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PRODUCTION OF LEATHER

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The present invention relates to improvements in leather manufacture and it particularly relates to the improvements in the dehairing of skins and hides.

Although amines have been known to have dehairing properties, they have never been commercially utilized with any degree of success unless in combination with strong alkalies, such as lime, alkali metal sulphides, and so forth.

Proteolytic enzymes have also been suggested for utilization in the dehairing of skins and hides, but it has not in the past been found feasible to combine the amines together with proteolytic enzymes, although each of these dehairing elements produced individually effects and qualities of the finer leather, which it was desired to attain in combination in such final product.

It has now been found by the utilization of certain proteolytic enzymes and particularly by the utilization of enzymatic products derived by the cultivation of bacteria, as for example *Bacillus subtilis* and *mesentericus*, at predetermined pH ranges, at desired temperatures and in desired concentrations, that certain amines may be most satisfactorily employed, in conjunction with such proteolytic enzymatic unhairing liquors to produce leather of a most satisfactory grade.

Simple amines, such as methylamine and ethylamine may be satisfactorily utilized under the specific conditions and with the specific types of enzymes to be described.

It has also been found very suitable for this purpose to use such simple amines in mixtures with compound amines which include an aliphatic nucleus containing from 2 to 6 carbon atoms, and which contain at least two substituent groups, such as the hydroxy group, the carboxy group, or another amino group.

Among the amines which may be used, singly but preferably in mixtures, are monodi-, and triethanolamines, the hydroxy-aminoalkanes, diaminopropanols, polyamino-polyhydroxyaliphatic compounds, N-hydroxyalkylaliphatic diamines, N-hydroxyamino alkyl-aliphatic diamines, various other aliphatic amino compounds, which amino group may carry alkyl radicals, in which there are one or more hydroxy and amino groups in the main or subsidiary aliphatic chains or both.

The preferred process contemplates that the enzyme be utilized in the presence of amino acids and/or hydroxy amines and/or diamines, which are preferably placed in the unhairing bath.

The pH of the unhairing bath should preferably range from about 8.5 to 11.5 with an optimum between 9 and 11. Under certain conditions the pH values may also range down to a value of 8.

The baths containing the amines and the proteolytic enzyme are preferably maintained at a temperature range from about 25 to 45 degrees C. with a preferred range at 25 to 35 degrees C.

The amount of the amine should preferably not be more than 5% of the weight of the skin and the preferred range is between 1 and 5%. The proteolytic enzyme is preferably utilized in quantity substantially less than about 2½% and usually less than 1% of the weight of the skin.

It has been found most suitable to incorporate in the dehairing bath relatively small quantities of phenolic bodies and/or pine oil. Phenolic bodies of a substantially higher molecular weight than ordinary phenol (C_6H_5OH), such as the cresylic acids and the naphthols may be readily employed.

Various enzymatic products may be used in activated condition. It has been found most suitable to use enzymes of bacterial or fungi origin combined mixed with their metabolic decomposition products, and these mixtures may also desirably contain papain, bromelin, pancreatin, trypsin and so forth.

The preferred enzyme compositions may be prepared by permitting *Bacillus subtilis* or *mesentericus, mucormucedo, Aspergillus oryzae* or *niger, Penicillium glaucum, Tryotrix tenuis* and so forth, to grow upon a suitable nutrient medium, containing starch and protein materials, and with mineral salts, such as the salts of potassium, magnesium, calcium and also ammonium salts and phosphates.

In the case of the *Bacillus subtilis*, and/or *mesentericus*, the nutrient materials may be prepared by treating bran, wheat or soya bean materials with sulphuric acid and then filtering.

The nutrient medium is preferably neutralized to a pH of between 7.5 to 9.5, is sterilized and then is inoculated with a pure culture of the Bacillus after its pH has been reduced by 1 to 2 units.

The culture is allowed to develop at room temperature or slightly thereabove, for example at a temperature of 30 to 40° C., while being maintained in relatively thin layers not exceeding one-half of one per cent in thickness, and it is preferably continuously supplied with sterile air.

After the culture has suitably developed, the growth of the bacteria is stopped and the entire liquor is sterilized by the addition of a suitable disinfectant.

This bacterial liquor containing the metabolic products is preferably combined with certain salts,

such as ammonium chloride (and it is also desirably combined with small amounts of reducing sulphur compounds, such as sodium sulphite and sodium bi-sulphite.

Instead of using a proteolytic enzyme, as above described, it is also possible to use in combination with said enzymes, or in place thereof, enzymes of the nature of pancreatin, trypsin, papain and/or bromelin.

In preparing the hides or skins for treatment with the combined enzyme and amine, it may be desirable to treat them first with a caustic alkali or caustic soda solution having concentrations between 0.05 to 0.3 normal. The preferred temperature range is from 20 to 40° C. with an average of about 30.

After the treatment with alkali, the skins or hides may be washed with water and thereafter treated with an alkali salt, such as borax. The skins or hides after treatment with the alkali solution and after washing may be treated with borax acid or with sodium bicarbonate in relatively dilute solution but in any case it is preferred that the pH of the hides be not reduced to less than 7 or more desirably to not less than 9.

The above preliminary treatment with caustic alkali, however, may be readily omitted.

After this treatment with the caustic alkali the skin or hides are most satisfactorily treated with the bath of the enzymatic dehairing agent containing the amine.

To give an illustrative example, 100 parts by weight of the skin or hides was placed in 400 parts by weight of water, to which was added 9 parts by weight of a 2% enzymatic liquor and 2.25 parts by weight of monoethanolamine. To the resultant bath was then added one-half part of a suitable phenolic mixture.

The pH of the bath was maintained between about 9.5 to 10 for two days and the temperature was maintained at about 34° C. The skins or hides which were then processed by subsequent bating and tanning operations were of most superior quality and appeared to have a most satisfactory grain and texture.

In another test calf skins after having been properly pretreated were put into a bath in an amount of 100 parts of skins to 450 parts of water. This bath contains 9 parts by weight of a bacterial enzymatic liquor, 2.25 parts by weight of ethylene diamine and one-half part of a phenolic mixture.

The pH of the solution was maintained between 10 and 11 for about two days and then was permitted to fall to 9.5.

The resultant skin after it had been dehaired and then subsequently bated and tanned was of most satisfactory quality.

It has been found quite desirable after the treatment with the enzyme-amine mixture to subject the skin subsequently to a second treatment with an enzyme bath devoid of the amine in substantially the same proportions as above given and/or also with a bath containing about 4.5 parts of the sodium carbonate to 450 parts by weight of water, which latter bath may also contain a small amount of caustic soda, such as about ½% of caustic soda.

What is claimed is:

1. A process of dehairing skins and hides which comprises subjecting the skins or hides to treatment with a bath containing a proteolytic enzyme and an amine devoid of carboxyl groups at a pH of between 8 to 11.

2. The process of dehairing skins and hides which comprises subjecting the skins or hides to a treatment with a dehairing bath containing a bacterial enzyme and a compound amine devoid of carboxyl groups.

3. The process of dehairing skins and hides which comprises subjecting the skins or hides to a treatment with a dehairing bath containing an enzymatic liquor derived from the cultivation of *Bacillus subtilis* and/or *mesentericus* and a compound amine devoid of carboxyl groups.

4. The process of dehairing skins and hides which comprises subjecting the skins or hides to a treatment with a dehairing bath containing a proteolytic enzyme and ethylene diamine.

5. The process of dehairing skins and hides which comprises subjecting the skins or hides to a treatment with a dehairing bath containing a proteolytic enzyme and a monoethanolamine at a pH between 9 to 11.

6. A process of dehairing skins and hides which comprises subjecting the skins or hides to treatment with an alkaline bath containing a proteolytic enzyme and amine compounds devoid of carboxyl groups.

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