United States Patent Office 2,857,317
Patented Oct. 21, 1958

2,857,317

TREATMENT OF SKINS AND HIDES

Otto Grimm, Darmstadt, Germany, assignor to Rohm & Haas G. m. b. H., Darmstadt, Germany

No Drawing. Application October 22, 1956
Serial No. 617,216

Claims priority, application Germany March 30, 1955

7 Claims. (Cl. 195—6)

This invention relates to an improvement in depilating skins and hides and in preparing them for tanning.

It is customary, in the production of leather, to treat skins and hides in an alkaline swelling lime after they have been soaked. In this way the hair and epidermis located above the derma are solubilized while hair roots and traces of epidermis remain in the follicles. This "scud" is removed in the alkaline bating following the alkaline liming. At the same time the collagen is loosened so that the tans can enter fully into action in the subsequent tanning process.

In order to obtain a complete removal of the "scud" by the action of proteolytic enzymes, the bating must be effected in an alkaline medium. Unfortunately, however, this frequently results in damage to the collagen by the proteolytic enzymes, and ultimately in an insufficiently firm grain for the leather.

I have already disclosed, in my earlier application Serial No. 533,227, filed September 8, 1955, of which this application is a continuation-in-part, that the enzymatic unhairing and dewooling of skins and hides can be carried out with the aid of proteolytic enzymes by applying the enzyme products in powdered form to green or soaked skins, preferably by sprinkling or dusting on the flesh side, and further that this mode of action has the advantage, over depilation in an aqueous bath, of resulting in a practically complete removal of the "scud."

I have now found that the advantageous results obtained by reason of the treatment described in my earlier application can be further enhanced by bating the skins and hides, thus depilated, in an acid bath having a pH of 3 to 5, preferably in the presence of neutral salt. The attack of the bating proteolytic enzymes on the collagen is sufficient when operating in an acid bath to effect the necessary loosening thereof, without however bringing about too strong a decomposition of the protein substance.

Most advantageously, the acid bating follows treatment of the enzymatically depilated skins and hides in swelling lime and, of course, precedes the tanning operation. The combination of depilating by applying enzyme products in powdered form to green or soaked skins followed by acid bating results, after tanning, in leathers having a most desirable firm grain.

The proteolytic enzymes that are preferred in the acid bating step are those formed from microorganisms, namely, the proteolytic enzymes from molds and bacteria. In addition to the proteolytic enzymes, carbohydrases formed from microorganisms and water-soluble mold lipases may also advantageously be employed. The addition of anhydrous phosphates has also proven favorable.

A skin from the soaking pit, i. e., one that has not been subjected to any alkaline treatment or swelling, is extremely resistant to depilatory enzymes. Consequently, such a skin is not in danger of forming leather having an undesirable grain. The unhaired skin is introduced in very clean form into the swelling lime and is thereupon fleshed, scudded and delimed. The enzymatic bating

which then is effected in an acid bath in accordance with the invention acts very gently on the completely fallen and unhaired skin. The production of a loose grain caused by the action of proteolytic enzymes on an unhaired hide under alkaline conditions is, therefore, avoided and instead, a highly desirable, firm grain is produced.

In some instances it may be advisable to combine a weak enzymatic bating in alkaline medium with the deliming. Such a treatment, however, is not sufficient for obtaining the bating effect so that the subsequent bating in an acid medium is in any event necessary.

If it is desired to pickle the unhaired hides at high acidity following treatment in the acid bating liquor and prior to the tanning operation, the necessary additional quantity of acid and neutral salt can be added to the bating liquor after the action of the enzymes has been completed. Tanning can then follow.

The advantages and utility of the invention will become further apparent from the following examples included to illustrate the best modes now contemplated for carrying out the invention. The percentages are based on the dry weight of the skins or hides treated.

Example 1

Dried goatskins were enzymatically softened, then washed and fulled for one-half hour with 3% mold tryptase from *Aspergillus flavus* without addition of water. The treated skins were unhaired after six hours, smoothed, washed and after-limed for two days with 400% of a sodium sulfide solution of 1° Bé. After this time, the treated skins were rinsed, de-swollen with ammonium chloride solution and then bated for twenty-four hours with

300% water at 20–24° C.
8% common salt
1.5% mold tryptase
1% ammonium sulfate

The pH of the bating liquor was maintained between 4 and 5.

Example 2

Salted sheepskins were soaked in the customary manner and then dusted, on the flesh side, with a powdered mixture of mold tryptase and carbohydrase derived from mold. After eighteen to twenty hours, the skins were dewooled, rinsed and after-limed for twenty-four hours with

300% water
3% sodium carbonate
3% concentrated sodium sulfide

After rinsing, the treated skins were de-swollen with ammonium sulfate and finally bated for eight hours with

300% water at 20–22° C., pH 4 to 5
8% salt
1% mold tryptase
0.25% carbohydrase derived from mold
0.5% ammonium sulfate

When the bating was ended, the skins were pickled in the liquor after 8% common salt and acid were added to reduce the pH to 2.5, whereupon tanning was accomplished with chromium salts.

Example 3

Salted calfskins were soaked in water, then after-treated for twelve hours with

500% water
0.2% bacterial protease
0.4% sodium bisulfite calc.
0.5% ammonium sulfate

The treated skins were then tumbled in the drum without addition of water for thirty minutes with

3% mold tryptase
0.5% sodium bisulfite calc.
0.5% ammonium sulfate

After eight hours, the treated skins were covered with

200% water at 26° C.
2% sodium calc.

After twelve additional hours, the treated skins were unhaired, rinsed and after-limed with 400% sodium sulfide solution of 0.8° Bé. After twenty-four hours, the skins were washed and then bated for eighteen hours at a pH of 4 to 5 with

300% water at 20° C.
8% common salt
1.5% bacterial protease
0.5% ammonium sulfate
0.25% sodium tripolyphosphate

Example 4

Dried goatskins were enzymatically soaked, then tumbled without addition of water for one hour with 3% bacterial protease from *Bacillus subtilis*. After eighteen hours, the treated skins were unhaired, then after-limed for twenty-four hours with 400% sodium sulfide solution of 1.5° Bé., then rinsed, de-swollen with ammonium chloride and bated for one hour at a pH of 8 to 8.5 with

300% water at 32° C.
0.2% pancreatic tryptase
0.8% ammonium sulfate

The skins were then bated for twenty-four hours in an acid medium having a pH of 3 to 5 with

300% water at 18–20° C.
8% salt
0.6% mold tryptase
0.6% ammonium sulfate.

It is to be understood that various modifications will readily become apparent to those skilled in the art upon reading this description. All such modifications are intended to be included within the scope of the invention as defined in the appended claims.

I claim:

1. A method for preparing a hide for tanning which comprises applying proteolytic enzyme, in powder form, to a hide, permitting enzymatic action to take place at ambient temperature without immersion in water, unhairing the treated hide, and bating the unhaired hide enzymatically in an acid bating liquor having a pH of from 3 to 5.

2. The method defined in claim 1 wherein the enzymes in the bating liquor are proteolytic enzymes.

3. The method defined in claim 2 wherein the bating liquor additionally contains carbohydrases.

4. The method defined in claim 2 wherein the bating liquor additionally contains water-soluble mold lipases.

5. The method defined in claim 2 wherein the depilated hide is bated in a weakly alkaline bating liquor before the acid bating.

6. A method for preparing a hide for tanning which comprises depilating the hide by applying to it a proteolytic enzyme in powder form and permitting enzymatic action to take place at ambient temperature without immersion in water, bating the depilated hide enzymatically in an acid bating liquor having a pH of from 3 to 5 and, after completion of the enzymatic action, pickling the hide by addition of acid and neutral salt to the bating liquor.

7. In a method for preparing a hide for tanning which includes depilating the hide by applying thereto a proteolytic enzyme in powder form and permitting enzymatic action to take place at ambient temperature without immersion in water, the improvement which comprises bating the depilated hide enzymatically in an acid bath having a pH of from 3 to 5.

References Cited in the file of this patent

UNITED STATES PATENTS

1,936,074	Tressler et al.	Nov. 21, 1933
2,157,969	Rohm	May 9, 1939
2,169,148	Jaeger et al.	Aug. 8, 1939
2,215,055	Rohm	Sept. 17, 1950