Title: AN ENVIRONMENTALLY FRIENDLY TANNING METHOD

Abstract: The present invention provides a system for tanning leather comprising from at least two tanning compositions to be used in sequence. First composition consists of zeolite having a Si to Al ratio from 0.7 to 2.5, treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in a zeolite structure which remains intact after said treatment; acidic metal salt; and a complexing agent. This first composition is in a form of a powdery solid having moisture content less than 25%. The second composition consists of the mere zeolite treated with concentrated aliphatic monocarboxylic acid. Moreover, a method for tanning leather using said system is provided subjecting the hide to be treated to a beam house treatment followed by a modified pickling stage using a solution having a baume value less than 5 and pH from 3 to 6.

Figure 1 A
AN ENVIRONMENTALLY FRIENDLY TANNING METHOD

The present invention relates to an environmentally friendly mineral tanning process. More specifically, the present invention relates to a mineral tanning process which is chromium free and produces waste waters with a low salt content. In addition, the present invention relates to a tanning chemical system providing suitable chemicals for the tanning stage.

Background

Tanning is one process stage in manufacturing animal skins into durable leather. In tanning the protein structure of the skin is permanently altered. The tanning process aims at, in addition to avoiding rotting of the skin, increasing resistance to water, humidity and usage together with increasing flexibility, anti-allergenic properties and visual attractiveness. Pretreatment processes are typically required before tanning can take place. These processes include e.g. splitting, deliming and/or pretanning processes like bating, decreasing, frizing and bleaching.

There are three dominating tanning methods; aldehyde or synthan tanning, mineral tanning predominated by chrome tanning and vegetable tanning. Each of these tanning agents produces leathers with different properties. However, increasingly environmentally friendly solutions such as chrome free or aldehyde free tanning agents are favoured, especially within e.g. automotive industry.

85% of the world's leathers are tanned with chromium salts which provide leather with very high shrinkage temperatures. For achieving this, the hides have to be pickled with acids to a pH of around 3 and below. At this pH the collagen swells considerably which may damage the collagen and hinders the uptake of the tanning agent. This is countered by large amounts of salt, typically 3-8% NaCl, on the hide weight. For an average to medium sized tannery this translates in a consumption of one to several Mtons per day. All of this salt ends up in the effluent. In turn, this creates various environmental problems related to both chromium with its toxic, cancer genic, mutagenic and allergenic potential as well as salt due to the large electrolyte load in the effluents. While chromium can be fairly easily removed from the effluent stream, the salt content of effluent is difficult and expensive to treat. Tanneries often exceed effluent norms regarding sodium and chloride and salt is considered as one of the most water polluting substances in the tanning industry today alongside with chromium.
Many replacement chemical systems to chromium have been proposed, but none gives as good results at moderate costs and only a handful of them are able to reduce or avoid the use of salt in order to decrease swelling.

The chromium tanning process further requires the use of additional chemicals such as buffering and basification solutions. Prior to the introduction of the basic chromium, several steps are required to produce a tannable hide including scudding, liming, introduction of alkali agents such as sodium hydroxide, deliming, restoring neutral pH, bating, or softening the skin with enzymes, and pickling i.e. lowering pH of the hide with salt and formic acid and sulphuric acid. The pH is very acidic when chromium is introduced to ensure that the chromium complexes are small enough to fit in between the fibres and residues of the collagen. Once the desired level of penetration of chrome into the hide is achieved, pH of the material is raised again i.e. "basified" to facilitate the process. At this stage, the chrome tanned skins obtain a bluish colour.

Costantini et al., "Studies on the tanning reactions of zeolite" in JALCA, vol. 95, 2000, pp. 125-137 discloses a study on the reactions involved in pretanning or tanning when using zeolite based masking agents. The hydrothermal stability of sodium aluminum silicate is considered to be too low for use in tanning solely by a zeolite. The role of pH and acidic solutions in aluminosilicate breakdown are emphasized and discussed in detail. The zeolite is first solubilised by water before adding a masking acid. The zeolite framework is broken down into soluble aluminum and silicon species such as [Al(H$_2$O)$_6$]$^{3+}$ by the use of the aqueous acid solution. The carboxylic acids used in solubilising are benzoic acid, acetic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, phtalic acid, maleic acid and fumaric acid. These acids are capable of forming complexes with the soluble aluminum. Maleic acid and phtalic acid are considered the only possible carboxylic acids to elevate the shrinkage temperature to an acceptable level. The shrinkage temperatures are determined by differential scanning spectroscopy. The hides are pretanned before the actual tanning.

Sodium aluminium silicate used for tanning leather must be added in the acidic phase with the result that it hydrolyses to alkaline aluminium salts and polysilicic acids. As the sodium aluminium silicate does not fully penetrate into the skin and become an active tanning agent prior to the decomposition, the tanning action will be restricted to the outer layers of the hide.
Salt free tanning has so far been based on novel organic tannages using reactive organic compounds that require strict temperature and/or pH control which renders the processes difficult to be carried out reproducibly and successfully.

For an average to medium sized tannery, the pickling step translates in a salt consumption of one to several million tons per day. All of this salt ends up in the effluent and becomes waste requiring further treatment steps and increasing the processing costs. In turn, the resulting chemical residues create various environmental problems related to both chromium with its toxic, carcinogenic, mutagenic and allergenic potential, as well as, salt due to the large electrolyte load in the effluents. While chromium can be fairly easily removed from the effluent stream in a post processing step, the salt content of the effluent is more difficult and expensive to treat. This often leads to the problem of tanneries exceeding effluent norms concerning sodium and chloride. Moreover, salt is already considered as one of the most water polluting substances in the tanning industry today alongside with chromium.

**Summary of the invention**

One object of the present invention is to provide a tanning process which is chromium free.

Another object is to provide a tanning process which provides a reduced salt load into the waste waters originating from the hide treatment.

A further object of the present invention is to provide toxic free tanning chemical system suitable for carrying out the tanning of hides, and providing an adequate shrinkage temperature for the tanned leather.

A yet further object of the present invention is to provide a tanning chemical system suitable for providing the desired tactovisual performance for the tanned leather.

In the first aspect of the present invention an environmentally friendly tanning system is provided as depicted by claim 1.
In the second aspect, a method is provided for tanning leather using a mineral tanning system resulting in chromium free waste water with strongly reduced salt load as depicted by claim 13.

The new tanning agent system is a dual component system, optionally formulated in a single formulation. This system has one component as a slow release or time differed release component. This component consist of an acidic metal salt, modified zeolite carrying mono and/or polycarboxylic or hydroxy carboxylic acids and/or so called non-swelling acids. The non-swelling acids are aromatic compounds carrying sulfonic acid groups, optionally with a low amount of hydroxyl groups. The second component is a self buffering base, ideally with tanning power in its own right, and optionally formulated as a slow release or time differed release substance.

**Figures**

Figure 1 shows XRD (X-ray diffraction) chart from Zeolite 4A (figure A) and from zeolite treated with concentrated formic acid according to the present invention (figure B).

Figure 2 shows the experimental results of dosing sequences performed using the tanning system of the present invention.

**Detailed description of the invention**

Unlike with chromium tanning, a regular pickling stage is not needed to be fully completed in using the tanning method of the present invention. A modified pickling with less salt may be performed. pH prior to tanning system addition is preferably set at pH less than 6, more preferably from 4.0 to 5.5 where no or little swelling occurs. Most preferably the pH is set within pH values of 4.5-5.0. Addition of the acidic tanning system composition (first composition) of the present invention will drop the pH quickly to level preferably below pH 4, but not preferably lower than pH 3.3, where the tanning agent penetrates the hide. Moderate controlled swelling that occurs in this pH range is preferably controlled by the presence of a minimum amount of polyvalent counterions originating from the acidic tanning
agent itself. Once penetration is complete, the second buffering and selfbasifying composition (second composition) of the present invention is added. The second composition slowly raises the pH and introduces the additional chemicals suitable for tanning into the hide inducing a crosslinking of the collagen protein fibres though in situ formation of aluminium-hydroxy-silica oligomers, thus stabilizing the hide. The tanning system of the present invention is selfbasifying and selfbuffering to the final pH suitable to achieve the tanning reactions, preferably from pH 4.0 to 5.5, more preferably to pH 4.2 to 5.0.

By the term "intact" is meant that the structure as defined by the atomic and molecular structure of a crystal remains after an acid treatment unchanged compared to the structure before said acid treatment.

By the term "tanning system" is meant a combined set of chemical compositions i.e. a multiple component system used together for enabling a tanning action at a tanning stage during hide processing.

By "baume value" is meant the amount of salt in water, originally defined by the amount of sodium chloride in water (mass fraction of salt content of the water).

By the term "modified pickling" is meant a pickling stage wherein the salt concentration is less that in a regular pickling stage. Preferably the salt amount is described by the baume value of the solution which shall be less than 5 for the modified pickling stage of the present invention.

By the term "beam house treatment" is meant the steps in the production of leather between curing and tanning. Regular beamhouse operations typically include soaking, liming, removal of extraneous tissues i.e. unhairing, scudding, and fleshing, deliming, banking, drenching, and pickling. The presently used term "beam house treatment" excludes the regular pickling stage which is replaced by a modified pickling stage.

By "shrinkage temperature", Ts, is meant a temperature measured according to ASTM D6076 - 08 Standard Test which method is designed to determine the temperature at which a thoroughly wetted leather specimen experiences shrinkage.

Shrinkage occurs as a result of hydrothermal denaturation of the collagen protein molecules which make up the fiber structure of the leather. The shrinkage temperature of leather is influenced by many different factors, most of which appear to af-
fect the number and nature of crosslinking interactions between adjacent polypeptide chains of the collagen protein molecules. The value of the shrinkage temperature of leather is commonly used as an indicator of the type of tannage or the degree of tannage, or both. In the present invention Ts is the temperature at which a thoroughly wetted leather experiences shrinkage.

In the first aspect of the present invention a tanning system is provided which is able to replace chromium compounds in a tanning stage in leather processing. In addition, the system of the present invention is able to simultaneously replace the buffering and/or basification agents required in e.g. chromium tanning process. Moreover, the use of the system of the present invention provides process waste waters that have a strongly reduced salt load. The system of the present invention can thus be used instead of all the three typically used chemicals; basic chromium sulphate, the buffering agent and the basifying agent which will streamline the tanning process considerably and reduce processing costs.

A yet further advantage in using the system according to the present invention is that the colour hue of the final tanned leather will be whitish instead of being bluish as is the case when using chrome tanning.

Moreover, the cationic charge of the leather product after the tanning is higher than of a chrome treated leather which improves the uptake of anionic fat liquoring, dyestuffs and anionic retanning compounds. The filling effect when using the tanning system of the present invention is more pronounced than that of a chrome treated leather, which allows for savings in post tanning compounds.

The shelf life or storability of the leather product intermediate after tanning according to the present invention is on a very good level. The obtained whitish colour in combination with the high uptake of dyestuffs enables very pronounced colours for the leather end product after the treatment according the the present invention.

The present invention provides a system for tanning leather which comprises at least two tanning compositions to be used in sequence.

The first composition (i) consist of (a) a zeolite, (b) an acidic metal salt, and (c) a complexing agent. The zeolite has a Si to Al ratio from 0.7 to 2.5 and is treated with concentrated aliphatic monocarboxylic acid. The concentration of this monocarboxylic acid is high, more than 84% by weight. The essentially aqueous free acid treatment results in a zeolite structure which remains intact after said treatment.
This means that the zeolite structure is not disrupted or disintegrated but preserves its original structural form as before the acid treatment. This first composition (i) is in a form of a powdery solid having moisture content less than 25 %, preferably less than 20 % by weight.

The second composition (ii) of the system of the present invention consist of a zeolite having a Si to Al ratio from 0.7 to 2.5 treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment. This second composition is also in a form of a powdery solid having moisture content less than 25 %, preferably less than 20 % by weight.

In a preferred embodiment the first (i) and/or the second (ii) composition may be formed into separate entities by agglomeration, coating, encapsulating or embedding them into a matrix. Preferably, a slow release base or buffer material coating is applied or the composition is encapsulated using a buffer material. The advantage in encapsulation is that a one-component product is enabled which is very convenient for the industry.

In order to provide as effective acidity as possible per unit volume and as efficient acidifying and tanning response as possible, the use of concentrated aliphatic monocarboxylic is favoured. Preferably, the concentration of the monocarboxylic acid to be used is 84 % by weight or more, more preferably 90 % or more, most preferably 95 % or more, such as 99%. A concentrated acid is preferred in order to provide as low moisture content for the end product as possible. The dry or dried zeolite is preferred as moisture affects, for example, handling properties of the powdery product such as flowability.

The zeolite treated with concentrated aliphatic monocarboxylic acid is obtained by a following preparation method: First the zeolite is introduced into a reactor, or another vessel suitable for withstanding the required treatment conditions. The provided zeolite is kept in motion while concentrated monocarboxylic acid is introduced onto the zeolite residing inside the reactor. It is essential to control the temperature in the treatment process; the aliphatic monocarboxylic acid is preferably introduced in a spray form i.e. slowly and uniformly enough into the reactor in order to ensure that a homogenous solid powdery composition is obtained and maintained, similar to the original zeolite powder, and simultaneously the temperature of this mixture may be controlled. The temperature of the mixture should stay low enough, at a critical value of 50 °C or below, preferably below 50 °C, to avoid un-
wanted reactions to take place as the treatment of the monocarboxylic acid with the zeolite is exothermic. Such unwanted reactions originate from heat peaks, and additionally, too high temperature causes volatilization of the acid. Unwanted reactions may comprise degradation of the zeolite structure such as decomposition, decreased effect of acid loading, formation of hard particles or other undesired or detrimental side effects. By the term “spray” is meant a small droplet size atomised liquid flow. A spray is generally taken to mean a dynamic collection of drops dispersed in gas. The process of forming a spray is called atomisation. A spray nozzle is typically used to generate the spray. The main characteristics of the spray is to distribute the material over a specified cross section and to generate a liquid surface area. A man skilled in the art is able to select the most appropriate spray technology depending on the reactor configuration. Preferably, a suitable spray is provided by a nozzle atomizer capable of injecting a spreading spray with a small droplet size, preferably in the range from 0.01 to 1 mm diameter. The mass transfer rate of the acid may be adjusted by measuring the temperature of the resulting zeolite-acid mixture and setting the mass transfer rate into a value wherein this temperature is still below the critical value. Spraying may be performed continuously or discontinuously. The zeolite needs to be in motion inside the reactor. Preferably, this motion is vigorous enough in order to ensure good uniformity for the acid contact and to avoid generation of local hot spots. A preferred option is to use a drum reactor or the like wherein the rotation speed may be adjusted according to the mixing needs. A skilled person is able to optimize the mixing to maintain a uniform temperature below the critical value. In a preferred embodiment the reactor is equipped with a cooling system to ensure that the temperature of the mixture is maintained below the critical temperature. More preferably, a drum reactor with a cooling casing or jacket is utilised. There are several other commercially available options for cooling in a reactor set up suitable for the present use which may be applicable and within the expertise of a skilled person.

In the present invention the monocarboxylic acid treatment to zeolite is performed using a concentrated acid i.e. essentially nonaqueous acid whereby the zeolite framework remains intact. The compositions of system of the present invention has been analysed and the results have shown that no breakdown or disintegration take place (figures 1: A and B). Figure A depicts an XRD (X-ray diffraction) chart from Zeolite 4A for reference showing, for example, the main peak at 8° (2 theta). When this zeolite is treated with concentrated formic acid according to the present invention the main peak is still clearly visible as shown by the figure B i.e. the zeolite structure remains intact.
The structures and reactivity of zeolites can be modified by confining specific molecules into the small pores therein. For example, hydrogen form of zeolites typically prepared by ion exchange are powerful solid state acids and can facilitate to host acid catalysed reactions. Synthetic zeolites can be tailor made to fulfil the specific uses aimed at.

The zeolites of the present invention preferably comprise essentially of Al and Si oxides. The zeolite comprised in the system of the present invention is preferably a basic zeolite. More preferably, the pH of the basic zeolite is about 10. The zeolites to be used are microporous aluminosilicate minerals with open three-dimensional framework structures built of SiO₄ and AlO₄ tetrahedra linked to each other by shearing all the oxygen atoms to form regular intra crystalline cavities and channels of molecular dimensions. These frameworks are typically negatively charged and attract positive cations that reside in cavities to compensate the negative charge of the framework. Preferably, alkali metals or earth alkaline metals are included into the zeolites of the present invention. More preferably the zeolites comprise Na, K, Ca or Ba aluminosilicates.

In the zeolite of the present invention the ratio of Si to Al is from 0.7 to 2.5. Preferably, the ratio is from 0.7 to 1.2, and more preferably from 0.7 to 1.1 such as from 0.9 to 1.1 or very close to unity. If silicon to aluminum ratio is too high, acid solubility will decrease or may even disappear.

In a preferred embodiment the alkali or earth alkaline metal:Si:Al ratio of the zeolite is about 1:1:1, the alkali metal being preferably sodium which is the most convenient cation.

In one embodiment the zeolite is selected from the group of faujasit, zeolite A, and mordenite, zeolite X, which have a nearly maximal aluminium content possible in the tetrahedral framework, or the mixtures thereof. Preferably the zeolite is type A. The number of cation exchange sites is the highest in these zeolites rendering them highly selective for polar or polarizable molecules.

In another embodiment the zeolite is selected from zeolites defined by their CAS numbers of 1344-00-9, 1318-02-1 and/or 1318-02-1.

Preferably, the zeolite has a low moisture content of less than 20% by weight, more preferably less than 10%, most preferably less than 7 %, such as less than 5 %, or even 4% or less. The lower the water content, the better the adsorption potential of formic acid leading to enhanced flowability of the zeolite/formic acid com-
pound. The zeolite may be dried, preferably oven dried, before subjecting it to monocarboxylic acid treatment. According to one embodiment zeolite A4 having a pore size of 4 Å is preferred. Especially, the combination of oven dried zeolite A4 treated with formic acid was found to exhibit an excellent performance. Preferably, the zeolites and the impregnated zeolites used in the system of the present invention do not include any heavy metals or toxic metals such as chrome.

The amount of the aliphatic monocarboxylic acid sprayed onto zeolite is within the ratio of from 5 to 50 % by weight. Preferably, the ratio of said aliphatic monocarboxylic acid to zeolite is from 5 to 40 % by weight, more preferably from 7 to 35 %, most preferably from 10 to 30 % such as from 5 to 30 % by weight. The pore size and amount of the zeolite may cause some variation on the desired outcome. The ratio is further to some extent dependent on the quality of the acid used.

In a preferred embodiment, for formic acid the preferred ratio is from 7 to 30 %, more preferably from 8 to 28 %, such as from 10 to 25 %. The characteristic smell of formic acid becomes clearly evident when the ratio exceeds 40% by weight.

In another preferred embodiment, for acetic acid the preferred ratio is from 7 to 35 %, most preferably from 10 to 34 %, such as from 13 to 33 %, providing an optimum balance between acidity and flowability of the compound.

The system of the present invention includes a zeolite which is specifically treated with an aliphatic monocarboxylic acid. The monocarboxylic acid is preferably concentrated monocarboxylic acid which is specifically impregnated or diffused into the zeolite structure i.e. reacted with the used zeolite. The monocarboxylic acid is preferably an aliphatic carboxylic acid with a low water content, preferably less than 15%, more preferably less than 5 % by weight. The use of lower aliphatic monocarboxylic acid, preferably C1-C3, is found advantageous contrary to the prior teaching such as e.g. Costantini et al. as it provides an enhanced ability to penetrate into the zeolite structure and pores therein compared to higher monocarboxylic acids.

The aliphatic monocarboxylic acid to be used in the first composition of the system according to the present invention is preferably selected from the group consisting of formic acid, propionic acid, glycolic acid and acetic acid, most preferably said aliphatic monocarboxylic acid is formic acid.

In a preferred embodiment of preparing the zeolite treated with aliphatic monocarboxylic acid concentrated, formic acid, most preferably 99% by weight formic acid,
is sprayed onto zeolite, preferably a basic zeolite of type A or X. The critical temperature in this case is 50 °C, preferably 45 °C, most preferably 35 °C such as 30 °C.

In another preferred embodiment concentrated acetic acid, preferably 99% by weight acetic acid, is sprayed onto zeolite, preferably a basic zeolite of type A or X. The critical temperature in this case is 50 °C, preferably 45 °C, most preferably 35 °C such as 30 °C.

In yet another preferred embodiment concentrated propionic acid, preferably 99% by weight propionic acid, is sprayed onto zeolite, preferably a basic zeolite of type A or X. The critical temperature in this case is 50 °C, preferably 45 °C, most preferably 35 °C such as 30 °C.

When all the monocarboxylic acid is dosed into the reactor the reaction is completed. After cooling down to room temperature the product is ready. The product has a shelf life of at least several months, possibly years. Preferably, the product is coated or encapsulated after cooling.

As the pore volume of the zeolite varies the amount of carboxylic acid readily impregnated may vary accordingly.

The acidic metal salt in the first composition of the system of the present invention is preferably an aluminum salt, more preferably aluminium sulphate. Aluminum salts are acidic, so they aid in suppressing the tanning reaction during the first step. The amount of the acidic salt is preferably from 40 to 80 % by weight, more preferably from 50 to 70 % by weight, most preferably from 50 to 65 % by weight, such as 50 to 55 % by weight. The sulphate salt aids in buffering the tanning solution and results in enhanced performance in combination with the monocarboxylic acid, preferably formic acid, treated zeolite. The rise in pH during tanning is delayed and the tanning procedure is more controlled when using sulphate salt. The hide becomes tanned to the core and the tanning is more efficient. The tanning effect will be restricted to the hide surface if mere zeolite is used without the monocarboxylic acid, and the core will become inflexible and unyielding. Despite of the addition of a sulphate salt a monocarboxylic acid impregnation is required. The addition of the metal salt further aids in preserving or even lowering the final temperature of the composition which tends to increase due to the exothermic reaction between the zeolite and the monocarboxylic acid.
The complexing agent in the first composition of the system of the present invention is preferably selected from aliphatic monocarboxylic acid having a pKa value from 2.7 to 5.3, preferably from 3 to 5. More preferably, the complexing agent is selected from the group consisting of citric acid, malic acid, tartaric acid, glycolic acid, lactic acid, phtalic acid, acrylic acid and homo, tert and co-polymers thereof with other ethylenically unsaturated substances or mixtures thereof. Most preferably the complexing agent is citric acid, malic acid or tartaric acid. Especially favoured is citric acid. The complexing agent provides additional buffering in the system and helps fixate the tanning agent in the collagen structure. The amount of the complexing agent is preferably from 4 to 30 % by weight, more preferably from 5 to 20 % by weight, most preferably from 6 to 15 % by weight, such as from 7 to 12 % by weight, or even from 7 to 10 % by weight. It was found that the most preferred amount gives the optimum balance in buffering and fixation.

The first composition preferably further comprises complexing agent(s) with acidic character. This complexing agent is preferably selected from EDTA, DTPA, phosphonic acid or citric acid, amino-acids, polypeptides based on amino acids such as aspartic acid, glutamic acid, lysine, histidine, arginine or phenylalanine. Finally, polysilicic acid, resinsyntans and oligomeric condensation resins i.e. syntans with sulfonic acid groups or phosphonic acid groups can be applied. Optionally non swelling acids such as aromatic sulfonic acids may be used.

The zeolite of the second composition of the system according to the present invention is made accordingly to the zeolite of the first composition and has the same preferred features as described above.

Together with the second composition a slow acting base may further be introduced. The slow acting base is preferably magnesium oxide, sodium carbonate or sodium formate. The slow acting base provides a gradual and/or smooth basification reaction throughout the entire cross-section of the hide, without an overloading of tanning agent on the grainside of the hide.

Both compositions of the system according to the present invention are powdery solid compositions having flowability equal to the zeolite before said monocarboxylic acid treatment. The appearance of the compositions is a solid powder, and it has preferable the same flowability as the zeolite used as precursor i.e. the treatment according to the invention does not degrade the handling properties. The solid appearance provides handling advantage compared to e.g. liquid tanning agents. The compositions of the tanning system of the present invention have rea-
sonable solubility in acidic aqueous solutions, especially at pH of about 3.5 – 4.0 which is the typical pH for tanning.

The dosing ratio of the first composition to the second composition of the system is preferably such that the pH of the aqueous solution comprising the hide is lowered by addition of the first composition to a value from 3.3 to 4 and increased by the addition of the second composition to a value from 4.2 to 5.0. In terms of amounts of these two compositions this means preferably from 3 - 6 % by weight referring to the limed weight of the hides. The pH of the aqueous solution containing the hides to be treated is regulated by the amount of each composition to be introduced.

Depending on the hide the tanning system may be realized by several sequential additions of the two different compositions. In a preferred embodiment the first composition is introduced once and the second composition multiple times, preferable two or three times, depending on the desired pH increase aimed at.

A slow release base or buffer may be introduced together with the tanning system of the present invention or included thereto.

In the second aspect, the present invention provides an environmentally friendly method for tanning leather comprising the following steps of

subjecting the leather hide to be treated to a beam house treatment, and

subjecting the hide in aqueous solution to a modified pickling stage with a solution having a baume value less than 5, and pH from 3 to 6, preferably from 4.5 to 5.5; and

adding to said modified pickling stage a tanning system comprising at least two tanning compositions to be used in sequence;

adding at least once a first tanning composition consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment; aluminum salt; and a complexing agent; said composition being in a form of a powdery solid having moisture content less than 25 % to said hide to be treated; and
adding at least once a second tanning composition consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment said second composition being in a form of a powdery solid having moisture content less than 25%.

After tanning the hide is treated by regular processing steps well know to a person skilled in the art of leather tanning.

he baume values in the typical chromium tanning processes are from 5 to 10. In the modified picking stage of the present invention the salt concentration may be strongly reduced down to 30 g/l, even to 1 g/l, or possibly even zero corresponding to a solution having a baume value less than 5, preferable less than 3, more preferably less than 1.

The subsequent waste water originating from this process typically feature conductivity values about 4 – 8 times lower than associated with a typical chrome sulphate process.

The pH of the modified pickling stage may be adjusted more neutral, preferably to a value from 3 to 6, more preferably from 3.5 to 5.5.

The third aspect of the present invention provides an alternative method for tanning leather comprising the steps of

subjecting the leather hide to be treated to a beam house treatment for forming a hide solution prior to tanning, including a modified picking stage with a solution having a baume value less than 5 and pH from 3.8 to 5.5; and

adding to said hide solution at least once a tanning system comprising at least two tanning compositions;

a first tanning composition consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment; aluminum salt; and a complexing agent; said composition being in a form of a powdery solid having moisture content less than 25% to said hide to be treated; and
a second tanning composition consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment said second composition being in a form of a powdery solid having moisture content less than 25%;

which are combined into a single formulation.

In this embodiment optionally the two compositions of the tanning system used in the tanning process are combined into a singly formulated compounded tanning agent, where the different tanning steps being such as final pickling, full penetration, crosslinking, buffering and basification, are controlled through the different solubility rates of the single compositions in the float. This may require, especially for the final basification step, the use of a protecting or slow release base or buffer. Technologies are known to those skilled in the art, e.g. coatings, encapsulation or matrix embedded actives. Ideally the protective coating or matrix would be formed by a slow dissolving compound with synergistic potential to the main tanning formulation or to the leather making process in general or by derivates of fats and oils being active as fatliquors in the process. The active release of the tanning formulation which is encapsulated or embedded may be triggered, for example, enzymatically or by varying temperature profiles in the process.

The combined tanning formulation comprises powdery solid particles of said two compositions, having flowability equal to zeolite before said monocarboxylic acid treatment. This formulation and/or compositions therein are preferably coated, encapsulated or embedded in a matrix, more preferably by a slow release base or buffer material.

The system according to the present invention has been found environmentally beneficial in tanning solutions as it simplifies the tanning process while retaining an overall affordable processing. Furthermore, this composition may absorb further liquids such as free formic acid, glutaraldehyde, metyol resins, and the like, that are known to be beneficial in tanning and leather finishing processes.

The tanning system of the present invention has the advantage that it can directly replace the chrome tanning agent typically used in the hide manufacturing pro-
cess. No substantial changes into the process flow chart are required. In a typical
mineral tanning process the hide is pickled with formic acid containing solution at a
pH from 2.8 to 3.4 before addition of the tanning agent. This necessitates the use
of a sodium formate buffer for buffering the solution, and a slow acting base such
as magnesium oxide or sodium bicarbonate for basification in order to achieve the
final pH close to 4 for completing the tanning. The tanning system of the present
invention already contains the buffer. If necessary, it dissolves at the pH from 3.5
to 3.8 in a salt free pickle based on formic acid or other acids known in the state of
the art to be used at the pickling stage and self-basifies to pH of about 4-5 in
about 8 h. The use of the system of the present invention thus removes the need
for a separate buffering and/or basifying, as well.

One advantage in using the tanning system of the present invention is that the
waste solution will be chromium-free and can be easily exposed of, or even recy-
cled. A further advantage is that the actual hide or leather product originating from
the tanning process is also totally chrome-free.

The process of the present invention allows for a simplified tanning process where
most or even all of the salt, and buffers like sodium formate and basification
agents like MgO, that are typically associated with a so-called wet blue process
i.e. chrome containing tanning process are exchanged by a more acidic and a less
acidic compounds of aluminum, silicate and organic acids or even a single com-
ponent formed thereof. A further advantage is that the amount of pickling acids
can be reduced, especially inorganic portion which contributes to salt load in the
effluent. Also the final tanning pH is considerably higher than with conventional
chrome tanning processes facilitating the downstream further process of re-
tanning.

A further benefit of the process of the present invention is that tanning agent ex-
haustion is considerably higher with organic acid "doped" aluminium silicates than
with chromium salts and that there is a minimized salt load in the effluents and no
hazardous waste is created such as Cr shavings or sludges. The intermediate
leather product after tanning is preferably further processed, retanned, fat liquored
and finished in a similar fashion to the chromium tanned leather. Also, the inter-
mediate product can be stored using the appropriate storage conditions and pre-
servatives, known in the art. The colour of the intermediate is a bright white base
colour that does not change in time. This enables advantages during dyeing, allowing colour fastness and all type of colour shades even without the use of bleaching synthans. Furthermore, the higher amount of cationic anchoring sites provided by the method of the present invention compared to the state of the art enables better exhaustion of the subsequent retanning, dyeing and fattliquoring agents which are generally of anionic character. This results in further decrease in the effluent loads.

The use of the method of the present invention provides chrome-free leather having a high shrinkage temperature, Ts, which is higher than 65 °C, preferably higher than 70 °C, more preferably higher than 72°C, such as 75 °C, and which does not have a bluish colour hue but a whitish one. Preferably, the leather product obtained is tanned to the core and provides an especially soft touch sensation.

The invention is further illustrated by the following non-limiting examples.

**Examples**

**Example 1**

Bovine hide having limed weight of about 10 kg was pickled with formic acid and sulfuric acid and a regular amount of salt (baume value 5) at pH of 4.

At this pH, a first composition of the tanning system namely composition A with following composition details was added:

- 52% by weight aluminum sulphate 14 *H₂O (from Kemira)
- 40% by weight of formic acid treated zeolite (zeolite 87 % by weight treated with 13 % by weight of formic acid (purity 99%) (from Kemira)
- 8% by weight citric acid, anhydrous (from Jungbunzlauer Austria AG)

Composition A was added in two (2) dosings of 2.5% by weight each, with a reaction time of 90 minutes after both additions.

The pH values after the reaction steps were: After the first dosing 3.83; after the second dosing 3.57.

Subsequently, composition B was added consisting of formic acid treated zeolite (zeolite 87 % by weight treated with 13 % by weight of formic acid (purity 99%)}
(from Kemira). Composition B was added in two (2) dosings of 1.5% by weight each, with a reaction time 90 minutes after first dosing and overnight reaction after second dosing.

The pH values after the reaction steps were: After the first dosing 3.9, after the second dosing 4.15.

The shrinkage temperature $T_s$ obtained was 75 °C, and the leather was processed into automotive crust. The final shrinkage temperature was 80°C. The obtained strength values of the leather were on the same level as those obtained using the conventional application of a known mineral tanning agent (Kemira product, TANFOR) starting at pH = 3.1, with the same dosing scheme as described above and basifying to pH 4.4. The leather exhibited a pleasant soft touch and is in no way distinguishable from the leathers that started with a lower pH.

This example demonstrates that it is possible to start from the pH range of basification using an appropriate acid/base balance in the dosing and formulation of composition A and composition B.

**Example 2**

Twenty grams of dehydrated hide was soaked in distilled water until it was fully rehydrated (water content 60%). The hide was dehydrated after deliming, so that is was reactive and accessible to tanning agent. Acetone and equipment similar to drycleaning equipment was used in the dehydration process.

Pieces of approx. 2 by 4 inch were cut from the dehydrated hide. Per formulation, 50 grams of rehydrated hide was put in a small container that was closed water tight. The containers were put in a rotating drum to mimic the mechanical action and float/hide contact as in a tanning drum. In this lab scale tanning setup, up to 9 different formulations can be tested at the same time.

From experience, it is known that this laboratory equipment correlates strongly with results obtained with fresh/salted hides and tannery machinery on trial and industrial scale.

The rehydrated hide was pickled with 0.3% by weight formic acid and 0% by weight sodium chloride in a float of 50%. The pH was 3.8.

As tanning agent, composition A and B of example 1 were used. The following dosing scheme was applied:
Composition A 5% by weight, reaction time 180 minutes. pH after reaction 3.8.
Composition B 1.5% by weight, reaction time 90 minutes. pH after reaction 4.4.
Composition B 1.5%, reaction time 90 minutes. pH after reaction 4.5.

The shrinkage temperature was determined using a thermostatic water bath, set at different temperatures. The outline of the samples were drawn on paper, and the outline was compared after immersing for 1 minute at a certain temperature. The temperature was increased after each successful comparison, until the temperature was found where the leather piece was smaller than the original outline after 1 minute immersion. In doing so, a shrinkage temperature between 75 °C and 76.5 °C was achieved. This proves that with a mineral tannage with a very reduced salt load in the pickle, a shrinkage temperature over 65 °C can be achieved.

Example 4

Twenty grams of dehydrated hide was soaked in distilled water until it was fully rehydrated (water content 60%). The hide was dehydrated after deliming, so that it was reactive and accessible to tanning agent. Acetone and equipment similar to drycleaning equipment was used in the dehydration process.

Pieces of approx. 2 by 4 inch were cut from the dehydrated hide. Per formulation, 50 grams of rehydrated hide was put in a small container that was closed water tight. The containers were put in a rotating drum to mimic the mechanical action and float/hide contact as in a tanning drum. In this lab scale tanning setup, up to nine (9) different formulations can be tested at the same time.

From experience, it is known that this laboratory equipment correlates strongly with results obtained with fresh/salted hides and tannery machinery on trial and industrial scale.

The rehydrated hide was pickled without any salt or sodium chloride in a float of 50%. The pH was 4.8.

As tanning agent, composition A according to example 1 was dosed (5%).

The following dosing scheme was applied:

Composition A 5% by weight, reaction time 180 minutes. pH after reaction 3.8.
Composition B 1.5% by weight, reaction time 90 minutes. pH after reaction 4.7.
Composition B 1.5% by weight, reaction time 90 minutes. pH after reaction 4.8.
The shrinkage temperature was determined using a thermostatic water bath, set at different temperatures. The outline of the samples were drawn on paper, and the outline was compared after immersing for 1 minute at a certain temperature. The temperature was increased after each successful comparison, until the temperature was found where the leather piece was smaller than the original outline after 1 minute immersion. In doing so, a shrinkage temperature between 75.5 °C and 76.5 °C was achieved. This proves that with a mineral tannage without salt in the pickle, a shrinkage temperature over 65°C can be achieved.

10 Example 5

Figure 2 shows experimental results of dosing sequences performed using composition A and composition B and different starting pH. All experiments were performed with beaume value 5. The hides varied between 14 kg and 17 kg in limed weight.

15 Composition A had following composition:

- 52% by weight aluminum sulphate 14 H₂O (from Kemira)
- 40% by weight of formic acid treated zeolite (zeolite 87 % by weight treated with 13 % by weight of formic acid (purity 99%) (from Kemira)
- 8% by weight citric acid, anhydrous (from Jungbunzlauer Austria AG)

20 In Curve A, a starting pH of 4.03 was chosen. Curves B, C, and D feature starting pH 3.54, 3.38, and 3.19 respectively. First 5% of composition A was dosed, referring to the limed weight. After 3 hours, pH values were checked. It is seen that despite the wide variation in starting pH, the pH after composition A converges to around 3.3 – 3.7.

25 Subsequently, composition B was added consisting of formic acid treated zeolite (zeolite 87 % by weight treated with 13 % by weight of formic acid (purity 99%, from Kemira). Composition B was added in two (2) dosings of 1.5% by weight each, with a reaction time 90 minutes after first dosing and overnight reaction after second dosing.

30 It is seen that the small differences in pH during the tanning process, compared to wide variation in starting conditions, are maintained. Shrinkage temperature around 75 °C was achieved for all experiments and after post tanning the leathers
were indistinguishable from each other. This experiment proves that the formulation of composition A can converge a wide range of starting conditions into a smaller pH range prior to basification by composition B.
Claims

1. A system for tanning leather, characterized in that said system comprises at least two tanning compositions first of which is an acidic tanning composition (i) and the second is a buffering and selfbasifying composition (ii) for use in sequence to provide a tanning effect, wherein

the first composition (i) consists of zeolite having a Si to Al ratio from 0.7 to 2.5, treated with concentrated aliphatic monocarboxylic acid selected from the group consisting of formic acid, propionic acid, glycolic acid and acetic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in a zeolite structure which remains intact after said treatment; acidic metal salt which is an aluminum salt; and a complexing agent; said first composition being in a form of a powdery solid having moisture content less than 25 %, and

the second composition (ii) consists of zeolite having a Si to Al ratio from 0.7 to 2.5 treated with concentrated aliphatic monocarboxylic acid selected from the group consisting of formic acid, propionic acid, glycolic acid and acetic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in a zeolite structure which remains intact after said treatment, said second composition being in a form of a powdery solid having moisture content less than 25 %.

2. The system according to claim 1, wherein the ratio of said aliphatic monocarboxylic acid to zeolite is from 5 to 40 % by weight, preferably from 5 to 35 % by weight.

3. The system according to claim 1 or 2, wherein said aliphatic monocarboxylic acid has a pKa value from 2.7 to 5.3, preferably from 3 to 5.

4. The system according to claim 1 or 2, wherein said aliphatic monocarboxylic acid is is formic acid.

5. The system according to any one of the claims 1-4, wherein the acidic metal salt is an aluminium sulphate,

6. The system according to any one of the claims 1-5, wherein the acidic metal salt is in an amount from 40 to 80 % by weight, preferably from 50 to 70 % by weight.

7. The system according to any one of the claims 1-6, wherein the complexing agent is selected from the group consisting of citric acid, malic acid, tartar-
ic acid, glycolic acid, lactic acid, phtalic acid, acrylic acid and homo, tert and copolymers thereof, preferably citric acid, malic acid or tartaric acid.

8. The system according to any one of the claims 1-7, **wherein** the complexing agent is in an amount from 4 to 30 % by weight.

9. The system according to any one of the claims 1-8, **wherein** said system comprises powdery solid compositions having flowability equal to the zeolite before said monocarboxylic acid treatment.

10. The system according to any one of the claims 1-9, **wherein** said system further comprises an acidic complexing agent, preferably EDTA, DTPA, phosphonic acid, aspartic acid, glutamic acid, lysine, histadine, arginine or phenylalanine or citric acid.

11. The system according to any one of the claims 1-10, **wherein** said system further comprises a slow acting base, preferably magnesium oxide, sodium carbonate or sodium formate.

12. The system according to any one of the claims 1-11, **wherein** the dosing ratio of the first composition to the second composition is such that the pH of the aqueous solution comprising the hide is lowered by addition of the first composition to a value from 3.3 to 4 and increased by the addition of the second composition to a value from 4.2 to 5.0.

13. A method for tanning leather, **characterized** in that said method comprises the steps of

subjecting the hide to be treated to a beam house treatment followed by

a modified pickling stage which is modified compared to a regular pickling stage in that a solution having a baume value less than 5, preferable less than 3, more preferably less than 1, and pH from 3 to 6 is used; and

subsequently subjecting the hide to a tanning stage using a tanning system comprising at least two tanning compositions to be used in sequence;

adding at least once a first tanning composition (i) consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid selected from the group consist-
ing of formic acid, propionic acid, glycolic acid and acetic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment; aluminum salt; and a complexing agent; said composition being in a form of a powdery solid having moisture content less than 25 % to said hide to be treated; and

adding at least once a second tanning composition (ii) consisting of a zeolite treated with concentrated aliphatic monocarboxylic acid selected from the group consisting of formic acid, propionic acid, glycolic acid and acetic acid, the concentration of said monocarboxylic acid being more than 84% by weight, resulting in zeolite structure which remains intact after said treatment said second composition being in a form of a powdery solid having moisture content less than 25 %.
Figure 1 A

Figure 1 B.
Figure 2
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C14C3/04  C01B39/02  C1103/12

ADD.

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)

C14C  C01B  C11D

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 practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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Further documents are listed in the continuation of Box C. See patent family annex.

*S* Special categories of cited documents:

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Neugebauer, Ute
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