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(54) **Product and process for obtaining of chrome free leather**

(57) The invention relates to a product for leather tanning and to a process for using the former in tanning bovine and sheep hides. The product according to the invention consists of 8-5% technical grade sulfuric acid, 3-10% unrecyclable metallurgic waste (selected so as to have a composition of min. 95% Ti, min. 95% Zr, max. 5% Al, max. 1% Fe and max. 0.5% V), 10...20% technical grade sodium citrate, 1.0...4.0% technical grade magnesium oxide, having the appearance of a gray-white powder with a content of 8-18% titanium and zirconium metal oxides, a so that the ratio of TiO_2:ZrO_2 ranges between 1:1 and 3:1 and the pH value of 10% solution is 1.8...2.2 and to a chromium-free bovine and sheep hide tanning process for semi-processed **chrome-free wet-white leather,** in which said powder tanning product is used.

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Description

[0001] The invention relates to a product and process of obtaining free-of-chrome tanned leathers with applications in the field of leather processing.

[0002] It was not until the dawn of the 20th century that the advent of chrome tanning created a universally traded commodity in the form of wet-blue. An intermediate product, wet-blue is bought and sold around the globe and provides the basis for more than 80% of total leather production [1]. Wet -blue is obtained from raw hides / skins with basic chrome sulphate tanning, which is the standard tanning procedure. In general, chromium (III) tanning agents uptake under typical technological conditions is of the order of 60 - 80 % of the offered quantities (typical offer: 80-90 kg Cr-tanning salts/t of pelt weight), with 3-7 kg Cr^{3+}/t of raw hides /skins (2-7g Cr(III)/Lt of exhaust tanning liquor) discharged with the process effluent.

[0003] Within this framework of industrial needs high levels of excess Cr(III)-tanning products remain a potential threat and hazard to the environment or contribute significantly to the amount of recalcitrant pollutants. Consequently, there is mounting pressure on tanners to reduce levels of Cr(III)- tanning agents employed during leather manufacture and their discharge with the outflow of tannery treatment plant.

[0004] Even though there is no legislation or norm that requires that chromium (III) should be absent from leathers, maximum allowable concentrations have been stipulated for the total chromium or chromium (III) content in leather digests or extracts, whereas an even stricter concurrent legislative requirement has been imposed for chromium (VI) absence (non detectable) in most finished leathers. In particular, Chromium (VI) and its salts are classified as known carcinogens not used for tanning and normally absent from chromium (III) tanning salts.

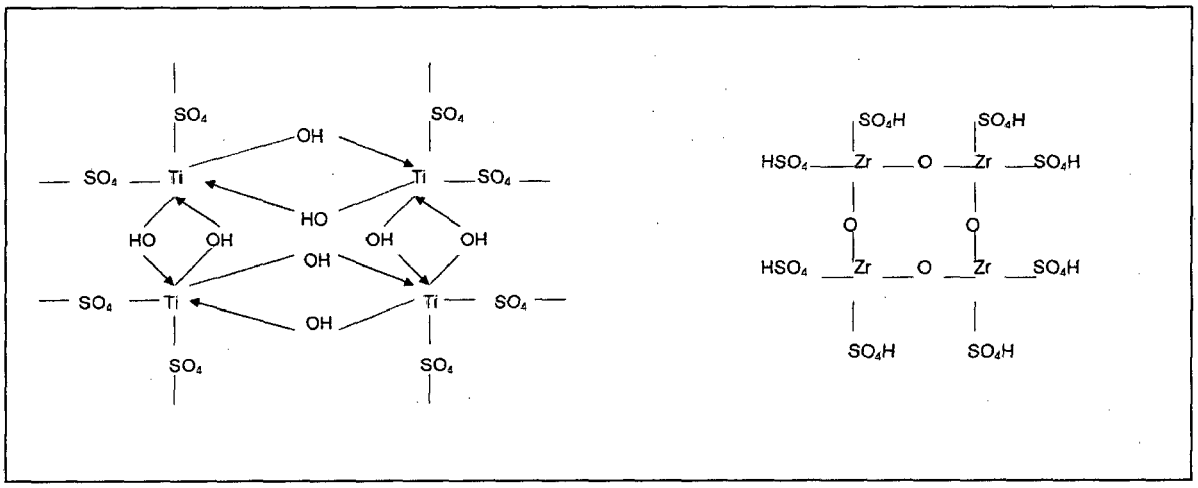
[0005] Leather and fur sector produce also leather wastes. The tannery can only transfer 1/3 of raw hides and skins into leather or other marketable products, while the rest has to be disposed/ incinerated. Leather wastes also contain chromium (III) due to tanning process. Chromium can occur in different oxidation states and its compounds behave differently. Most Cr(VI) compounds are highly toxic and classified as MAK III A 2 carcinogens. So, leather waste containing chromium is considered toxic for environment and man and is an important environmental issue for the footwear industry in recent decades. Also, it is a big problem with current costs in leather waste management in leather, fur and footwear sector.

[0006] On the other hand, interest in the impact of leather on the consumer's health and sense of well being are progressively increasing. There has been discussion about hazardous chemicals in consumer goods made of leather. The purchaser and the public are paying increasing attention to this phenomenon, which is prompting the introduction of relevant regulations by authorities and new labels by private organizations.

[0007] For these reasons, in the past few years, the tanning sector has been working to discover new tanning agents that give leather similar properties to those given by chromium (III) salts.

[0008] Accordingly, Al (III), Zr (IV) [2, 3], Ti (III and IV) [4, 5, 6, 7], Fe -salts [8], their mixed salts [9], and most recently nano-silicates [10] and sodium water glass [11] were tested as effective partial or total chromium replacement mineral tanning agents for the production of a reversibly or irreversibly tanned new intermediate semi-processed product and commodity: "wet-white" leather.

[0009] It is known that Ti(IV) forms compounds with tanning properties, but they are difficult to obtain, as titanium salts can be completely hydrolysed with the separation of the metatitanic acid insoluble in water (TiO_3H_2). In order to be used in leather tanning, titanium sulphate-based compounds are masked with formate, phtalate, glutamate, citrate, tartrate, acetate and are basified using agents such as sodium sulphite / magnesium oxide / ammonia, hexamethylene tetramine; at low pH they are fixed in leather due to $H^+ {}^-O_4S(TiO)_nSO_4^- {}^+H$ complexes which react with functional groups of collagen, but also by physical deposition in the interfibrillary gaps of collagen as it is shown in the figure below (left).



[0010] It is known that Zr(IV) forms complexes with tetrameric structures (see figure, right). Easy hydrolysis of zirconium complexes and their precipitation in the form of oxihydrates lead to the formation of white oxide sediments inside the fibrous structure of collagen, which stabilize collagen structure and provide the leathers with a white colour and very good fullness. However, according to some authors [12], Zr tanning compounds bind to polar amine groups of side chains of collagen, leaving the carboxyl groups unblocked, so that leather pretanned with zirconium salts does not hinder subsequent binding of chromium used for retanning to carboxyl groups.

[0011] In this respect, the following patents are known:

Patent CN101033494 (A)/2007 [13] describes an inorganic tanning composition containing sodium silicate, aluminum sulphate, zirconium synthesis of sodium sulphate which can be used in leather tanning resulting in leathers with a shrinkage temperature of 105°C.

Patents RU2112809/1998 [14] and RU2103372(C1)/1998 [15] relate to tanning compositions based on titanyl sulphate solution obtained by processes involving complicated and expensive crystallization, filtration and precipitation treatments.

Patent JP2006213915 (A)/2006 [16] describes a tanning composition based on titanium dioxide produced by thermal decomposition and used as tanning preventive agent.

Patent IT1262542 (B)/1996 [17] refers to a process of leather pre-tanning for the production of wet-white leather using products based on titanium salts. The process takes place in the pickling bath, then the skins are left in a moist environment for more than 30 hours before subsequent further tanning and other operations, and it involves a lengthy leather processing.

Patent EP0290143 (A1)/1988 [18] relates to a tanning agent comprising a composition of a mixed of aluminum (III) and titanium (IV) ions masked with a poly(hydroxyl) monocarboxylic acid, an alkali metal salt and a process for pretanning, tanning and retanning of hides and skins, using the tanning agent, alone or in conjunction with other tanning agents.

Patents RO103051 (B1)/1992 [19], RO103050 (A2)/1991 [20] and RO103050 (B1)/1992 [21] present tanning compositions based on chromium and aluminum salts and tanning processes for bovine leather. However, these methods have the disadvantage of using chromium salts, even if in a lesser concentration.

[0012] The key factor in the manufacture of chrome-free leather is pretanning the skins into wet-white.

[0013] The technical problem solved by the invention consists in producing a mixed tanning product based on titanium and zirconium, which eliminates the disadvantages of tanning products based on Ti or Zr in that the product acts synergistically in leather, through the complexes of the two metals, and provides increased stability of collagen fixing bonds, as well as a bovine leather tanning process using the complex tanning product in order to obtain semi-processed chrome-free wet white leather.

[0014] The tanning product according to the invention eliminates disadvantages of known tanning agents in that it contains 8-15% technical grade sulfuric acid of min. 95% concentration, 3-10% unrecyclable mixed metallurgic waste (selected so as to have a composition of min. 95% Ti, min. 95% Zr, max. 5% Al, max. 1% Fe and max. 0.5% V), 15-25% technical grade sodium citrate, and 1.0-4% technical grade magnesium oxide, having the appearance of a gray-white powder with a content of 8-18% Ti and Zr metal oxides, so that the ratio of TiO_2:ZrO_2 ranges between 1:1 and 3:1 and the pH value of 10% solution is 1.8-2.2.

[0015] The process of tanning bovine raw hides or sheep skins according to the invention for obtaining semi-processed

chrome-free wet-white leather, which consists in the fact that it employs the tanning product obtained in an amount equivalent to 2-6% metal oxides relative to pelt weight, added directly in the pickling float, with the following parameters: 30-80% float ratio, pH=2.7-3.1, temperature of 25-26°C, density of 1.055- 1.060 g/cc, which lowers the float pH to 1.1-1.3, with dermal tissue penetration time 10-20 min., then the float pH is increased to 3.7-3.9, when the tanning product is fixed into the leather, using 1.5-2.5% basification agent based on magnesium oxide, resulting in semi-processed **wet-white leather** with the following characteristics: 7.5-10% metal oxide content, 10-18% ash content, shrinkage temperature of 68-82°C, pH of the aqueous extract 3.6-4.1. Wet-white leathers obtained can be further processed in a conventional manner, using existing equipment in tanneries, yielding chrome- free leather.

[0016] Economical and ecological advantages:

- Valorization of metallurgical waste;
- Obtaining "chrome-free leather" according to special requirements of automotive leathers, upholstery leathers, clothing leathers);
- Wet-white is a new wet stock to be commercialized;
- Implementation of new tanning process at industrial scale does not require new equipment or investments;
- No risk of Cr(VI) formation;
- Glossy dyeings, especially for fashion items;
- The quality of the crust (retanned) leathers is directly comparable with that resulting from conventional process;
- Leather is free of heavy metals, and therefore suitable for allergic persons;
- Improved scope for sorting at the pretanned stage;
- Effluents without chromium which are easier and cheaper to treat;
- Solid wastes without chromium can be valorized easier and cheaper as fertilizer, for gelatin, glue or other industrial products;
- Cost minimization by reduction of pollution in the leather manufacturing process;
- Elimination of chrome shavings (wastes), which represent approx. 5-10% of the hide weight.
- Wet-white leathers have a higher biodegradability rate than wet-blue leathers, contributing to a more sustainable production in the leather and footwear sector.

[0017] Two examples for the reproduction of the invention consisting in the tanning product and the tanning process using the above product.

Example 1:

[0018] Mixed tanning product for raw bovine hides or sheep skins, obtained in an antiacid reaction vessel with jacket for temperature control, anchor stirrer and exhaust of gases resulting from synthesis, in which are added 48% industrial water, 12% technical grade sulfuric acid of min. 95% concentration and 7% unrecyclable mixed metallurgic waste selected so as to have a composition of min. 95% Ti, min. 95% Zr, max. 5% Al, max. 1% Fe and max. 0.5% V, with intermittent stirring and heating at 90°C until complete dissolution, then 20% sodium citrate previously dissolved in 25% water is added and stirring continues at a temperature of 90°C for 180 minutes, the mixture is cooled at 30-35°C and 2.6% magnesium oxide is added while stirring for 300 minutes until reaching a final pH of 1.6 for the composition in the form of solution, then the composition is filtered, concentrated and dehydrated through freeze-drying or atomisation, resulting in a gray-white powder with a content of 15% titanium and zirconium oxide content, for a TiO_2:ZrO_2 ratio of 1:1 and a pH value of 2.1 for the 10% solution. The composition of the tanning product obtained is the following: 4.45% Ti, 4.40% Zr, 9.85 Mg, 0.28%Al, 0.18% Fe, 0.09% V.

Example 2:

[0019] Pickled bovine hides are subjected to the tanning operation in a rotating drum of 7-14 rpm, in the pickling float with the following parameters: 50% float ratio, pH=2.8-2.9, temperature of 25-26°C, density of 1.060-1.055g/cc with an amount equivalent to 5% titanium and zirconium metal oxides from the mixed tanning product obtained according to Claim 1, relative to pelt weight, directly in the float, when float pH decreases to 1.2, it is stirred for 15 minutes, then penetration of tanning product into leather is visually checked by the presence of violet-blue colour in the leather section, stirring continues for 120 minutes, during which leathers become light coloured and the float transparent, pH increases to 1.8, then the basification operation is performed by adding 1.5% technical grade MgO relative to pelt weight and float temperature is raised from 25°C to 30°C and the drum is rotated for another 300 minutes, with the final pH of the tanning float of 3.9. The resulting wet-white leathers have a smooth grain, pleasant appearance, white colour, very good fullness and a shrinkage temperature of 72°C, which allows subsequent mechanical operations of wringing, splitting and shaving. Chemical characteristics of wet-white leathers are: 2.2% extractable substances, 3.83% metal oxides, 10% ash content,

4.43 pH of aqueous extract. Elemental analysis shows that wet white leathers contain: 1.38 mg/Kg Ti, 1.34mg/Kg Zr, 0.009mg/Kg Fe, 0.015mg/Kg Al, 0.005mg/Kg V. Leathers are further processed by retanning and finishing in a conventional manner.

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Claims

1. Mixed product for tanning bovine raw hides or sheep skins **characterized by** the fact that in consists of 8-15% technical grade sulfuric acid of 95-96% concentration, 3-10% unrecyclable metallurgic waste (selected so as to have a composition of min. 95% Ti, min. 95% Zr, max. 5% Al, max. 1% Fe and max. 0.5% V), 15-25% technical grade sodium citrate, 1.0-4.0% technical grade magnesium oxide, obtained in the form of a gray-white powder with a content of 8-18% Ti and Zr metal oxides, so that the ratio of TiO_2:ZrO_2 ranges between 1:1 and 3:1 and the pH

value of 10% solution is 1.8-2.2.

2. Process of tanning bovine raw hides or sheep skins using a powder tanning product, defined in claim 1, in order to obtain semi-processed **chrome-free wet-white leather, characterized by** the fact that an amount of tanning product equivalent to 2-6% metal oxides relative to pelt weight is added directly in the pickling float, with the following parameters: 30-80% float ratio, pH=2.7-3.1, temperature of 25-26°C, density of 1.055- 1.060 g/cc, which lowers the float pH to 1.1-1.3, with dermal tissue penetration time 10-20 min., then the float pH is increased to 1.8-2.2 and the tanning product is fixed into the leather using 1,5-2,5% basification agent based on magnesium oxide, with the final pH of the tanning float of 3.7-3.9, resulting in **chrome-free wet-white leather** with the following characteristics: 7.5-10% metal oxide content, 10-18% ash content, shrinkage temperature of 68-82°C, pH of the aqueous extract 3.6-4.1, 1.38 mg/Kg Ti, 1.34mg/Kg Zr, 0.009mg/Kg Fe, 0.015mg/Kg Al, 0.005mg/Kg V.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 46 4004

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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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
Munich	24 July 2015	Neugebauer, Ute

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