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TREATMENT OF HIDES

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This invention relates to a method of unhairing and liming green and salted skins and hides.

The treatment of softened, rinsed skins and hides with depilatory proteolytic enzymes to remove hair and wool from the hides in a completely undamaged condition is known in the art. As soon as the hair or wool is sufficiently loosened, it is removed from the hides, which are then limed with alkaline swelling baths, such as of lime and sulfides. Skins, the hair of which is to be loosened enzymatically, may also be treated before dehairing with a soda solution in order to facilitate removal of hair without attack of the hair. Further, it is known in the art to use pancreatic enzymes during the softening process, if liming and depilation are to be accomplished by means of lime, in order to improve the unsatisfactory hair loosening caused by a pure lime treatment.

In all the processes mentioned above, the recovery of hair and wool requires special techniques in which the hair or wool is removed by hand or by machine.

It is also known to lime green and salted skins and hides, after softening and rinsing, with sulfide-containing or lime-sulfide-containing baths. Such processes are only used, however, when damage to the hair is acceptable. Often such high concentrations of sulfides are employed in order to speed the liming process that the hair becomes completely pulped, that is, so fully dissolved or decomposed as to be removable by washing of the hides at the conclusion of the process, whereby the requirements for a mechanical dehairing are saved. Such methods, however, involve the great disadvantage that not only are fat-wrinkles strongly prominent in the finished leather, but also that a considerable raising of the grain is involved which cannot fully be repaired during the further working of the leather. In the finished leather, the raised grain has a very unpleasant appearance and influences leather quality, since the leather is not sufficiently fine-grained and also the raised grain interferes with the removal of soil from the leather.

It has now been found that the treatment of green and salted skins and hides with sulfide-containing or lime-sulfide-containing baths can be improved during the course of liming if the skins and hides, after softening and rinsing according to any suitable process, are pretreated with solutions, preferably neutral solutions, of fungus proteases or bacterial proteases and are then directly treated with sulfides or with lime and sulfides without removal of hair and without rinsing. The liming and dehairing chemicals are added directly to the enzyme solution after the latter has worked for the required time on the skins and hides. In this manner, sufficient sodium sulfide can be employed that hair is fully pulped and can be removed afterwards by simple rinsing, without concern for the effect of the treatment on the quality of the leather. In particular, treatment of skins and hides in this manner produces a fine, delicate, flat, tight, and smooth grain, that is an unraised grain, in which fat-wrinkles are practically unapparent, and from which soil can easily be removed.

The enzymes employed can be used in any suitable manner. To increase their effect, carbohydrases, particularly oligases produced by micro-organisms, can be combined with the proteolytic enzymes. By oligases are meant those enzymes which, in contrast to polyases such as alpha- and beta-amylases, only split lower saccharides such as occur in the polypeptide chains of non-collagenaceous proteins. These polypeptide chains, in particular, contain only a minimal content of glucose, galactose, and mannose. Probably the two saccharides last mentioned are substantially absent. This good effect is not obtained with pancreatic tryptase probably because the unchanged cells of animal skin contain inhibitors which influence its action.

The proteolytic enzymes employed can be used either alone or together with other materials such as salts, for example soluble ammonium salts or soluble sulfites and nitrites such as sodium sulfite, sodium nitrite, and the like.

It is possible to carry out this enzymatic pretreatment in a neutral, alkaline, or acid solution. It is particularly advantageous to work in a neutral solution since the alkalinity of the subsequent liming treatment is not affected. Nevertheless, it is possible also to work with weakly alkaline solutions. If weakly acid solutions are employed, the influence of the solutions on the subsequent alkaline liming must be taken into acount.

The process of the present invention can be carried out at room temperatures (18°–25° C.) or at elevated temperatures. When working at room temperatures, the softened and subsequently rinsed skins are suitably treated for from about 12 to about 24 hours with the solution of proteolytic enzyme before the liming chemicals are added. If elevated temperatures are employed, that is 25–30° C., a shorter period of presoftening can be used, for example a two to four hour softening with agitation. Then the hides are washed with running water and the warm enzyme solution added. After only three to five hours, the liming chemicals can be added to the same bath. The period of treatment with lime and sodium sulfide varies according to the kind of leather to be produced. For example, in the production of chrome leather from cowhide, a liming period of about 14 to about 18 hours is sufficient. However, longer periods up to 24 hours or longer may be used with this or other types of leather.

The method of the invention is to be distinguished from enzymatic softening processes usually employed only with dried raw goods in that attack of collagenaceous fiber structure requires more enzyme and in the fact that the hides are not rinsed after the present enzymatic treatment. If, by exception, proteolytic enzymes are used for enhancement of the softening of salted skins and hides, very small amounts are employed, e.g. only about 0.1 percent by weight of an enzyme preparation having an enzyme value of 4000 according to A. Küntzel "Gerbereichemisches Taschenbuch," Theodor Steinkopff, Dresden and Leipzig, Sixth Edition, 1955, page 86.

Green skins and hides do not require any softening in the usual sense, but only a short rinsing to remove blood and dirt. Thus, enzymatic softening agents are never employed for such raw goods.

The method of the invention is distinguished from enzymatic hair removal methods in that according to the present invention the hides are not depilated after treatment with enzyme, but are directly treated with conventional chemicals having a swelling effect, such as with sodium sulfide alone or together with lime. Also, the

amounts of enzyme employed according to the present invention are insufficient for an enzymatic dehairing. For example, if it is desired to depilate salted cowhide enzymatically, a bath treatment with about 300–500 percent of water (based on the weight of the hides) and about 7.5 percent of bacterial protease having an enzyme value of 4000 would require at least three days in which to act. In contrast, according to the method of the present invention, only about 0.6 to 2 percent of bacterial protease having an enzyme value of 4000 is employed in such amounts of water for only 2 to 24 hours at temperatures of from 18°–30° C.

Thus, in enzymatic dehairing processes employing baths, large quantities of enzyme are required in order to bring about depilation after a considerably long time such as two or three days. The use of such large quantities of enzyme is only economically justifiable if the skins or hides treated carry valuable wool or hair which must be recovered in an undamaged condition. In contrast, the present method involves an enzymatic treatment employing only small amounts of enzyme, requiring much shorter periods of time, and retaining the advantages of an enzymatic depilation such as the formation of a smooth, fine, and close grain while operating in a much simpler and cheaper manner, i.e. in a much shorter time and with a savings in the cost of chemicals, wages, and energy, particularly since hair need not be removed with dehairing machines, but is simply removed in the liming vessel by agitating or paddling and washing. The present method, thus, is particularly suitable when treating skins and hides, the hair or wool of which is expendable.

A better understanding of the present invention and of its many advantages will be had by reference to the following examples given by way of illustration.

Example 1

Salted calfskins were softened in conventional manner, rinsed, and then treated at a pH of 7.0–7.5 for 12 hours with a solution containing:

	Percent
Water at 18–20° C.	300
Fungus protease from *Aspergillus parasiticus* having an enzyme value of 4000 determined by the method of Küntzel earlier referred to	1
Sodium nitrite	0.4
and	
Ammonium chloride	0.4

After this period the following materials were added to the aforementioned bath without intermediate rinsing:

	Percent
Sodium sulfide (60–62 percent)	2
Sodium hydrosulfide	1
and	
Hydrated lime	2.5

The skins were dehaired after 18–24 hours.

Example 2

Dry salted cowhides were softened in the usual manner, rinsed, and then treated for 24 hours at a pH between 7.0 and 7.5 with:

	Percent
Water at 20–22° C.	300
and	
Bacterial protease from *Bacillus subtilis* having an enzyme value of 4000	1.5

After this period, the following were added to the same bath without intermediate rinsing:

	Percent
Sodium sulfide (60–62 percent)	2.5
and	
Hydrated lime	2.5

After 24 hours the pulped hair was removed by rinsing. The skins were then fleshed, split, bated, and pickled.

Example 3

Salted cowhides were softened for 4 hours at 26° C. with agitation, washed with warm water, and then treated for 3 to 4 hours at a pH of 6.5 to 7 with:

	Percent
Water at 28–30° C.	300
Bacterial protease from *Bacillus subtilis* having an enzymatic activity corresponding with an enzyme value of 4000 and a content of oligases, such as glucosidases, galactosidases, and mannosidases corresponding with a β-glucosidase value of 0.013 according to K. Myrbäck, "Enzymatische Katalyse" published by Walther de Gruyter, 1953, page 45	1
Calcined sodium sulfite	0.4
Calcined sodium bisulfite	0.3
and	
Ammonium sulfate	0.4

Without rinsing,

	Percent
Sodium sulfide (60–62 percent)	3.0
and	
Hydrated lime	2.5

were added to the same bath. After 18 hours, the pulped hair was removed by rinsing. The limed hides were next fleshed, split, bated, and pickled.

Example 4

Green calfskins, that is, skins not preserved with the use of salt, were washed for 30 minutes with running water to remove blood and dirt (such raw goods require no special softening), and then treated for 6 hours at a pH of 7 with:

	Percent
Water at 22–23° C.	300
Fungus protease from *Aspergillus flavus* having an enzyme value of 4000	0.5
and	
Basterial protease having an enzyme value of 4000	0.5

After this time,

	Percent
Sodium sulfide (60–62 percent)	2.8
and	
Hydrated lime	3.0

were added to the bath without intermediate rinsing of the hides. After another 18 hours, the pulped hair was removed by rinsing, and the limed hides were fleshed, split if desired, bated and then further treated in a manner usual for tanned leather.

Although specific embodiments have ben herein shown and described, it is to be understod that they are illustrative and are not to be construed as limiting on the scope and spirit of the invention.

I claim:

1. The method of unhairing and liming green and salted skins and hides which comprises contacting said skins and hides, after softening and rinsing, with an aqueous solution of a proteolytic enzyme, said enzyme being present in amounts effective for attack of the collagenaceous fiber structure of said skins and hides but insufficient to cause unhairing, and then destroying hair on said skins and hides by pulping the addition of alkaline sulfide liming chemicals, and then removing the pulped hair from said skins and hides by rinsing.

2. The method as in claim 1 wherein said aqueous solution additionally contains dissolved salts selected from the group consisting of ammonium salts, sulfites, and nitrites.

3. The method as in claim 1 wherein carbohydrase is additionally present in said aqueous solution.

4. The method as in claim 3 wherein said carbohydrase is an oligase produced by a micro-organism.

5. The method as in claim 1 wherein said proteolytic enzyme has an enzyme value of 4000 and is present in an amount of 0.6 to 2 percent.

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