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(54) **AMMONIUM AND BORIC ACID FREE DELIMING AGENT, A DELIMING PROCESS AND A USE THEREOF**

(57) The present invention discloses an ammonium and boric acid free deliming agent, which comprises amino acid component and no ammonium compound; the amino acid component comprising amino acid, amino acid salt, and/or protein hydrolysate which contains amino acid and/or amino acid salt. The present invention also discloses a deliming process by using said deliming agent and the use of amino acid, amino acid salt and/or protein hydrolysate as deliming agent. The deliming agent not containing boric acid or ammonium salts is environmentally friendly and has good deliming effect.

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Description

FIELD OF THE INVENTION

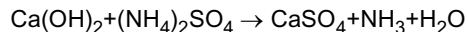
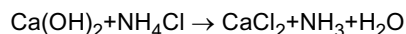
[0001] The present invention relates to ammonium and boric acid free deliming agent, and to a leather deliming process by using the said deliming agent. The present invention also related to a use of amino acid, amino acid salt and/or protein hydrolysate as deliming agent.

DESCRIPTION OF THE RELATED ART

[0002] It's well known that in the leather manufacturing process, pretreatments for raw pelts should be done before tanning and crusting. Liming is one of the pretreatments to remove hair and unwanted proteins usually by soaking the pelts in a lime bath. Then it is necessary to delime the pelts so as to bring them into a proper state of alkalinity. Deliming is about removing calcium hydroxide from pelts including surfaces and inner parts thereof and lowering pelts pH value until around 8. During the deliming, if pH value of the pelts decreases too fast, excessive deliming happens and leads to surface acid swelling. To prevent grain damage and acid swelling, mild deliming should be carried out by applying satisfactory deliming agents which have good buffering capacity and sufficient in lime removal.

[0003] Conventional deliming agents used in leather industry were mainly based on ammonium salts, such as ammonium sulfate, ammonium chloride, etc. US 2,318,454, which was granted May 4, 1943 used ammonium salt as deliming component. Ammonium salts have been widely accepted in leather industry due to the following characteristics: i) cheap raw material prices compared with organic compounds; ii) buffering effect, which provides a narrow pH range in deliming float and prevents the surface damage of the pelts and a mild removal of lime from the limed pelt. Ammonium salts are known as good buffering agents in deliming recipes, that generate leather with clean surface, even dying property and good handle feeling.

[0004] When ammonium salts are used for deliming purpose, they react with calcium hydroxide which are physically and chemically bonded on the limed pelt. For instance, the reactions between ammonium sulfate or ammonium chloride and calcium hydroxide are illustrated below:



[0005] Ammonium based deliming agents have two shortcomings, which limit their application in industry. The disadvantages are: i) the ammonia released during deliming leads to the workers' exposure in unsafe environment; ii) the high $\text{NH}_3\text{-N}$ content in tannery effluent made it necessary to perform $\text{NH}_3\text{-N}$ removal, which increases the cost and duration in wastewater treatment.

[0006] Due to the high $\text{NH}_3\text{-N}$ pollution induced by ammonium salts, three categories of acids have been explored as deliming agents in literature and patents: i) inorganic acid, like boric acid; ii) small molecular organic acids, including lactic acid, citric acid, succinic acid, or adipic acid; iii) macromolecule, such as polyimides, polysuccinimide and hydroxy polysuccinimide.

[0007] Boric acid has very good buffering effect in deliming float and was used as the alternative deliming agent, which enables even deliming across the thick pelts and generates leather with good quality. However, boric acid has reproductive toxicity and is listed in SVHC (substance of very high concern) according to REACH (Registration, evaluation, authorization and restriction of chemicals). A buffering system which has low impact on workers' health and environment is currently lacking.

[0008] CN 102010917A mentions an ammonia free deliming agent, which is the combination of two organic acids. One organic acid is a small molecular organic acid, such as citric acid, or succinic acid; the other organic acid is gluconic acid or sulfosalicylic acid. However, the above used small molecular organic acids have very limited buffering effect in liming float.

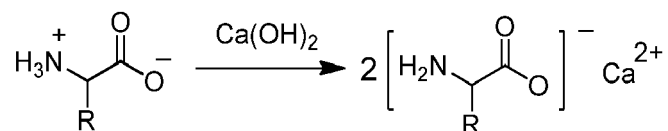
[0009] WO 2013/107233 also discloses an ammonia free deliming agent. The deliming agent comprises polysuccinimide or hydroxy polysuccinimide. Polyimides, polysuccinimides are polymers, which are slow in penetrating into thick limed pelts.

[0010] Since the use of ammonium salts, numerous trials have been done to seek for a safe, sufficient and mild deliming agent. However, for many years, environmental friendly deliming agents which have comparative deliming capacity as ammonium salt and high penetration rate needs to be developed.

SUMMARY OF THE INVENTION AND ADVANTAGES

[0011] Disclosed is an ammonium and boric acid free deliming agent. The deliming agent comprises amino acid component. The deliming agent has high lime dissolving value and good buffering capacity during deliming process, and ensures zero add-on $\text{NH}_3\text{-N}$ load originating from liming agents, resulting in low $\text{NH}_3\text{-N}$ load in deliming effluent. According to the present invention, the final $\text{NH}_3\text{-N}$ value in effluent is around 100 ppm.

[0012] The deliming with amino acids was implemented via the below route:



[0013] After reacting with hydroxide ion, the protonated amine groups generate amine compounds, which are weak bases and provide buffering capacity for the system. Good buffering capacity allows the pH value to decline gradually and to prevent acid swelling on the grain layer.

[0014] After reacting with calcium ion, the carboxylic groups form soluble calcium salts, enabling the effective removal of lime and produce wet blue/wet white with clean surface.

[0015] Amino acids in the present invention can be individually used in the deliming agent or combined with some additives, and achieve good deliming effect with no help of ammonium salts, thus enabling the replacement of conventionally used boric acid and ammonium salts. The invention also discloses a deliming process and the use of amino acids in the deliming agent.

[0016] Compared with ammonium based deliming agents, the present invention provides environmentally friendly deliming agents. The present deliming agent has the following features: i) amino acids are utilized as deliming agent, which are safe compounds both to environment and workers; ii) amino acids will not introduce $\text{NH}_3\text{-N}$ burden into deliming effluent, therefore the reduction of $\text{NH}_3\text{-N}$ generated in deliming process can be achieved.

[0017] Compared with the known ammonium free deliming agents, the present deliming agent has good deliming effect which is almost equal to ammonium salts and will not cause acid swelling.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The object of the present invention is therefore to provide an ammonium and boric acid free deliming agent, which comprises amino acid component and no ammonium compound; the amino acid component comprises amino acid, amino acid salt, and/or protein hydrolysate which contains amino acid and/or amino acid salt.

[0019] The amino acid component could mean any component so long as it comprises amino acid and/or amino acid ion and could react with Ca(OH)_2 without bringing any negative effect to deliming. The amino acid component in the present invention could comprise amino acid, amino acid salt, and/or protein hydrolysate which contains amino acid and amino acid salt.

[0020] The amino acid in the present invention is the commonly known amino acid which contains amine and carboxyl functional group, along with a side-chain (R group) specific to each amino acid. Amino acid having good buffering capacity and lime dissolving ability is preferably used in the present invention. Preferably, the amino acid is α -amino acid, which has both the amine and the carboxyl functional group attached to the α -carbon atom. The generic formula of the α -amino acid is $\text{H}_2\text{NCH(R)COOH}$ in most cases.

[0021] In a preferred embodiment, the amino acid comprises at least one selected from the group consisting of glycine, alanine, valine, leucine, isoleucine, phenylalanine, tryptophan, tyrosine, histidine, serine, threonine, cysteine, aspartic acid, glutamic acid, asparagine, glutamine, lysine, arginine, proline, methionine and selenocysteine. Based on amounts of experiments, it was found that glycine, serine, asparagine, leucine, glutamine and/or lysine are more preferably.

[0022] The amino acid in the present invention can be natural or synthesized amino acid. All the stereoisomers of amino acid can be used in the present invention, such as D-, L-, or D,L- amino acid.

[0023] The amino acid salt in the present invention is preferably water soluble amino acid salt. The common amino acid salt which will not precipitate with calcium ion could be used in the present invention. The amino acid salt preferably comprises alkali metal salt and/or hydrochloride salt. The alkali metal is preferably sodium and/or potassium.

[0024] The protein hydrolysate is a mixture of amino acids and/or amino acid salts, which could be prepared according to the conventional method, for example by splitting proteins with acid, alkali, and/or enzyme. All proteins that could be hydrolyzed into amino acid and/or amino acid salt can be used in the present invention. Preferably, the protein hydrolysate comprises collagen hydrolysate and/or keratin hydrolysate. The degree of hydrolysis is not limited in the present invention, so long as there is amino acid in the protein hydrolysate. The hydrolyzation into high content of amino acids level is

preferred.

[0025] The deliming agent in the present invention could further comprise organic acid and/or carbon dioxide, the organic acid herein excluding amino acid. The organic acids for use in the present invention are those that are commonly used in leather manufacturing processes. Preferably, the organic acid comprises at least one selected from the group consisting of lactic acid, citric acid, adipic acid, malonic acid, succinic acid, glutaric acid, and gluconic acid; more preferably succinic acid and adipic acid. The combination of the amino acid component and the organic acid could realize better deliming efficiency.

[0026] The deliming agent in the present invention could further comprise additives. The additives which come into consideration in the present invention are the conventional additives in leather manufacturing industry. The preferable additive is oxidizing agent and/or catalyst. The preferable additive comprises at least one selected from the group consisting of manganese sulfate, manganese chloride, manganese acetate, sodium formate, potassium formate, sodium hydrogen sulfite, sodium metabisulfite, potassium metabisulfite, sodium acetate, potassium acetate, sodium sulfate, potassium sulfate, sodium hydrosulfate, potassium hydrosulfate, sodium percarbonate and potassium percarbonate.

[0027] The content of the amino acid component in the deliming agent is calculated according to the content of the total amino acids and amino acid salts in the deliming agent. For the protein hydrolysate, the amino acid and amino acid salt in the protein hydrolysate is used to calculate the content of the total amino acids and the amino acid salts. The content of the total amino acids and the amino acid salts in the deliming agent could be chosen according to the conventional methods in leather process industry. It is particular advantageous that the content of the total amino acids and the amino acid salts in the deliming agent is 40-100 wt%, more preferably 55-100 wt%, further more preferably 70-100 wt%, most preferably 80-100 wt%, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additives.

[0028] The content of the organic acid in the deliming agent could be chosen according to conventional methods in leather process industry, preferably is 25 wt% or less; more preferably 5-20 wt%; most preferably 5-10 wt%, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additives.

[0029] The content of the additives in the deliming agent could be chosen according to conventional method in leather process industry, preferably is 25 wt% or less, more preferably 20 wt% or less, most preferably 10 wt% or less, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive.

[0030] In a preferred embodiment, the deliming agent comprises the amino acid component in which the content of the total amino acids and the amino acid salts is 55-100 wt%, 0-20 wt% of the organic acid and 0-25 wt% of the additive, wt% is all based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additives; and the amino acid component is glycine, asparagine, glutamine, lysine, leucine, serine, collagen hydrolysate and/or keratin hydrolysate.

[0031] In a more preferred embodiment, the deliming agent comprises the amino acid component in which the content of the total amino acids and the amino acid salts is 80-100 wt%, 0-10 wt% of the organic acid and 0-10 wt% of the additives, wt% is all based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive; the amino acid component is glycine, lysine, serine, leucine, collagen hydrolysate and/or keratin hydrolysate.

[0032] Another object of the present invention is to provide a deliming process, comprising deliming step: deliming limed pelt with the deliming agent of the present invention.

[0033] The pelt in the present invention could be also referred to as hide in the leather manufacturing field. The pelt could come from common mammals used in the leather manufacturing field, such as cattle, sheep, pig, deer, or from common birds.

[0034] In a preferred embodiment, the deliming process comprises: (A) a pre-deliming step: pre-liming the limed pelt with the additive, the organic acid and/or the carbon dioxide; and (B) the deliming step: deliming the limed pelt with the deliming agent.

[0035] The step (A) preferably comprises (i) washing the limed pelt with water, removing the float; (ii) pre-liming the limed pelt with the additive, and the organic acid and/or carbon dioxide; and (iii) when the pH value of float is about 8, draining the float.

[0036] In a preferred embodiment, if the deliming process doesn't comprise the pre-deliming step (A), the deliming step (B) shall be conducted as deliming the limed pelt in an aqueous solution of the deliming agent.

[0037] The additive in step (A) is the same additive mentioned above in the deliming agent.

[0038] The organic acid in step (A) is the same organic acid mentioned above in the deliming agent.

[0039] In step (A), the amount of the additive could be chosen according to conventional methods in the leather manufacturing process, preferably is 0.05-0.3 wt% of the limed pelt.

[0040] In step (A), the amount of the organic acid could be chosen according to conventional methods in the leather manufacturing process, preferably is 0.1-0.5 wt% of the limed pelt.

[0041] The amount of the water in step (i) or in the aqueous solution of the deliming agent could be chosen according to conventional methods in leather manufacturing process, preferably is 300 wt% of the limed pelt or less, more preferably 200 wt% of the limed pelt or less, based on the total weight of the limed pelt.

[0042] The step (B) preferably comprises: (iv) deliming the limed pelt with the deliming agent; and (v) ending the deliming step.

[0043] In the deliming step, the amount of the deliming agent is calculated based on the amount of the total amino acids and the amino acid salts in the deliming agent. The amount of the total amino acids and the amino acid salts in the deliming agent is preferably 1-10 wt% of the limed pelt, more preferably 1-5 wt% of the limed pelt, most preferably 1-2.5 wt% of the limed pelt.

[0044] The deliming process in the present invention could be conducted in the conventional temperature range, preferred is 5°C-35°C, more preferred is 25°C-35°C.

[0045] The end of the deliming step could be decided according to conventional methods in leather process industry. Preferably, when the cross section of a cut of the pelt turns to colorless upon the addition of phenolphthalein, and the float of deliming step is 6-8.8, more preferably is about 8, the deliming step could be ended. The time of the deliming step is preferably from 1 to 6 hours, more preferably from 1 to 3 hours.

[0046] The "about 8" in the invention refers to 8 ± 0.8 .

[0047] During the deliming step, pH value of the float is preferably monitored.

[0048] The limed pelt could be limed according to conventional liming methods in leather process industry.

[0049] Another object in the present invention is to provide use of amino acid, amino acid salt or protein hydrolysate which contains amino acid and/or amino acid salt as a deliming agent.

[0050] Another object in the present invention is to provide use of amino acid, amino acid salt or protein hydrolysate which contains amino acid and/or amino acid salt as buffer in a deliming agent.

[0051] In the present invention, all the technical features mentioned above could be freely combined to form the preferred embodiments.

[0052] The present invention has the following benefits: (1) raw material does not contain boric acid, and is compliant with safe operation; (2) without using ammonium salts and hence greatly reduces the ammonia-nitrogen values in the effluent; (3) no ammonia releasing during deliming process, which facilitates safe operation; (4) amino acids have good buffering capacity during deliming pH range, which enables the successful lime removal from the limed pelts without inducing acid swelling especially on the grain layer; (5) amino acids have high solubility in water and small molecules which enables fast penetration into limed pelts; (6) the formation of soluble calcium salts between amino acids compounds and lime resulting in high lime removal efficiency, which enables a clean pelt surface and soft handle feeling of the crust.

EMBODIMENTS

[0053] The following examples serve to illustrate the invention, but they are not intended to limit it thereto:
Raw materials: organic acid mixture: 50 wt% of succinic acid, 50 wt% of adipic acid.

Example 1

[0054] Cattle hide which has been soaked and limed in conventional way was used for the application trial. The deliming process comprises the following steps:

(A) Pre-deliming step:

(i) Limed pelt (weight 16 kg, thickness 7 mm) was washed in the drum with 150 wt% (wt% is based on the weight of the limed pelt) of water at 30 °C; the float was drained after 10 minutes;

(ii) Pre-deliming the limed pelt with mixture of 100 wt% of water, 0.15 wt% of sodium metabisulfite and 0.3 wt% of the organic acid mixture at 30 °C for 30 minutes, wt% is all based on the weight of the limed pelt; and

(iii) Measuring the pH value of float (8.2) and drain the float again; and

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 2.0 wt% of glycine, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.4, ending the deliming step, the deliming degree is 100%.

[0055] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 2

[0056] Cattle hide which has been soaked and limed in conventional way was used for the application trial. The deliming process comprises the following steps:

- (A) Pre-deliming step is the same as example 1;
(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 2.5 wt% of lysine, wt% is all based on the weight of the limed pelt; and
(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.6, ending the deliming step, the deliming degree is 100%.

[0057] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 3

[0058] Cattle hide which has been soaked and limed in conventional way was used for the application trial. The deliming process comprises the following steps:

- (A) Pre-deliming step is the same as example 1;
(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 4 wt% of leucine, wt% is all based on the weight of the limed pelt; and
(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.5, ending the deliming step, the deliming degree is 100%.

[0059] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 4

[0060] Cattle hide which has been soaked and limed in conventional way was used for the application trial. The deliming process comprises the following steps:

- (A) Pre-deliming step is the same as example 1;
(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.8 wt% of the organic acid mixture, 1 wt% of sodium formate, 4 wt% of arginine, wt% is all based on the weight of the limed pelt; and
(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 7.6, ending the deliming step, the deliming degree is 100%.

[0061] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 5

[0062] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0063] The content of the amino acids in the collagen hydrolysate is 40 wt%.

[0064] The deliming process comprises the following steps:

- (A) Pre-deliming step is the same as example 1;
(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture,

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0.15 wt% of sodium metabisulfite, 6 wt% of collagen hydrolysate, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.5, ending the deliming step, the deliming degree is 100%.

[0065] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 6

[0066] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0067] The content of the amino acids in the keratin hydrolysate is 43 wt%.

[0068] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 5 wt% of keratin, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.5, ending the deliming step, the deliming degree is 100%.

[0069] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 7

[0070] Cattle hide which has been soaked and limed in conventional way was used for the application trial. The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 2.0 wt% of glycine and 2.0 wt% of lysine, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.2, ending the deliming step, the deliming degree is 100%.

[0071] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 8

[0072] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0073] The content of the amino acids in the collagen hydrolysate is 70 wt%.

[0074] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.8 wt% of the organic acid mixture, 1 wt% of sodium formate, 3.5 wt% of collagen hydrolysate, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein and the pH value of float is 7.8, ending the deliming process, the deliming degree is 100%.

[0075] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 9

[0076] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0077] The content of the amino acids in the collagen hydrolysate is 70 wt%.

[0078] The deliming process comprises the following steps:

(A) Pre-deliming step:

(i) Limed pelt (weight 7 kg, thickness 3.5 mm) was washed in the drum with 150 wt% (wt% is based on the weight of limed pelt) of water at 30 °C; the float was drained after 10 minutes;

(ii) Pre-deliming the limed pelt with mixture of 100 wt% of water, 0.15 wt% of sodium metabisulfite and 0.3 wt% of organic acid mixture at 30 °C for 30 minutes, wt% is all based on the weight of limed pelt; and

(iii) Measuring pH value of float (8.2) and drain the float again; and

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.2 wt% of sodium metabisulfite, 1.5 wt% of collagen hydrolysate, wt% is all based on the weight of the limed pelt; and

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein and the pH value of float is 7.6, ending the deliming step, the deliming degree is 100%.

[0079] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 10

[0080] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0081] The content of the amino acids in the keratin hydrolysate is 43 wt%.

[0082] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15wt% of sodium metabisulfite, 5wt% of keratin hydrolysate, wt% is all based on the weight of the limed pelt;

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.5, ending the deliming step, the deliming degree is 100%.

[0083] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 11

[0084] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0085] The content of the amino acids in the keratin hydrolysate is 28 wt%.

[0086] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 6.5 wt% of keratin hydrolysate, wt% is all based on the weight of the limed pelt;

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.3, ending the deliming step, the deliming degree is 100%.

[0087] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Example 12

[0088] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0089] The content of the amino acids in the collagen hydrolysate is 40 wt%.

[0090] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step:

(iv) Deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 6wt% of collagen hydrolysates solution, wt% is based on the weight of the limed pelt;

(v) After 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein and the pH value of float is 8.5, ending the deliming process, the deliming degree is 100%.

[0091] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Comparative example 1

[0092] Cattle hide which has been soaked and limed in conventional way was used for the application trial.

[0093] The deliming process comprises the following steps:

(A) Pre-deliming step is the same as example 1;

(B) Deliming step: delime the limed pelt with 0.2 wt% of the organic acid mixture, 0.15 wt% of sodium metabisulfite, 1.5 wt% of ammonium sulfate and 0.5 wt% of ammonium chloride; after 120 min, when the cross section of the cut of the pelt gives no color with the addition of phenolphthalein, the pH value of float is 8.5, ending the deliming process, the deliming degree is 100%.

[0094] Thereafter, using the conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dyeing and fat-liquoring.

Table 1

Examples	Deliming agent (wt%, based on the total weight of organic acid, additives, and amino acids)		
	Organic acids	Additives	Amino acids
1	8.5%	6.4%	85.1%
2	7.0%	5.3%	87.7%
3	4.6%	3.4%	92.0%
4	13.8%	17.2%	69.0%
5	7.3%	5.4%	87.3%
6	8.0%	6.0%	86.0%
7	/	/	100.0%
8	18.8%	23.5%	57.7%
9	13.8%	13.8%	72.4%
10	8.0%	6.0%	86.0%
11	9.2%	6.9%	83.9%
12	7.3%	5.4%	87.3%

[0095] All the floats of example 1-12 and comparative example 1 were taken to check $\text{NH}_3\text{-N}$ value. The deliming results and the crust effect of each of the examples are shown in Table 2.

Table 2

Examples	Deliming agent	pH			Penetration time (min)	NH ₃ -N value	Crust Evaluation
		60 min	90 min	120 min			
Comparative 1	Ammonium salts	6.5	7.6	8.5	120	1900 ppm	Good
1	Glycine	6.2	7.5	8.4	120	70 ppm	Good
2	Lysine	6.8	7.9	8.6	120	80 ppm	Good
3	Leucine	6.5	7.8	8.5	120	80 ppm	Good
4	Arginine	5.5	6.9	7.6	120	60 ppm	Good
5	Collagen hydrolysate	6.2	7.7	8.5	120	100 ppm	Good
6	Keratin hydrolysate	6.5	7.7	8.5	120	70 ppm	Good
7	Glycine + Lysine	6.5	7.4	8.2	120	100 ppm	Good
8	Collagen hydrolysate	5.8	7.2	7.8	120	80 ppm	Good
9	Collagen hydrolysate	5.6	6.8	7.6	120	60 ppm	Good
10	Keratin hydrolysate	6.5	7.7	8.5	120	70 ppm	Good
11	Keratin hydrolysate	6.5	7.4	8.3	120	80 ppm	Good
12	Collagen hydrolysate	6.2	7.7	8.5	120	100 ppm	Good

[0096] As shown in Table 2, deliming with ammonium salts, glycine, lysine, leucine, arginine, collagen hydrolysate, keratin hydrolysate achieved the end pH value of around 8, which means that amino acids have similar buffering capacity with ammonium salts. In addition to that, the deliming effluent of amino acids has NH₃-N value around 100 ppm, which is less than 5% of ammonium salts deliming effluent. Low NH₃-N value can significantly reduce effluent treatment time and cost.

[0097] The crusts obtained from all the examples have even color, soft handle feeling and very fine grain, which is comparable with comparative example 1.

Claims

1. An ammonium and boric acid free deliming agent, which comprises amino acid component and no ammonium compound; the amino acid component comprising amino acid, amino acid salt, and/or protein hydrolysate which contains amino acid and/or amino acid salt.
2. The ammonium and boric acid free deliming agent according to claim 1, wherein the amino acid is α -amino acid.
3. The ammonium and boric acid free deliming agent according to claim 1 or 2, wherein the amino acid comprises at least one selected from the group consisting of glycine, alanine, valine, leucine, isoleucine, phenylalanine, tryptophan, tyrosine, histidine, serine, threonine, cysteine, aspartic acid, glutamic acid, asparagine, glutamine, lysine, arginine, proline, methionine and selenocysteine.
4. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the amino

acid salt comprises alkali metal salt and/or hydrochloride salt.

5. The ammonium and boric acid free deliming agent according to claim 4, wherein the alkali metal is sodium and/or potassium.
6. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the protein hydrolysate comprises collagen hydrolysate and/or keratin hydrolysate.
7. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the deliming agent further comprises organic acid and/or carbon dioxide.
8. The ammonium and boric acid free deliming agent according to claim 7, wherein the organic acid comprises at least one selected from the group consisting of lactic acid, citric acid, adipic acid, malonic acid, succinic acid, glutaric acid, and gluconic acid; preferably is succinic acid and adipic acid.
9. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the deliming agent further comprises additive.
10. The ammonium and boric acid free deliming agent according to claim 9, wherein the additive comprises at least one selected from the group consisting of manganese sulfate, manganese chloride, manganese acetate, sodium formate, potassium formate, sodium hydrogen sulfite, sodium metabisulfite, potassium metabisulfite, sodium acetate, potassium acetate, sodium sulfate, potassium sulfate, sodium hydrosulfate, potassium hydrosulfate, sodium percarbonate and potassium percarbonate.
11. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the content of the amino acid component in the deliming agent is calculated according to the content of the total amino acids and amino acid salts in the deliming agent, the content of the total amino acids and the amino acid salts in the deliming agent being 40-100 wt%, preferably 55-100 wt%, more preferably 70-100 wt%, most preferably 80-100 wt% wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive.
12. The ammonium and boric acid free deliming agent according to claim 7 or 8, wherein the content of the organic acid in the deliming agent is 25 wt% or less, preferably 5-20 wt%, more preferably 5-10 wt%, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive.
13. The ammonium and boric acid free deliming agent according to claims 9 or 10, wherein the content of the additive in the deliming agent is 25 wt% or less, preferably 20 wt% or less, more preferably 10 wt% or less, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive.
14. The ammonium and boric acid free deliming agent according to any one of the preceding claims, wherein the deliming agent comprises the amino acid component in which the content of the total amino acids and the amino acid salts is 55-100 wt%, 0-20 wt% of the organic acid and 0-25 wt% of the additive, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive; the amino acid component is glycine, asparagine, glutamine, lysine, leucine, serine, collagen hydrolysate and/or keratin hydrolysate.
15. The ammonium and boric acid free deliming agent according to claim 14, wherein the deliming agent comprises the amino acid component in which the content of the total amino acids and the amino acid salts is 80-100 wt%, 0-10 wt% of the organic acid and 0-10 wt% of the additive, wt% is based on the total weight of the total amino acids, the amino acid salts, the organic acid and the additive.
16. A deliming process, comprising deliming step: deliming limed pelt with the ammonium and boric acid free deliming agent as defined in any one of the preceding claims.
17. The deliming process according to claim 16, comprising the following steps:
 - (A) a pre-deliming step: pre-liming the limed pelt with the additive, the organic acid and/or the carbon dioxide; the organic acid as defined in claim 8, the additive as defined in claim 10; and
 - (B) the deliming step: deliming the limed pelt with the deliming agent.

18. The deliming process according to claim 17, wherein the step (A) comprises (i) washing the limed pelt with water, removing the float; (ii) pre-liming the limed pelt with the additive, and the organic acid and/or carbon dioxide; and (iii) when the pH value of float is about 8, draining the float.

5 19. The deliming process according to claim 17 or 18, wherein in step (A), the amount of the additive is 0.05-0.3 wt%, preferably 0.1-0.5 wt% of the limed pelt.

10 20. The deliming process according to at least one of claims 17-19, wherein the step (B) comprises: (iv) deliming the limed pelt with the deliming agent; and (v) ending the deliming step.

21. The deliming process according to at least one of claims 16-20, wherein the amount of the deliming agent is calculated based on the amount of the total amino acids and the amino acid salts in the deliming agent, the amount of the total amino acids and the amino acid salts in the deliming agent is 1-10 wt%, preferably is 1-5 wt%, more preferably is 1-2.5 wt% of the limed pelt.

15 22. Use of amino acid, amino acid salt or protein hydrolysate which contains amino acid and/or amino acid salt as a deliming agent.

20 23. Use of amino acid, amino acid salt or protein hydrolysate which contains amino acid and/or amino acid salt as buffer in a deliming agent.

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EUROPEAN SEARCH REPORT

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