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3,076,749

METHOD OF UNHAIRING SKINS AND HIDES
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No Drawing. Filed June 20, 1960, Ser. No. 37,062
Claims priority, application Germany June 24, 1959
10 Claims. (Cl. 195—6)

This invention relates to methods for unhairing skins and hides.

It is known in the art that lime and sulfides, particularly sodium sulfide, are effective for the removal of hair from skins and hides. Also, sulfur compounds which are reducing agents, such as sulfites, bisulfites, and hyposulfites, show some effect as hair loosening agents. Nevertheless, methods of removing hair employing the latter compounds are of little practical value, because the hair removal is completely unsatisfactory. Thus, hair removal is not uniform. Large amounts of chemicals are used and the treatment requires strongly alkaline solutions. Also, when dry rawhides are treated, the process may take several days. In contrast, the use of sulfides, to be sure, brings about a removal of hair. However, when small amounts of sulfides are used, hair removal is scanty, and when large amounts are employed, the hair is attacked or fully destroyed, leaving the hair roots unremoved from the hide. Thioglycolates, also used in the prior art for unhairing, show only a very weak hair loosening effect at a pH below 8. Above pH 9, hair is strongly attacked by this reagent.

Softened skins and hides have also been treated in the prior art with pulverized proteolytic enzymes or enzyme pastes whereby a very good removal of hair can be effected. However, such treatment requires relatively large amounts of enzyme, and is very expensive.

It has now been found that skins and hides may be unhaird without any attack of the hair by presoftening the hides by a suitable process such as washing in water, then further softening the hides with a powdered or pasty enzyme product containing a proteolytic enzyme, and then treating the hides with inorganic neutral salts of the alkali metals and of ammonium and/or sulfur compounds which are reducing agents.

By this process, the need for expensive enzyme preparations can be reduced to a minimal amount, while nevertheless a complete removal of hair is effected. In the unhairing, the hair is maintained fully integral and can be removed together with the hair roots, any adhering residue of epidermis, pigments, and sebaceous glands.

It is emphasized that neither the amount of enzyme used in the softening according to the invention, nor the amount of neutral salts and/or reducing sulfur compounds employed in the present unhairing process is sufficient alone to bring about a removal of hair.

In view of the experiences of the prior art in unhairing with sulfur-containing reducing agents, it is a surprising result that the hair-removing efficiency of these compounds can be improved by a prior treatment of hides and skins with a relatively small amount of the enzyme to give a useful, sure, and cheap method for removing hair.

As proteolytic enzymes, the proteases formed by microorganisms and bacteria are particularly desirable for use in the process of the invention. Pancreatic tryptase is also useful. As concerns the enzyme concentrates employed in the specific examples herein, reference is made to the "Gerbereichemisches Taschenbuch," by A. Kuntzel, Theodor Steinkopff, publishers, Dresden and Leipzig, 1955, page 86. The enzyme softening of the invention is conveniently effected by felting water-soaked and softened hides with from 0.05 percent to 1.5 percent, preferably

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with from 0.1 percent to 1 percent, of the enzyme, the percentages being by weight of the hides treated. These amounts of enzyme are substantially smaller than the amounts used in the prior art to effect unhairing and alone, in the absence of the further treatment of the hides as contemplated by this invention, are insufficient to effect a satisfactory unhairing.

The felting of the hides is carried out for from 15 minutes to 2 or 3 hours, suitably for from 30 minutes to an hour, after which the enzymes are permitted to work on the hides for an additional period of from 30 minutes to an hour, or two or three hours. The unhairing effects produced according to the invention are even more pronounced if the proteolytic enzyme is combined with oligases, particularly with the glucosidases and galactosidases found in almond emulsin (synaptase). These are enzymes which act only on oligosaccharide, but do not decompose polysaccharides. Reference is made to the book by K. Myrback, "Enzymatische Katalyse," Walter de Gruyter & Company, Berlin, W. 35, 1935, pages 44-45, concerning the enzymatic efficiency of these oligases. The oligases are suitably used in combination with enzymes in amounts of between about 0.05 percent to 0.5 percent, preferably about 0.1 to 0.3 percent, by weight of hides treated.

Similarly, the sulfur-containing reducing agents mentioned herein can be combined with proteases in the softening process (cf. Examples 2, 5, 6, 7 infra). Those of these compounds which contain oxygen are particularly suitable in such combinations, and are suitably used in amounts of from about 0.1 percent to 5 percent, preferably about 0.2 percent to 2 percent, based on the weight of hides treated. By such combinations, the unhairing effects of the process can be augmented.

Advantageously, wetting agents can be used together with the enzymes. Cationic wetting agents, known to the art for hide treating, or non-ionogenic wetting agents of the same type as ethylene oxide condensation products preferably having 6-16 polymerized ethylene-oxide oxyhydrocarbon units are particularly effective.

The simultaneous use of enzymes with the inorganic neutral salts used for post-treating the enzyme-softened hides does not accomplish a satisfactory unhairing.

In the enzyme treatment, the pH of the hides suitably is kept at a weakly alkaline to weakly acid pH, e.g. between about 5.5 and 8, preferably between about 6.0 and 7.5. The same pH range is employed when the enzymes are combined with sulfur containing reducing agents as hereinbefore described.

After enzymatic softening, the hides are next treated with inorganic neutral salts and/or sulfur containing reducing agents. The salts are suitably employed in the presence of from about 30 to 100 percent, preferably of from about 30 to 50 percent, of water, based on the weight of the skins or hides being treated. The use of larger amounts of water, such as in amounts of 200 to 300 percent by weight of the hides is not excluded, but requires a correspondingly greater amount of salt. In case a painting process is indicated, the salt solutions can be used with the addition of a thickening agent such as kaolin and applied to the fleshy side of the enzymatically softened hides and skins.

The inorganic neutral salts most suitable for use in the invention are the salts, with alkali metals and ammonium, of strong inorganic acids such as the inorganic oxy-acids (e.g. sulfates, nitrates, chlorates, etc.) or the hydrohalic acids (e.g. chlorides, iodides, etc.), or of other strong acids such as thiocyanic acid. The salts are employed, with the amounts of water mentioned above, in amounts of from about 0.1 percent to about 10 percent, preferably from about 0.2 percent to 7 percent or 0.5 percent to 5 percent, by weight of the hides treated. Anionic, cationic,

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and non-ionic wetting agents known to the art for hide treating can be combined with the solutions of neutral salts.

As sulfur containing reducing agents used in combination with enzymes in the softening treatment, or alone or in combination with neutral salts in treating the enzyme-softened hides, soluble sulfur compounds containing oxygen, or soluble oxygen-free compounds are suitable. Soluble inorganic reducing sulfo-salts are particularly suitable, specifically those containing sulfur atoms having a valence less than +6. Soluble sulfites, bisulfites, thio-sulfates, hyposulfites, sulfides, and hydrosulfides are particularly advantageous. Salts of thioacids such as thioglycolic acid can also be used to advantage. The metal ion of the soluble salts is not critical, but sodium compounds are usually employed commercially because of cost. Where sulfides are used in the present process, they are employed in amounts only $\frac{1}{50}$ to $\frac{1}{4}$ the amounts previously used in the art for complete unhairing using sulfides alone. Such prior art processes also undesirably destroy the hair, as noted earlier.

These reducing agents are used in amounts similar to those described for the neutral salts, in corresponding amounts of water.

The simultaneous use of neutral salts and reducing sulfur-containing agents, particularly those which contain oxygen, has shown itself to be particularly advantageous (cf. Examples 3, 6, 7 infra). When combinations of the salts are used, the total amount of treating agents used falls within the limits mentioned herein for the substances used separately.

The aqueous media containing the salts and/or sulfur compounds are suitably maintained weakly alkaline or weakly acid, at values like those mentioned for the enzyme treatment. However, when oxygen-free sulfur containing reducing agents are employed, a strongly alkaline pH, for example between about 9 and 10 to 12 or 13, is suitable.

The sulfur-containing reducing agents can be used in combination with non-ionic or anionic wetting agents known to the art in hide treating.

In both the enzymatic softening step and the subsequent application of neutral salts and/or sulfur-containing reducing agents, the unhairing is readily and conveniently effected at room temperature (about 18°–20° C.), and can even be accomplished at lower temperatures such as 10°–15° C. The use of higher temperatures is also satisfactory, and is in no way excluded.

A better understanding of the invention and of its many advantages can be had by reference to the following illustrative examples.

Example 1

Indian goatskins were pre-softened with water for 24 hours and then enzymatically softened, without addition of water, by placing them in a vessel with 0.5 percent mold fungus protease in powdered form, calculated on the weight of the pre-softened hides, and 0.1 percent of a preservation agent. The skins were felted for one hour. After standing an additional hour, 50 percent of water and 1 percent of sodium nitrate were added. After a felting period of another hour the hides were set aside. After 24 hours, the hair was removed therefrom. The action of the mold fungus protease and the sodium nitrate took place in media at pH 7.

Example 2

Dried Indian goatskins were softened in water for 24 hours and then enzymatically softened by placing in a vessel, without addition of water, with 0.6 percent of mold fungus protease in powdered form, calculated on the weight of the pre-softened skins, 0.5 percent sodium sulfate, and 0.1 percent of a preservation agent. The skins were felted for 1 hour. After 1 hour of standing, 50 percent of water and 1 percent of potassium nitrate were added, and the skins were felted for an additional hour,

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after which they were set aside for 24 hours. The hair was then removed from the hides. The mold fungus protease medium was at a pH between 7 and 7.5; the solution containing sodium nitrate had a pH of 7.

Example 3

Dried Spanish goatskins were pre-softened in water for 24 hours and thereafter enzymatically softened by placing in a vessel, without addition of water, with 0.5 percent mold fungus protease, calculated on the weight of the pre-softened skins, and 0.1 percent of a preserving agent. The skins were felted for 1 hour. After 1 hour's standing, 50 percent of water, 1 percent of calcined sodium sulfite, and 1.2 percent of potassium chloride were added. The skins were felted for 1 hour and allowed to stand for 24 hours. The hair was then removed. The action of the mold fungus protease and the salts took place in media with a pH of 7.

Example 4

Salted red cowhides were pre-softened with water, rinsed, and then put in a vessel, without addition of water, for additional softening with 0.75 percent mold fungus protease in powdered form, calculated on the weight of the pre-softened hides, and 0.1 percent of a preservation agent. The hides were then felted for 30 minutes. After standing for 1 hour, 50 percent of water and 1 percent of ammonium chloride were added. After an additional hour's felting, the hides were set aside for 24 hours and the hair was then removed. The action of the mold fungus protease and of the ammonium chloride took place in solutions at a pH of 7.

Example 5

Salted black cowhides were pre-softened with water. After rinsing, the hides were additionally softened by agitating for 30 minutes in a vessel, without the addition of water, with 0.5 percent bacterial protease in powdered form, 0.2 percent of almond emulsin having a beta-glucosidase value of 0.01 and 0.5 percent calcined sodium bisulfite. After one hour's standing, 50 percent of water and 1 percent of ammonium chloride were added. After felting for 10 minutes, the hides were set aside for 24 hours and then unhaired. The protease medium had a pH of 6–6.5; that of the ammonium chloride was at pH 7.

Example 6

Dried Chinese goatskins were presoftered for 48 hours with water and after rinsing were further treated, during the course of an hour's felting, in a vessel with 0.8 percent bacterial protease in powdered form, calculated on the weight of the presoftered hides, 0.2 percent of almond emulsin having a beta-glucosidase value of 0.01, 0.8 percent of sodium bisulfite, and 0.8 percent of ammonium sulfate. After 2 hours' standing, 50 percent of water, 3 percent of calcined sodium sulfite, and 1 percent of potassium chloride were added. After an additional hour's felting, the hides were set aside for 24 to 36 hours and then unhaired. For Indian goatskins, half the quantity of enzyme/salt mixture is sufficient in the softening treatment. The action of the enzyme took place at pH 6–6.5. The solution of sodium sulfite and potassium chloride was at pH 7.

Example 7

Dried Indian goatskins were presoftered for about 36 hours with water. After rinsing, they were felted for one hour in a vessel with 0.4 percent bacterial protease, calculated on the weight of the presoftered hides, 0.6 percent sodium bisulfite, and 0.6 percent ammonium sulfate. After standing for 1 hour, 50 percent water, 1.5 percent sodium sulfite, and 1 percent sodium chloride were added. After an additional 1 hour period of felting, the hides were set aside for 24 hours and then unhaired. By inclusion with the protease of 0.1 percent of a polyglycol

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ether wetting agent prepared by condensing 10 moles of ethylene oxide with 1 mole of an alkyl phenol, the water presoftening period can be reduced for 24 hours. The action of the bacterial protease took place at pH 6; the action of the sodium sulfite and sodium chloride at pH 7.

Example 8

Indian goatskins previously softened by a 48 hour treatment with water were further softened by 1 hour's felting in a vessel with 1.0 percent of pancreatic trypsin in powdered form, calculated on the weight of the presoftened hides. After 2 hours' standing, 50 percent water, 1 percent ammonium sulfate, and 0.5 percent of potassium chloride were added. After an additional one hour's felting, the hides were set aside for 36 hours and then unhaired. The action of the pancreatic trypsin took place in a medium at pH 7-7.5, that of the salts at pH 7. The unhairing effect can be increased by raising the pH of the salt solution to pH 9, for example by the addition of soda.

Example 9

Dried Indian goatskins were presoftened with water and then felted for 30 minutes with 0.5 percent of mold fungus protease, calculated on the weight of the presoftened hides, and 0.3 percent of a preservation agent. After two hours' standing, 50 percent of water and 5 percent of anhydrous sodium thiosulfate were added. After another 30 minutes of felting, the hides were allowed to stand overnight. After 24 hours, they were dehaired. The action of the mold fungus protease was in a medium at pH 6.5-7; the solution of sodium thiosulfate had a pH of 7.

Example 10

Kid hides were presoftened with water and then felted for 30 minutes with 0.4 percent bacterial protease, 0.3 percent of a preserving agent, 0.2 percent of calcined sodium sulfite, and 0.4 percent ammonium sulfate. After 2 hours' standing, 50 percent of water and 2 percent of sodium sulfite (or 1.75 percent sodium sulfite with 0.25 percent sodium hyposulfite—which is even more efficacious) were added. After another 30 minute long felting period, the hides were left to stand overnight. After about 24 hours, the hides were unhaired. The action of the bacterial protease occurred at pH 6.5-7; the action of the sodium sulfite at pH 7.5. The use of 50 to 250 percent of water together with between 2 and 10 percent of calcined sodium sulfite alone, without the prior protease treatment, gives no loosening of hair from the hides.

Example 11

Calfskins, presoftened and rinsed with water, were felted for 30 minutes with 0.6 percent bacterial protease, 0.4 percent calcined sodium bisulfite, and 0.8 percent of ammonium sulfate. After 2 hours' standing, 50 percent water and 3 percent of calcined sodium sulfite were added. After an additional 30 minutes of felting, the hides were allowed to stand, and were unhaired after 24-36 hours. The action of the bacterial protease takes place in a medium at pH 6-6.5; the action of the sodium sulfite takes place in a medium at pH 7.5-8.

If, in place of 50 percent water and 3 percent sodium sulfite, 250 percent water, 3 percent sodium sulfite, and 1 percent of mold fungus protease are used, a somewhat longer period is required for unhairing.

Example 12

Red cowhides, presoftened with water and then rinsed, were felted for one-half hour with 0.6 percent bacterial protease, 0.5 percent sodium bisulfite, and 0.4 percent ammonium sulfate. After one hour's standing, 50 percent water and 4 percent of sodium sulfite were added and felted for an additional 30 minutes. The hides were then left to stand and were unhaired after about 40 hours. The action of the bacterial protease was in a medium at

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pH 6-6.5; that of the sodium sulfite in a medium at pH 7.5-8.

Example 13

Goatskins were presoftened with water, rinsed, and then felted for one hour with 0.5 percent mold fungus protease, calculated on the weight of the presoftened skins. After two hours' standing, 50 percent water and 0.5 percent of 60-62 percent sodium sulfide were added. Felting continued for an additional hour, and then the hides were set aside. After 24 hours, they were unhaired. The action of the mold fungus protease was at pH 7; that of the sodium sulfide at pH 12-13. If the presoftened hides or hides fully softened with water are treated only with 50 percent of water and 0.5 percent of sodium sulfide (60-62 percent), no loosening of the hair is observed.

Example 14

Water softened goatskins were felted for one-half hour with 0.5 percent mold fungus protease and 0.3 percent of a preserving agent. After 3 hours' standing, 50 percent of water, 2 percent of 98 percent thioglycolic acid neutralized with ammonia were added. After an additional 30 minutes of felting, the hides were set aside and after 24 hours were dehaired. The action of the mold fungus protease and the thioglycolic acid was at pH 7. If water presoftened or fully softened goatskins are felted for one-half hour with 50 percent of water and with 2 percent of ammonia-neutralized 98 percent thioglycolic acid—without protease treatment—and are then set aside for 24 hours, a hair loosening of only 30 to 40 percent is observed, whereas skins treated with mold fungus protease according to the example can be dehaired 100 percent after 24 hours.

The criticality of the two-step process of the invention is shown by the results of comparative unhairing techniques in Examples 15 and 16 below.

Example 15

A dried Indian goatskin was washed and soaked with water for 24 hours and divided into 4 parts. The first part was felted for 1 hour with 0.5 percent by weight of skin of a mold fungus protease without addition of water. After 24 hours, 20 to 25 percent of the hair on the skin was loosened.

The second part of the skin was felted for one hour with 50 percent water and 1 percent of sodium nitrate. After 24 hours, no loosening of hair was observable.

The third portion of the skin was felted for one hour with 0.5 percent by weight of the mold fungus protease and 1 percent by weight of sodium nitrate without the addition of water. After 24 hours, about 20 percent of the hair had been loosened.

The fourth part of the skin was felted for 1 hour with 0.5 percent of mold fungus protease without the addition of water. After an additional hour, 50 percent of water and 1 percent of sodium nitrate were added and the skin was felted for 30 minutes. The treated hide was then set aside. After 24 hours from the beginning of the treatment, substantially 100 percent of the hair could be removed from the skin. The other neutral salts mentioned earlier herein give corresponding results when employed according to the last-mentioned methods. Potassium thiocyanate and ammonium chloride are especially effective.

Example 16

An Indian goatskin was softened with water and divided into 4 parts. The first part was felted for 30 minutes with 3 percent of mold fungus protease, calculated on the weight of the softened hide, according to the process described in German Patent 1,026,038, without the addition of water. After 24 hours, 100 percent of the hair could be removed.

A second part of the skin was felted with 0.5 percent mold fungus protease for 30 minutes. After 24 hours, about 15 percent of the hair was loosened.

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A third portion of the skin was felted for 30 minutes with 50 percent of water and 2 percent of calcined sodium sulfite, both calculated on the weight of the softened skin. After 24 hours, there was practically no loosening of the hair.

The fourth part of the skin was treated with 0.5 percent of mold fungus protease for 30 minutes. After 2 hours, 50 percent of water and 2 percent of calcined sodium sulfite were added and the skin felted for an additional 30 minutes. After 24 hours, calculated from the beginning of the enzymatic treatment, substantially 100 percent of the hair was easily removable. The mold fungus protease used had an enzyme value above 5000.

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

What is claimed is:

1. The method of unhairing hides which consists essentially of softening water-soaked hides by contacting them with an amount of a powdered proteolytic enzyme insufficient to cause substantial loosening of hair, and then contacting the softened hides, at a pH between about 5.5 and 8, with at least one reagent selected from the group consisting essentially of sulfur containing reducing agents and inorganic neutral salts of the alkali metals and ammonium.

2. The method of unhairing hides which consists essentially of softening water-soaked hides by contacting them with an amount of a powdered proteolytic enzyme insufficient to cause substantial loosening of hair, and then contacting the softened hides, at a pH between about 5.5 and 8 and in the presence of from about 30 percent to 250 percent of water by weight of the softened hides, with at least one reagent selected from the group consisting essentially of sulfur containing reducing agents and inorganic neutral salts of the alkali metals and ammonium.

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3. The method of claim 1 wherein said sulfur containing reducing agent is a compound containing oxygen.

4. The method of claim 1 wherein said sulfur containing reducing agent is a oxygen-free compound.

5. The method of claim 1 wherein soaked hides are contacted with a proteolytic enzyme in the presence of oligases.

6. The method of claim 1 wherein the hides, during the course of treatment, are additionally contacted with a wetting agent.

7. The method of claim 6 wherein said wetting agent is a polyglycol ether, the molecules of which comprise 6 to 16 polymerized units of ethylene oxide.

8. The method of claim 6 wherein said wetting agent is contacted with the hides together with said reagent selected from the group consisting essentially of sulfur containing reducing agents and inorganic neutral salts of the alkali metals and ammonium.

9. The method of claim 1 wherein said proteolytic enzyme is the enzyme of a micro-organism.

10. The method of claim 1 wherein said hides and proteolytic enzyme are contacted at a pH between about 5.5 and 8.

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