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PROCESS FOR THE TREATMENT OF HIDES
AND SKINS

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In the usual processes for unhairing hides prior to tanning, the hairs or, as the case may be, the skins are badly damaged partly by chemical and partly by bacterial action. There either occurs a very intensive decomposition of the skin substance and a considerable damage to the grain, or the hairs obtained according to the previous processes are no longer to be regarded as suitable starting out materials for the hair working-up industry, especially for the manufacture of felts and hair yarns. It is true that various proposals have been made in order as far as possible to exclude a damaging of the skins and hair during liming and treatment in the lime pit of skins and hides. For this purpose the additional use, for example, of protective colloids such as albumen and its decomposition products, sulphite waste liquor or carbohydrates, of ammonium salts, organic nitrogen compounds, saponins as well as of soluble silicates, has been proposed. Although a better preservation of the hairs was, to some extent, achieved by these additions, the removal of the hairs from the skins was, on the other hand, thereby rendered more difficult. The problem of easily removing the hairs including the particularly firmly embedded root hairs from the skins and recovering them without loss in an undamaged condition whilst, at the same time, obtaining the skin and especially the grain in a condition which guarantees a faultless result in the final tanned leather is thus not solved by any of these processes.

A process has now been found which renders possible not only the obtaining of the whole of the hairs including the root hairs in an unchanged condition, but also an extraordinary protection of the hide and the grain and thereby an excellent result in the finished leather, which process is, moreover, in general capable of being carried out in a shorter time and with smaller quantities of chemicals than the usual liming processes.

In order to achieve this the soaking process and the liming process must be cut out in a certain way and must be adjusted to one another, as is more fully described in the following:

The process consists of pre-soaking, main soaking and liming. If desired, the pre-soaking and the main soaking can be combined, but this is less advantageous.

The pre-soaking takes place in weak alkaline aqueous solution with a bath quantity of preferably 400–800% and a pH value of between 8 and 11.8, but in any event below 12, which is adjusted by the use of buffer salts, such as sodium

phosphates, sodium bicarbonate and the like. The temperature of the treatment is advantageously from 18–20° C., but may also be lower. It is possible, temperatures of above 30° are to be avoided as they cause an excessively strong development of bacteria.

The main soaking similarly takes place in weak alkaline aqueous solution of pH 8 to 11.8, preferably with the addition of larger quantities of salt than in the pre-soaking and with a further addition of a fatty alcohol sulphate which is also soluble in the form of its alkaline earth salts. Those fatty alcohol sulphates which have unsaturated double bonds or contain from 6 to 12 carbon atoms in their chains and which are produced according to Patents Nos. 1,968,793, 1,968,794 and 1,968,797 are especially suitable for this purpose. As such may be mentioned the sulphates of the alcohols which result from the catalytic reduction of the first runnings of the fatty acids from paraffin oxidation.

In addition to the alkaline reacting buffer salts mentioned, sulphides, especially sodium sulphide or ammonium sulphide, as well as polysulphides and sulph-hydrates can also be used especially in those cases where the soaking and/or the liming takes place in the vat.

Lime, if desired with the addition of sodium sulphide, is preferably used for the liming treatment. The above mentioned fatty alcohol sulphates can also be additionally used here. The quantity of the bath amounts in the case of the vat liming to about 400% and in that of the pit liming to from 500 to 800% calculated on the raw weight of the skins. The duration amounts in the case of the vat liming to about 24 hours, in that of pit liming to about 3 to 4 days.

It has been found that owing to the thorough soaking with moderately alkaline solutions, the subsequent liming process is prepared much better and more effectively than by the usual materially stronger alkaline soaking liquids or pre-liming baths. The especially favourable condition of the skin obtained by the soaking treatment, together with the special effect of the fatty alcohol sulphates which are also employed, render it possible to complete the treatment with a shorter duration of liming and with a smaller quantity of sodium sulphide and, in some cases, even entirely without sulphide, whereby the pelt and especially the grain are preserved. The fatty alcohol sulphates assist the action of the liming chemicals on the hair papillae and thereby materially contribute to the loosening out of the securely embedded root hairs. Moreover, it has

been determined that these fatty alcohol sulphates exercise a loosening and solvent effect on the intercellular albuminous substances of the skin such as albumens, globulins and mucines without, however, in the slightest degree attacking the collagen fibre. This special effect of the fatty alcohol sulphates can best be illustrated as follows.

If a piece of bullock skin is placed into a weakly alkaline solution of a suitable fatty alcohol sulphate (for example a mixture of the sodium salts of the fatty alcohol sulphuric acid esters with 6 to 12 carbon atoms, obtained from the first runnings of the distillation of the alcohols corresponding to the coconut oil acids) then after a comparatively short time slimy albuminous substances separate on the bottom of the vessel. Other wetting-out agents, such as sulphonated oils or aromatic sulphonic acids, which have already been proposed as additions to the soaking bath do not show this behaviour. The albumen solvent effect of the fatty alcohol sulphates, however, does not extend to the collagen fibres but only to the so-called inter-cellular substances of the skin. Consequently, no disadvantageous changes of the skin, especially damage to the grain or reduction of the yield of the finished leather occur. If, for example, a pelt which has been limed according to the previously known processes is placed in a weakly alkaline fatty alcohol sulphate solution, the liquid will remain clear for a long time and no odour of foulness occurs. In this case the inter-cellular substances have already previously, to the largest extent, been dissolved out by the liming treatment, and the fatty alcohol sulphate exerts no further influence on the skin substance. Thus, only those albuminous substances are removed from the skin by the fatty alcohol sulphate which must, in any event, be dissolved out of the skin for the purpose of satisfactory tanning and finishing of the leather.

EXAMPLES

(1) A. VAT LIMING

Raw material: Salted large animal skins, e. g. bullocks and horse skins. (The percentages refer to the weight of the salted skins.)

Pre-soaking

(a)	or	(b)	or	(c)
500-800% bath		500-800% bath		500-800% bath
1 kg. trisodium phosphate per cbm.		500 g. disodium phosphate		100 g. NaHCO_3
		200 g. Na_2S conc. (or		200 g. Na_2S conc. (or
		100 g. NaOH) per cbm.		100 g. NaOH) per cbm.

pH values of the solutions:

(a)	(b)	(c)
pH=11.5	pH=10.6	pH=10.1
	with NaOH	with NaOH
	pH=11.2	pH=11

Temperature of the soaking bath: 18-20°C.

Duration of soaking treatment: Overnight.

Main softening (pre-liming)

(a)	(b)	(c)
500-800% bath	500-800% bath	500-800% bath
10-12 kg. trisodium phosphate	4 kg. disodium phosphate	11 kg. NaHCO_3
1.2-1.4 kg. HCl conc.	2 kg. Na_2S conc.	2 kg. Na_2S conc.
0.25 kg. fatty alcohol sulphate (ammonium salt) per cbm.	0.25 kg. fatty alcohol sulphate (ammonium salt) per cbm.	0.25 kg. fatty alcohol sulphate (ammonium salt) per cbm.

pH values of the solutions:

(a)	(b)	(c)
pH=11.5-11.8	pH=11.6	pH=11

Temperature of the soaking bath: 18-20°C.

Duration of soaking treatment: 24 hours.

Liming in the vat for a, b and c: about 400% bath

12 kg. burnt lime	
0.4 kg. Na_2S conc.	
0.3 kg. fatty alcohol sulphate	
Duration of liming: 48 hours.	
Liming temperature: 22 to 25°C.	

B. PIT LIMING

Raw material: Heavy sun-dried bullocks or bulls skins.

Pre-soaking

Cleaning of the skins in water, to which about 100 grms. of caustic soda per cbm. can be added. Soaking time: 1 day.

Main soaking

700-1000% bath, calculated on the dry weight.	
200 grms. NaOH or 800 grms. disodium phosphate + 100 grms. NaOH	
95 grms. sodium salt of ricinoleic acid-butylester-sulphuric acid ester	
50 grms. methyl-cyclohexanol	
Temperature of soaking bath: about 18°C.	
Duration: 4-5 days (after 3 days the skins are felled if necessary).	

Pre-liming

500-800% bath calculated on the dry weight.	
200 grms. NaOH or 800-1000 grms. disodium phosphate + 100 grms. NaOH	
275 grms. fatty alcohol sulphate (ammonium salt)	
Pre-liming time: 24 hours.	
Temperature: 18-20°C.	

Main liming

500-800% bath calculated on the weight of the soaked skins.	
12 kg. burnt lime (or calcium hydrate)	
600 grms. Na_2S conc.	
275 grms. fatty alcohol sulphate (ammonium salt)	
Liming time: 3-4 days.	
Liming temperature: 22-25°C.	

(2) A. VAT LIMING

Raw material: Salted skins of large animals.

Pre-soaking

500-800% bath.	
0.67 kg. disodium phosphate	
1.33 kg. sodium bicarbonate	
2 kg. sodium sulphide conc.	
Soaking time: 24 hours.	
Temperature: 18-20°C.	

Main soaking

500-800% bath.	
1.67 kg. disodium phosphate	
3.33 kg. sodium bicarbonate	
5 kg. sodium sulphide conc.	
0.3 kg. fatty alcohol sulphate	
Soaking time: 24 hours.	
Temperature: 18-20°C.	

Liming in the vat: pure white lime treatment

400% bath.	
10-12 kg. burnt lime	
0.2 kg. fatty alcohol sulphate	
Liming time: about 24 hours.	
Temperature: 22-25°C.	

B. PIT LIMING

Raw material: Salted skins of large animals.

Pre-liming

500-800% bath.	
0.17 kg. disodium phosphate	
0.35 kg. sodium bicarbonate	
0.3-0.5 kg. sodium sulphide conc.	
Soaking time: 24 hours.	
Temperature: 18-20°C.	

Main soaking

500-800% bath.	
0.33 kg. disodium phosphate	
0.67 kg. sodium carbonate	
1 kg. sodium sulphide conc.	
0.3 kg. fatty alcohol sulphate	
Soaking time: 24 hours.	
Temperature: 18-20°C.	

Liming

500-800% bath.	
12 kg. burnt lime	
0.4 kg. sodium sulphide conc.	
0.2 kg. fatty alcohol sulphate	
Liming time: 3 days.	
Temperature: 22-25°C.	

After the liming the skins are unhaired on this machine (Leidgen or Roller unhairing machine) or by hand. Care must be taken to see that both before and during the unhairing the skins be not chilled, i. e. do not come into contact with cold water. The further working is continued in the usual manner.

In the foregoing examples, except where otherwise expressly stated, the term "fatty alcohol sulphate" means a mixture of the sodium salts of the sulphuric acid esters of the fatty alcohols with 6 to 12 carbon atoms, as are present in the first runnings of the alcohols obtainable by catalytic reduction of the fatty acids of coconut oil.

Similar results may, for example be achieved with the following fatty alcohol sulphates:

Sodium salt of dodecyl sulphuric acid ester.

Ammonium salt of hexadecenyl sulphuric acid ester.

Sodium salt of undecenyl sulphuric acid ester.

The process is suitable not only for bullock and horse skins, but also for calf-, goats-, and sheep-skins, as well as for other skins of similar character in which the preservation of hair is important. The hairs, including all the root hairs, can very easily be removed according to the process described, and they are so firm, smooth and shiny that they can only be compared with sheared hairs. They constitute a raw material, of very high value, for the hair using industry. Bullocks hairs, obtained in the manner described can, for example be utilized up to 30% in the manufacture of woollen blankets.

The pelts obtained according to the process are elastic, tender and smooth in the grain and yield an excellent leather. In the subsequent enzyme bating the quantity of the enzyme can be reduced, or for example when manufacturing sleek leather it can be entirely omitted. The process is therefore in every respect progressive and industrially valuable.

I claim:

1. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath in presence of such fatty alcohol sulphuric acid esters as are easily soluble in water even in the form of their alkaline earth salts, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said esters being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

2. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterized in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, also containing alkali sulphide, in presence of such fatty alcohol sulphuric acid esters as are easily soluble in water even in the form of their alkaline earth salts, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said esters being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

3. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath in presence of sulphates of unsaturated fatty alcohols, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said sulfates being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

4. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, also containing alkali sulphide, in presence of sulphates of unsaturated fatty alcohols, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said sulfates being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

5. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, in presence of sulphuric acid esters of the fatty alcohols from the first runnings of the coconut oil alcohols and the palm kernel oil alcohols, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said esters being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

6. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, also containing alkali sulphide, in presence of sulphuric acid esters of the fatty alcohols from the first runnings of the coconut oil alcohols and the palm kernel oil alcohols, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said esters being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

7. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, in presence of oleyl alcohol sulfate, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said sulfate being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

8. A process for the preparation of hides and skins for tanning whilst preserving the hairs characterised in that the hides and skins are first subjected to an alkaline soaking at a pH value between 8 and 11.8 and are then treated in an alkaline liming bath, also containing alkali sulphide, in presence of oleyl alcohol sulfate, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said sulfate being employed in an amount which has a dissolving action on intercellular albuminous

material sufficient to effect together with the liming treatment the loosening of the root hairs.

9. A process for the preparation of hides and skins for tanning whilst preserving the hairs comprising first soaking said hides and skins in an alkaline soaking bath of a pH value less than 12 and then subjecting said hides and skins to an alkaline liming bath, said soaking and liming baths each containing a sulfuric acid ester of a fatty alcohol whose alkaline earth salts are readily soluble in water at a temperature less than 30° C., the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said ester being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

10. A process for the preparation of hides and skins for tanning while preserving the hairs comprising first soaking said hides and skins in an alkaline soaking bath of a pH value less than 12 and then subjecting said hides and skins to an alkaline lime bath, said soaking and lime baths each containing a sulfuric acid ester of fatty alcohol selected from the group consisting of fatty alcohols of 6 to 12 carbon atoms and a higher molecular unsaturated fatty alcohol, the effective strength of the soaking solution and liming bath being insufficient either singularly or collectively to destroy the root hairs, and said ester being employed in an amount which has a dissolving action on intercellular albuminous material sufficient to effect together with the liming treatment the loosening of the root hairs.

11. A liming bath for alkaline soaked hides containing lime, sodium sulfide in a quantity insufficient to damage the hair present and approximately 0.2 to 0.3 kgs. per cubic meter of the bath solution of a sulfuric acid ester of a fatty alcohol whose alkaline earth salts are easily soluble in said bath.

12. A liming bath for hides which have been softened in an alkaline bath having a pH value ranging between 8 and 11.8 which comprises lime, sodium sulfide in a quantity insufficient to damage the hair present and a sulfuric acid ester of a fatty alcohol of 6 to 12 carbon atoms.

13. A liming bath for hides softened in an alkaline softening bath having a pH value below 12 containing lime, a sharpening agent in a quantity insufficient to damage the hair present and a sulfuric acid ester of an unsaturated fatty alcohol of 18 carbon atoms.

14. A liming bath for hides softened in an alkaline softening bath having a pH value below 12 containing approximately 12 kgs. of burnt lime and approximately 0.3 kg. per cubic meter of the liming bath of the sodium salt of a sulfated fatty alcohol whose alkaline earth salts are readily soluble in said liming bath.

15. A liming bath for hides soaked in an alkaline softening bath having a pH value below 12 containing per cubic meter not less than about 10 kgs. of burnt lime and not less than about 0.2 kg. of a water soluble salt of a sulfated fatty alcohol whose alkaline earth salts are readily soluble in said liming bath.

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