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(54) Title: TANNAGES

(57) Abstract: A novel tannage comprises the reaction product of a quaternary phosphonium compound (e.g. tetrakis hydroxymethyl phosphonium chloride or sulphate) with a vegetable tanning agent (e.g. mimosa, chestnut, wattle, tara, myrobalan or quebracho). There is also provided a method for the production of such a tannage.
TANNAGES

FIELD OF THE INVENTION

This invention relates to a novel tanning compound for tanning of hides and skin. The tanning processes using the compound can be carried out without using chromium.

This invention also relates to a method for producing tannages, which tannages comprise the reaction products of quaternary phosphonium compounds with natural tanning agents. The present invention further relates to tannages made by the said method, to the use of such tannages in treating animal skins and to tanned skins obtained thereby.

BACKGROUND OF THE INVENTION

Processing of hides and skin has hitherto involved the use of chromium based tanning compounds, the dominant tanning agent used worldwide at the present. Chromium is a toxic metal compound now deemed environmentally unfriendly. Pressure towards production of non-chrome leather is mounting as the industry strives to meet the increasingly stringent regulations attached to chromium and to solid waste disposal, as well as the demand for product safety and recyclability. Some European countries are already beginning to restrict the use of leather containing chromium. A number of alternative tanning agents like aluminium chloride, aluminium sulphate, titanium sulphate and a double salt of ammonium and titanium sulphate have been tried but these do not give leather with the hydrothermal characteristics as obtained with chromium. Alternative organometallic aluminium complexes were also studied and a patent also established for the application of basic aluminium formate or acetate with polycarboxylic acid [British Patent 2153844 (1984)]. This
gives hydrothermal stability, as measured by the shrinkage temperature of the leather, similar to that of chromium, but does not solve some of the environmental concerns. Syntans (synthetic tanning agents) have been used for about 90 years. These are mostly based on naphthalene or phenol-formaldehyde condensation products. They give leather with shrinkage temperatures around 70 – 75°C. These leathers cannot be compared in their performance with chrome-containing leather. Oxazolidines, [British Patent 1481508 (1973)], tetrakis hydroxy methyl phosphonium chloride, [US patent 2732278 (1956)], and tetrakis hydroxy methyl phosphonium salts, [NZ Patent 244515 (1997)] are environmentally friendly but give leather with shrinkage temperatures of only around 85°C. Moreover, they do not give satisfactory leather when used alone. Only when subsequently tanned with chromium or vegetable tanning agents do these reagents give satisfactory leather.

In US 2,732,278, a two-step tanning process is disclosed which requires tanning with tetrakis hydroxymethyl phosphonium chloride followed by retanning with a vegetable tannin. The shrinkage temperatures of these leathers did not exceed 90°C.

Accordingly, there is still a need for a simple, chromium free tanning process, and for tannage compounds useful in such processes.

**SUMMARY OF THE INVENTION**

In a first aspect, the present invention provides a tannage of the formula:

\[
\begin{align*}
\text{CH}_2 & \quad \text{R}^1 \\
\text{R}^2 \text{H}_3 \text{C} & \quad \text{P} \quad \text{CH}_2 \text{OA} \\
\text{CH}_2 & \quad \text{R}^3
\end{align*}
\]
wherein A is a polyphenol containing tanning agent, and R¹, R² and R³ are selected from –OH or X wherein X is chloride, sulphate or phosphate; with the proviso that only one of R¹, R² and R³ is X.

In a second aspect, the present invention provides a method for producing a tannage, said tannage comprising the reaction product of a quaternary phosphonium compound and a vegetable tanning agent, in which the phosphonium compound and the vegetable tanning agent are mixed together in a weight ratio of 1:5 or greater, optionally in the presence of water, the mixture being subsequently heated at a minimum temperature of 80°C for up to 20 hours.

The present invention further provides a tannage which has been produced by the method described in the immediately-preceding paragraph.

The present invention yet further provides the use of the said tannage in the treatment of animal skins, as well as tanned skins which have been so treated.

Preferably, the tanning agent A is a vegetable tanning agent.

The present invention still further provides a process for tanning a hide or skin which process comprises treating the hide or skin with 1 to 30% by weight (based on weight of the hide or skin) of a tannage compound of the invention.

Desirably, the tanning process is carried out at a pH of between 2.5 to 8.5, and at a temperature of from 10°C to 45°C.

As a pre-step or further step, the process comprises treating the hide or skin with a further tanning agent.
While the invention is broadly as defined above, it will be appreciated by those persons skilled in the art that it is not limited thereto and that it also includes embodiments of which the following description provides examples.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides in a first aspect a tannage of the formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{H}_3 \quad \text{C} \quad \text{P} \quad \text{CH}_2 \quad \text{OA} \\
\text{CH}_2 & \quad \text{R}^3
\end{align*}
\]

wherein A is a polyphenol containing tanning agent, and R^1, R^2 and R^3 are selected from -OH or X, wherein X is chloride, sulphate or phosphate; with the proviso that only one of R^1, R^2 and R^3 is X.

Preferably, X is chloride or sulphate.

Preferably, the tanning agent A is a vegetable tanning agent. Any suitable vegetable tanning agent known in the art may be used. Preferred vegetable tanning agents include condensed or hydrolysed agents e.g. mimosa extract, chestnut extract, wattle extract, tara extract, myraborlam extract and quebracho extract, but are not limited thereto.

As the reader will appreciate, the novel tannage of the invention is a condensate product which may be synthesised by condensing vegetable tanning agents discussed above, and tetrakis hydroxymethyl phosphonium
chloride and tetrakis hydroxymethyl sulphate, according to known condensation techniques or as set out herein.

In one preferred method of making such tannages, the tannage is synthesised by reacting 25 to 65 parts, preferably 45 to 50 parts of a condensed vegetable tanning agent with 75 to 35 parts, preferably 35 to 45 parts of a tetrakis hydroxymethyl phosphonium salt. The process may additionally include the use of 0-15% water and is carried out at a temperature of between 30°C to 60°C, preferably 40°C to 50°C for 2 to 6 hours, preferably 4 hours, and with constant stirring.

Under the conditions of the aforesaid process, the quaternary phosphonium compound may not be completely reacted with the tanning agent and would therefore have to be removed as an unwanted by-product of the reaction.

We have now found that, by decreasing the amount of quaternary phosphonium compound relative to the tanning agent and by increasing the temperature and time of the reaction, we can produce a tannage in which the amount of residual phosphonium compound is minimised or eliminated and which exhibits commercially-useful tanning properties when applied to animal skins.

We have also, most unexpectedly, found that equally advantageous tannages can be produced by the reaction of a vegetable tanning agent with a phosphonium compound which is the condensation product of a tetrakis (hydroxymethyl) phosphonium salt and urea, thiourea or an amine.

Accordingly, in a second aspect, the present invention provides a method for producing a tannage, said tannage comprising the reaction product of
a quaternary phosphonium compound and a vegetable tanning agent, in which the phosphonium compound and the vegetable tanning agent are mixed together in a weight ratio of 1:5 or greater, optionally in the presence of water, the mixture being subsequently heated at a minimum temperature of 80°C for up to 20 hours.

The present invention further provides a tannage which has been produced by the method described in the immediately-preceding paragraph.

The present invention yet further provides the use of the said tannage in the treatment of animal skins, as well as tanned skins which have been so treated.

Preferably, the quaternary phosphonium compound is a phosphonium salt such as tetrakis (hydroxymethyl) phosphonium sulphate (hereinafter THPS) or tetrakis (hydroxymethyl) phosphonium chloride (hereinafter THPC).

Alternatively, the quaternary phosphonium compound may comprise the condensation product of THPS or THPC with an organic nitrogen compound such as urea, thiourea or an amine.

Preferably, the vegetable tanning agent is a condensed or hydrolysed tanning agent, for example, mimosa, wattle, chestnut, quebracho, tara or myrabolam. Most preferably, the vegetable tanning agent is a condensed tanning agent such as mimosa.

The present invention still further provides a process for tanning a hide or skin which process comprises treating the hide or skin with 1 to 30%, preferably 5 to 25%, and most preferably 10 to 15% by weight of a
tannage compound of the invention (all percentage weights being based on the weight of the hide or skin).

Desirably, the tanning process is carried out at a pH of between 2.5 to 8.5, preferably between 4.0 to 6.5 and most preferably between 4.4 and 6.5, at a temperature of from preferably from 15°C to 45°C, preferably from 20°C to 40°C and most preferably at 35°C.

The tanning process may be effected for 2 to 10 hours, most preferably from 4 to 8 hours and most preferably for 4 hours.

In the method according to the second aspect of the present invention, the reaction can suitably be carried out in the presence of water. For example, the reaction mixture can comprise 12.5% by weight of the quaternary phosphonium compound, 50% by weight of the vegetable tanning agent and 37.5% by weight of water, all percentages being calculated on the total weight of the reaction mixture and the gross weight of each reactant. In this description, "gross weight" includes both the "active" and "inactive" weights of the individual reactant.

We have found that heating the reaction mixture for up to about 20 hours at 80°C leads to a substantially complete reaction between the quaternary phosphonium compound and the vegetable tanning agent, as evidenced by, for example, n.m.r. spectrographic analysis. A shorter reaction time has been found to lead to a less complete reaction and the consequent residue of the phosphonium compound in the reaction mixture.

In a further preferred embodiment the tanning process also employs an aluminium tanning agent such as aluminium salts selected from aluminium chloride, aluminium sulphate, aluminium acetate and aluminium formate, but again are not limited thereto. The aluminium salts may be used in the
process at levels between 0.1 to 5%, preferably 0.5 to 2% by weight of the hide or skin.

The applicant has discovered that the use of aluminium salts with the novel tannage compounds of the invention increases the shrinkage temperature of the resulting leather to a range of from 98°C to 120°C.

In a particular preferred process, tanning with a novel tannage compound of the invention is effected for 30 minutes to 4 hours, preferably 1 hour, after which an aluminium salt is added. In this preferred process the aluminium salt is basic aluminium formate and tanning is carried out at pH 4.0, generally for 6 hours.

The process may further comprise other standard tanning steps known in the art. This includes degreasing of pickled skins prior to tanning, fatliquoring, and drying of skins following tanning.

Preferably, the hides or skins are pickled and optionally degreased prior to tanning.

The tanning process may further comprise a pre-tanning step or a further tanning step comprising tanning with known tanning agents. The tanning agents used in these additional steps may include known chrome, aluminium or vegetable tanning agents but are not limited thereto.

Using the novel compounds of the invention, tanning can be effected as a one-step, chromium-free process. This simplifies known art processes, considerably lessens impact on the environment, while still providing hides or skins with high hydrothermal stability. Moreover, testing shows that the performance properties of the leather produced are comparable to those of chromium-containing leather, as compared to leathers tanned by
two step processes using tetrakis hydroxymethyl phosphonium salts, followed by separate tanning steps. The novel tanning compound operates by reacting with skin or hide protein as evidenced by the considerable increase in the hydrothermal stability of the tanned hides and skin.

The present invention will be illustrated by way of the following non-limiting examples.

In Examples 1 to 9, the term "NPM" denotes a compound produced by the reaction of a phosphonium compound with mimosa extract and "NPC" denotes a compound produced by the reaction of a phosphonium compound with a chestnut extract.

**EXAMPLE 1**

Use of Compound NPM and Compound NPC as a solo tanning agent

Pickled lamb skins at pH 1.5 were degreased and the pH adjusted to 3.5 and were allotted at random for tannage with various tanning agents as set out in Table 1 below. Following a standard method these pelts were tanned individually in a computer controlled Dose drum at 12 rpm for 5 hours gradually raising the pH of the tanning bath with sodium formate and sodium bicarbonate to pH 5.5 – 6.5 and maintaining the temperature at 35°C. The shrinkage temperature, which is a measure of tanning, was determined following prescribed method IUP 16 of the International Union of Leather Technologists and Chemists. The leathers were fatliquored and crusted out together following a standard process. The results were as given in Table 1 below:-
Table 1

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage temperature, °C (after 5 hour tannage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrakis hydroxy methyl phosphonium (THPS) alone</td>
<td>82</td>
</tr>
<tr>
<td>Mimosa Extract alone</td>
<td>76</td>
</tr>
<tr>
<td>Compound NPM alone</td>
<td>88</td>
</tr>
<tr>
<td>Compound NPC alone</td>
<td>89</td>
</tr>
</tbody>
</table>

This result indicates the tanning power of Compounds NPM and Compound NPC which were superior to tetrakis hydroxy methyl phosphonium (THPS) and vegetable tanning materials. The tanned leather could be dried normally under usual tannery conditions. While THPS tanned pelt dried out firm typical of a formaldehyde tanned leather, the pelt tanned with Compound NPM gave leather which was almost white, soft and pliable, similar in feel and appearance to a commercially saleable East India (E.I.) tanned leather.

EXAMPLE 2

Use of Compound NPM and Compound NPC as a pretanning agent

Pickled lamb skins were degreased and their pH adjusted to 3.5. Following a standard method these pelts were tanned with THPS in a computer controlled Dose drum at 12 rpm for 5 hours gradually raising the pH of the tanning bath with sodium formate and sodium bicarbonate to pH 5.0 – 5.5 and maintaining the temperature at 35°C. The shrinkage temperature, which is a measure of tanning, was determined following prescribed method IUP 16 of the International Union of Leather Technologists and Chemists. These skins were then allotted at random for further tannages with
various known mineral tanning agents. Tannages were conducted with the novel Compound NPM, with known THPS with combinations of NPM or THPS and various aluminium salts. The results were as given in Table 2 below:

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>THPS alone</td>
<td>82</td>
</tr>
<tr>
<td>THPS + aluminium chloride, basic (1% Al₂O₃)</td>
<td>88</td>
</tr>
<tr>
<td>THPS + aluminium sulphate, basic (1% Al₂O₃)</td>
<td>87</td>
</tr>
<tr>
<td>THPS + aluminium formate, basic (1% Al₂O₃)</td>
<td>88</td>
</tr>
<tr>
<td>THPS + aluminium acetate, basic (1% Al₂O₃)</td>
<td>89</td>
</tr>
<tr>
<td>THPS + titanium sulphate (1% Al₂O₃)</td>
<td>88</td>
</tr>
<tr>
<td>THPS + Synektan TAL (1% Al₂O₃)</td>
<td>88</td>
</tr>
<tr>
<td>Compound NPM alone</td>
<td>90</td>
</tr>
<tr>
<td>Compound NPM + aluminium chloride, basic (1% Al₂O₃)</td>
<td>97</td>
</tr>
<tr>
<td>Compound NPM + aluminium sulphate, basic (1% Al₂O₃)</td>
<td>99</td>
</tr>
<tr>
<td>Compound NPM + aluminium acetate, basic (1% Al₂O₃)</td>
<td>100</td>
</tr>
</tbody>
</table>

THPS alone gave leather with a lower shrinkage temperature than the novel tanning compound, Compound NPM. THPS and aluminium combination tannages gave shrinkage temperatures lower than those achieved with the novel compound alone. In comparison, the novel compound in combination with known aluminium salts gave considerably higher shrinkage temperatures, and in particular with a known basic aluminium formate, gave leather which stood the boil (shrinkage temperature above 100°C) when tested following the method prescribed in IUP 16 of the International Union of Leather Technologists and Chemists.
EXAMPLE 3

Effect of concentration of Compound NPM and basic aluminium formate combination tannages

Pickled lamb skins were degreased and the pH adjusted to 3.5. Pelts were tanned in a computer controlled Dose drum at 12 rpm with varying concentrations of the Compound NPM for 5 hours, gradually raising the pH of the tanning bath with sodium formate and sodium bicarbonate to pH 5.25 and maintaining the temperature at 35°C. The shrinkage temperature was measured following prescribed method IUP 16 of the International Union of Leather Technologists and Chemists. These were then further tanned with 9.12% basic aluminium formate (1% Al₂O₃) and the final pH of the tanning baths were adjusted to pH 4.4 – 4.6. The shrinkage temperature of these pelts were re-measured as above. The leathers were fatliquored and crusted out together following a standard process. The results were as given in Table 3 below:-

Table 3

<table>
<thead>
<tr>
<th>Compound NPM alone</th>
<th>Shrinkage temperature, ºC</th>
<th>Final tannage (after aluminium treatment)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After NPM tannage</td>
<td></td>
</tr>
<tr>
<td>5% Compound NPM</td>
<td>87</td>
<td>98</td>
</tr>
<tr>
<td>6% Compound NPM</td>
<td>88</td>
<td>99</td>
</tr>
<tr>
<td>7% Compound NPM</td>
<td>87</td>
<td>99</td>
</tr>
<tr>
<td>8% Compound NPM</td>
<td>87</td>
<td>99</td>
</tr>
<tr>
<td>10% Compound NPM</td>
<td>88</td>
<td>105</td>
</tr>
<tr>
<td>15% Compound NPM</td>
<td>90</td>
<td>102</td>
</tr>
<tr>
<td>20% Compound NPM</td>
<td>90</td>
<td>105</td>
</tr>
</tbody>
</table>
The crust leather when assessed for feel and overall quality, was found to give an optimum result with 10 - 15% Compound NPM. At lower applications, the leather appeared empty and hard while at higher applications, the leather was heavy, fuller and darker.

EXAMPLE 4

Use of Compound NPM and basic aluminium formate combination tannages

Pickled lamb skins were degreased and the pH adjusted to 3.5. These pelts were tanned with 15% Compound NPM in a computer controlled Dose drum for 5 hours gradually raising the pH of the tanning bath with sodium formate and sodium bicarbonate to pH 5.20 and maintaining the temperature at 35°C. The shrinkage temperature was measured following method IUP 16 of the International Union of Leather Technologists and Chemists. These were then separated, allotted at random for further tannages with varying amounts of basic aluminium formate (0.5% to 2.0% Al₂O₃). One set was adjusted to pH 3.2 with oxalic acid and another set was processed without lowering the pH to find out the effect of combination tannage with basic aluminium formate at different pH. The leathers were fatliquored and crusted out following a standard process. The results were as given in Table 4 below:-

Table 4

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low initial pH (pH adjusted to 3.2)</td>
</tr>
<tr>
<td>Compound NPM alone</td>
<td>105</td>
</tr>
<tr>
<td>with 0.5% Al₂O₃ as basic aluminium formate</td>
<td>105</td>
</tr>
</tbody>
</table>
These results show that 0.5% Al₂O₃ is sufficient to give a shrinkage temperature above 100°C. Higher percentages at high initial pH did not significantly improve the shrinkage temperature and it was also not necessary to lower the pH before the addition of basic aluminium formate to achieve the highest shrinkage temperature. With increases in the percentage of aluminium formate used, the colour of the leather became increasingly paler, 1% Al₂O₃ giving the optimum quality of leather.

EXAMPLE 5

Combination tannages of Compound NPM and basic aluminium formate

Pickled lamb skins were degreased and pH adjusted to 4.5. These were then divided in three randomised sets. Following a standard method, one set (Set A) was tanned with 10% Compound NPM in a computer controlled Dose drum for 4 hours gradually raising the pH to 5.0 – 5.5 with sodium formate and sodium bicarbonate, maintaining the temperature at 35°C. The shrinkage temperature was measured following method IUP 16 of the International Union of Leather Technologists and Chemists. Further tannage was then given with 9.12% of basic aluminium formate (1% Al₂O₃) in the same bath, gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The second set (Set B) was tanned with 10% Compound NPM for 1 hour and then pH was raised to 4.0. Then 9.12% of basic aluminium formate (1% Al₂O₃) was added in the same bath,
15 gradually adjusting the pH to 4.4 – 4.5, keeping the total time of tannage the same as the first set. The third set (Set C) was tanned with 10% Compound NPM for only 20 minutes and then 9.12% of basic aluminium formate (1% Al₂O₃) was added in the same bath, gradually adjusting the pH to 4.4 – 4.5, keeping the total time of tannage the same as the first set. The shrinkage temperature was re-measured. Then all sets were dyed with 2% Sandoderm Brown R, Clariant, Switzerland for 30 minutes and fatliquored and crusted out following a standard procedure. The results were as given in Table 5 below:-

**Table 5**

<table>
<thead>
<tr>
<th>Tanning time</th>
<th>Shrinkage temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set A</td>
</tr>
<tr>
<td></td>
<td>Neck</td>
</tr>
<tr>
<td>6 hours</td>
<td>99</td>
</tr>
<tr>
<td>Overnight</td>
<td>99</td>
</tr>
</tbody>
</table>

These results showed that 1% Al₂O₃ is sufficient to give a shrinkage temperature above 100°C in a total tanning period of some 6 hours. A longer period of tanning did not improve the shrinkage temperature. Addition of basic aluminium formate after an hour tannage with the novel tanning agent at pH 4.0 gave optimum quality leather and is the currently preferred system.

**EXAMPLE 6**

**Tanning with a modified Compound NPM2**

The tanning compound is synthesised in a laboratory five neck reaction vessel by reacting a mixture of 400g of tetrakis hydroxy methyl phosphonium sulphate (Ex. Albrite & Wilson, UK) and 150g water with a
gradual addition of 450g of mimosa extract powder (Ex. Wattle Development Board, South Africa) at a temperature of 45°C. The reaction was continued for 4 hours with constant stirring and maintaining temperature at 45°C-50°C. The yield was about 86-93% (w/w).

Hereinafter these compounds referred in this preparation will be denoted by Compound NPM2. The pH (10% solution of the compound) was 2.85 to 3.45.

Eight pickled lamb skins at pH 1.8 were degreased and their pH adjusted to 4.5. These were then divided into four sets at random. Following a standard method, one set was tanned with 15% Commercial mimosa extract powder in a computer controlled Dose drum at 12 rpm for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was measured following method IUP 16 of the International Union of Leather Technologists and Chemists. The second set was tanned with 15% commercial mimosa extract powder in a computer controlled Dose drum for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was measured. Further tannage was continued in the same bath with 2% of tetrakis hydroxy methyl phosphonium sulphate (75% active) for 60 minutes at pH 3.90 and then 9.12% of basic aluminium formate (1% Al₂O₃) was added in the same bath and run for an hour, then gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The third set was tanned with 10% Compound NPM2 in a computer controlled Dose drum for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was measured following the prescribed method. Further tannage was continued in the same bath with 9.12% of basic aluminium formate (1% Al₂O₃) and run for an hour, then gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The fourth set was chrome tanned with 6% basic chrome sulphate (33% basic, 25% Cr₂O₃) following a standard method. The
shrinkage temperature was measured as before. The results were as given in Tables 6 to 20 below:

**Table 6**

<table>
<thead>
<tr>
<th>Tanning system</th>
<th>Shrinkage temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 hours</td>
</tr>
<tr>
<td></td>
<td>neck</td>
</tr>
<tr>
<td>15% mimosa extract</td>
<td>76</td>
</tr>
<tr>
<td>15% mimosa + 2% THPS + 1% Al₂O₃</td>
<td>75</td>
</tr>
<tr>
<td>10% Compound NPM2 + 1% Al₂O₃</td>
<td>-</td>
</tr>
<tr>
<td>Chromium reagent</td>
<td>89</td>
</tr>
</tbody>
</table>

All these leathers were then fatliquored and crusted out following a standard method, conditioned and tested for physical properties following relevant methods of the International Union of Leather Technologists and Chemists. The results are given in Tables 7 to 10.

**Table 7:** Comparative grain strength of lamb skin leather tanned with or without chromium

<table>
<thead>
<tr>
<th>Tanning process used</th>
<th>Load at grain crack (kg)</th>
<th>Distension at grain crack (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% mimosa extract</td>
<td>30.4</td>
<td>9.0</td>
</tr>
<tr>
<td>15% mimosa + 2% THPS + 1% Al₂O₃</td>
<td>39.4</td>
<td>9.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.9</td>
<td>10.7</td>
</tr>
<tr>
<td>10% Compound NPM2 + 1% Al₂O₃</td>
<td>36.4</td>
<td>9.9</td>
</tr>
<tr>
<td>Chromium reagent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These data are all indicative of satisfactory strength and are consistent with commercial chrome tanned leather.
Table 8: Comparative tear strength of lamb skin leather tanned with or without chromium

<table>
<thead>
<tr>
<th>Tanning process used</th>
<th>Tear strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>avg</td>
</tr>
<tr>
<td>15% mimosa extract</td>
<td>51.9</td>
</tr>
<tr>
<td>15% mimosa + 2% THPS + 1% Al₂O₃</td>
<td>33.4</td>
</tr>
<tr>
<td>10% Compound NPM2 + 1% Al₂O₃ Chromium reagent</td>
<td>45.9</td>
</tr>
<tr>
<td></td>
<td>45.3</td>
</tr>
</tbody>
</table>

These data are all indicative of satisfactory tear strength and are consistent with commercial chrome tanned leather.

Table 9: Comparative tensile strength and elongation at break properties of lamb skin leather tanned with or without chromium

<table>
<thead>
<tr>
<th>Tanning process used</th>
<th>Tensile strength (N/mm²)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>avg</td>
<td>SD</td>
</tr>
<tr>
<td>15% mimosa extract</td>
<td>16.7</td>
<td>5.2</td>
</tr>
<tr>
<td>15% mimosa + 2% THPS + 1% Al₂O₃</td>
<td>20.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.7</td>
<td>1.4</td>
</tr>
<tr>
<td>10% Compound NPM2 + 1% Al₂O₃ Chromium reagent</td>
<td>18.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

These data are all indicative of satisfactory strength and are consistent with commercial chrome tanned leather.

Table 10: Comparative softness measurements of lamb skin leather tanned with or without chromium
These data are all indicative of softness properties similar or better than those of commercial chrome tanned leather.

5  EXAMPLE 7

Combination tannages with Compound NPM2

The tanning compound is synthesised in a laboratory five neck reaction vessel by reacting a mixture of 400g of tetrakis hydroxy methyl phosphonium sulphate (Ex. Albrite & Wilson, UK) and 150g water with a gradual addition of 450g of mimosa extract powder (Ex. Wattle Development Board, South Africa) at a temperature of 45°C. The reaction was continued for 4 hours with constant stirring and maintaining temperature at 45°C-50°C. The yield was about 86-93% (w/w). Hereinafter these compounds referred in this preparation will be denoted by Compound NPM2. The pH (10% solution of the compound) was 2.85 to 3.45.

The tanning compound is synthesised by reacting 45 to 50 parts of commercial mimosa extract powder with 40 parts of tetrakis hydroxy methyl phosphonium sulphate and 10 parts water at 40 – 45°C for 4 hours with constant stirring. Hereinafter this compound referred in this preparation will be denoted by Compound NPM2.
Pickled lamb skins at pH 1.6 were degreased and their pH adjusted to 4.5. These were then divided into four sets at random. One set (Set A) was tanned with 15% commercial mimosa extract powder in a computer controlled Dose drum for 4 hours, maintaining the temperature at 35°C. The shrinkage temperature was measured following method IUP 16 of the International Union of Leather Technologists and Chemists. Further tannage was continued in the same bath with 2% of tetrakis hydroxy methyl phosphonium sulphate (75% active) for 30 minutes at pH 3.90 and then 9.12% of basic aluminium formate (1% Al₂O₃) was added and run for an hour, then gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The second set (Set B) was tanned with 15% of another commercial mimosa extract powder in a computer controlled Dose drum for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was measured. Further tannage was continued in the same bath with 2% of tetrakis hydroxy methyl phosphonium sulphate (75% active) for 30 minutes at pH 3.90 and then 9.12% of basic aluminium formate (1% Al₂O₃) was added and run for an hour, then gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The third set (Set C) was tanned with 10% Compound NPM2 in a computer controlled Dose drum for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was re-measured. Then 9.12% of basic aluminium formate (1% Al₂O₃) was added in the same bath and run for an hour, then gradually adjusting the pH to 4.4 – 4.5. The shrinkage temperature was re-measured. The fourth set (Set D) was the same as the third set except, before addition of the aluminium formate, the pH of the bath was reduced to 3.5 – 4.0 with oxalic acid.

All these leathers were fatliquored and crusted out together following a standard process. The shrinkage temperature results were as given in Table 11 below:-
Table 11

<table>
<thead>
<tr>
<th>Tanning time</th>
<th>Set A</th>
<th>Set B</th>
<th>Set C</th>
<th>Set D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neck</td>
<td>butt</td>
<td>neck</td>
<td>butt</td>
</tr>
<tr>
<td>7 hours</td>
<td>114</td>
<td>116</td>
<td>112</td>
<td>119</td>
</tr>
<tr>
<td>Overnight</td>
<td>114</td>
<td>115</td>
<td>112</td>
<td>118</td>
</tr>
</tbody>
</table>

5 These results showed that 1% $\text{Al}_2\text{O}_3$ is sufficient to give a shrinkage temperature above 100°C in a total tanning period of about 6 to 7 hours. A longer period of tanning did not improve the shrinkage temperature. These leathers were sent to a commercial tannery for finishing under normal production condition. They had no problem in finishing these non-chrome leathers. The leather was assessed as of good quality and no different from commercial chrome tanned lamb skin nappa leather. Dyeing was very uniform and overall quality was assessed as satisfactory. The results of physical tests, conducted following relevant methods of the International Union of Leather Technologists and Chemists (IULTC) are given in Tables 12 to 15.

Table 12: Grain strength of lamb skin leather tanned without chromium

<table>
<thead>
<tr>
<th>Tanning process</th>
<th>Load at grain crack (kg)</th>
<th>Distension at grain crack (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>19.9</td>
<td>9.4</td>
</tr>
<tr>
<td>Set B</td>
<td>27.9</td>
<td>9.7</td>
</tr>
<tr>
<td>Set C</td>
<td>27.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Set D</td>
<td>21.9</td>
<td>8.6</td>
</tr>
</tbody>
</table>
These data are all indicative of satisfactory strength and consistent with commercial chrome tanned leather.

Table 13: Tear strength of lamb skin leather tanned without chromium

<table>
<thead>
<tr>
<th>Tanning process</th>
<th>Breaking load (N) avg</th>
<th>SD</th>
<th>Tear strength (N/mm) avg</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>33.8</td>
<td>3.4</td>
<td>34.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Set B</td>
<td>44.8</td>
<td>6.5</td>
<td>32.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Set C</td>
<td>41.3</td>
<td>6.2</td>
<td>34.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Set D</td>
<td>46.5</td>
<td>12.5</td>
<td>52.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>

These data are all indicative of satisfactory tear strength and consistent with commercial chrome tanned leather.

Table 14: Tensile strength of lamb skin leather tanned without chromium

<table>
<thead>
<tr>
<th>Tanning process</th>
<th>Breaking load (N) Avg</th>
<th>SD</th>
<th>Tensile strength (N/mm²) avg</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>140.3</td>
<td>19.2</td>
<td>13.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Set B</td>
<td>152.3</td>
<td>42.5</td>
<td>11.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Set C</td>
<td>194.4</td>
<td>27.9</td>
<td>17.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Set D</td>
<td>209.6</td>
<td>51.2</td>
<td>24.0</td>
<td>2.9</td>
</tr>
</tbody>
</table>

These data are all indicative of satisfactory strength and consistent with commercial chrome tanned leather.
Table 15: Elongation at break of lamb skin leather tanned without chromium

<table>
<thead>
<tr>
<th>Tanning process</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
</tr>
<tr>
<td>Set A</td>
<td>32.5</td>
</tr>
<tr>
<td>Set B</td>
<td>37.5</td>
</tr>
<tr>
<td>Set C</td>
<td>20.2</td>
</tr>
<tr>
<td>Set D</td>
<td>23.1</td>
</tr>
</tbody>
</table>

These are all indication of satisfactory elongation properties and consistent with commercial chrome tanned leather.

The concentrated exhaust tanning bath when analysed for aluminium content was found to contain only 77.2 ppm aluminium (as Al). This liquor, when diluted as per normal tannery conditions and discharged into the effluent stream will contain only about 3.8 ppm aluminium, which is well below the general toxic level criteria applied to aquatic life (100 ppm if pH higher than 6.5 and 5 ppm if pH is lower than 6.5). Similarly, the crust leather from Set B and Set C when analysed for free formaldehyde content as per the method prescribed in JIS 1041 (Japanese Industrial Standard), was found to contain only 10.6 and 19.7 mg/kg of leather respectively.

EXAMPLE 8

The tanning compound is synthesised by reacting 45 parts of commercial mimosa extract powder FS with 40 parts of tetrakis hydroxy methyl phosphonium sulphate and 15 parts water at 45 – 50°C for 4 hours with constant stirring. Hereinafter this compound referred to in this preparation will be denoted by tanning compound Ecotan CSP.
Eighteen pickled lamb skins (pH = 1.6) were degreased and pH adjusted to 4.5. These were then divided in three sets at random, each containing six skins. One set (Set A) was tanned with 15% commercial mimos extract powder ME in a computer controlled Dose drum for 4 hours, maintaining the temperature at 35°C. The shrinkage temperature was measured following the prescribed method, IUP 16 of the International Union of Leather Technologists & Chemists. The second set (Set B) was tanned with 3% tetrakis hydroxy methyl phosphonium sulphate (75% active) for 30 min and then pH was gradually raised with sodium formate and sodium bicarbonate to pH 6.5 over 4 hours. The shrinkage temperature was measured following the prescribed method, IUP 16 of the International Union of Leather Technologists & Chemists. These skins were then subjected to a further tannage with a gradual addition of 15% commercial mimos extract powder ME as per the known state of art of retannage of tetrakis hydroxy methyl phosphonium sulphate (THPS) pretanned leather (the so called wet white leather) in a computer controlled Dose drum for 4 hours maintaining the temperature at 35°C. The shrinkage temperature was measured. The third set (Set C) was tanned with 15% Ecotan CSP for 60 min (pH 4.0) and then the pH was gradually raised with sodium formate and sodium bicarbonate to pH 6.5. The shrinkage temperature was measured following the prescribed method, IUP 16 of the International Union of Leather Technologists & Chemists. The final shrinkage temperature of these leather were as given below:-

<table>
<thead>
<tr>
<th>Set A (Mimosa)</th>
<th>SHRINKAGE TEMPERATURE, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>76</td>
</tr>
</tbody>
</table>
All these leathers were fatliquored in the same manner with commercial fatliquors (5% Chromopol UFBW + 2% Coripol ZXK + 1% Chromopol SG-all products sourced from TFL, Germany) and crusted out following a standard process. The crusted leathers when assessed visually were found to differ considerably in their appearance, feel, handle and colour. The colour of Ecotan CSP tanned leather was almost white in comparison with the mimosa tanned control and the THPS pretanned and subsequently mimosa retanned leather. All these skins were then tested for their physical properties following the relevant methods of test of the International Union of Leather Technologists & Chemists. The results given in Tables 16 to 22 are indications of considerable difference between the leather obtained by the sequential use of THPS and mimosa and the novel product, Ecotan CSP.

**Table 16: Colour values of lamb skin leather tanned without chromium (measured against standard white tile)**

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>White tile</td>
<td>95.87</td>
<td>-0.77</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>84.71</td>
<td>4.81</td>
<td>18.22</td>
<td>21.29</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>89.93</td>
<td>2.86</td>
<td>14.0</td>
<td>14.77</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>92.62</td>
<td>1.52</td>
<td>11.78</td>
<td>11.51</td>
</tr>
</tbody>
</table>
Table 17: Weight of lamb skin leather without chromium (g/sq ft)

<table>
<thead>
<tr>
<th>Sample from process</th>
<th>WEIGHT, G/SQ FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (Mimosa)</td>
<td>74.27</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>60.00</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>68.48</td>
</tr>
</tbody>
</table>

Table 18: Softness of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Softness, BLC values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>1.89</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>3.59</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Table 19: Grain strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Load at grain crack (kg)</th>
<th>Distension at grain crack (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>SD</td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>34.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>19.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>32.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
### Table 20: Tear strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Breaking load (N)</th>
<th>Tear strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>74.1</td>
<td>11.2</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>44.7</td>
<td>8.8</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>69.2</td>
<td>14.8</td>
</tr>
</tbody>
</table>

### Table 21: Tensile strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Breaking load (N)</th>
<th>Tensile strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>306.3</td>
<td>83.8</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>118.2</td>
<td>20.5</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>304.1</td>
<td>101.3</td>
</tr>
</tbody>
</table>

### Table 22: Elongation at break of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
</tr>
<tr>
<td>Set A (Mimosa)</td>
<td>40.0</td>
</tr>
<tr>
<td>Set B (THPS + mimosa)</td>
<td>54.8</td>
</tr>
<tr>
<td>Set C (Ecotan CSP)</td>
<td>43.0</td>
</tr>
</tbody>
</table>
These data provide evidence of considerable difference between the leather obtained by the sequential use of THPS and mimosa and the novel product, Ecotan CSP.

5 EXAMPLE 9

The tanning compound is synthesised by reacting 45 parts of commercial mimosa extract powder FS with 40 parts of tetrakis hydroxy methyl phosphonium sulphate and 15 parts water at 45 – 50°C for 4 hours with constant stirring. Hereinafter this compound referred in this preparation will be denoted by tanning compound Ecotan CSP.

Twelve pickled lamb skins (pH = 1.6) were degreased and pH adjusted to 4.5. These were then divided into two sets at random, each containing six skins. One set (Set A) was tanned with 15% commercial mimosa extract powder ME in a computer controlled Dose drum for 4 hours, maintaining the temperature at 35°C. The shrinkage temperature was measured following the prescribed method, IUP 16 of the International Union of Leather Technologists & Chemists. These skins were then further tanned in the same bath with 9.12% of basic aluminium formate (1% Al₂O₃) for an hour, then gradually the pH of the bath was adjusted with alkali to pH 4.4 – 4.5. The shrinkage temperature was remeasured. The second set (Set B) was tanned with 15% Ecotan CSP for 60 min and the pH was gradually raised with sodium formate and sodium bicarbonate to pH 6.5. The shrinkage temperature was measured following the prescribed method, IUP 16 of the International Union of Leather Technologists & Chemists. These skins were then further tanned with 9.12% of basic aluminium formate (1% Al₂O₃) for an hour, then gradually the pH was adjusted with alkali to pH 4.4 – 4.5 following a similar process as given for Set A. The shrinkage temperature was remeasured.
All these leathers were fatliquored in the same manner with commercial fatliquors (5% Chromopol UFBW + 2% Coripol ZXK + 1% Chromopol SG—all products ex TFL, Germany) and crusted out following a standard process. The crusted leather was then tested for their physical properties following the relevant methods of the International Union of Leather Technologists & Chemists. Even though, the final shrinkage temperature of these leathers from both Sets A & B was similar (114°C), the appearance, feel, handle, weight (g/sq ft) and colour were characteristically different. The leather with the novel tanning compound was considerably softer and the colour considerably lighter. The results given in Tables 23 to 29 are indications of considerable difference between the leather obtained by the sequential use of mimosa and aluminium tanning agent and the novel product, Ecotan CSP and aluminium tanning agent.

Table 23: Colour values of lamb skin leather without chromium (measured against standard white tile)

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>CIELAB values</th>
<th>ΛE</th>
</tr>
</thead>
<tbody>
<tr>
<td>White tile</td>
<td>L*: 95.87</td>
<td>a*: -0.77</td>
</tr>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>L*: 68.84</td>
<td>a*: 7.14</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>L*: 82.68</td>
<td>a*: 1.7</td>
</tr>
</tbody>
</table>

Table 24: Weight of lamb skin leather without chromium (g/sq ft)

<table>
<thead>
<tr>
<th>Sample from process</th>
<th>Weight (g/sq ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>68.48</td>
</tr>
</tbody>
</table>
### Table 25: Softness of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Softness, BLC values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
</tr>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>3.10</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>3.92</td>
</tr>
</tbody>
</table>

### Table 26: Grain strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Load at grain crack (kg)</th>
<th>Distension at grain crack (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>29.8</td>
<td>6.0</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>31.8</td>
<td>10.7</td>
</tr>
</tbody>
</table>

### Table 27: Tear strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Breaking load (N)</th>
<th>Tear strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>65.4</td>
<td>8.0</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>60.3</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Table 28: Tensile strength of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Breaking load (N) Avg</th>
<th>SD</th>
<th>Tensile strength (N/mm²) Avg</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>301.7</td>
<td>96.9</td>
<td>14.9</td>
<td>4.6</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>237.1</td>
<td>59.0</td>
<td>13.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 29: Elongation at break of lamb skin leather without chromium

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Elongation at break (%) Avg</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>43.7</td>
<td>8.0</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>41.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The aluminium contents in the exhaust baths were as given below:-

<table>
<thead>
<tr>
<th>SAMPLE FROM PROCESS</th>
<th>Aluminium content (as Al) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (Mimosa + aluminium)</td>
<td>131.2</td>
</tr>
<tr>
<td>Set B (Ecotan CSP + aluminium)</td>
<td>49.5</td>
</tr>
</tbody>
</table>
These results indicate that leathers with satisfactory but considerably different properties are obtained by the novel product and aluminium tanning agent. In particular, the leathers tanned with Ecotan CSP and aluminium had better colour and softness than leathers tanned with mimosa and aluminium. The aluminium content of the exhaust bath was also different and considerably better for the novel compound, Ecotan CSP.

In the following Examples, EXAMPLES 10 and 11 illustrate the method of producing tannages in accordance with the present invention. EXAMPLES 12, 13 and 14 illustrate the use of the tannages of EXAMPLES 10 and 11 in the treatment of animal skins.

Example 10

In this Example, the quaternary phosphonium compound used was tetrakis (hydroxymethyl) phosphonium sulphate (THPS) in 75% w/w aqueous solution. The vegetable tannage used was mimosa.

The weight ratio of "active" amounts of THPS and mimosa in this Example was 1:5.3.

THPS (75% w/w, 12.5g) Mimosa (50g) and water (37.5g) were mixed together in a sample jar, which was placed in an oven preheated to 80°C.

The sample jar was removed from the oven and shaken at 30 minute intervals and then returned to the oven. The total heating time was 20 hours.

At regular intervals a sample was taken and analysed by $^{31}$P-NMR spectroscopy. The results are given in Table 30 below.
TABLE 30

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Area % Phosphonium Products</th>
<th>Area % Residual THPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>64</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>8</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

After 8 hours at 80°C, 85% of the THPS had reacted with the Mimosa to give a reddish/brown viscous liquid. The product after 8 hours is water-soluble, but after 20 hours its solubility is reduced.

Example 11

In this Example, the quaternary phosphonium compound used was a condensate of THPS and urea (weight ratio THPS: urea being 4:1), available under the Registered Trade Mark ALBRITE®CS4. The vegetable tannage used was again mimosa.

The weight ratio of "active" amounts of THPS and mimosa in this Example was 1:5.

ALBRITE®CS4 (12.5g), Mimosa (50g) and water (37.5g) were mixed together in a sample jar, which was placed in a oven preheated to 80°C.
The sample jar was removed from the oven and shaken at 30 minute intervals and then returned to the oven. The total heating time was 8 hours.

After 8 hours a sample was removed from the oven and analysed by $^{31}$P-NMR spectroscopy. The NMR indicated that there was 85% of a broad polymeric phosphonium product and 15% of unreacted THPS.

Examples 12 to 14

These Examples illustrate the use of the products of Examples 1 and 2 as tanning agents.

The tanning method used was as follows:

A portion of pickled domestic ovine pelt (100g) and salt (8% by weight) was floated to 200% with the addition of 0.4% by weight of a 50% w/w solution of a sequestrant comprising amino-tris (methylene phosphonic acid) and available under the Registered Trade Mark BRIQUEST®301-50A. The float was rotated for 20 minutes. The pH of the float was found to be 1.8. After this time, 2.0% by weight sodium formate was added, followed by a further 30 minutes' rotation, to allow adjustment of the pH to 3.6 to 3.8.

One of the tanning products of Example 10 or Example 11 (4% or 8% by weight) was added and rotation continued for 3 hours. The float was then basified to pH 6.0 by the addition of 1% by weight sodium bicarbonate every 30 minutes, over a total period of 90 minutes.
The pelt was removed, washed and fat-liquored and subsequently tested for shrinkage temperature in accordance with the Industry Standard Test Method IUP16 (SLP 18).

The results are compared in TABLE 31 below:

**TABLE 31**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Tanning Product</th>
<th>Dosage %</th>
<th>Shrinkage Temp (°C)*</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Ex.1 (20 hours)</td>
<td>N/A</td>
<td>N/A</td>
<td>Tanning Product did not dissolve in float</td>
</tr>
<tr>
<td>4</td>
<td>Ex. 1 (8 hours)</td>
<td>4 8</td>
<td>68 74</td>
<td>Red-coloured complex formed at pH &gt; 4.8</td>
</tr>
<tr>
<td>5</td>
<td>Ex. 2 (8 hours)</td>
<td>4 8</td>
<td>63 68</td>
<td>Tanning Product of higher viscosity than in Example 4.</td>
</tr>
</tbody>
</table>

*Shrinkage temperature of an untreated pelt was 55°C.

Comparison of the results of Examples 13 and 14 (where, in both cases, a red-coloured iron complex formed at pH above 4.8) indicated that complex formation using the tanning product of Example 10 (THPS/mimosa) was more noticeable than when using the tanning product of Example 11 (THP-urea/mimosa). Complex formation with either tanning product was more pronounced at 8% dosage than at 4% dosage.
36

CLAIMS

1. A tannage of the formula

\[
\begin{align*}
R^3 & \quad H_2 \quad C & \quad P & \quad CH_2 \quad O\quad A \\
\quad | & & | \\
\quad CH_2 & \quad R^1 & \quad CH_2 \quad R^2
\end{align*}
\]

wherein A is a polyphenol-containing tanning agent, and R^1, R^2 and R^3 are selected from –OH or X, where X is chloride, sulphate or phosphate, with the proviso that only one of R^1, R^3 and R^3 is X.

2. A tannage according to Claim 1, in which X is chloride or sulphate.

3. A tannage according to Claim 1 or 2, in which A is a vegetable tanning agent.

4. A tannage according to Claim 3, in which the tanning agent comprises mimosa extract.

5. A tannage according to Claim 3, in which the tanning agent comprises chestnut extract, wattle extract, tara extract, myrabolam extract or quebracho extract.

6. A method for providing a tannage according to any one of Claims 1 to 5, the method comprising reacting a quaternary phosphonium compound with a vegetable tanning agent, in a ratio by weight of from 35:65 to 25:75, at a temperature of from 30°C to 60°C, for 2 to 6 hours.
7. A method according to Claim 6, in which the phosphonium compound and the vegetable tanning agent are mixed together in a weight ratio of 1:5 or greater, optionally in the presence of water, the mixture being subsequently heated at a minimum temperature of 80°C for up to 20 hours.

8. A method according to Claim 6 or 7, in which the quaternary phosphonium compound is tetraakis (hydroxymethyl) phosphonium sulphate or tetraakis (hydroxymethyl) phosphonium chloride.

9. A method according to Claim 6 or 7, in which the quaternary phosphonium compound comprises a condensation product of tetraakis (hydroxymethyl) phosphonium sulphate or tetraakis (hydroxymethyl) phosphonium chloride with an organic nitrogen compound.

10. A method according to Claim 9, in which the organic nitrogen compound is urea, thiourea or an amine.

11. A method according to Claim 9 or 10, in which the quaternary phosphonium compound comprises the condensation product of tetraakis (hydroxymethyl) phosphonium sulphate and urea.

12. A tannage produced by the method of any one of Claims 6 to 11.

13. The use of a tannage according to Claim 12 in the treatment of animal skins.

15. A process for tanning a hide or skin comprising treating said hide or skin with from 1 to 30% by weight (based on the weight of said hide or skin) of a tannage according to any one of Claims 1 to 5.

16. A process according to Claim 15, carried out at a pH of from 2.5 to 8.5 and at a temperature of from 15°C to 45°C for from 2 hours to 10 hours.

17. A process according to Claim 15 or 16, further including an aluminium tanning agent at a level of from 0.1% to 5% (based on the weight of said hide or skin).

18. A process according to Claim 17, in which the aluminium tanning agent is aluminium chloride, aluminium sulphate, aluminium acetate or aluminium formate.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 CI4C3/12

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 CI4C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
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<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 3 104 151 A (FILACHIONE EDWARD M ET AL) 17 September 1963 (1963-09-17) column 1, line 23; examples 7,10</td>
<td>1-3,6,8, 12-14</td>
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<td>A</td>
<td>DE 197 24 468 A (CIBA GEIGY AG) 18 December 1997 (1997-12-18) page 2, line 12 - page 3, line 40 examples 1,6</td>
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<td>A</td>
<td>US 2 732 278 A (FILACHIONE E.M.) 24 January 1956 (1956-01-24) cited in the application column 1, line 21 - column 2, line 26 example 6</td>
<td>1,6,8, 12-14</td>
</tr>
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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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Date of the actual completion of the international search

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Authorized officer

Neugebauer, U

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<th>Patent family member(s)</th>
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