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ART OF BATING HIDES AND SKINS

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This invention relates to the art of bating hides and skins.

Before hides and skins are tanned or converted into commercial leather they are subjected to a number of processes. For example, after the hides or skins have been flayed, cured and soaked, they are treated for dehairing. This treatment loosens the hair so that it can easily be removed. One of the common methods of treatment for loosening hair consists in soaking the skins or hides in a lime solution, either with or without the addition of sulfides, red arsenic or other chemicals. It has also been proposed to effect the loosening of the hair by certain enzymatic methods, such use of enzymes being usually carried out after the skins have been first subjected to an alkaline bath. After the hides or skins have been subjected to the lime or alkaline process, they are usually partly neutralized.

As a result of the lime treatment, the fibres of the hides or skins have more or less resilience or elasticity and the presence of lime or soda, in the form of free alkali or alkaline salts, causes a swelling of the hides or skins. Before the hides or skins can be tanned, they must be "brought down" or "reduced", particularly in the production of light and soft leather, in order to remove this elastic or resilient condition, render the hides or skins soft, supply and flaccid, and to remove the alkaline swelling. To this end, the hides or skins are subjected to a process known as deliming or bating or puering. This process normally consists in "neutralizing" the hides or skins to a pH ranging from slight acidity to about 10, ordinarily in the presence of proteolytic enzymes.

This neutralizing or lessening of alkalinity may be achieved in various ways. For example, it has been proposed to use inorganic acids such as sulfuric, hydrochloric and boric acids and organic acids such as lactic, formic, acetic and butyric acids. The result of such treatment is the removal from the hides or skins of a large amount or all of the lime, in the form of soluble salts.

As another example, one of the earliest known methods of deliming, or puering, was to treat the hides and skins in a bath formed from animal manure. This method involves a violent fermentation, with the formation of various acids, more particularly large amounts of CO_2.

The deliming process is usually, though not necessarily, carried out in the presence of proteolytic enzymes which act on certain constituents of the hides or skins. The enzymes or enzymatic products used for this purpose may be derived from various sources, such, for example, as pancreas glands or from preparations which contain the proteases of various plants or molds or other micro-organisms, e. g., bacterial proteases. They may, of course, be generated by micro-organisms during the above mentioned process of fermentation.

While this neutralizing process is necessary, not only for the purposes mentioned but also because the presence of the lime in the hides or skins is undesirable in subsequent operations, it has been found that when the hides and skins are subsequently treated with acids, as in the tanning process, the otherwise harsh action of the acids is somewhat mitigated if there is present one or more relatively insoluble salts of a basic nature. While the fermenting process just referred to results in a large part of the lime being retained in the form of such a salt, namely, calcium carbonate, the advantages of its presence are far outweighed by the disadvantages incident to the fermentation process itself. In fact, because the fermentation method of bating is so objectionable, for a variety of reasons, it has, to a large extent, been replaced in commercial practice by safer methods. One serious objection is that the process is practically uncontrollable and the hides or skins may be and frequently are badly damaged if the fermentation goes too far. Again, the bacteria necessarily present are apt to injure the skins and hides. A further objection is that the process is attended by an evil smell. In addition, the degree of evolution of CO_2 gas is uncontrollable and is apt to be more violent than is desirable.

It is an object of the present invention to provide a bate and a method of bating hides and skins that results in the presence therein of one or more relatively insoluble salts of a basic nature and that, at the same time, avoids the objectionable features of the methods above referred to.

Other objects and advantages of the invention will be apparent from the ensuing description.

According to the present invention, I use as a bating agent for offsetting or neutralizing the alkalinity of the lime and soda, one or more salts of ammonia that will react with the lime to form relatively insoluble salts of a basic nature. For this purpose I have found that the carbonates, bicarbonates and carbamates of ammonia are suitable and satisfactory. Such salts react with the lime to form relatively insoluble calcium carbonates, with the result that, while the alkalinity of the lime is offset or neutralized, so that the skins are properly "bated", lime is retained in the

skins in the form of relatively insoluble salts of a basic nature. That is, the advantages of the old fermentation process are retained but the dangers and disadvantages of fermentation are avoided. Not only is no forced fermentation necessary but any incidental fermentation that might naturally occur can be prevented since the bating operation may be carried out in the presence of disinfectants. Moreover, by controlling the amount of ammonium salts used, it is possible to control the extent to which the swelling is reduced and the extent to which the lime, in the form referred to, is retained.

Depending on the desired amount of retained calcium salts, the ammonium carbonates, bicarbonates or carbamates may be used alone or in connection with other deliming agents, such as various acids, organic or inorganic, for example, sulfuric, hydrochloric, acetic, formic and carbonic acids, or other ammonium salts such as chlorides and sulfates. These other neutralizing agents may be added either simultaneously with the ammonium carbonates, bicarbonates or carbamates or before or after the addition of the latter.

It is not essential to add the ammonium carbonates, bicarbonates or carbamates as such, since such salts may be generated during the process. For example, the desired ammonium salt or salts may be obtained by adding ammonia and CO_2; or by adding ammonium salts, such as chlorides or sulfates, and neutralizing the formed ammonia with CO_2; or by adding mixtures of sodium bicarbonate and ammonium salts, such, for example, as chlorides and sulfates. While sodium bicarbonate has previously been proposed as a neutralizing agent, such use with limed skins has not proved satisfactory, apparently because of the formation of caustic soda which is retained by the skins and prevents proper "falling" and neutralization. When used, however, in conjunction with ammonium salts, such as chlorides, for example, there is formed, by reaction, ammonium carbonate or bicarbonate and sodium chloride.

During the action of ammonium carbonates, bicarbonates or carbamates on limed skins, ammonia is driven off. If it is desired to neutralize this ammonia, it may be accomplished by adding an acid, preferably a weak acid such as boric or carbonic or a weak organic acid, such as amino acids, or acid salts such as ammonium or sodium bisulfates or bisulfites. If the above salts or stronger acids are used they should be added after the main action of the ammonium carbonates, bicarbonates or carbamates is over but if weak acids are used they may, if desired, be added simultaneously with the ammonium salts themselves.

The formed ammonium may also be removed to a considerable extent by expelling it by mechanical treatment in a more or less open vessel, such, for example, as a paddle, at a temperature of 80° F. or more.

In carrying out the invention to what is now considered the best advantage, the calcium carbonate or other calcium salt should be precipitated in an amorphous form. This can be attained by keeping the pH on the alkaline side, about 7.0 or higher, during the whole bating procedure. I have also found that it is advantageous to use small amounts of phosphates in the bating liquor, for example, from 2% to 60% of the ammonium carbonates, bicarbonates or carbamates used. The presence of magnesium salts also aids in the formation of amorphous calcium carbonate, etc. Therefore, if the lime used in the alkaline beamhouse process was deficient in magnesium oxide, magnesium salts may be added.

The ammonium carbonates, bicarbonates or carbamates, with or without the other ammonium salts or the acids above mentioned, may also be used in combination with proteolytic enzymes or enzymatic products derived from various sources, for example, pancreas glands or preparations containing the proteases of various plants or molds, or other micro-organisms, for example, bacterial proteases. If the enzyme preparations are used in a dry precipitate or are absorbed on wood flour, etc., a dry bating compound may be obtained by mixing such enzymatic preparations in a dry state with ammonium carbonates, bicarbonates or carbamates, with or without other ammonium salts or with or without acids, such as boric or amino acids, in a dry form, or with or without salts of phosphoric acid, such as di-ammonium mono-phosphate or mono-ammonium di-phosphate.

While the amounts of materials and the conditions under which they are used may vary widely, I have found the procedure set forth in the following examples to give satisfactory results, producing leather of superior and improved quality.

In the examples here given, the specified weight of hides or skins is to be understood to be "white weight", i. e., weight after dehairing and fleshing. It is also to be understood that the basis of the bating liquor is water, the amount used varying as desired. The usual range is from one part water to two to five parts hides or skins by weight.

Where a disinfectant is specified, any suitable disinfectant may be used, for example, those disclosed in U. S. Patent 1,985,267.

Where enzyme preparations absorbed on wood flour are specified, it is to be understood that the weight given includes both the absorbed and the absorbing material.

Example 1

Subject kipskins to a lime solution sharpened with sodium sulphide for about four days. Take out skins and unhair and flesh the same according to known practice. For 3450 pounds of these skins, add to the bating liquor about four pounds of an enzyme preparation of bacterial origin, about one pound ammonium bicarbonate and about twenty-two pounds ammonium sulfate. Subject the skins to a bating treatment in such liquor at about 92° F. for about one hour. Finish the skins for chrome leather in usual known manner.

Example 2

Soak and unhair wet salted India skins in customary lime bath. After unhairing and fleshing, wash with water for about 15 minutes. For 2000 pounds of skins, add to the bating liquor about ten pounds of proteolytic enzyme preparation and about twenty pounds of a mixture consisting of about 33% ammonium carbonate, about 66% ammonium sulfate and about four pounds disinfectant. Bate overnight in a paddle at about 94° F.

Example 3

Soak goatskins as usual and subject to an alkaline swelling bath containing both lime and

caustic soda. After a few days, partly neutralize the skins and subject the same to an unhairing bath containing bacterial proteases. Unhair and flesh in usual manner. For 1000 pounds of skins, add to the bating liquor about ten pounds of a bating preparation comprising about 75% of a proteolytic enzyme absorbed on wood flour and about 25% ammonium carbonate. Add a disinfectant. Bate overnight at about 90° F.

Example 4

Soak and unhair goatskins in customary lime bath. After unhairing and fleshing, bate 1000 pounds of skins overnight in a bating liquor to which has been added seven and one-half pounds of an enzyme preparation and about twenty-two and one-half pounds of a mixture containing about 80% ammonium carbonate, about 10% ammonium sulfate and about 10% urea by weight. Bate overnight at about 88° F.

Example 5

For the added bating material of Example 4, substitute about five pounds of a pancreatic bating preparation and about twenty-five pounds of a mixture consisting of about 60% ammonium chloride and about 40% sodium bicarbonate. Bate at 82° F. to 96° F.

Example 6

For the added bating material of Example 4, substitute about seven and one-half pounds of a proteolytic enzyme preparation absorbed on wood flour and about an equal amount by weight of ammonium bicarbonate. Add a disinfectant. Bate overnight at 82° F. to 96° F.

Example 7

For the added bating material of Example 4, substitute about five pounds of a proteolytic enzyme preparation absorbed on wood flour and about fifteen pounds of a mixture consisting of about 42% sodium bicarbonate, about 54% ammonium chloride and about 4% di-ammonium mono-phophate. Bate at 82° F. to 96° F.

Example 8

Soak and unhair goatskins in customary lime bath. After unhairing and fleshing, bate 2000 pounds of skins overnight in a paddle containing a bating liquor to which has been added about sixteen pounds of a mixture consisting of about equal amounts by weight of a pancreatic enzyme absorbed on wood flour and ammonium bicarbonate. Bate about four hours at about 90° F.

Example 9

Soak and unhair goatskins in the customary lime bath. After unhairing and fleshing, treat 2000 pounds of skins overnight in a liquor to which has been added about ten pounds ammonium bicarbonate.

What is claimed is:

1. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing at least one reagent tending to react with part of the lime in the hides or skins to form soluble salts, and also containing an ammonium salt which will form, by reaction with part of the lime, a relatively insoluble salt of a basic nature.

2. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing an enzymatic preparation and an ammonium salt which will form, by reaction with the lime in the hides or skins, a relatively insoluble salt of a basic nature.

3. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing an enzymatic preparation, at least one reagent tending to react with part of the lime in the hides or skins to form soluble salts, and also containing an ammonium salt which will form, by reaction with part of the lime, a relatively insoluble salt of a basic nature.

4. The process of bating hides and skins which comprises subjecting limed skins or hides to a bating liquor to which has been added two ammonium salts, one of which forms, by reaction with the lime in the hides or skins, a relatively soluble calcium salt and the other of which forms, by reaction with the lime, a relatively insoluble calcium salt of a basic nature.

5. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing an ammonium salt which will form, by reaction with the lime in the hides or skins, a relatively insoluble salt of a basic nature, the bating material also containing a phosphate.

6. A bating liquor for bating hides or skins comprising at least one reagent tending to react with the lime in the hides or skins to form soluble salts and at least one ammonium salt which will form, by reaction with the lime, a relatively insoluble salt of a basic nature.

7. A bating liquor for bating hides or skins comprising an enzymatic preparation and an ammonium salt which will form, by reaction with the lime in the hides or skins, a relatively insoluble salt of a basic nature.

8. A dry material for use in a bating liquor and which comprises a mixture of an enzymatic preparation and an ammonium salt selected from the group consisting of carbonates, bicarbonates and carbamates.

9. The process of bating hides and skins which comprises subjecting limed hides and skins to a bating material containing an ammonium salt which will form, by reaction with the lime in the hides or skins, a relatively insoluble salt of a basic nature, the bating material also containing a magnesium salt.

10. A composition of matter, in dry form, for use in a bating liquor and comprising a mixture of an enzymatic preparation, an ammonium salt which, in the liquor, will tend to form, by reaction with lime, a relatively insoluble salt of a basic nature, and a substance which, in the bath, will tend to react with lime to form soluble salts.

11. A composition of matter, in dry form, for use in a bating liquor and comprising a mixture of an enzymatic preparation, an ammonium salt which, in the liquor, will tend to form, by reaction with lime, a relatively insoluble salt of a basic nature, a substance which, in the bath, will tend to react with lime to form soluble salts, and a phosphate.

12. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing at least one reagent tending to react with part of the lime in the hides or skins to form soluble salts, and also containing an ammonium salt selected from the group consisting of carbonates, bicarbonates and carbamates.

13. The process of bating hides and skins which comprises subjecting limed hides or skins to a bating material containing an enzymatic

preparation and an ammonium salt selected from the group consisting of carbonates, bicarbonates and carbamates.

14. A bating liquor for bating hides and skins comprising an enzymatic preparation and an ammonium salt selected from the group consisting of carbonates, bicarbonates and carbamates.

15. The process of bating hides and skins which comprises subjecting limed hides and skins to a bating material containing an enzymatic preparation, at least one reagent tending to react with part of the lime to form soluble salts, and an ammonium salt selected from the group consisting of carbonates, bicarbonates and carbamates.

16. A dry material for use in a bating liquor for limed skins and hides, which comprises a mixture of an enzymatic preparation and an ammonium salt which will form, by reaction with the lime in the hides or skins, a relatively insoluble salt of a basic nature.

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