement of the pH of the retanned hides is preferably carried out by adding to the tumbler containing hides, in percentages by weight on the weight of the hides to be treated, 50-200% of water, preferably around 100% and 1,5-3%, preferably 2% of ammonium bicarbonate (pH regulator) so as to enhance the pH to a value of 6-7. Then the tumbler is placed in rotation for a period of 60-120 minutes, preferably 90 minutes and, at the end of the rotation an abundant washing with running water is carried out.

[0025] The enhancement of the acid pH typical of the retanned hides to a value around the neutrality advantageously allows to prepare the hides in the best way for the subsequent treating steps and it results to be particularly suitable for obtaining a good softness of the hides in said subsequent steps.

[0026] In the method according to the invention, the optional treatment of the retanned hides with the mixture of acrylic resins is preferably carried out in the tumbler containing the hides to be treated by adding therein, in percentages by weight on weight of the hides, 100-300% of water, preferably around 200% and 3-5% of a watery solution of acrylic resins.

[0027] Then the tumbler is placed in rotation for a period of 30-90 minutes, preferably 60 minutes and, at the end of the rotation, an abundant washing with running water is carried out.

[0028] Preferably, the acrylic resins useful in the method according to the invention are composed of polymers and co-polymers of the methacrylic acid, the percentage by weight of the resins in the solution is of around 40% and the pH of the solution is comprised between 4,2 and 5,5.

[0029] The treatment of the retanned hides with the mixture of acrylic resins advantageously confers to the hide the proper degree of fulness to touch.

[0030] A very important aspect of the present invention is given by the lubrication step (step b). In accordance with the present invention, such lubrication step is

carried out by treating the hides in a tumbler with an emulsion obtained by mixing under agitation 70-90 parts by weight on the total weight of the emulsion of an organic phase constituted of hydrophobic synthetic oils and 10-30 parts by weight of a watery phase constituted of an emulsion of silicone compounds.

[0031] The hydrophobic synthetic oils constituting the organic phase preferably have anionic character, i.e. they comprise anionic organic units. A preferred product for the organic phase is sold by Dermacolor s.r.l. with the name of DERMADOL W 300 and it comprises a mixture of syntetical oils able to confer waterproofing to the hide.

[0032] The silicone compounds constituting the emulsion of the watery phase are chosen from the group comprising silane and siloxane compounds and respective polymeric products of condensation. A preferred product for the watery phase is constituted of a watery emulsion of dimethylpolysiloxane.

[0033] Preferably, the emulsion used in the lubricating process is prepared in situ and it is used in percentages by weight on the weight of the hides to be treated comprised between 8% and 15%. After adding the emulsion to the hides, the tumbler is placed in rotation for a period of 60-120 minutes, preferably 90 minutes and, at the end of the rotation, an abundant washing with running water is carried out.

[0034] The above specified lubricating treatment confers to the hides characteristics of softness, waterproofing, transpiration and elasticity desired for the final application.

[0035] The lubricated hides as specified above are dried in a conventional way, e.g. by means of vacuum applications and windy conditioning for then being selected for the following manufacturing steps.

[0036] In accordance with a preferred embodiment of the invention, before subjecting the selected hides to dyeing (step c), it is preferred to carry out on the same a second lubricating treatment with the same emulsion used for the first lubrication.

[0037] Preferably, for the second lubrication treatment the emulsion is used in proportions from 2% to 8% by weight on the weight of the dried hides.

[0038] This second lubricating treatment allows to improve, i.e. enhancing, the characteristics of softness, waterproofing/transpiration and elasticity already conferred to the hides in the previous lubrication.

[0039] In the method according to the invention, the lubricated hides (in one or two steps as specified above) are then subjected to the dyeing treatment.

[0040] In accordance with the invention, the dyeing is carried out by adding to the hides to be dyed placed in a tumbler, 100-300% by weight on the weight of the hides of water and 1-6% by weight of a dyeing agent of a conventional type chosen according to the colour which is to be conferred to the final hide. The tumbler is then placed in rotation according to the normal dyeing times.

[0041] In accordance with a preferred embodiment of the invention, in the dyeing step, the hides are further treated with a solution containing 1-3% by weight of cationic acrylic resins.

[0042] These resins act as auxiliaries for dyeing, facilitating the fixing of the chosen dyeing agent to the hide and thus allow the improvement of the characteristics of fastness of the colour.

[0043] The dyeing is generally completed by a fixing step which allows to bind permanently in the pores of the hides all the chemical products used in the previous treatments (es. lubrication and dyeing).

[0044] In the method according to the invention, carrying out the fixing by treating the hides in a tumbler with a watery emulsion comprising silicone compounds and with metallic salts has resulted advantageous.

[0045] The silicone compounds are preferably chosen from the group comprising silane and siloxane compounds and their respective polymeric products of condensation whereas the nature of the metallic salts varies according to the chosen dyeing agent. Suitable metallic salts are chosen among chromium, aluminium and zirconium salts.

[0046] Preferably, the fixing treatment is carried out by adding in the tumbler containing the dyed hides, in percentages by weight on the weight of the hides, 100-300% of water, preferably 200%, 0,5-3% of silicone emulsion and 3-6% of metallic salts.

[0047] The leather obtained with the method according to the invention has high qualities and characteristics of softness, waterproofing, transpiration, elasticity, fullness to touch, colour fastness and stability, washability, fastness to light and to fading, which fully satisfy the standards required by the international rules in this field.

[0048] In particular, as regards the characteristic of colour fastness, which is strictly correlated with washability, it has surprisingly been discovered that the leather obtained according to the invention has mean values on the scale of the grey in the range of 4-5 as determined according to the international rule IUF 423.

[0049] According to this international rule, samples of dyed leather are coupled with particular non-dyed fabrics, agitated in a neutral solution of synthetic detergent and then rinsed and dried. At this stage the variations of colour on the samples as well as the degree of migration of the colour on the accompanying fabrics are evaluated by comparing them with the scale of the grey. The results are then expressed in values of the scale of the grey variable from 1 to 5 wherein a significant bleaching of the hide and/or a significant migration of the colour from the hide to the coupling fabric correspond to the minimum value of 1 whereas the maximum value of 5 is given to a leather that, at the end of the test, has no variation of the colour of the leather and/or colouring of the accompanying fabric.

[0050] In the case of the leather obtained according to the method of the invention, from washing tests on samples coloured with 50 different colours and associ-

ated with accompanying fabrics having fibres of materials chosen among cellulose acetate, cotton, nylon, polyester, acrylic fibres and wool, mean values have been detected in the range 4-5 both as regards the colour variation of the hide (colour fastness) and the dyeing of the accompanying fabric.

[0051] The leather according to the invention also has improved characteristics of transpiration and waterproofing. As regards transpiration, measures on samples of leather carried out according to the international rule IUP 15 have shown transpiration values (i.e. permeability to water vapour) higher or equal to 10 mg/cm² h and generally comprised between 10 and 15 mg/cm² h.

[0052] Instead, as regards waterproofing, measures on samples of leather carried out according to the international rule IUP 10 have shown values of resistance to the penetration of water comprised between 90 and 120 minutes with absorption of water varying from 10% to 15% by weight on the weight of the examined sample of leather.

[0053] The leather obtained according to the method of the invention also has excellent elasticity characteristics. In fact, from measures of resistance to the traction (e.g. by means of the rules ISO 3376 or IUP 6) a breaking load higher or equal to 12 N/mm² and a stretch higher or equal to 40% have been detected.

[0054] Without being linked to any scientific theory it is believed that the improvement of all these characteristics is reached thanks to the peculiarity of the treatment steps of the hides provided in the method according to the invention and to the peculiarity of the chemical compositions used in these treatment steps.

[0055] More particularly, it is believed that the improved characteristics of colour fastness, washability, fastness to light and to fading (characteristics strictly connected one another) are reached thanks to the use, during the dyeing steps, of dyeing agents selected together in association with cationic acrylic resins as auxiliaries of dyeing and of the peculiarity of the fixing of said agents to the hide.

[0056] In particular, the use of the above dyeing agents together with the auxiliaries of dyeing in the above described ways would allow the dyes themselves to adequately penetrate into the pores of the hides whereas by means of the fixing said dyes would form very strong chemical bonds with the hides in correspondence with active sites in their pores.

[0057] Instead, as regards the improvement of the characteristics of softness, waterproofing, transpiration and elasticity it is believed that such improvement is reached thanks to the use of the particular emulsions with their oily and watery phases used in the lubricating steps.

[0058] In particular, the use of these particular emulsions in the above indicated proportions and modes would allow a sufficient and uniform penetration of the hide by the fatty substances contained in the emulsions,

which fatty substances would thus form interactions of various type with the collagen matrix of the hide. The bond among fatty substances of the hide would be then highly reinforced during the fixing treatment thus ensuring to the hide the desired characteristics of softness, transpiration, waterproofing and elasticity.

[0059] The main advantage of the leather obtained through the method according to the invention lies in the fact that it can be efficiently subjected to washing with neutral detergent at a temperature of around 40°C without any substantial structural alteration of the hide (e.g. loss of elasticity and/or shrinking) and of the softness, and without any release and variation of colour.

[0060] Therefore, the leather obtained according to the invention is advantageously suitable for being used as it is alone or coupled to other natural or synthetic fibres for manufacturing washable items, e.g. in the field of clothing, footwear, leather goods and furnishing.

[0061] In this use, advantageously the leather does not need further specific finishing treatments.

[0062] The method according to the invention is efficiently applicable to all the raw hides of natural origin with particular reference to bovine and ovogoaty hides.

[0063] Obviously a skilled in the art can apply several modifications and variations to the above described method, in order to satisfy occasional and specific needs, all of them included in the scope of the invention, as defined in the following claims.

Claims

1. A method for manufacturing washable leather comprising the preparation, in a conventional way, of tanned hides starting from raw hides and **characterised in** the fact that it comprises the additional steps of:

- a) subjecting the tanned hides to retanning,
- b) subjecting said retanned hides to at least a lubricating treatment with an emulsion obtained by mixing 70-90 parts by weight of an organic phase constituted of synthetic hydrophobic oils and 10-30 parts by weight of a watery phase constituted of an emulsion of silicone compounds,
- c) subjecting said retanned and lubricated hides to dyeing with a dyeing agent possibly in association with cationic acrylic resins,
- d) subjecting the dyed hides obtained from step c) to a fixing treatment with a watery emulsion comprising silicone compounds and metallic salts.

2. A method according to claim 1, further comprising

before step b), at least one of the following steps:

- treating said retanned hides with a pH regulating agent so as to enhance the pH to a value of around 6-7,
- treating said retanned hides possibly after having enhanced their pH to 6-7 with a watery solution of acrylic resins.

3. A method according to claim 1 or claim 2, wherein said retanning step is carried out by treating the tanned hides in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

50-200% water,

5-6% chromium oxide

0,5-0,6% sodium bicarbonate.

4. A method according to any of the previous claims, wherein two lubricating steps of said retanned hides are provided by means of a treatment of the same respectively with 8-15% and 2-8% by weight on the weight of the hides of said emulsion obtained by mixing 70-90 parts by weight of an organic phase constituted of synthetic hydrophobic oils and 10-30 parts by weight of a watery phase constituted of an emulsion of silicone compounds.

5. A method according to claim 4, wherein said synthetic oils comprise anionic organic units.

6. A method according to claim 4 or claim 5, wherein said silicone compounds are chosen from the group comprising silane and siloxane compounds and respective polymeric products of condensation.

7. A method according to any of the claims from 4 to 6, wherein said watery phase is constituted of an emulsion of dimethylpolysiloxane.

8. A method according to any of the previous claims, wherein said dyeing step is carried out by treating said retanned and lubricated hides in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

100-300% water

1-6% dyeing agent

1-3% cationic acrylic resins.

9. A method according to any of the previous claims, wherein said fixing step is carried out by treating the

dyed hides in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

100-300% water

0,5-3% emulsion comprising silicone compounds

3-6% metallic salts.

10. A method according to any of the claims 2 to 9, wherein said treating step of the hides retanned with a pH regulating agent is carried out in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

50-200% water,

1,5-3% ammonium bicarbonate.

11. A method according to any of the claims 2 to 10, wherein said treating step of the hides retanned with a watery solution of acrylic resins is carried out in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

100-300 % water,

3-5% watery solution of acrylic resins.

12. A method according to any of the previous claims, wherein the conventional preparation of the tanned hides provides the use of a chromium tanning agent so as to obtain Wet Blue hides.

13. A method according to any of the previous claims, further comprising before the retanning step (step a), the step of subjecting the tanned hides to a bleaching treatment with sodium hydrosulphite and oxalic acid.

14. A method according to claim 13, wherein said bleaching treatment of the retanned hides is carried out in a watery bath comprising the following ingredients in percentages by weight on the weight of the hides:

100-300% water

1-3% sodium hydrosulphite

0,3-1% dislubricating agent chosen among fatty acids and soaps.

0,7-1,5% oxalic acid.

15. Washable leather obtainable by means of a method

according to any of the previous claims.

16. Washable leather according to claim 15, **characterised in that** it has a colour fastness measured on the scale of the grey comprised between 4 and 5. 5
17. Washable leather according to claim 15 or claim 16, **characterised in that** it has a permeability to water vapour higher or equal to 10 mg/cm² h, preferably comprised between 10 and 15 mg/cm² h. 10
18. Washable leather according to any of the claims 15 to 17, **characterised in that** it has a resistance to water penetration comprised between 90 and 120 minutes with an absorption of water varying from 10% to 15% by weight on the weight of the leather. 15
19. Washable leather according to any of the claims 15 to 18, **characterised in that** it has a breaking load higher or equal to 12 N/mm² and a stretch higher or equal to 40%. 20
20. Use of a washable leather according to any of the claims 15 to 19 in the manufacturing of clothing items, footwear, leather goods and furnishing. 25
21. Chemical composition for use in the lubricating treatment of retanned hides comprising in percentages by weight on the weight of the composition 70-90% of an organic phase constituted of synthetic hydrophobic oils and 10-30% of a watery phase constituted of an emulsion of silicone compounds, said organic and watery phases being mixed one another before said use in order to form an emulsion. 30
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EUROPEAN SEARCH REPORT

Application Number
EP 03 42 5647

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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 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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