Title: COMPOSITION COMPRISING CHROMIUM SALTS FOR TANNING

Abstract: Solutions of chromium salts which contain at least one low molecular weight carboxylic acid and have a Schorlemmer basicity of not more than 25% and a pH of less than 2.8 in the aqueous liquor are suitable for the pickle-free tanning of pelts, it surprisingly being possible to use short action times.
Composition comprising chromium salts for tanning

The present invention relates to a composition comprising (a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schorlemmer basicity of not more than 25%, (b) alkali metal sulphates and (c) optionally water; and a process for tanning unpickled pelts with a strongly acidic solution of the composition in water.

In tanning with mineral salts, the one-bath process, which comprises the steps of pickling, tanning with chromium salt and basifying, has become established. During pickling, the animal hide which has been digested and degreased in the beamhouse is treated with strong acids, for example sulphuric acid or hydrochloric acid, and salts, for example sodium chloride. By means of this treatment, the degree of dissociation of the carboxyl groups in the collagen is reduced so that the animal hide has a low pH of less than 2. In this pH range, the fixing of the chromium salts is greatly reduced and the permeation of the salts is increased. The tanning effect is then displayed by an increase in the pH to about 3.5 to 6. For this purpose, when basifying the liquor, alkaline compositions are added in amounts (for example magnesium oxide or sodium carbonate) such that the optimum value for the tanning is established. For this method of tanning, chromium salts have a Schorlemmer basicity of at least 30%.

Large amounts of chemicals are required for this form of tanning, which leads to a high level of pollution of the wastewater. The residual content of, for example, chromium salts in the liquor necessitates an afferent treatment for reducing the chromium content in the wastewater. Improvements have therefore been proposed in order to increase the liquor exhaustion and reduce the consumption of chemicals in order to meet ecological requirements and to increase the cost-efficiency.

It is also known that organic acids, such as, for example, formic acid, are added to the pickle without being able to eliminate the disadvantages described above.

The use of smaller amounts of low molecular weight organic acids, for example formic acid, acetic acid or oxalic acid, or salts thereof, e.g. sodium formate, sodium acetate or sodium oxalate, for masking the chromium salts is also known. Such products are commercially available. Alternatively, small amounts of these complex-active compounds can be added to
the liquors for tanning. The Schorlemmer basicity is also at least 30% in the case of chromium sulphates modified in this manner. By means of this method, the reliability of the tanning process is increased. However, the fact that the tanning capacity of the chromium compound is reduced since polynuclear chromium complexes are present is disadvantageous.

US-A-4,715,861 recommends treating pickled pelts or pelts during the pickling initially with aldehyde- or ketocarboxylic acids, for example glycolic acid, in order to increase the exhaustion of the liquor and to reduce the consumption of chromium salts. The steps of pickling and of basifying are, however, still necessary. Aldehyde and keto acids are physiologically unsafe and require special protective measures. The effect of the aldehyde and keto acids consists in the reaction with amino groups of collagen, which leads to an increase in the acidity of the pelt and hence better chromium uptake.

EP-A-0 822 263 describes a process for tanning with chromium salts, in which pelts are treated with 3-hydroxybutyraldehyde, and pickling and basifying are dispensed with. As a result of reaction of the aldehyde group with amino groups of the collagen, the isoelectric point is reduced so that chromium salts penetrate sufficiently and basifying is superfluous. WO 00/66793 discloses the same process using α- or β-hydroxyaldehydes. The agents used for the pretreatment are volatile compounds which can be handled only with difficulty in tanneries. Furthermore, aldehydes are physiologically unsafe. The use of these processes requires special protective means, which cancels out the advantages of dispensing with pickling and basifying from economic points of view.

Brazilian Published Patent Application PI 0004255-7 A discloses chromium complexes of chromium salts and oligomeric masking agents having a low Schorlemmer basicity of from 10 to 20%. They are suitable for tanning pelts without pickling and basifying. The required penetration is achieved by the low basicity, these agents penetrating only slowly owing to their excessively high molecular weights and therefore being unconvincing.

Processes for the direct tanning of pelts from the beamhouse have not become established owing to the existing disadvantages, although said direct tanning is extremely desirable owing to the ecological and economic advantages.

It has now surprisingly been found that existing disadvantages can be avoided and more rapid and uniform penetration and a higher uptake of basic chromium salts in the pelt and hence also greater exhaustion of the liquor are achieved, excellent complete tanning of the pelts and hence very good physical properties (for example, tensile strength, ultimate tensile
strength, stitch tear resistance) are obtained, the salt consumption (for example, sodium chloride) is reduced, pickling and basifying are avoided and the time required for complete tanning is reduced if the pelts for tanning are treated with an effective amount of a reaction product of (a) chromium sulphates having a Schorlemmer basicity of from 30 to 50% and (b) amounts of low molecular weight carboxylic acids sufficient for the formation of mononuclear chromium salts, in aqueous and weakly acidic liquor.

The invention firstly relates to a composition comprising
(a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schorlemmer basicity of not more than 25%,
(b) an alkali metal sulphate, and
(c) optionally water,
(d) the pH of a 10 percent strength by weight solution of the composition in water being not more than 2.8.

Mono- and polycarboxylic acids are known. The mono- and polycarboxylic acids preferably have a molecular weight of not more than 200, preferably not more than 160 and particularly preferably not more than 120. Some examples of mono- and dicarboxylic acids are formic acid, acetic acid, propionic acid, lactic acid, methoxyacetic acid, monochloro- or monofluoroacetic acid, oxalic acid and malonic acid. The carboxylic acids may be used individually or as a mixture of at least two carboxylic acids.

The Schorlemmer basicity of the mononuclear chromium salt is preferably not more than 23% and particularly preferably not more than 21%. The lower limit may be, for example, at least 14% and preferably at least 16%.

The pH of the composition according to definition (d) is preferably not more than 2.5. The lower limit of the pH may be, for example, 0.2 and preferably 0.5.

The amount of the mononuclear chromium salt in the composition may be, for example, from 5 to 30% by weight and preferably from 10 to 20% by weight, calculated as the content of Cr₂O₃.

The alkali metal sulphate is preferably potassium sulphate or particularly preferably sodium sulphate. The amount of the alkali metal sulphate may be, for example, the remaining amount up to 100% by weight. The complete drying of the composition is difficult and
technically complicated owing to the water of hydration bound to the chromium salt. It is therefore more advantageous if small amounts of water are present in the composition, for example up to 15% by weight and more preferably up to 10% by weight.

The composition according to the invention may be present as an aqueous solution, as an aqueous concentrate or as a solid, water-soluble formulation. The amount of the composition according to the invention in aqueous solution and aqueous concentrates may be, for example, from 35 to 85% by weight, preferably from 40 to 70% by weight. The solid composition can, as mentioned above, contain up to 15% by weight and more preferably up to 10% by weight of water, owing to the difficult drying. The solid composition may be powder or granules. Concentrates having a water content of less than about 35% are highly viscous and difficult to handle, particularly when filling and removing from containers. These water contents are therefore less preferred.

The composition according to the invention may additionally contain agents customary in the tannery, for example solvents, standardizing agents and fungicides.

The composition according to the invention is obtainable by reacting an aqueous solution of chromium sulphates having a Schorlemmer basicity of, for example, from 30 to 50%, which contains alkali metal sulphates, with low molecular weight mono- or polycarboxylic acids.

Chromium salts for tanning have long been known and are commercially available as solid or liquid formulations. They are sulphates of trivalent chromium. The products available are generally mixtures of basic chromium sulphates and alkali metal sulphates, such as, for example, sodium sulphate, since the basicity is established by adding alkali metal hydroxides. The basicity is established by means of the amount of alkali metal hydroxides, which is stated in percent Schorlemmer. In this context, a basicity of 0% is assigned to pure chromium sulphate and a basicity of 100% to pure chromium hydroxide. Forms in between, such as, for example, Cr(OH)SO₄, have a basicity of 33.3%.

The chromium sulphates used for the preparation of the composition preferably have a Schorlemmer basicity of from 30 to 50%, more preferably from 30 to 45%, and particularly preferably from 30 to 42%. Such chromium sulphates are standard products for the tanneries and are commercially available or can be prepared in a simple manner.

The preparation of the composition according to the invention can be effected in a simple manner by dissolving chromium sulphates in water and adding the desired amount of alkali
metal hydroxides. Commercially available products are advantageously used. Specifically, it is possible to add the desired amount of carboxylic acid, optionally as an aqueous solution, to the aqueous solution of chromium sulphate and alkali metal sulphate, and then to stir, optionally with heating, until the carboxylic acids have dissolved. Heating may mean up to 100°C and preferably up to 50°C. The reaction is expediently carried out at room temperature.

On the one hand, the basicity of the chromium sulphate and, on the other hand, the pH are adjusted with the amount of the mono- and polycarboxylic acids. It is possible to add less than stoichiometric amount or an excess, based on the Cr₂O₃ present in the solution. The molar ratio of chromium sulphate, based on Cr₂O₃ to carboxylic acid may be, for example, from 1:0.1 to 1:1.5, preferably from 1:0.2 to 1:1.

A typical composition according to the invention can be prepared from an amount of water of, for example, 45-55% by weight, an amount of chromium sulphate, calculated as Cr₂O₃, of, for example, 10-20% by weight, and an amount of carboxylic acid of, for example, 4-10% by weight, the remaining amount to 100% by weight being an alkali metal sulphate.

The reaction product obtained can, if necessary and desired, be worked up by removing water to give aqueous solutions, aqueous concentrates or solid formulations. The removal of water can be effected by heating, optionally in vacuo. Solid formulations can be obtained by means of freeze-drying, spray-drying, fluidized-bed drying, granulation or removal of water with heating, optionally in vacuo, and milling of the dried product to give powders. Liquid and solid compositions according to the invention have no substantial differences with regard to their outstanding tanning effect.

Aqueous concentrates can be prepared in a simple manner directly in the tannery. Such concentrates can, however, also be supplied as the prepared solution. Pulverulent or granulated solid compositions are preferred delivery forms, owing to the smaller volume. However, it is also possible to supply dilute aqueous solutions which can be used directly as tanning liquor, particularly if the amount of hides to be tanned is not too large.

Furthermore, it is possible to fill chromium sulphates and carboxylic acids according to the amounts used into containers and thus to supply the tanneries, so that it is possible to prepare the liquor for tanning with formation of mononuclear chromium salts directly in the tannery.
The invention also relates to a kit, consisting of two containers, which each contain:

(a) a chromium sulphate having a Schorlemmer basicity of from 30 to 50% and an alkali metal sulphate, in the form of an aqueous solution, of an aqueous concentrate or of a solid formulation, and

(b) at least one low molecular weight mono- or polycarboxylic acid, either as such, in aqueous solution or as an aqueous concentrate.

Amounts and molar ratios are as stated above.

The invention furthermore relates to a process for the preparation of a liquor for tanning pelts, comprising an aqueous solution of chromium salts, wherein

a) a chromium salt having a Schorlemmer basicity of from 30 to 50% as a mixture with an alkali metal sulphate, in the form of an aqueous solution, of an aqueous concentrate or of a solid formulation, and

b) at least one low molecular weight mono- or polycarboxylic acid, either as such, in aqueous solution or as an aqueous concentrate,

c) are mixed in molar ratios and amounts in water, and allowed to react with formation of mononuclear chromium salts having anions of low molecular weight carboxylic acids and sulphate anions, such that the mononuclear chromium salts have a Schorlemmer basicity of not more than 25%, the pH of the aqueous solution is not more than 2.8, and the amount of chromium salt in the liquor is from 1 to 8% by weight of chromium trioxide (Cr₂O₃), based on the weight of the pelt.

The molar ratios and amounts are preferably chosen so that the pH of the aqueous solution is not more than 2.5 and, for example, from 2.5 to 0.2 and in particular from 2.5 to 0.5.

The composition according to the invention is outstandingly suitable for tanning pelts in aqueous liquor, it being possible completely to dispense with pickling and basifying, and optionally only smaller amounts of electrolyte salts are added to the water, for example up to 5% by weight, based on the dry weight of the pelt. The electrolyte salt used is mainly sodium chloride. The pH of the liquor at the beginning of the process is strongly acidic. The optimum pH required for effective tanning in the aqueous liquor is automatically established after addition of the composition, since basic components present in the pelt as a result of the pretreatment increase the pH. After the end of the tanning, the pH has increased to about 3 to 3.5.
The invention furthermore relates to a process for tanning unpickled pelts by the action of chromium(III) sulphates in aqueous liquor, which is characterized in that an effective amount of a composition comprising

(a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schölemmer basicity of not more than 25%,
(b) an alkali metal sulphate, and
(c) optionally water,
(d) the pH of a 10 percent strength by weight solution of the composition in water being not more than 2.8,

is added to the pelt in aqueous liquor and allowed to act on the pelt.

In the context of the invention, effective amount means that from 1 to 8% by weight and preferably from 1.5 to 5% by weight of chromium trioxide (Cr2O3) are present in the liquor, based on the weight of the pelt. The amount is calculated in the tannery, usually on the basis of the theoretical content of chromium trioxide.

The process according to the invention can be carried out by introducing washed pelts into water, adding a salt, for example sodium chloride, to the liquor, and allowing to act for a short time on the pelts. The composition according to the invention for tanning is then added, which composition can be allowed to act, for example, for about 2 to 10 hours at room temperature. Heating is then effected and the reaction time is allowed to continue, for example, for up to 10 hours. The temperature may be up to 50°C and preferably up to 45°C. After the tanning, the leather obtained is washed and is then ready for further processing. The pH of the liquor after the tanning may be from 3 to 5.5.

The invention also relates to the use of a composition containing

a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schölemmer basicity of not more than 25%,

b) an alkali metal sulphate, and
c) optionally water,

d) the pH of a 10 percent strength by weight solution of the composition in water being not more than 2.8,

for tanning pelts in aqueous liquor.

The examples which follow explain the invention in more detail.
A) Preparation of compositions

**Example A1:** Solution of chromium sulphate, lactic acid and formic acid
In a stirred vessel, 109.3 g of a solution of 18 g of formic acid (85% strength) and 42.7 g of lactic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 30 minutes at room temperature. The composition contains 12.49% by weight of Cr₂O₃ and has a Schorlemmer basicity of 20.6% and a density of 1.47 g/cm³ at 20°C. The pH of the composition is 1.40 and the pH of a 10 percent strength by weight solution in water is 2.42.

**Example A2:** Solution of chromium sulphate, lactic acid and formic acid
In a stirred vessel, 108.3 g of a solution of 23 g of formic acid (85% strength) and 37.7 g of lactic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 15 minutes at room temperature. The composition contains 12.40% by weight of Cr₂O₃ and has a Schorlemmer basicity of 20.0% and a density of 1.47 g/cm³ at 20°C. The pH of the composition is 1.40 and the pH of a 10 percent strength by weight solution in water is 2.39.

**Example A3:** Solution of chromium sulphate and oxalic acid and formic acid
In a stirred vessel, 109.3 g of a solution of 28.5 g of oxalic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 30 minutes at from 40 to 50°C. Thereafter, after cooling to 30°C, 32.8 g of formic acid (85% strength) are added and stirring is effected for a further 15 minutes. The composition contains 14.49% by weight of Cr₂O₃ and has a Schorlemmer basicity of 19.2% and a density of 1.63 g/cm³. The pH of the composition is 0.98 and the pH of a 10 percent strength by weight solution in water is 2.27.

**Example A4:** Powder comprising chromium sulphate, lactic acid and formic acid
109.3 g of a solution of 18 g of formic acid (85% strength) and 42.7 g of lactic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 30 minutes at room temperature. The composition is dried in a
water jet vacuum at 60°C. The green residue is then milled to give a powder. The pH of a 10 percent strength by weight solution in water is 2.48.

**Example A5:** Powder comprising chromium sulphate, lactic acid and formic acid
109.3 g of a solution of 23 g of formic acid (85% strength) and 37.7 g of lactic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 15 minutes at room temperature. The composition is dried in a water jet vacuum at 60°C. The green residue is then milled to give a powder. The pH of a 10 percent strength by weight solution in water is 2.46.

**Example A6:** Powder product comprising chromium sulphate and oxalic acid and formic acid
109.3 g of a solution of 28.5 g of oxalic acid in water are added to a solution of 830 g of chromium(III) sulphate and sodium sulphate [Schorlemmer basicity 33% (theoretically Cr(OH)SO₄; 15% by weight content of Cr₂O₃)]. Stirring is then effected for 30 minutes at from 40 to 50°C. Thereafter, after cooling to 30°C, 32.8 g of formic acid (85% strength) are added and stirring is effected for a further 15 minutes. The composition is dried in a water jet vacuum at 60°C. The green residue is then milled to give a powder. The pH of a 10 percent strength by weight solution in water is 2.45.

**B) Use examples**

**Example B1:** Tanning of hides (Swiss bull)
20% by weight of water are added to 50 kg (dry weight) of delimed, bated, unsplit and washed hides (Swiss bull) in a tanning drum and then 3% by weight of NaCl are added. The liquor is allowed to act for 15 minutes. Thereafter, 10% by weight of the undiluted composition according to example A1 and 0.1% by weight of fungicide (Acticide 4A⁵) are added and allowed to act for 6 hours at room temperature. The temperature is then increased to 44°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.25, and the liquor contains only 0.15% by weight of chromium. The hides have been completely tanned.

**Example B2:** Tanning of hides (Russian cows)
20% by weight of water are added to 300 kg (dry weight) of delimed, bated, unsplit and washed hides (Russian cows) in a tanning drum and then 3% by weight of NaCl are added. The liquor is allowed to act for 15 minutes. Thereafter, 10% by weight of the undiluted composition according to example A1 and 0.1% by weight of fungicide (Acticide 4A⁵) are
added and allowed to act for 6 hours at room temperature. The temperature is then increased to 44°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.0. The hides have been completely tanned.

Example B3: Tanning of hides (Brazilian zebu)
20% by weight of water are added to 35 kg (dry weight) of delimed, bated, unsplit and washed hides (Brazilian zebu) in a tanning drum and then 3% by weight of NaCl are added. The liquor is allowed to act for 15 minutes. Thereafter, 10% by weight of the undiluted formulation according to example A2 and 0.1% by weight of fungicide (Acticide 4A®) are added and allowed to act for 6 hours at room temperature. The temperature is then increased to 42°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.4. The hides have been completely tanned.

Example B4: Tanning of hides (Russian cows)
20% by weight of water are added to 30 kg (dry weight) of delimed, bated, unsplit and washed hides (Russian cows) in a tanning drum and then 3% by weight of NaCl are added. The liquor is allowed to act for 15 minutes. Thereafter, 10% by weight of the undiluted formulation according to example A3 and 0.1% by weight of fungicide (Acticide 4A®) are added and allowed to act for 6 hours at room temperature. The temperature is then increased to 44°C and the liquor is allowed to act for a further 8 hours. The tanned hide is then removed and washed. The pH of the liquor is from 3.2 to 3.3 and the liquor contains only 0.16% by weight of chromium. The hides have been completely tanned.

Example B5: Tanning of hides (Swiss bull)
20% by weight of water are added to 50 kg (dry weight) of delimed, bated, unsplit and washed hides (Swiss bull) in a tanning drum and then 3% by weight of NaCl are added. The liquor is then allowed to act for 15 minutes. Thereafter, 6% by weight of the pulverulent formulation according to example A4 and 0.1% by weight of fungicide (Acticide 4A®) are added and the liquor is allowed to act for 6 hours at room temperature. The temperature is then increased to 40°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.23, and the liquor contains only 0.08% by weight of chromium. The hides have been completely tanned.
Example B6: Tanning of hides (Swiss bull)
20% by weight of water are added to 50 kg (dry weight) of delimed, bated, unsplit and washed hides (Swiss bull) in a tanning drum and then 3% by weight of NaCl are added. The liquor is then allowed to act for 15 minutes. Thereafter, 6% by weight of the pulverulent composition according to example A5 and 0.1% by weight of fungicide (Acticide 4A®) are added and the liquor is allowed to act for 6 hours at room temperature. The temperature is then increased to 40°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.20, and the liquor contains only 0.20% by weight of chromium. The hides have been completely tanned.

Example B7: Tanning of hides (Swiss bull)
20% by weight of water are added to 50 kg (dry weight) of delimed, bated, unsplit and washed hides (Swiss bull) in a tanning drum and then 3% by weight of NaCl are added. The liquor is then allowed to act for 15 minutes. Thereafter, 6% by weight of the pulverulent composition according to example A6 and 0.1% by weight of fungicide (Acticide 4A®) are added and the liquor is allowed to act for 6 hours at room temperature. The temperature is then increased to 40°C and the liquor is allowed to act for a further 9 hours. The tanned hide is then removed and washed. The pH of the liquor is 3.04, and the liquor contains only 0.13% by weight of chromium. The hides have been completely tanned.
Patent Claims

1. Composition comprising
   a) a mononuclear chromium salt having anions of low molecular weight
      carboxylic acids and sulphate anions, the mononuclear chromium salts having
      a Schorlemmer basicity of not more than 25%,
   b) an alkali metal sulphate, and
   c) optionally water,
   d) the pH of a 10 percent strength by weight solution of the composition in water
      being not more than 2.8.

2. Composition according to Claim 1, characterized in that the carboxylic acids are
   formic acid, acetic acid, proplionic acid, lactic acid, methoxyacetic acid, monochloro-
   or monofluoroacetic acid, oxalic acid and malonic acid.

3. Composition according to Claim 1, characterized in that the Schorlemmer basicity of
   the mononuclear chromium salt is from 16% to not more than 23%.

4. Composition according to Claim 1, characterized in that the amount of the chromium
   salt is from 5 to 30% by weight, calculated as the content of Cr₂O₃, and the remaining
   amount is the alkali metal sulphate and optionally water.

5. Composition according to Claim 1, characterized in that it is present as an aqueous
   solution, as an aqueous concentrate or as a solid, water-soluble formulation.

6. Composition according to Claim 5, characterized in that the amount of the
   composition in aqueous solution and aqueous concentrates is from 35 to 65% by
   weight.

7. Composition according to Claim 6, characterized in that the aqueous concentrate
   contains more than 40 and up to 70% by weight of water.

8. Composition according to Claim 6, characterized in that, as a solid composition, it is a
   powder or granules which may contain up to 15% by weight of water.
9. Composition obtainable by reacting an aqueous solution of chromium sulphates having a Schorlemmer basicity of from 30 to 50%, which contains alkali metal sulphates, with low molecular weight mono- or polycarboxylic acids.

10. Composition according to Claim 9, characterized in that the molar ratio of chromium sulphate, based on Cr₂O₃, to carboxylic acid is from 1:0.1 to 1:1.5.

11. Composition according to Claim 9, characterized in that the amount of water is 45-55% by weight, the amount of chromium sulphate, calculated as Cr₂O₃, is 10-20% by weight, and the amount of carboxylic acid is 4-10% by weight, the remaining amount to 100% by weight being an alkali metal sulphate.

12. Kit consisting of two containers which each contain:
   (a) a chromium sulphate having a Schorlemmer basicity of from 30 to 50% and an alkali metal sulphate, in the form of an aqueous solution, of an aqueous concentrate or of a solid formulation, and
   (b) at least one low molecular weight mono- or polycarboxylic acid, either as such, in aqueous solution or as an aqueous concentrate.

13. Process for tanning unpickled pelts by the action of chromium(III) sulphates in aqueous liquor, characterized in that an effective amount of a composition containing
   (a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schorlemmer basicity of not more than 25%,
   (b) an alkali metal sulphate, and
   (c) optionally water,
   (d) the pH of a 10 percent strength by weight solution of the composition in water being not more than 2.8,
   is added to the pelt in aqueous liquor and allowed to act on the pelt.

14. Process according to Claim 13, characterized in that from 1 to 8% by weight of chromium trioxide (Cr₂O₃), based on the weight of the pelt, is present in the liquor.
15. Use of a composition containing
   a) a mononuclear chromium salt having anions of low molecular weight carboxylic acids and sulphate anions, the mononuclear chromium salts having a Schorlemmer basicity of not more than 25%,
   b) an alkali metal sulphate, and
   c) optionally water,
   d) the pH of a 10 percent strength by weight solution of the composition in water being not more than 2.8,

for tanning pelt in aqueous liquor.

16. Process for the preparation of a liquor for tanning pelt, comprising an aqueous solution of chromium salts, characterized in that
   a) a chromium sulphate having a Schorlemmer basicity of from 30 to 50% as a mixture with an alkali metal sulphate, in the form of an aqueous solution, of an aqueous concentrate or of a solid formulation, and
   b) at least one low molecular weight mono- or polycarboxylic acid, either as such, in aqueous solution or as an aqueous concentrate,
   d) are mixed in molar ratios and amounts in water, and are allowed to react with formation of mononuclear chromium salts having anions of low molecular weight carboxylic acids and sulphate anions, such that the mononuclear chromium salts have a Schorlemmer basicity of not more than 25%, the pH of the aqueous liquor is not more than 2.8 and the amount of chromium salt in the liquor is from 1 to 8% by weight, calculated as chromium trioxide (Cr₂O₃), based on the weight of the pelt.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C14C3/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C14C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>GB 547 129 A (ARTHUR SAMUEL CALLAGHAN; ICI LTD; JOHN BURCHILL; RONALD ERNEST HUNNAM) 14 August 1942 (1942-08-14) page 1, line 68 - page 2, line 36 example 1</td>
<td>1-16</td>
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<tr>
<td>A</td>
<td>US 4 919 680 A (WEHLING BERNHARD ET AL) 24 April 1990 (1990-04-24) column 2, line 16 - column 4, line 5</td>
<td>1-16</td>
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<td>A</td>
<td>US 4 715 861 A (LOTZ WERNER ET AL) 29 December 1987 (1987-12-29) cited in the application page 1, line 52 - page 2, line 7 example 1</td>
<td>1-16</td>
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Further documents are listed in the continuation of box C.

| Patent family members are listed in annex. |

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