⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 291 165 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 88303209.6

㉒ Date of filing: 11.04.88

(51) Int. Cl.⁴: **C14C 3/04 , C14C 3/28**

㉚ Priority: 24.04.87 EP 87400962

㊸ Date of publication of application:
17.11.88 Bulletin 88/46

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) Tanning Agent.

(57) A composition, suitable for use as a tanning agent in the preparation of leather, comprising a mixture of aluminium sulphate and a magnesium salt. The composition may also contain a titanium salt, optionally stabilised with a complexing agent, especially a poly(hydroxy)aliphatic-carboxylic acid. The composition may also contain or be used in conjunction with conventional mineral or vegetable tanning agents, such as chromium or zirconium salts. It may also be used with or contain an internal basifying agent, for control of pH during the tanning process, such as calcium carbonate or dolomite.

The tanning agents may be used for the prepraation of pre-tanned ("wet-white" or "dry-white") or fully tanned leathers, especially in conjunction with small quantities of chrome tanning agents, and produce leathers having generally superior properties to conventionally tanned leathers. The invention also includes pre-tanning, tanning and re-tanning processes using the new tanning compositions and pre-tanned, tanned and re-tanned leathers arising from these processes.

Tanning Agent

This specification describes compositions suitable for use as a sole or co-tanning agents in the preparation of leather and to tanning processes using the compositions.

State of the Art

Aluminium compounds are probably the oldest known tanning agents, having been used in the preparation of leathers, with such adjuvents as flour and egg yolk, in the ancient Arabic and Mediterranean civilisations. However, the sensitivity of aluminium salts to hydrolysis and the susceptibility of leather tanned therewith to hydrolysis at temperatures below 100°C have led to its replacement by salts of more effectively coordinated metals, such as chromium, which provide more robust protection of the leather.

However, chromium (III) salts have a number of serious disadvantages, viz,

(1) the substantial blue coloration of leather arising from the use of a chrome tanning agent which causes problems with the preparation of pale-shade or undyed leathers and causes dulling with stronger shades;

(2) the extensive and complex procedures required (a) to prevent premature precipitation of the chromium while ensuring that the pH is raised as tanning proceeds & (b) to ensure completion of tanning (maturing or aging) before subsequent treatments; and

(3) the concern about the toxicity of chromium (III) which make its presence undesirable in industrial effluents and the waste products of the leather industry, such as shavings and off-cuts; concern about the ecological effects of high levels of chromium in effluents and dumps of scrap leather has, from time to time, led to the temporary closure of tanneries by governments and local authorities.

Various alternative tanning agents and compositions, which overcome one or more of these problems, have been proposed but none of these has proved as commercially effective as chromium (III) salts in imparting a permanent protection to leather.

In an attempt to overcome the ecological and colour problems associated with chromium, recent efforts have concentrated upon colourless mineral tanning agents based upon aluminium (III), titanium (IV) and mixed complexes of these metals. Although these are less toxic and non-colouring they are less effective, more pH sensitive and require more sophisticated processes for their manufacture and use. Furthermore, the complexing (masking) agents required to keep such metals, especially titanium, in solution during the tanning process actually interfere with their tanning efficiency by competition, with the collagen, for the metal ions. Throughout this specification the proportions of metal salts in the various tanning compositions and the proportions of mineral tanning agents with respect to hides are expressed as weight percentages of the metals in the form of their oxides, even though the metals may be present as salts.

The First Tanning Composition

A new composition of metal ions has now been found which can be used in a simple and robust process for the preparation of non-coloured leather and can also be used in combination with any of the other known tanning agents, especially chromium salts, to improve their performance, particularly in those features where the use of the known agents give rise to problems.

According to a first aspect of the present invention there is provided a composition, suitable for use as a tanning agent in the preparation of leather comprising aluminium sulphage and at least one magnesium salt in which the amount of magnesium salt, expressed as MgO, is from 15% to 110% by weight with respect to the aluminium sulphate, expressed as Al_2O_3.

The composition may contain one or more other salts of aluminium, such as a polychloride or a salt with an organic acid, provided that the amount of aluminium sulphate, expressed as Al_2O_3, is at least 40% by weight with respect to the total amount of aluminium salts, expressed as Al_2O_3, in the composition.

The composition preferably contains from 35% to 90% by weight of the magnesium salt. The magnesium may be in the form of salt with any suitable mineral acid, such as sulphuric or hydrochloric acid, or an organic acid, such as acetic acid. It is however, preferably the salt of a strong acid and especially magnesium sulphate, which may be prepared by the reaction of a basic magnesium compound, such as $MgCO_3$ or MgO, with sulphuric acid.

Without prejudice to the scope of the invention, the presence of the water-soluble magnesium salt is believed to hold the aluminium ions, and those of any auxiliary mineral tanning agent, in solution during the tanning process in manner that allows the smooth take up of the aluminium and other metal ions by hides to produce leather. The soluble salts of magnesium are believed to modify the behaviour of aluminium salts, whether basified or not, with regard to the acidity of the solutions, the astringency of the solutions in tanning, their flocculation indices, their properties of dispersion from hydrogels to hydrosols during agitation in the tanning barrel, the partial peptisation of the solutions of titanium or aluminium and titanium, and their resistance to hydrolysis.

The Second Tanning Composition

It has been found that the addition of titanium salts does not detract from the performance of the present composition and such salts can improve the grain structure and fullness of the leather. The present invention thus encompasses a second composition comprising the the above-defined composition of aluminium and magnesium salts and a titanium salt or a mixture of titanium and aluminium salts, especially water-soluble or stabilised salts of titanium and aluminium. Such salts may be stabilised with organic complexing agents containing hydroxy and/or carboxy groups, e.g polyols, hydroxycarboxylic acid, phenols and naphthols or their water-soluble salts, such as citric, tartaric, phthalic, glucoheptanoic gluconic and aldolised naphtholsulphonic acids and/or their alkali metal salts. Masked complexes of titanium and aluminium and the masking agents therefor, suitable for incorporation into the present composition, are described in GB 2,068,999 and GB 2,165,859. Preferred complexing agents are gluconic, glucoheptanoic acid and their alkali metal salts. The second composition may contain up to two moles of complexing agent per mole of total metal oxides but preferably contains from 0.35-1.5 mole/mole. The composition conveniently contains from 30% to 125% by weight of one or more titanium salts, expressed as TiO_2, with respect to the total amount of aluminium salts, expressed as Al_2O_3 (i.e. molar ratios of Al_2O_3:TiO_2 from 0.8:1 to 8:1 and preferably from 0.8:1 to 4:1). Where the second composition contains additional aluminium salts, the afore-mentioned proviso should still apply, i.e. the amount of aluminium sulphate, expressed as Al_2O_3, should comprise at least 40% by weight with respect to the total amount of aluminium salts, expressed as Al_2O_3. The second composition preferably comprises a mixture of aluminium and titanium sulphates in the weight ratio 2:1 (expressed as Al_2O_3 and TiO_2), containing about one mole of sodium gluconate per mole of aluminium and titanium salts taken together (expressed as Al_2O_3 and TiO_2).

The Third Tanning Composition

The first or the second composition may be mixed with one or more auxiliary tanning agents, which may be vegetable or mineral to form a third composition in accordance with the present invention. Preferred mineral auxiliary tanning agents are chromium and zirconium salts and the third composition, containing a chromium salt, can be used in place of chromium salts alone for the tanning of leather.

The third tanning composition may contain up to 500%, but more preferably contains from 10% to 300% by weight of the auxiliary tanning agent with respect to the weight of the aluminium salts or aluminium and titanium salts (expressed as oxides) in the first or second composition. It is further preferred that the third tanning composition a mixture of the second tanning composition with, as auxiliary tanning agent, from 10% to 300%, more especially from 35% to 250%, by weight of a chromium or zirconium salt (expressed as Cr_2O_3) or ZrO_2) with respect to the weight of aluminium and titanium salts (expressed as $Al_2O_3 + TiO_2$).

The use of the first, and more especially the second, tanning composition in conjunction with a conventional chromium salt tanning agent allows a substantial reduction, up to 70% (expressed as Cr_2O_3) with respect to the amount of hides) in the amount of chromium used, with only a slight reduction in the protection of the leather against hydrolysis. For example, a tannage containing 0.45% of the second tanning composition (as $Al_2O_3 + TiO_2$) and 0.8% of a chromium salt (as Cr_2O_3) will give a fully tanned leather having a shrinkage temperature greater than 90°C which is adequate for most purposes. The shrinkage temperature can be raised to around 100°C by increasing the quantity of the second tanning composition, preferably to within the range 1% to 2%. In a conventional tanning process it is generally necessary to use about 3% chromium salts (expressed as Cr_2O_3) to achieve a shrinkage temperature of 95-100°C. The significant reduction in chromium usage achievable with the third composition, has advantages in reduced coloration of the leather and reduced amounts of chromium salts in the solid effluents from tanning, such as splits and shavings, and in the liquors after tanning. Lower proportions of the chromium salts (with proportional benefits) may be used where a lower shrinkage temperature can be tolerated.

As already indicated, the use of the second tanning composition in conjunction with about 200% (by weight with respect to the second tanning agent, expressed as oxides) of a standard chromium salt tanning agent allows a substantial reduction, of up to 70% by weight (expressed as Cr_2O_3 with respect to the amount of hides), in the amount of chromium used in a tanning process, with only a slight reduction in the protection of the leather against hydrolysis. Increasing the proportion of the second tanning composition will raise the shrinkage temperature back to the level achievable by a full 3% chrome tannage.

Although the third tanning agent has been presented herein as a prepared composition it is not necessary to make it up before introduction into the tanning bath. In fact it is preferable to prepare the composition in situ, i.e. in the tanning bath by separate addition of the first or second tanning agent (or its various components) and the auxiliary tanning agent. In fact the two tanning agents can be added at different times during the tanning process, with either the present first or second tanning agent being added before or after the auxiliary tanning agent so that partial tanning with either is performed before addition of the other.

The Fourth Tanning Composition

Any of the above-defined tanning compositions conveniently contains one or more basic salts of alkaline earth metals, especially calcium, with a weak acid, to act as an internal pH control, while the tanning agent is acting on the hides, and to adjust the final pH of the tannage to the most efficient level, between 3.5 and 4.5. Such a composition containing a basic salt of an alkaline earth metal forms a fourth aspect of the present invention. The amount of the alkaline earth metal salt, hereinafter referred to as the "internal pH controller", expressed as oxide, is preferably from 25% to 200%, especially from 35% to 180%, by weight with respect to the total weight of aluminium salts and other metal salts having a tanning action, expressed as oxides, in the composition. A preferred internal pH controller is a salt of an alkaline earth metal with a weak acid, especially one containing calcium, such as calcium carbonate or dolomites.

The First Tanning Process

According to a further aspect of the present invention there is provided a process for the preparation of leather which comprises treating skins or hides (hereinafter referred to collectively as "hides") with the first, second, third or fourth composition (hereinafter referred to as the first, second third or fourth tanning agent).

The tanning process is conveniently performed on the hides immediately after they have been pickled, preferably to a pH of from 2 to 4, and may be performed by addition of the composition to the pickling liquor or to a fresh liquor, such as 10% brine, added to the pickling bath containing the pickled hides after removal of the spent pickling liquor. The amount of the tanning agent used is conveniently from 0.5% to 30% and preferably from 0.5% to 5%, by weight of tanning components, i.e. aluminium salts, titanium salts and auxiliary tanning agents, expressed as oxides, based upon the weight of the hides. Tanning is conveniently performed by tumbling the hides in the liquor for a period of from 4 hours to 24 hours at or around ambient temperature.

A significant advantage of the present tanning process is that it is not necessary to make any adjustment of the pH of the tanning liquor. However, exhaustion of the bath and tanning is optimised if the fourth tanning agent, including an internal pH controller, such as calcium carbonate, is employed, because this ensures that the pH at the end of the tanning process is in the region or 3.5 to 4.5.

By means of the process using the first or second tanning agent, it is possible to obtain a "white" leather having a shrinkage temperature up to 80-85°C.

Hides which have been treated by means of the present process with the first or second tanning agent are generally only partially protected against hydrolysis and are susceptible to shrinkage in water at temperatures above 80-85°C and such partial tanning is referred to herein as "pre-tanning". However, hides which have been pre-tanned in accordance with the present process can be subsequently retanned, even after drying and rewetting, which means that they can be pre-tanned and dried for protection, immediately after they have been removed from the animal, and subsequently stored and/or transported to another location, in a dry condition, at a reduced weight and with reduced risk of bacterial spoilage. Pre-tanned leather from the first process can be used directly, where pre-tanning is sufficient to produce a leather of the quality required for a particular application, e.g. the production of finished sheepskins which will not be subjected to high temperature cleaning processes and in which "whiteness" is important.

Hides which have been pre-tanned in accordance with the present process and dried can be re-wetted, e.g. in a new pickling bath or in 10% brine, and re-tanned in accordance with local practice. The re-tanning can be carried out with the present tanning composition, with any other mineral or vegetable tanning agent or with the third tanning agent.

The mechanical treatments, such as splitting and shaving, to which tanned leathers are generally submitted before finishing treatments are applied, can be given to the pre-tanned hides before the re-tanning operation. This has the advantage that the more expensive re-tanning and finishing agents are only applied to material which has commercial utility after tanning and that the waste materials from the mechanical treatments are not contaminated with the salts of heavy metals, such as chromium, which are commonly employed in re-tanning.

If the first tanning process involves the use of an auxiliary agent, the hides can be treated with a pre-formed tanning composition, i.e. the third or fourth tanning agent, or they may be treated, simultaneously or consecutively, with the first, second or fourth tanning agent and the auxiliary tanning agent, such as a chromium salt, in either order.

It has been found that the the pre-tanned or fully tanned leathers resulting from the use of the present agents and processes, especially those using the second, third and fourth tanning agents, are plumper (and retain their plumpness during subsequent treatments) than conventionally tanned or pre-tanned leathers which means that splitting and shaving can be performed more accurately and with less waste of leather. This increased plumpness improves the quality of the leather, which has better "plastic metal elasticity" i.e. shape retaining characteristics. This means that hides can be converted into quality leathers having a better "feel" than they can by the use of conventional agents and processes. Because the present agents and processes give rise to improvements in the quality of leather and the quality can be judged more accurately at the pre-tanning stage, the tanner can have greater freedom and confidence in the selection of tanned and pre-tanned leathers for the later and expensive finishing stages which are so vital to the production of top quality leathers.

The Second Tanning Process

According to a further aspect of the present invention there is provided a second process for the preparation of leather which comprises treating a hide which has been pre-tanned in accordance with the first process with the first, second, third or fourth tanning agent.

The process conditions for the second process (hereinafter referred to as "re-tanning") are substantially the same as those for the first process. It is preferred, however, that the starting material is a leather which has been pre-tanned with the first or second tanning agent and that the re-tanning is performed with the third tanning agent, containing an auxiliary tanning agent.

Where the second tanning process involves the use of an auxiliary agent, the pre-tanned leather can be treated with a pre-formed tanning composition, i.e. the third or fourth tanning agent, or it can be treated, simultaneously or consecutively, with the first, second or fourth tanning agent and the auxiliary tanning agent, such as a chromium salt, in either order.

The auxiliary tanning agent may vegetable or mineral, and in the latter case is a conveniently a water-soluble salt of a metal such as chromium (III), zirconium or titanium. The use of the auxiliary tanning agent permits the achievement of any advantages associated with the auxiliary tanning agent (e.g. the use of chromium or zirconium allows the achievement of higher shrinkage temperature) without the complex processing conditions (e.g. temperature, pH and agitation variations) required when the auxiliary tanning agent is used alone. Furthermore, there is a significant reduction in the coloration and toxicity problems encountered when chromium is the main, or sole, tanning agent. The use of the present first and second tanning agents allows reductions in the usage of auxiliary agents, such as chromium salts, of up to 70% compared with normal usages, without any significant reduction in the resistance of the tanned leather to hydrolysis. In this way it is possible to obtain leathers which are resistant to shrinkage in boiling water yet have only a very faint blue colour. Furthermore, by careful selection of process conditions and the inclusion of an internal pH controller (fourth tanning agent), the tanning bath liquor can be virtually exhausted with respect to chromium, or other heavy metals, at the end of the tanning process. Such a liquor does not present the disposal problems associated with the liquors from normal mineral tanning processes which frequently contain large amounts of heavy metals. Thus, the accumulation of toxic waste materials, such as shavings and tannage waste liquors containing significant proportions of chromium salts, can be largely avoided and the waste disposal problems associated with the use of chrome tanning agents and processes can be greatly reduced.

Because the present invention allows a significant reduction (up to 70%) in the quantity of chromium required to achieve a fully tanned leather (with shrinkage temperature around 100°C) the blue coloration associated with conventional chrome tanning of leather is significantly reduced. It has been found that this permits the more effective coloration of the leather with standard acid dyes. The new tanning agents permit the achievement of brighter deep shades and truer pastel shades. It has also been found that the dyes exhaust more fully into leather tanned with the present compositions which, in turn, allows more efficient use of dyes with less waste in the dye bath. It has also been found that any defects in the leather, such as scarring or other surface damage, arising from damage to the hides either on the animal or after skinning, are more effectively masked by conventional dyes when the leather is tanned with the present tanning agents and processes in place of conventional tanning processes. This means that the quality of hides can be upgraded by use of the present tanning agents and processes.

Without prejudice to the scope of the invention, it is believed that the advantages arising from the use of the present agents and processes, particularly those involving an aluminium or aluminium/titanium tannage or either of these in conjunction with a minor proportion of chromium tannage, are at least in part due to the different structure of the derived leather. Microscopic examination of leathers from the present processes shows that they have a more fibrous or textured structure, akin to that of the original hide, in comparison with conventionally chrome tanned leathers.

The present invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

Examples 1 to 8

The eight compositions, C1 to C8, in Table 1 were prepared by mixing the indicated quantities of the named components and adding sufficient water to give, in each case, a final total metal oxide content (Al_2O_3 + TiO_2) of 2.4%.

Table 1

Component	C1	C2	C3	C4	C5	C6	C7	C8
$Al_2(SO_4)_3 18H_2O$	134	54	54	54	13.4	134	134	134
$MgSO_4 7H_2O$	87		148		5.4			120
$MgNa_2(SO_4)_2 4H_2O$		17		59		130	118	
$Ti(SO_4)_2$(a)							54	
$Ti(NH_4)_2(SO_4)_3$(b)						50		
Basic $AlCl_n$(c)			72		124			
Masked Al/Ti(d)		129	309		96			
Unmasked Al/Ti(e)								100

Notes

(a) Unmasked titanium oxysulphate containing the equivalent of 38.2% TiO_2 and 46.1% H_2SO_4 (in grams).

(b) Unmasked tiatanium ammonium sulphate containing the equivalent of 20.0% TiO_2 and 25.0% H_2SO_4 (in grams).

(c) Aluminium polychloride ((WAC from ATOCHEM) of basicity 50 containing the equivalent of 10% Al_2O_3 and 9.2% chlorine of the general formula $Al_n(OH)_mCl_{(3n-m)}$ (in grams)

(d) Mixed solution of Al and Ti sulphates masked with sodium glucoheptonate (see GB 2,165,859) containing 40g/l of equivalent Al_2O_3, 20g/l of equivalent TiO_2 and 1 mole of masking agent per mole of total metal oxides (TiO_2 + Al_2O_3) (in cc).

(e) Unmasked solution of Ti and Al sulphates containing equivalent of 50g/l TiO_2, 70g/l Al_2O_3 and 300g/l H_2SO_4 (in cc)

The eight compositions had the properties shown in Table 2.

Table 2

Properties	C1	C2	C3	C4	C5	C6	C7	C8
$Al_2SO_4)_3$ wrt. total Aluminium salts as Al_2O_3	100	65	100	100	100	100	100	100
MgO equivalent wrt. $Al_2(SO_4)_3$ (as Al_2O_3)	69	15	85	85	15	76	69	71
pH at 20°C(a)	2.9	3.3	3.2	3.3	3.4	1.8	1.8	1.8
pH (72 hour)(a)	2.9	3.5	3.4	3.4	3.7	1.8	1.8	1.8
Ti wrt. Al as TiO_2 & Al_2O_3	0	12.5	30	0	50	48.5	101	18.1
Masking Agent	-	+	+	-	+	-	-	-

Notes

(a) Compositions C6, C7 & C8 were basified to pH 3.4 with Na_2CO_3 before addition to the tanning barrel.

Examples 9 to 16

Each of the compositions C1 to C8 was used to tan calf hide, pickled to pH 3.5, by the following procedure..

To a tanning barrel containing 100 parts of pickled hides was added 50 parts of the composition (containing 1.2 parts of Al_2O_3 + TiO_2) and 1.5 parts of $CaCO_3$. The barrel was rotated continuously at 3-5 rpm for 4 hours and then intermittently (1 hour stationary; 1 hour rotating) for 4 hours. At the end of 8 hours the temperature had risen to 35-38°C. The properties of the leathers are given in Table 3.

Table 3

Properties	C1	C2	C3	C4	C5	C6	C7	C8
Shrinkage Temperature (°C)	74	77	75	77	75	78	78	80
Final pH of Tannage without Basification	4.0	4.2	4.2	4.2	4.2	3.5	3.5	3.5

In the following examples the quantities of materials used are indicated as percentages based on the weight of hides unless otherwise indicated.

Example 17

This tanning process permits the preparation of pre-tanned hides which can be stored or transported in the wet form ("wet whites") and subjected to the standard mechanical operations of sawing, shaving and splitting, prior to re-tanning to a finished leather. In this case it is not the intention to produce a leather having all the quantities of fullness and suppleness associated with finished leathers but to permit the selection, storage or transport of hides in a convenient and stable form and the application of orientation and levelling operations which are generally applied after full tanning.

The pre-tanning operation was performed upon bulls hide having a thickness after pickling from 4.5-11mm, which is recognised as a difficult material to tan.

The wet hides (100 parts) after dehairing, liming, deliming and pickling to pH 3.2-3.5 were placed in a tanning barrel with 20% of their weight of water and 8% of their weight of NaCl and rotated for 10 minutes. Then an amount of Composition C4 containing 2.5 parts of Al_2O_3 was added followed by 1.5 parts of $CaCO_3$. Rotation was continued at 3-5 rpm for 6 hours when the temperature of the contents had risen to about 37°C after which intermittent rotation (1 hour stationary and 1 hour rotation) was continued for a further 4 hours. The final pH of the tanning liquor was about 3.5.

The leather obtained had a fine grain and was perfectly white, i.e. the natural skin colour. It had a shrinkage temperature of 77°C.

Example 18

This concerns a procedure for the preparation of pre-tanned hides for storage after drying and their subsequent re-wetting and re-tanning to full permanent leather.

The process was performed on calf-skin having a thickness from 3.5-7mm after pickling to a pH of 3.2-3.5.

The pickled hides were placed in a tanning barrel containing 80% of their weight of water and 10% of NaCl. After 15 minutes of rotation 1% as metal oxides (Al_2O_3 + TiO_2) of Composition C2 and 1.5% of $CaCO_3$ was added. After 4 hours rotation the pH of the liquor was 3.5 and the hides had a shrinkage temperature of 69°C. After a further 2 hours rotation the pH rose to 3.8 and the shrinkage temperature of the hides was 75°C. Then 6% (wrt to the hides) of a commercial cationic agent having a fat liquor effect, comprising an organic salt of a substituted aliphatic amine (pH 4.9) (EDUNINE B from ICI - EDUNINE is a registered trade mark) was added and rotation was continued for a further 2½ hours. The pH of the bath rose to 4.4 and the shrinkage temperature of the hides was 78°C.

The dried pre-tanned hides had a fine grain with a normal fullness and a creamy white colour. They could be re-wetted without difficulty and subjected to a classical chrome tanning operation without any problem.

Example 19

A simple tanning process using chromium sulphate alone followed by the addition of a simple composition of aluminium and magnesium to demonstrate the effectiveness of the latter in conjunction with a typical chrome tanning agent.

Calf hides pickled to pH 3.5 in a liquor at 80% volume were treated in a pickling bath with with 3%, measured as Cr_2O_3, of a salt of chromium at 33°Sch and the bath was rotated for 4 hours. The pH was then 2.7 and the shrinkage temperature of a sample of the leather was 67°C. Then 2.05%, as oxide (Al_2O_3 + TiO_2), of Composition C6, prebasified to pH 3.4 with Na_2CO_3 and 1.5% of $CaCO_3$ were added to the same bath and rotation continued for 5 hours when the pH of the bath was about 3.8. The leather had a shrinkage temperature of 92°C, a pale blue colour and a fine grain. It was ready for the usual complementary mechanical and chemical treatments.

Example 20

A tanning barrel containing 100 parts of calf hides, pickled to pH 2.8, 60 parts of water at 18°C and 10 parts of NaCl was rotated for 10 minutes.

To the barrel was then added 30 parts of the Chrome Tanning Agent 1 identified below and rotation continued for 4 hours at 2-3 rpm when the pH was 2.6. There was then added 2.4% as oxides (Al_2O_3 + TiO_2) of Composition C8, prebasified to pH 3.4 with Na_2CO_3 and 2% $CaCO_3$. After rotation for a further 4 hours the pH was 3.8 and the leathers were a light red-brown colour. After draining the bath the leathers were rinsed with 150% water containing 0.1% $Na_2S_2O_5$ (bath pH: 3.7).

The resulting leathers were very fine grained, smooth and a pale beige colour. They had a shrinkage temperature of 95°C.

Chrome Tanning Agent 1

This was an organo-metallic tannin, comprising a chrome salt complexed with aldolised beta-naphthol sulphonic acid (A-BNSA), neutralised with ammonia and re-acidified with acetic acid, of which a solution of 28% dry extract contains:

A-BNSA: 62.5g/1
Cr_2O_3: 23.0g/1
Na_2SO_4: 141.0g/1
or:

A-BNSA/Cr salt complex:	132
sodium sulphate:	141
acetic acid:	6
water:	721
Total:	1000 (of liquid product).

Example 21

To 100 parts of dewoolled, limed, delimed and pickled (to pH 2) sheepskins, after rotation in a tanning barrel for 10 minutes in 100 parts of 10% brine at 20°C, was added 2.4% (as total oxides, Al_2O_3 + TiO_2) of Composition C3 and 3% $CaCO_3$. The barrel was rotated for 4 hours after which the pH was 4 and a sample of the dried skin had a shrinkage temperature of 79°C. There was then added 4% of a condensate of naphthalene sulphonic acid (SYNEKTAN ACN from ICI, SYNEKTAN is a registered trade mark) and 20% of an extract of Gambier (vegetable tannin). After a further 4 hour period of rotation the pH was still 4 and the leather had a shrinkage temperature of 78°C. After treatment with 4% of sulphonated neats foot oil for 1½ hours the pH of the bath was 4. The shrinkage temperature of the leather was 90°C and it was full, of fine grain and orange coloured.

Example 22

Woolled sheepskins, pickled to pH 2.6 were stirred for 2 hours in a paddled tanning vessel containing 30 litres of 6% NaCl brine per skin at 20°C after which the pH of the solution was 2.8. To this bath was added 2.7g g/litre of liquor (as total oxides, Al_2O_3 + TiO_2) of Composition C4 and 2g/litre of liquor of $CaCO_3$. After 4 hours continuous and a further 12 hours intermittent agitation, sufficient to raise the temperature to 35°C, there were added 10 litres of water at 60°C per skin and agitation continued for a further 4 hours. After draining the bath and washing and draining the skins their pH was about 3.5. The skins had a shrinkage temperature of 80°C, were white on the flesh side and had perfectly white wool, in contrast to similar skins tanned with chrome salts.

Example 23

A dry tanning agent was made by mixing 90.4 parts of a dried form of Composition C3 and 9.6 parts of $CaCO_3$.

Calf-skins, pickled to pH 3.6 were placed in a fresh bath of 80% water, 20 NaCl and 0.1% formic acid and rotated for 20 minutes when the pH was 3.5. To the bath was added 3% of a commercial $Cr_2(SO_4)_3$ - (CHROMOSAL B from Bayer) and rotation continued for 4 hours when the pH of the bath was 2.7.

There was then added 4%, as oxide (Al_2O_3 + TiO_2), of the dry tanning agent and 20% of water, based on the weight of skins. After 3 hours rotation the pH of the bath was 3.1 and the shrinkage temperature of the leather was 80°C. After standing for 16 hours and a further 20 minutes of rotation the pH was 3.4 and the shrinkage temperature of the leather was 90°C.

There was then added 0.3% of sodium orthophthalate and rotation was continued for 1½ hours when the pH was 4 and the shrinkage temperature of the leather was 98°C.

The bath was then drained and the leather re-tanned with 6% of the dry tanning agent, followed by a classical nourishing operation with 7% of a commercial agent, TRUPON DX (from Trumpier).

The resulting leather was fined grained, of a white or very light blue colour and a very even texture.

Example 24

Calfskins, pickled to pH 3 were rotated in a tanning barrel with 80% water and 10% NaCl for 15 minutes when the pH was 3.6. There was then added 6% of the dry tanning agent used in Example 23 and 3% of dry $(CH_3COO)_3Zr$ (TANFIX NBS from Hoechst). After 9 hours rotation the pH was 3.5 and the leathers were perfectly impregnated and had a slight tackiness which disappeared on drying. The dried leathers were fine grained, pale rosy beige in colour and had a shrinkage temperature of 88°C.

Example 25

Pickled and degreased sheepskins were rotated in a tanning barrel for 20 minutes with 50% water and 5% salt (pH: 3.2). To the barrel was then added 1% of chromium sulphate (33° Sch) (as Cr_2O_3) and 0.09% of Composition C9 (as Al_2O_3 + TiO_2). After rotation for 1 hour the pH had risen to 2.9 and the shrinkage temperature was 70°C. After rotation for a second hour the pH fell to 2.7. There was then added a further 0.81% of Composition C9 and rotation was continued. After 2 hours the pH was 3.2 and after 3 hours the pH was 3.3 and the shrinkage temperature had risen to 100°C and after 6 hours the pH had settled at 3.5. The barrel was then drained and the leather washed by rotation with water for 10 minutes at 35°C followed by water (100%) containing 0.4% soda ash and 0.04% antiseptic (BUSAN) for 45 minutes. The resulting leather had a very pale blue coloration and could be converted into a high quality finished leather by treatment with conventional finishing agents.

Composition C9 is a composition of 80 parts of the masked Al/Ti component (d) described in Table 1 and 20 parts of $MgSO_4$.

Claims

1. A composition, suitable for use as a tanning agent in the preparation of leather comprising aluminium sulphate and at least one magnesium salt in which the amount of magnesium salt, expressed as MgO, is from 15% to 110% by weight with respect to the aluminium sulphate, expressed as Al_2O_3.

2. A composition according to Claim 1 containing other aluminum salts provided that the amount of aluminium sulphate, expressed as Al_2O_3, is at least 40% by weight with respect to the total amount of aluminium salts, expressed as Al_2O_3, in the composition.

3. A composition according to Claim 1 or Claim 2 in which the amount of the magnesium salts, expressed as MgO, is from 35% to 90% by weight, with respect to the total amount of aluminium salts in the composition, expressed as Al_2O_3.

4. A composition according to any one of Claims 1 to 3 wherein the magnesium is in the form of a salt with a mineral acid.

5. A composition according to Claim 4 wherein the magnesium salt is magnesium sulphate.

6. A composition according to any one of Claims 1 to 5 also containing, as internal pH controller, from 25% to 200% by weight a basic salt of an alkaline earth metal, with respect to the total weight, in the composition, of aluminium salts and other metal salts having a tanning action, expressed as oxides.

7. A composition according to Claim 6 wherein the pH controller is calcium carbonate or a dolomite.

8. A composition according to any one of Claims 1 to 7 also containing from 30% to 125% by weight of a titanium salt, expressed as TiO_2, with respect to the total amount of aluminium salts, expressed as Al_2O_3.

9. A composition according to Claim 8 in which the titanium ions are stabilised by the presence of a complexing agent.

10. A composition according to Claim 9 wherein the complexing agent is a an organic complexing agent containing hydroxy and/or carboxy groups.

11. A composition according to Claim 10 wherein the complexing agent is selected from polyols, hydroxycarboxylic acids, phenols, naphthols and salts thereof with alkali metals.

12. A composition comprising a mixture of composition according to any one of Claims 1 to 11 with up to 500% by weight with respect to the aluminium and titanium salts (expressed Al_2O_3 and TiO_2) of an auxiliary tanning agent.

13. A composition according to Claim 12 wherein the auxiliary tanning agent is a mineral or vegetable tannin.

14. A composition according to Claim 13 containing, as auxiliary tanning agent, from 10% to 300% by weight of a chromium or zirconium salt (expressed as Cr_2O_3 or ZrO_2) with respect to the weight of aluminium and titanium salts (expressed as Al_2O_3 and TiO_2).

15. A process for the pretanning or tanning of raw hides comprising the treatment of the raw hides with a tanning composition according to any one of Claims 1 to 11.

16. A process for tanning of hides or the retanning of pre-tanned hides comprising the treatment of the raw or pre-tanned hides with tanning composition according to any one of Claims 12 to 14.

17. A process according to Claim 15 or Claim 16 wherein the raw hides have been previously pickled to a pH from 2 to 4.

18. A process according to any one of Claims 15 to 17 wherein the amount of tanning composition is from 0.5% to 30% by weight of tanning components expressed as oxides, with respect to the weight of the raw or pre-tanned hides.

19. A process for the retanning of hides which have been pre-tanned in accordance with the process of Claim 15 comprising the treatment of the pretanned hides with a composition according to any one of Claims 12 to 14.

20. A pre-tanned or tanned leather produced by a process according to any one of Claims 15, 17 and 18.

21. A tanned or re-tanned leather produced by a process according to any one of Claims 16 to 19.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 3209

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-1 603 169 (J.K. TULLIS) * Claims *	1,2,4,5,15,17,20	C 14 C 3/04 C 14 C 3/28
X	BE-A- 333 358 (I.G. FARBENINDUSTRIE) * Claim; page 2, paragraph 2; page 4, example 7 *	1-5,15,18,20	
A,D	GB-A-2 165 859 (BRITISH LEATHER CONFEDERATION) * Abstract *	8-11	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 14 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-08-1988	GIRARD Y.A.

CATEGORY OF CITED DOCUMENTS

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