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(54) **A DELIMING PROCESS**

(57) The present invention disclosed a deliming process, comprising a deliming step: deliming the limed pelt with a deliming agent which is free of ammonium and boric acid, the deliming agent comprising protein hydrolysate, the protein hydrolysate being produced according to a method comprising the following steps: (A) hydrolyzing hair, shavings, trimmings and/or feathers to generate amino acid and/or amino acid salt, then obtaining the protein hydrolysate. The present invention utilizes the waste from leather manufacturing as the raw material for deliming process, realizing recycling and significantly enhancing the concept of "closed loop" process and realizing a friendly and mild deliming process, which enables a clean pelt surface and soft handle feeling of the crust.

EP 3 425 069 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a deliming process.

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. Liming is one of the pretreatments to remove hair and unwanted proteins usually by soaking the pelts in a lime bath. Beamhouse process in leathering manufacturing accounts for 80% of organic waste in effluent and sludges. Among these, around 70% comes from liming process. In general, there are two liming technologies, hair burning and hair saving. Hair saving technology removes the hair from the skin by attacking the hair roots and keeps the hair shaft intact, which allows the easy separation of the hair from the effluent by simple filtration. Compared with hair burning technology, hair saving is equally economic and has ecological benefit; thus, it is the dominate liming technology when the local government has certain requirements on effluent emission. However, limed hair usually has short fiber and is contaminated with strong alkaline chemicals, this limits its application in textile and carpet manufacturing industries.

[0003] One technical route for hair treatment is to extract valuable protein like keratin and keratin pieces and using them as surfactant or as functional additives in personal care products. Another method is isolating of single valuable amino acids from the hair hydrolysates for pharmaceutical and fine chemical industries. These routes technically allow for high value-added utilization of hair. However, the high demand on technical control of the hydrolysis process and purification requires additional investment, as well as the big consumption of water resource during purification steps (1 Ton pure amino acid consumes around 200 Tons of water) inhibits the utilization of limed hair. Most of the hair is dumped on the vacant site around the tanneries, leading to foul smell and environmental problems due to long time storage. Leather industry has been seeking an economic and ecological approach for recovering of products from the limed hair during the past one and half century.

[0004] After liming, deliming is required to bring pH value of pelt to a proper state of alkalinity. Deliming is about removing calcium hydroxide from pelts including surfaces and inner parts thereof and lowering pH value of pelts 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 are sufficient in lime removal.

[0005] 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 on May 4, 1943 used ammonium salt as deliming component. Ammonium salts have been widely accepted in leather industry due to the following characteristics: 1) cheap raw material compared with organic compounds; 2) 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.

[0006] When ammonium salts are used for deliming purposes, 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 as below:

$$Ca(OH)_2+NH_4Cl \rightarrow CaCl_2+NH_3+H_2O$$

$$Ca(OH)_2+(NH_4)_2SO_4 \rightarrow CaSO_4+NH_3+H_2O$$

[0007] Ammonium based deliming agents have two shortcomings, which limit their applications in industry. The disadvantages are: 1) the ammonia released during deliming leads to the workers' exposure in unsafe environment; 2) the high NH_3-N content in tannery effluent makes it necessary to perform NH_3-N removal, which increases the cost and duration of wastewater treatment.

[0008] Due to the high NH_3-N pollution induced by ammonium salts, three categories of compounds have been explored as deliming agents in literature and patents: 1) inorganic acid, like boric acid; 2) small molecular organic acids, including lactic acid, citric acid, succinic acid, or adipic acid; 3) macromolecules, such as polyimides, polysuccinimide and hydroxy polysuccinimide.

[0009] 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). Buffering system which has low impact on workers' health and environment are

lacking.

[0010] 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 limed pelt.

[0011] WO 2013/107233A 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.

[0012] Since the use of ammonium salts, numerous trials have been done to seek a safe, sufficient and mild deliming agent. However, for many years, environmentally friendly deliming agents which has comparative deliming capacity as ammonium salt and high penetration rate needs to be developed.

[0013] During the leather manufacturing process, another waste, chrome contaminated shavings and trimmings, are generated. These shavings and trimmings account for 60% of solid waste in leather industry. The very small content of chrome limits the further application of collagen waste, resulting in the high cost of solid waste disposal in the tannery. The leather industry is keen to more economic approach for chrome contaminated shavings and trimmings.

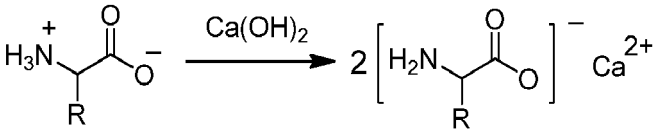
[0014] Till now, there is no solution in leather manufacturing industry that could both apply the waste hair, shavings and trimmings to the deliming process to realize "closed-loop" processing and realize a mild deliming process with good deliming effect without the existence of ammonium salts and boric acids.

SUMMARY OF THE INVENTION AND ADVANTAGES

[0015] Disclosed is a deliming process of leather manufacture. The deliming process comprises a deliming step: deliming the limed pelt with a deliming agent which is free of ammonium salts and boric acid, the deliming agent comprising protein hydrolysate, the protein hydrolysate being produced according to a method comprising the following steps: (A) hydrolyzing hair, shavings, trimmings and/or feathers to generate amino acid and/or amino acid salt, then obtaining protein hydrolysate.

[0016] The deliming agent has high lime dissolving value and good buffering capacity during deliming process, and ensures zero add-on NH_3-N load originating from liming agents, resulting in low NH_3-N load in deliming effluent. According to the present invention, the final NH_3-N value in effluent is around 100 ppm.

[0017] The active component of the protein hydrolysate is amino acids and/or amino acid salts. Deliming with amino acids or amino acid salt is implemented via the below route:



[0018] 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 prevent acid swelling on the grain layer.

[0019] While 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.

[0020] Protein hydrolysate of the present invention could be individually used in the deliming agent or combined with some additives, and achieve good deliming effect with no help of ammonium salts, which enables the replacement of conventional boric acid and ammonium salts.

[0021] Compared with ammonium salt based deliming agents in the deliming process, the deliming process of the present invention is more environmentally friendly. The deliming agent of the present invention has the following features: 1) protein hydrolysates are utilized as deliming agent; they are safe compounds both to environment and workers; 2) amino acids in protein hydrolysate will not introduce NH_3-N burden into deliming effluent, therefore the reduction of NH_3-N generated in deliming process can be achieved; 3) 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; 4) the deliming agent can be obtained by hydrolyzing limed hair or chrome contaminated shavings or trimmings from leather manufacturing process. This decreases the cost of the deliming agent and solves the issue of waste of limed hair, shavings and trimmings, and prevents the environmental pollution caused by disposal of contaminated keratin and collagen based solid waste.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The objective of the present invention is therefore to provide a deliming process comprising a deliming step: deliming the limed pelt with a deliming agent which is free of ammonium and boric acid, the deliming agent comprising protein hydrolysate, the protein hydrolysate being produced according to a method comprising the following steps: (A) hydrolyzing hair, shavings, trimmings and/or feathers to generate amino acid and/or amino acid salt, then obtaining the protein hydrolysate.

[0023] In step (A), the hair refers to all kinds of animal hair and/or human hair so long as the hair comprises keratin. The feathers in step (A) refer to all kinds of bird feathers so long as the feathers comprise keratin.

[0024] In step (A), the shavings or trimmings are solid waste from leather manufacturing process. The shavings or trimmings in step (A) refer to all kinds of hair or leather shavings or trimmings so long as the shavings or trimmings comprise collagen.

[0025] In step (A), hydrolyzing can be done via conventional protein hydrolysis method so long as amino acids can be generated by hydrolyzing. The hydrolyzing method can be acid, alkali and/or enzyme hydrolysis, preferably acid hydrolysis.

[0026] In a preferred embodiment, the acid hydrolysis comprises the following steps: (a-1) hydrolyzing hair, shavings, trimmings and/or feathers in inorganic acid solution I at 80-130 °C, (a-2) removing the insoluble substances by pressure filtration, (a-3) neutralizing the filtrate with ammonium free alkaline compounds to pH value of 4-7 and obtaining protein hydrolysate solution, and optionally (a-4) spraying dry the protein hydrolysate solution and obtaining the protein hydrolysate.

[0027] The protein hydrolysate used in the deliming agent can be in the form of protein hydrolysate solution obtained in step (a-3), as well as in the form of dried protein hydrolysate obtained in step (a-4).

[0028] In step (a-1), the inorganic acid of the inorganic acid solution I is conventional inorganic acid used in the leather manufacturing process, preferably comprising at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid. The content of the inorganic acid in the inorganic acid solution I can be chosen according to the conventional method, preferably is 5-40 wt%. In step (a-1), the time of hydrolyzing can be chosen according to the conventional method, preferably is 1-10 hours. In step (a-3), the pH value is preferably 5-6.5.

[0029] When hydrolyzing the hair in step (a-1), the amount of hair is preferably 10-50 wt%, more preferably 20-50 wt%, most preferably 30-50 wt%, based on the total weight of the inorganic acid solution I and the hair. The content of the inorganic acid in the inorganic solution I is preferably 10-38 wt%. The hydrolysis of hair is preferably conducted at 80-130 °C. The time of hydrolyzing hair is preferably 2-8 hours.

[0030] When hydrolyzing the shavings and/or the trimmings in step (a-1), the amount of the shavings and the trimmings is preferably 40-80 wt%, more preferably 50-75 wt%, based on the total weight of the inorganic acid solution I, the shavings and the trimmings. The content of the inorganic acid in the inorganic acid solution I is preferably 10-40 wt%. The hydrolysis of the shavings and/or the trimmings is preferably conducted at 80-130 °C. The time of hydrolyzing the shavings and/or the trimmings is preferably 2-7 hours.

[0031] In step (a-3), the basic compound is conventional basic compound used in the leather manufacturing process, preferably comprising at least one selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate.

[0032] In a preferred embodiment, when hydrolyzing the hair in step (A), the hair can be limed hair. The limed hair is preferably pretreated before hydrolyzing. The pretreatment for the limed hair could be done according to the conventional method to remove grease, dirt and contaminated chemicals, preferably comprising the steps: (i) washing the limed hair with inorganic acid solution II, (ii) neutralizing the inorganic acid solution II to pH value of 5-8, and (iii) removing the effluent, drying and obtaining the pretreated hair.

[0033] In step (i), the content of the inorganic acid in the inorganic acid solution II is preferably 0.3-2 mol/L. The amount of the inorganic acid solution II is preferably 3-20 times, more preferably is 3-10 times the weight of the limed hair. The inorganic acid of the inorganic acid solution II is conventional inorganic acid used in the leather manufacturing process, preferably comprising at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid. The time of washing is preferably 1-5 hours. The washing is preferably conducted under stirring.

[0034] In step (ii), alkaline can be used to neutralize the inorganic acid solution II, the alkaline can be conventional alkaline used in the leather manufacturing process, preferably comprising at least one selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate. The amount of the alkaline can be chosen according to conventional method used in the leather manufacturing process to adjust the pH value to 5-8.

[0035] In step (iii), the drying is preferably conducted at 30-60 °C.

[0036] In a preferred embodiment, when hydrolyzing the shavings and/or the trimmings in step (A), the shavings and/or the trimmings can be chrome containing shavings and/or trimmings. The chrome containing shavings and/or trimmings are preferably pretreated before hydrolyzing. The pretreatment for the chrome containing shavings and/or trimmings

can be done according to the conventional method to remove dirt, preferably comprising the steps: (iv) washing the chrome containing shavings and/or trimmings with water, removing the dirt, soaking in the solution of calcium oxide, glucose and water; (v) removing water, (vi) acid dechroming with inorganic acid solution III to dissociate the chromium from the shavings and trimmings, and (vii) sufficient washing to remove chromium and obtaining the pretreated shavings and/or trimmings.

[0037] In step (iv), the amount of the water is preferably 3-20 times of the weight of the chrome containing shavings and trimmings, more preferably 3-10 times. The time of washing is preferably 1-5 hours. The washing is preferably conducted under stirring.

[0038] In step (iv), soaking is to open the fiber structure in the chrome containing shavings and/or trimmings. The content of calcium oxide in the solution is preferably 1- 3 wt%, based on the weight of water. The content of glucose in the solution is preferably 0.1-0.3 wt%, based on the weight of water. The time of soaking is preferably 2-4 days.

[0039] In step (vi), the content of the inorganic acid in the inorganic acid solution III is preferably 4-15 wt%. The inorganic acid of the inorganic acid solution III is conventional inorganic acid used in the leather manufacturing process, preferably comprising at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid. The time for acid dechroming depends on the dissociation of chromium, preferably is 0.5-2 hours.

[0040] In a preferred embodiment, the deliming agent can further comprise organic acid and/or carbon dioxide, the organic acid herein excluding amino acid. The organic acid which comes into consideration in the present invention is the one that is commonly used in leather manufacturing process. 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 is succinic acid and/or adipic acid. The combination of the protein hydrolysate and the organic acid can realize better deliming efficiency.

[0041] In a preferred embodiment, the deliming agent can further comprise additives. The additives which come into consideration for use in the present invention is any of the conventional additives used in leather manufacturing process. The preferable additive is y 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.

[0042] In a preferred embodiment, the deliming agent preferably further comprises amino acid component. The amino acid component means any component so long as it comprises amino acid and/or amino acid ion and can react with $Ca(OH)_2$ without bringing any negative effect to deliming. The amino acid component for use in the present invention preferably comprises amino acid, amino acid salt, and/or other protein hydrolysate which contains amino acid and/or amino acid salt. In the present invention, the other protein hydrolysate means the one that is not obtained according to the step (A).

[0043] The amino acid for use 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 acids is $H_2NCH(R)COOH$ in most cases.

[0044] In a preferred embodiment, the α-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 experiments, it was found that glycine, serine, asparagine, leucine, glutamine and/or lysine is more preferable.

[0045] The amino acid for use in the present invention can be natural or synthetized amino acid. All the stereoisomers of amino acid can be used in the present invention, such as D-, L-, or D,L- amino acid.

[0046] The amino acid salt for use in the present invention is preferably water soluble amino acid salt. The common amino acid salt which will not precipitate with calcium ion can be used in the present invention. The amino acid salt is preferably alkali metal salt and/or hydrochloride salt. The alkali metal is preferably sodium and/or potassium.

[0047] The other protein hydrolysate is preferably collagen hydrolysate and/or keratin hydrolysate. The degree of hydrolysis is not limited in the present invention, so long as there is amino acid or salt thereof in the other protein hydrolysate. The hydrolyzation into high content of amino acids level is preferred.

[0048] The total content of the protein hydrolysate and 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 are used to calculated the content of the total amino acids and amino acid salts. The content of the total amino acids and the amino acid salts in the deliming agent can be chosen according to conventional methods in leather manufacturing industry. It is particularly advantageous that the content of the total amino acids and amino acids salts in the deliming agent is preferably 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 amino acids,

the amino acid salts, the organic acid and the additives.

[0049] The content of the organic acid in the deliming agent can be chosen according to conventional methods in leather manufacturing process, preferably is 40 wt% or less; more preferably 5-20 wt%; most preferably 5-10 wt%, wt% is based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

[0050] The content of the additive in the deliming agent can be chosen according to conventional methods used in leather manufacturing process, preferably is 25 wt% or less, more preferably 1-10 wt%, wt% is based on the total weight of the amino acids, the amino acid salts, the organic acid and the additives.

[0051] In a preferred embodiment, the deliming agent comprises the protein hydrolysate in which the content of the total amino acids and the amino acid salts is 55-94 wt%, 5-20 wt% of the organic acid and 1-25 wt% of the additives, wt% is all based on the total weight of the amino acids, the amino acid salts, the organic acid and the additives. The preferred protein hydrolysate, the preferred organic acid and the preferred additive all can be respectively or together chosen according to the above preferred solutions.

[0052] In a more preferred embodiment, the deliming agent comprises the protein hydrolysate in which the content of the total amino acids and the amino acid salts is 80-90 wt%, 5-10 wt% of the organic acid and 5-10 wt% of the additive, wt% is all based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

[0053] In the present invention, 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 1-5 wt% of the limed pelt, more preferably 1-2.5 wt% of the limed pelt.

[0054] In a preferred embodiment, the deliming step includes the following steps: (b-1) a pre-deliming step: pre-liming the limed pelt with the additive, and the organic acid and/or the carbon dioxide; and (b-2) deliming the limed pelt with the deliming agent.

[0055] The step (b-1) preferably comprises: (viii) washing the limed pelt with water, removing the float; (ix) pre-deliming the limed pelt with the additive, and the organic acid and/or carbon dioxide; and (x) when the pH value of float is about 8, draining the float.

[0056] The additive in step (b-1) is the same additive mentioned above in the deliming agent.

[0057] The organic acid in step (b-1) is the same organic acid mentioned above in the deliming agent.

[0058] In step (b-1), the amount of the additive can be chosen according to conventional methods used in the leather manufacturing process, preferably is 0.05-0.3 wt% of the limed pelt.

[0059] In step (b-1), the amount of the organic acid can be chosen according to conventional methods used in the leather manufacturing process, preferably is 0.1-0.5 wt% of the limed pelt.

[0060] When the deliming step doesn't include pre-deliming step (b-1), the deliming step is be conducted as deliming the limed pelt with an aqueous solution of the deliming agent.

[0061] The amount of water in step (viii) or in the aqueous solution of the deliming agent can be chosen according to conventional methods used in leather manufacturing process, preferably is 300 wt% of the limed pelt or less, more preferably 200 wt% of the limed pelt or less.

[0062] The step (b-2) preferably comprises: (xi) deliming the limed pelt with the deliming agent; and (xii) ending the deliming step.

[0063] The step (b-1) or (b-2) can be conducted at conventional temperature, preferred is 5-35 °C, more preferred 25-35 °C.

[0064] The end of the deliming step can be decided according to conventional methods used in leather manufacturing process. Preferably, when the cross section of a cut of the pelt turns to colorless upon the addition of phenolphthalein, and the float of the deliming step is 6-8.8, more preferably is about 8, the deliming step can be ended. The time of the deliming step is preferably from 1 to 6 hours, more preferably from 1 to 3 hours.

[0065] The "about 8" in the present invention refers to 8 ± 0.8.

[0066] During the deliming step, pH value of the float is preferably monitored.

[0067] The pelt in the present invention can be also explained 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, or deer.

[0068] The limed pelt could be limed according to conventional liming methods used in leather manufacturing process.

[0069] In the present invention, all the technical features mentioned above can be freely combined to form the preferred embodiments.

[0070] The present invention has the following benefits: (1) The utilization of the waste (limed hair, chrome containing shavings and/or trimmings) from leather manufacture turns the tannery waste into raw material for deliming process, realizing the recycling and significantly enhancing the concept of "closed loop" process; (2) raw material for deliming process does not contain boric acid, which is compliant with safe operation; (3) without using ammonium salts, greatly reducing the ammonia-nitrogen values in the effluent; (4) no ammonia releasing during deliming process, which facilitates safe operation; (5) protein hydrolysate has good buffering capacity within deliming pH range, which enables the success lime removal from the limed pelts without inducing acid swelling especially on the grain layer; (6) protein hydrolysate has high solubility in water and small molecules which enables fast penetration into limed pelts; (7) the formation of

soluble calcium salts from 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

[0071] 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

[0072] The pretreatment of the limed hair was conducted by: (i) 1500g limed hair was added into 10 L, 0.3 mol/L hydrochloric acid solution (inorganic acid solution II), then the mixture was stirred for 2 hours; (ii) neutralization with sodium hydroxide solution to pH 6; and (iii) filtration was conducted to remove the effluent and hair was dried at 50 °C for 2 hours to obtain 1000g pretreated hair.

[0073] The keratin hydrolysate solution used in the following deliming process was obtained according to the following steps:

(a-1) hydrolyzing the pretreated hair: 1000g pretreated hair was added to 1000 mL, 38 wt% hydrochloride solution (inorganic acid solution I) in autoclave at 80 °C, 0.6-1 MPa for 3 hours under stirring;
(a-2) after cooling down, solid particles were removed from the solution via press-filtration; and
(a-3) the filtrate was collected and neutralized with sodium hydroxide solution to pH value of 6.0, the keratin hydrolysate solution (wherein the content of amino acids is 43 wt%) was obtained.

[0074] Cattle hide which had been soaked and limed in conventional way was used for the application trial.

[0075] The deliming process comprises the following steps:

(b-1) pre-liming step:

(viii) 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;
(ix) 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 for 30 minutes, wt% is all based on the weight of limed pelt; and
(x) Measuring pH value of float (8.2) and draining the float again;

(b-2) deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of organic acid mixture, 0.15wt% of sodium metabisulfite, 5wt% of keratin hydrolysate solution, wt% is all based on the weight of the limed pelt; 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%.

Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.

Example 2

[0076] The pretreatment of the limed hair was conducted by: (i) 1500g limed hair was added into 10 L, 0.3 mol/L hydrochloric acid solution (inorganic acid solution II), then the mixture was stirred for 2 hours; (ii) neutralization with sodium hydroxide solution to pH 6; and (iii) filtration was conducted to remove the effluent and hair was dried at 50 °C for 2 hours to obtain 1000g pretreated hair.

[0077] The keratin hydrolysate solution used in the following deliming process was obtained according to the following steps:

(a-1) hydrolyzing the pretreated hair: 1000g pretreated hair was added to 2000 mL, 10 wt% hydrochloride solution (inorganic acid solution I) in autoclave at 130 °C, 0.6-1 MPa for 6 hours under stirring;
(a-2) after cooling down, solid particles were removed from the solution via press-filtration; and
(a-3) the filtrate was collected and neutralized with sodium hydroxide solution to pH value of 6.0, the keratin hydrolysate solution (wherein the content of amino acids is 28 wt%) was obtained.

[0078] Cattle hide which had been soaked and limed in conventional way was used for the application trial.

[0079] The deliming process comprises the following steps:

(b-1) pre-liming step:

(viii) 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;
(ix) 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 for 30 minutes, wt% is all based on the weight of limed pelt; and
(x) Measuring pH value of float (8.2) and draining the float again;

(b-2) deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of organic acid mixture, 0.15 wt% of sodium metabisulfite, 6.5 wt% of keratin hydrolysate solution, wt% is all based on the weight of the limed pelt; 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%.

[0080] Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.

Example 3

[0081] The pretreated shavings and trimmings in step (a-1) were obtained by:

(iv) 300g wet-blue chrome containing shavings and trimmings were cut into small pieces, 1L water was added and the mixture was stirred for 2 hours; filtering to remove the dirt; soaking in the aqueous solution of 30g CaO, 9g glucose and 3L water, the soaking was carried out for 4 days; (v) removing water via pressure filtration; (vi) soaking in 300mL, 4wt% hydrochloride solution (inorganic acid solution III) in a flask for 2 hours; (vii) sufficient washing to remove chromium, draining the float and obtaining the pretreated shavings and/or trimmings.

[0082] The collagen hydrolysate solution used in the following deliming process was obtained according to the following steps:

(a-1) hydrolyzing the pretreated shavings or trimmings: 300g pretreated shavings and trimmings were added to 300 mL, 10 wt% hydrochloride solution (inorganic acid solution I) in autoclave at 130 °C, 0.6-1 MPa and stirred for 6 hours;
(a-2) after cooling down, solid particles were removed from the solution via press-filtration; and
(a-3) the filtrate was collected and neutralized with sodium hydroxide solution to pH value of 6.0, the collagen hydrolysate solution (wherein the content of amino acids is 40 wt%) was obtained.

[0083] Cattle hide which had been soaked and limed in conventional way was used for the application trial.

[0084] The deliming process comprises the following steps:

(b-1) pre-liming step: the same as in example 1;
(b-2) deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of organic acid mixture, 0.15 wt% of sodium metabisulfite, 6wt% of collagen hydrolysates solution, wt% is based on the weight of the limed pelt; 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%.

[0085] Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.

Example 4

[0086] The pretreated shavings and trimmings in step (a-1) were obtained by:

(iv) 300g wet-blue chrome containing shavings and trimmings were cut into small pieces, 1L water was added and the mixture was stirred for 2 hours; filtering to remove the dirt; soaking in the aqueous solution of 60g CaO, 3g glucose and 3L water, the soaking was carried out for 2 days; (v) removing water via filter-press; (vi) soaking in 300mL, 15wt% hydrochloride solution (inorganic acid solution III) in a flask for 0.5 hours; (vii) sufficient washing to remove chromium, draining the float and obtaining the pretreated shavings and/or trimmings.

[0087] The collagen hydrolysate solution used in the following deliming process was obtained according to the following steps:

(a-1) hydrolyzing the pretreated shavings or trimmings: 300g pretreated shavings or trimmings were added to 100 mL, 38 wt% hydrochloride solution (inorganic acid solution I) in autoclave at 90 °C, 0.6-1 MPa and stirred for 3 hours;
(a-2) after cooling down, solid particles were removed from the solution via press-filtration; and
(a-3) the filtrate was collected and neutralized with sodium hydroxide solution to pH value of 6.0, the collagen hydrolysate solution (wherein the content of amino acids is 70 wt%) was obtained.

[0088] Cattle hide which had been soaked and limed in conventional way was used for the application trial.
[0089] The deliming process comprises the following steps:

(b-1) pre-liming step: the same as in example 1;
(b-2) deliming the limed pelt with the deliming agent (Table 1) comprising 0.8 wt% of organic acid mixture, 1 wt% of sodium formate, 3.5 wt% of collagen hydrolysates solution, wt% is all based on the weight of the limed pelt; 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%.

[0090] Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.

Example 5

[0091] The collagen hydrolysate solution obtained in example 4 (amino acid content 70%) was used in example 5.
[0092] The deliming process comprises the following steps:

(b-1) pre-liming step:

(viii) Limed pelt (weight 7 kg, thickness 3.5 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;
(ix) 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 for 30 minutes, wt% is all based on the weight of limed pelt; and
(x) Measuring pH value of float (8.2) and draining the float again;

(b-2) deliming the limed pelt with the deliming agent (Table 1) comprising 0.2 wt% of organic acid mixture, 0.2 wt% of sodium metabisulfite, 1.5 wt% of collagen hydrolysate solution, wt% is all based on the weight of the limed pelt; 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%.

[0093] Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.

Comparative example 1

[0094] The deliming process comprises the following steps:

(b-1) pre-deliming step is the same as in example 1;
(b-2) deliming step:

[0095] Delime with 0.2 wt% organic acid mixture, 0.15 wt% of sodium metabisulfite, 1.5wt% of ammonium sulfate and 0.5 wt% of ammonium chloride, wt% is all based on the weight of the limed pelt; 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 8.4, ending the deliming process, the deliming degree is 100%.
[0096] Thereafter, using conventional methods, crust was obtained after bating, pickling, chrome tanning, retanning, neutralization, dying and fat-liquoring.
[0097] All the floats of example 1-5 and comparative example 1 were taken to check NH_3-N value. The deliming results and the crust effect of each of the examples are shown in Table 2.

Table 1

Examples	Deliming agent (wt%, based on the total weight of organic acid, additives, and amino acids)		
	Organic acids	Additives	Amino acids
1	8.0%	6.0%	86.0%
2	9.2%	6.9%	83.9%
3	7.3%	5.4%	87.3%
4	18.8%	23.5%	57.7%
5	13.8%	13.8%	72.4%

Table 2

Examples	Deliming agent	pH during deliming			Penetration time (min)	NH_3-N value	Crust Evaluation
		60 min	90 min	120 min			
Comparative 1	Ammonium salts	6.5	7.6	8.4	120	1900 ppm	Good
1	Keratin hydrolysate	6.5	7.7	8.5	120	70 ppm	Good
2	Keratin hydrolysate	6.5	7.4	8.3	120	80 ppm	Good
3	Collagen hydrolysate	6.2	7.7	8.5	120	100 ppm	Good
4	Collagen hydrolysate	5.8	7.2	7.8	120	80 ppm	Good
5	Collagen hydrolysate	5.6	6.8	7.6	120	60 ppm	Good

[0098] As shown in Table 2, deliming with ammonium salts, collagen hydrolysate, keratin hydrolysate achieved end pH value around 8, which means that amino acids have similar buffering capacity as ammonium salts. In addition to that, the deliming effluent of amino acids has NH_3-N value around 100 ppm, which is less than 5% of ammonium salts deliming effluent. Low NH_3-N value can significantly reduce effluent treatment time and cost.

[0099] 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. A deliming process comprising a deliming step: deliming the limed pelt with a deliming agent which is free of ammonium and boric acid, the deliming agent comprising protein hydrolysate, the protein hydrolysate being produced according to a method comprising the following steps: (A) hydrolyzing hair, shavings, trimmings and/or feathers to generate amino acid and/or amino acid salt, then obtaining the protein hydrolysate.

2. The deliming process according to claim 1, **characterized in that** in step (A), the hydrolyzing is acid hydrolysis, which comprises the following steps:

   (a-1) hydrolyzing hair, shavings, trimmings and/or feathers in inorganic acid solution I at 80-130 °C;
   (a-2) removing the insoluble substances by pressure filtration;
   (a-3) neutralizing the filtrate with ammonium free basic compounds to pH value of 4-7 and obtaining protein hydrolysate solution;

and optionally (a-4) spraying dry the protein hydrolysate solution and obtaining the protein hydrolysate.

3. The deliming process according to any one of claims 1-2, **characterized in that** in step (a-1), the inorganic acid of the inorganic acid solution I comprises at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid; the content of the inorganic acid in the inorganic acid solution I being 5-40 wt%.

4. The deliming process according to any one of the above claims, **characterized in that** when hydrolyzing the hair in step (a-1), the amount of hair is 10-50 wt%, preferably 20-50 wt%, more preferably 30-50 wt%, based on the total weight of the inorganic acid solution I and the hair; when hydrolyzing the shavings and/or the trimmings in step (a-1), the amount of the shavings and the trimmings is 40-80 wt%, preferably 50-75 wt%, based on the total weight of the inorganic acid solution I, the shavings and the trimmings.

5. The deliming process according to any one of the above claims, **characterized in that** when hydrolyzing the hair in step (a-1), the content of the inorganic acid in the inorganic solution I is 10-38 wt%; the hydrolysis of hair is conducted at 80-130 °C.

6. The deliming process according to any one of the above claims, **characterized in that** when hydrolyzing the shavings and/or the trimmings in step (a-1), the content of the inorganic acid in the inorganic acid solution I is 10-40 wt%; the hydrolysis of the shavings and/or the trimmings is conducted at 80-130 °C.

7. The deliming process according to any one of the above claims, **characterized in that** in step (a-3), the ammonium free basic compound comprises at least one selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate.

8. The deliming process according to any one of the above claims, **characterized in that** when hydrolyzing the hair in step (A), the hair is limed hair which is pretreated before hydrolyzing, the pretreatment for the limed hair comprising the steps: (i) washing the limed hair with inorganic acid solution II, (ii) neutralizing the inorganic acid solution II to pH value of 5-8, and (iii) removing the effluent, drying and obtaining the pretreated hair.

9. The deliming process according to any one of the above claims, **characterized in that**,
in step (i), the content of the inorganic acid in the inorganic acid solution II is 0.3-2 mol/L; the amount of the inorganic acid solution II is 3-20 times of the weight of the limed hair; the inorganic acid of the inorganic acid solution II comprises at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid;
in step (ii), alkaline is used to neutralize the inorganic acid solution II, the alkaline comprises at least one selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate.

10. The deliming process according to any one of the above claims, **characterized in that** when hydrolyzing the shavings and/or the trimmings in step (A), the shavings and/or the trimmings are chrome containing shavings and/or trimmings which are pretreated before hydrolyzing, the pretreatment for the chrome containing shavings and/or trimmings comprising the steps: (iv) washing the chrome containing shavings and/or trimmings with water, removing the dirt, soaking in the solution of calcium oxide, glucose and water; (v) removing water, (vi) acid dechroming with inorganic acid solution III, and (vii) washing to remove chromium and obtaining the pretreated shavings and/or trimmings.

11. The deliming process according to any one of the above claims, **characterized in that**,
in step (iv), the amount of the water is 3-20 times of the weight of the chrome containing shavings and trimmings; the content of calcium oxide in the solution is 1- 3 wt%, based on the weight of water; the content of glucose in the solution is 0.1- 0.3 wt%, based on the weight of water;
in step (vi), the content of the inorganic acid in the inorganic acid solution III is 4-15 wt%; the inorganic acid of the inorganic acid solution III comprises at least one selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid.

12. The deliming process according to any one of the above claims, **characterized in that** the deliming agent further comprises organic acid and/or carbon dioxide, and/or additive.

13. The deliming process according to claim 12, **characterized in that** 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 or adipic acid.

14. The deliming process according to claim 12, **characterized in that** 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.

15. The deliming process according to any one of claims 12-14, **characterized in that** the deliming agent further comprises amino acid component, the amino acid component comprises amino acid, amino acid salt, and/or other protein hydrolysate which contains amino acid and/or amino acid salt.

16. The deliming process according to claim 15, **characterized in that** 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; preferably consisting of glycine, serine, asparagine, leucine, glutamine and/or lysine; the amino acid salt comprises alkali metal salt and/or hydrochloride salt; the alkali metal is preferably sodium and/or potassium.

17. The deliming process according to any one of claims 12-16, **characterized in that** the content of the total amino acids and the amino acid salts in the deliming agent is 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 amino acids, the amino acid salts, the organic acid and the additive.

18. The deliming process according to any one of claims 12-17, **characterized in that** the content of the organic acid in the deliming agent is 40 wt% or less; preferably 5-20 wt%; more preferably 5-10 wt%, wt% is based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

19. The deliming process according to any one of claims 12-18, **characterized in that** the content of the additive in the deliming agent is 25 wt% or less, preferably 1-10 wt%, wt% is based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

20. The deliming process according to any one of claims 12-19, **characterized in that** the deliming agent comprises the protein hydrolysate in which the content of the total amino acids and amino acid salts is 55-94 wt%, 5-20 wt% of the organic acid and 1-25 wt% of the additive, wt% is all based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

21. The deliming process according to claim 20, **characterized in that** the deliming agent comprises the protein hydrolysate in which the content of the total amino acids and amino acid salts is 80-90 wt%, 5-10 wt% of the organic acid and 5-10 wt% of the additive, wt% is all based on the total weight of the amino acids, the amino acid salts, the organic acid and the additive.

22. The deliming process according to any one of the above claims, **characterized in that** 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 1-5 wt% of the limed pelt, preferably 1-2.5 wt% of the limed pelt.

23. The deliming process according to at least one of the above claims, **characterized in that** the deliming step includes the following steps: (b-1) a pre-deliming step: pre-liming the limed pelt with the additive, and the organic acid and/or the carbon dioxide; and (b-2) deliming the limed pelt with the deliming agent.

24. The deliming process according to any one of the above claims, **characterized in that** the step (b-1) comprises: (viii) washing the limed pelt with water, removing the float; (ix) pre-deliming the limed pelt with the additive, and the organic acid and/or carbon dioxide; and (x) when the pH value of float is 7.2-8.8, draining the float.

25. The deliming process according to any one of the above claims, **characterized in that** in step (b-1), the amount of the additive is 0.05-0.3 wt% of the limed pelt; the amount of the organic acid is 0.1-0.5 wt% of the limed pelt.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 18 1645

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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