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PROCESS FOR PREPARING HIDES

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26 Claims. (Cl. 149—2)

The invention relates to improvements in preparing hides, and more particularly to a process for depilating and bating skins and hides with the aid of mold tryptases.

The present application is a continuation-in-part of the following prior applications: Serial No. 70,890 filed March 25, 1936; Serial No. 104,147 filed October 5, 1936; and Serial No. 123,295 filed January 30, 1937.

In German application Serial No. R 97,257 filed September 4, 1936, and in my U. S. application Serial No. 123,295 filed January 30, 1937, there is described a process for depilating and bating skins and hides with the aid of mold tryptases especially tryptases cultured from aspergillus varieties, these being used in slightly alkaline to slightly acid solution, and, if desired, at elevated temperature, a feature being that chlorine-free and chromium-free oxidizing agents as well as sodium bisulphite, sodium sulphite, sodium thiosulphate, or similar sulphur-containing compounds are added to the mold tryptase solutions to serve as compounds adapted to promote enzymatic action. Aside from these, alkaline reacting salts may also be added.

Furthermore, in my German application Serial No. R 95,449 filed February 7, 1936, and in my U. S. application Serial No. 123,295, it is recited that the hides and skins may be pre-treated with sodium sulphite or similar sulphur-containing compounds, if desired, with the addition of soda, and then first subjected to the action of the mold tryptase solution together with chlorine-free and chromium-free oxidizing agents as activators. Pre-treatment with ammonia has been described in my German application Serial No. R 94,938 filed December 7, 1935 and in my U. S. application Serial No. 123,295.

The present application is related to the subject matter covered by application Serial No. 123,295 in that the same reagents may be used but differs from what is disclosed and claimed in said application in that the hair loosening or depilating agent is added in a separate step from the treatment with oxidizing and reducing agents. This step may be prior to the treatment with oxidizing agents, subsequent thereto or may be between the treatments with oxidizing and reducing agents.

In addition to the oxidizing and reducing agents recited, other agents could be used which facilitate the enzymatic action, e. g., wetting agents and organic compounds which contain hydroxyl groups, e. g., carbohydrates, alcohols, aliphatic oxy acids, phenols, naphthols.

Both in treating the skins with the mold tryptases as well as in the treatment with the recited inorganic substances, alkaline reacting salts, e. g., sodium carbonate may be used conjointly therewith. However, a separate subsequent treatment with swelling or non-swelling alkalies and/or alkaline reacting salts may be adjoined.

An alkali nitrite, nitrate, perborate, percarbonate or peroxide, or hydrogen peroxide may for example serve as the chlorine-free and chromium-free oxidizing agent used as set forth in my prior application Serial No. 123,295. In lieu of ammonia, ammonium salts such as ammonium chloride, ammonium sulphate, ammonium carbonate, may be used, together with alkaline reacting salts such as soda, sodium bicarbonate, borax, sodium phosphate, or alkalies like caustic soda or barium hydroxide.

Furthermore, the salt mixture may be used conjointly or separately for example so that the treatment with ammonia or with ammonia yielding salts either precedes or follows the treatment with the oxidizing and reducing agents.

This process is applicable both to salted as well as to dried skins. In working up salted skins it is preferable first to free these from adhering salt and to wash them out with water, whereupon they are soaked from 1 to 2 days with ordinary water, rinsed again, and then, in accordance with the invention brought directly into a solution of sodium nitrite, sodium sulphite, ammonium sulphate and soda.

In working up dried hides it has been found to be very desirable to allow a solution of oxidizing and reducing substances, if desired including ammonia, to act directly on the dried hides without a previous water soaking. Since the oxidizing and reducing acting compounds when used in this combination exert an appreciably greater softening action than water or neutral salts or weak alkalies such as ammonia, the soaking period is appreciably shortened.

After such soaking it is possible to use other known depilating and bating agents in addition to or in lieu of the mold tryptases. Among these may be mentioned alkalies, lime, the sulphides of the alkali metals and arsenic, arsenic being generally used in conjunction with lime.

For details concerning the application of these materials reference is directed to the illustrative examples given below.

It has already been proposed to activate vegetable or animal proteases by means of thio acids or their salts or even by means of other

oxygen containing compounds which contain sulphur in di- or tetravalent form and to use the enzyme solutions for depilating and bating of calf skins, using papain as the enzyme.

Furthermore it has been recommended to use papain in admixture with fungi tryptase for depilating and bating. Finally a method is known by which the depilating and bating are effected with the use of bacterial proteases, sodium bisulphite being indicated as the deliming or neutralizing agent.

It is also known that the action of papain as a depilating agent can be increased by pre-treating the hides with strongly ionized salts such as e. g., sodium nitrate, potassium iodide, magnesium bromide, potassium cyanide, etc.

Aside from the fact, that owing to the still relatively uncertain status of enzyme chemistry, it cannot be concluded from these proposals that pre-treatment with these compounds or their use conjointly with enzymes will also produce favorable results with mold tryptases, nevertheless novelty is inherent in the process of the application and consists in the combined use of oxidizing and reducing compounds, if desired together with ammonia, in a step separate from the treatment with the mold tryptases, thus producing unique and favorable results.

Example 1

Salted cattle hides are soaked for two days with ordinary water and then treated (per 100 kg. of soft weight) with the following for one hour:

Water	liters	200.0
Sodium sulphite	kilogram	.5
Ammonium sulphate	do	.5
Sodium nitrite	do	.6
Calcined soda	do	.45

The alkalinity of the solution corresponds to pH9 to 9.5. After reacting for one day, the hides are handled out and coated on both sides with a solution of:

Mold tryptase from *Aspergillus flavus*	kilogram	1
Water	liters	20

After 24 hours the hides are covered while in the pit with a solution of:

Water	liters	200
Calcined soda	kilograms	4

The alkalinity of this solution should be about pH 10. After 1 to 2 days the hides are depilated and then worked up without any subsequent bating.

The preliminarily softened hides may also be treated first with a solution of:

Sodium nitrite	kilogram	.6
Ammonium sulphate	do	.5
Calcined soda	do	.45
Water	liters	150.0

for one hour, to which may then be added a solution of .5 kg. of sodium sulphite in 50 liters of water—the treatment continued again for an hour, and the procedure continued as indicated above.

Example 2

The procedure is carried out as in the case of Example 1. In lieu of coating as described in that example, the hides are treated in a drum with:

Water	liters	200
Mold tryptase from *Aspergillus wentii*	kilograms	3

for one hour. The next day the following solution is added thereto:

Calcined soda	kilograms	4
Water	liters	20

After 1 to 2 days the hides may be depilated and are then worked up further as in Example 1.

Example 3

40 kg. of dry goat skins are softened for one day with

Water	liters	400
Sodium sulphite	kilogram	.4
Ammonium sulphate	do	.4
Sodium nitrate	do	.4
Calcined soda	do	.4

then stretched, and then placed in a fresh soaking bath of the same composition. After 1 to 2 days, when sufficiently softened, they are limed with:

Mold tryptase from *Aspergillus effusus*	kilograms	3
Water	liters	10

The hides are placed in a pit and after 24 hours covered with:

Water	liters	200
Calcined soda	kilograms	4

After 5 days they are depilated and worked up further without any subsequent bating.

Example 4

40 kg. of dry sheep skins are soaked in the manner indicated for Example 3, then coated on the fleshy side with:

Mold tryptase from *Aspergillus oryzae*	kilograms	3
Water	liters	10

After 24 hours the wool is removed; then they are after-treated for two days (per 100 kg. of hide weight) with a solution of:

Water	liters	300
Calcined soda	kilograms	3

They are then worked up further without any subsequent bating.

Example 5

Salted cattle hides are soaked for two days with ordinary water, then treated for one hour (per 100 kg. of soft weight) with:

Water	liters	200.0
Sodium sulphite	kilogram	.5
Ammonium sulphate	do	.5
Sodium percarbonate	do	.6
Calcined soda	do	.4

The alkalinity of the solution should be pH 9.5. After reacting for one day the hides are handled out and coated as in Example 1 with the mold tryptase solution.

Example 6

The procedure is carried out as in Example 5. In lieu of .6 kg. sodium percarbonate however, .6 kg. sodium perborate are used.

Example 7

Salted cattle hides are soaked for three days with ordinary water and then treated for one hour (per 100 kg. of soft weight) with:

Water	liters	200
Mold tryptase from *Aspergillus flavus*	kilograms	2

The next day a solution of:

Sodium sulphite	kilograms	1
Sodium nitrite	do	1
Ammonium sulphate	do	1
Calcined soda	do	6
Water	liters	40

are added. After treating for one hour the hides are allowed to repose over night. The alkalinity of this solution should be pH 10. After one day the hides are depilated and then worked up further without subsequent bating.

Example 8

The procedure is carried on as in Example 1. There is however added to the solution of sodium sulphite, ammonium sulphate, sodium nitrite and soda (per 100 kg. of soft weight) .3 kg. of olein alcohol sulphonate.

Example 9

The procedure is carried out as in Example 1. However, to the solution of sodium sulphite, ammonium sulphate, sodium nitrite and soda, .5 kg. of sodium lactate are added.

Example 10

40 kg. of dry goat skins are soaked for one day with:

Water	liters	400
Sodium sulphite	kilogram	.4
Ammonium sulphate	do	.4
Sodium nitrite	do	.4
Soda (calcined)	do	.4

then stretched and placed in a fresh soaking bath of the same composition. After 1 to 2 days the skins, if sufficiently softened, are limed as usual with lime-sodium-sulphide and bated with a pancreatic bating liquor.

I claim:

1. In a process which includes treating hides or skins in aqueous solution with (1) at least one oxidizing agent selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide, (2) a reducing agent comprising an oxygen containing sulphur compound and (3) a depilating and bating agent comprising a mold tryptase; the improvement wherein the treatment with the depilating and bating agent comprises a separate step from the treatment with the oxidizing and reducing agents.

2. Process according to claim 1, wherein a member of a group consisting of ammonia and compounds which produce ammonia acts on the hides and skins separately from the depilating and bating agent.

3. Process according to claim 1, wherein wetting agents act on the hides or skins separately from the depilating and bating agent.

4. Process according to claim 1, wherein an organic compound containing an hydroxyl group selected from a class consisting of carbohydrates, alcohols, aliphatic hydroxy-acids, acts on the hides or skins separately from the depilating and bating agent.

5. Process according to claim 1, wherein the said oxidizing agent and the said reducing agent act on the hides or skins together in one solution.

6. Process according to claim 1, wherein the said oxidizing agent and the said reducing agent act on the hides or skins in separate solutions.

7. Process according to claim 1, wherein the said oxidizing agent and the said reducing agent act on the hides or skins before the action of the depilating and bating agent.

8. Process according to claim 1, wherein the said oxidizing agent and the said reducing agent act on the hides or skins after the action of the depilating and bating agent.

9. Process according to claim 1, wherein at least one member of a group consisting of alkalies, lime, and sulphides of the alkalimetals is used as the depilating agent.

10. Process according to claim 1, wherein mold tryptase in neutral to weakly alkaline aqueous solution is used as the depilating and bating agent.

11. Process for producing ready-to-tan hides or skins including the steps of soaking dry hides or skins in aqueous solutions of (1) oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide and (2) oxygen-containing reducing compounds of sulphur and separately treating the soaked hides or skins with mold tryptase in neutral to weakly alkaline aqueous solution.

12. Process for producing ready-to-tan hides or skins including the steps of soaking dry hides or skins in aqueous solutions of (1) oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide and (2) oxygen-containing reducing compounds of sulphur and ammonia or compounds which produce ammonia and subsequently treating the soaked hides or skins with mold tryptase in neutral to weakly alkaline aqueous solution.

13. Process for producing ready-to-tan hides or skins including the steps of soaking salted hides or skins in water, treating the soaked hides or skins with (1) oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide and (2) oxygen-containing reducing compounds of sulphur in aqueous solution and separately treating the hides and skins with mold tryptase in neutral to weakly alkaline aqueous solution.

14. Process for producing ready-to-tan hides or skins including the steps of soaking salted hides or skins in water, treating the soaked hides or skins with (1) oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide and (2) oxygen-containing reducing compounds of sulphur and ammonia or compounds which produce ammonia in aqueous solution and separately treating the hides and skins with mold tryptase in neutral to weakly alkaline aqueous solution.

15. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur, in an aqueous solution, separately treating the hides or skins with mold tryptase in neutral to weakly alkaline

aqueous solution and depilating the hides or skins.

16. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur, in an aqueous solution, separately depilating the hides or skins and treating them with alkaline compounds selected from a group consisting of alkalies and alkaline reacting salts.

17. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur, in an aqueous solution, and thereafter with alkaline compounds selected from a group consisting of alkalies and alkaline reacting salts, and depilating the hides or skins.

18. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with a water-soluble sulphite, and an alkaline nitrite in aqueous solution and separately treating them with mold tryptase from an aspergillus in neutral to weakly alkaline solution.

19. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur and with a member of a group consisting of ammonia and compounds which produce ammonia, in an aqueous solution, separately treating the hides or skins with mold tryptase in neutral to weakly alkaline aqueous solution and depilating the hides or skins.

20. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur and with a member of a group consisting of ammonia and compounds which produce ammonia, in an aqueous solution, separately depilating the hides or skins and treating them with alkaline compounds selected from a group consisting of alkalies and alkaline reacting salts.

21. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with oxidizing agents selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide together with oxygen-containing reducing compounds of sulphur and with a member of a group consisting of ammonia and compounds which produce ammonia, in an aqueous solution, and thereafter with alkaline compounds selected from a group consisting of alkalies and alkaline reacting salts, and depilating the hides or skins.

22. Process for producing ready-to-tan hides or skins including the steps of treating hides or skins with a water-soluble sulphite, an alkaline nitrite, an ammonium salt and an alkaline reacting salt in aqueous solution and separately treating them with mold tryptase from an aspergillus in neutral to weakly alkaline solution.

23. In a process which includes treating hides or skins in aqueous solution with (1) at least one oxidizing agent selected from a group consisting of alkali nitrates, alkali nitrites, alkali percarbonates, alkali peroxides and hydrogen peroxide, (2) a reducing agent comprising an oxygen containing sulphur compound and (3) a depilating agent; the improvement wherein the treatment with the depilating agent comprises a separate step from the treatment with the oxidizing and reducing agents.

24. A process according to claim 1, wherein a carbohydrate acts on the hides or skins separately from the depilating and bating agent.

25. A process according to claim 1, wherein an alcohol acts on the hides or skins separately from the depilating and bating agent.

26. A process according to claim 1, wherein an aliphatic hydroxy-acid acts on the hides and skins separately from the depilating and bating agent.

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