Abstract:
The present invention relates to compositions for the retanning and fatliquoring of pre-tanned leather, to the process of preparing such compositions, to the use of these compositions for the preparation of leather (the term "leather" encompassing fur skins or pelts), as well as a novel type of leather that is obtainable by the use of these compositions.
Title: Composition and process for the retanning and fatliquoring of leather, and the leather prepared

The present invention relates to compositions for the retanning and fatliquoring of pre-tanned leather, to the process of preparing such compositions, to the use of these compositions for the preparation of leather (the term "leather" encompassing fur skins or pelts), as well as a novel type of leather that is obtainable by the use of these compositions.

Leather is a durable, flexible material created via the tanning of animal rawhide and skin. The leather manufacturing process is divided into three fundamental sub-processes: preparatory stages, tanning and crusting.

In the preparatory stages, hide or skin is prepared for tanning. After trimming, animal skin is soaked to remove salts and other solids, while restoring moisture when the skin was first dried. Then, the flesh side of the wet skin is scraped to remove any remaining traces of flesh or fat, and the skin is optionally dehaired. After an optional bating and pickling step, the skins are subjected to tanning. Other potential steps that may be part of the preparatory stages include preservation, liming, splitting, reliming, deliming, degreasing, frizzling, bleaching and depickling.

Tanning is the process of preserving the skins by soaking these in a bath for a period of time. Particularly, tanning converts the protein, and especially the collagen, of the raw hide or skin into a stable material that does not putrefy. Tanning is carried out by using either vegetable chemicals, using tannin and other ingredients derived from vegetable matter such as the bark of certain trees, by the use of chromium salts (giving so-called wet-blue leather), by the use of aldehydes (resulting in wet-white leather), by use of synthetic tannins (syntans), or other conventional techniques. The product prepared in this sub-process is called "pretanned leather".
As said, the present invention focuses on the sub-process of crusting, and especially on the chemical aspects thereof. Crusting is the process wherein the hide or skin is thinned, retanned, and lubricated. Often a coloring operation is included in the crusting sub-process. Any chemicals used or added during crusting must be fixed in place. The crusting process ends with drying and softening operations. This description of the crusting process is not complete; crusting may also include wetting back, sammyming, splitting, shaving, rechroming, neutralization, filling, stuffing, stripping, whitening, fixating, setting, conditioning, milling, staking and buffing.

The chemical aspects of the crusting process at least encompass re-tanning (optionally following neutralization, especially after chrome-tanning) and fatliquoring. Usually in the preparation of leather from pre-tanned hides, the re-tanning and fatliquoring is done in separate steps.

The purpose of re-tanning is to produce a further stabilization of the collagen network. This involves further processing of the stabilised collagen network and may comprise a further tannage (e.g. with combinations of chrome, vegetable, glutaraldehyde or syntan agent) when special characteristics such as perspiration resistance are required. Conditioning, softening, dyeing or bleaching may also be carried out.

Any kind of softer leather contains remarkable amounts (such as 5-20%) of fat. Fat is the basis of the flexibility of the leather, and it is said that the flexibility is due to the separation of the leather fibers from each other. The fiber elements dehydrated by tanning are coated with a fat layer to give leather the desirable softness and handle by a sort of lubrication; this coating with fat is called fathquoring. Fat prevents the sticking, glueing or adhesion of fibers, which occurs though a certain fiber separation is effected by tanning. At the same time, fatliquoring influences the physical properties of the leather, such as extensibility, tensile strength, wetting properties, waterproofness and permeability to air and water vapour.
Traditionally, fatliquoring is a very complicated process depending on many factors.

One such factor is the temperature of the liquor bath. With increasing temperatures, the small fat particles are more stable against coagulation. On the other hand, the fixation of fat by binding to the charged groups of treated animal skin is more prominent. Generally, a high temperature is 60°C, and a low temperature is about 35°C. The lower the temperature, the lower the uptake of fat; yet, the more even the fat distribution.

A further factor of interest in the fatliquoring system is the pH of the leather and the liquor float. Chrome leather as well as retanned chrome leather needs to have a pH high enough to maintain charged groups. Groups like sulfates, sulfonates and phosphates can act as surface active agents only in the neutralized state. Leather to be retanned, dyed and fatliquored needs to be neutralized in advance to a pH of about 5.5. After fatliquoring, the float must be acidified to a pH of about 4.5 or a bit lower to fix everything at the fiber.

In conventional, artisanal leather preparation, the neutralization, re-tanning and fixation steps require the use of a high amount of chemicals of often about 15 or even more compounds, and these steps take about 8-16 hours. This conventional process will be illustrated herein-below in comparative example 2.

There is a clear need in the art to reduce the amounts of chemicals needed, to save on the amount of water (and/or other solvents) required in the leather preparation process, and to save on the use of energy (both in the use of apparatuses and in transport).

In view of this need, reference is made to US-A-6,033,590. This US Patent describes a composition that allows the simultaneous re-tanning and fatliquoring of leather or pelts, already resulting in a substantial reduction of the total process time to about 5-6 hours in practical circumstances.
Particularly, the invention described in US-A-6,033,590 makes use of a composition, which is solid at a temperature below 40°C, and which comprises (a) 10-18 wt.% of a retanning agent; (b) 5-50 wt.% of a fatliquoring agent; optionally, (c) 0-55 wt.% of a neutralizing agent; and (d) additional optional components selected from the group consisting of carriers, colorants, impregnants, dressing agents and dressing auxiliaries, each based on the total weight of the composition; said composition being present in a form such that on addition of said composition to water at from 10-60°C in an amount such that the ratio of water to that composition is at least 8:1, said composition forms a homogeneous mixture in the water.

Suitable fatliquoring agents were said to be "the customary agents which are commonly used for the fatliquoring of leather" and preferably fatliquoring agents based on animal fat; fatliquoring agents based on vegetable fat; synthetic fatliquoring agents; mineral oils and other petrochemical products.

Preferably, the re-tanning agent, fatliquoring agent and any other additives are used as solutions or suspensions or else dispersions, and then to mix these followed by drying and especially spray-drying.

Although realizing a major step forward when compared to traditional processes, it was found that the compositions described in US-A-6,033,590 still have room for improvement: the leather prepared therewith still suffers from substantial swelling, the leather obtained is not soft by touching or feeling by hand and to be able to obtain soft leather additional fat liquors have to be added; and the process for obtaining the compositions using spray-drying is cumbersome.

It is an aim of the present invention to provide a composition which also allows the retanning and fatliquoring in one step, yet within a shorter period of time. In addition, it is an objective to provide a composition and a process leading to leather having less swelling, having a higher tear strength and/or having a higher tensile strength than conventionally prepared leather.
or leather prepared by the teaching of US-A-6,033,590. Moreover, it is desirable to have a composition leading to softer leather than obtained in the process of said US Patent.

In accordance with the present invention, it was found that one or more of the above objects could be met, when at least a part of the fatliquoring agent is formed by phospholipids. That is, in accordance with the present invention, the fatliquoring agent may consist for 100% of phospholipids, but provides also advantages when a considerable amount of the 10-50 wt.% fatliquoring agent is formed by phospholipid. Suitable ranges of phospholipids present in the 10-50 wt.% fatliquoring agent are at least 50 wt.% (drawn to the weight of the fatliquoring agent) of phospholipid, preferably at least 60 wt.%, more preferably at least 70 wt.%, up to 100 wt.% of phospholipid.

Hence, in a first aspect, the present invention relates to a composition for the retanning and fatliquoring of pre-tanned leather, comprising:

(a) 30-80 wt.% drawn to the total composition of a retanning agent;
(b) 10-50 wt.% drawn to the total composition of a fatliquoring agent comprising at least 50 wt.% (drawn to the weight of the fatliquoring agent) of phospholipid, preferably at least 60 wt.%, more preferably at least 70 wt.%, up to 100 wt.% of phospholipid; and
(c) optionally other crusting chemicals not being retanning agents and fatliquoring agents balancing to 100 wt.% of the total composition.

Preferred weight ranges are 40-70 wt.% (drawn to the total composition) for the retanning agent and 15-40 wt.% for the fatliquoring agent.

In a preferred embodiment, the phospholipid used as (part of) the fatliquoring agent is solid at ambient conditions (atmospheric pressure and a temperature of 25°C). In a more preferred embodiment, the total fatliquoring agent used is solid at ambient conditions.

In another preferred embodiment, the retanning agent is solid at ambient conditions.
The other crusting chemicals not being retanning agents and fatliquoring agents (c) may be selected from the same neutralizing agents and additives as taught in US-A-6,033,590, but also encompass inert filling materials and traces of moisture. Suitable materials of these other crusting chemicals not being retanning agents and fatliquoring agents are carriers, colorants, impregnants, dressing agents and dressing auxiliaries, alkali metal salts of inorganic and organic weak acids, aromatic sulfonic acids and aliphatic mono- or dicarboxylic acids. Preferably, the other crusting chemicals not being retanning agents and fatliquoring agents are selected from the group consisting of complexation agents, carriers, conventional dyes, surfactants, and stabilisers. In yet a further embodiment, these optional other components (c) are solid at ambient conditions.

In a very advantageous embodiment, the composition of the invention is solid at ambient conditions. Such a solid composition may be in the form of a powder.

Further, the invention relates to a process for preparing the composition of the invention, comprising mixing its components. In a preferred embodiment of this process the respective ingredients are solid at ambient conditions and are mixed in solid form. This embodiment may result in a dry powder. In this preferred embodiment of the present invention, wherein the composition is obtained by mixing solid components that are preferably in powder form, no spray-drying is required as in US-A-6,033,590, said prior art composition being obtained by mixing dissolved components and then subsequently spray drying those mixtures obtained. The preferred preparation of the composition of the present invention is easier to perform than the preparation using the spray-drying method of said US Patent.

In a further aspect, the invention relates to the use of its composition for retanning and fatliquoring of pre-tanned leather, pelts, skins, hides, leather intermediate products or non-finished leather. Or, the invention relates to a process for retanning or fatliquoring of pre-tanned leather, pelts,
skins, hides, leather intermediate products or non-finished leather comprising a one-step treatment with a composition according to the invention.

The composition of the invention, when used in the preparation of leather from pre-tanned leather, provides both retanning and fatliquoring, and results in leather that is soft by touching or feeling by hand and has very good tear strength and that has swollen less than 20% and preferably less than 18% in this preparation process.

The person skilled in the field to which the present invention relates, conventionally determines softness by touching/feeling (by hand) and comparing it with other materials/references.

Conventionally prepared leather swells between 10 and 40%, depending on type of pre-tanned leather. The leather made according to US-A-6,033,590 shows between 20% and 40% swelling. Swelling is measured by comparing the thickness (in millimeters) of the leather before and after the retanning and fatliquoring process. Less swelling has the advantage that less of the leather has to be shaved off prior to the retanning and fatliquoring process to obtain a similar thickness of the leather after the process resulting in lower amounts of waste and higher fiber density of the leather after the process.

For high quality leather according to the invention the requirements are a single edge tear strength equal to or higher than 25 N according to ISO 3377-1:2002, a double edge tear strength equal to or higher than 80 N according to ISO 3377-2:2003 and a maximum load in the tensile strength of higher than 120 N according to ISO 3376:2002.

These ISO norms are used under a relative humidity (RH) of 40-45% RH and at a temperature of 22°C, using test piece "standard".

The leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather is much softer than the leather obtained by applying the composition and procedure described in US-A-6,033,590. This will be illustrated in the working examples herein-
below, wherein the example illustrating the present invention does not require additional fathquoring agents to obtain soft leather (that is, a leather having a softness in line with conventionally prepared leather as described in comparative example 3), whereas additional fathquoring agents are needed to obtain soft leather when the composition and procedure of US-A-6,033,590 are employed.

Further, the leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather is stronger than the leather obtained by applying the composition and procedure described in US-A-6,033,590, as illustrated for both the tear strength and tensile strength as determined herein-below in the comparisons in the working examples.

Moreover, the leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather has swollen much less than leather obtained by applying the composition and procedure described in US-A-6,033,590.

In yet a further aspect, the present invention, hence, relates to the leather product that can be prepared in accordance with the present invention and that has unique properties in respect of swelling, tear strength, tensile strength and/or softness compared to leathers known in the state of the art.

The main advantages of the composition of the present invention and its preparation process over the conventional step-wise retanning and fathquoring process and over the composition and preparation described in US-A-6,033,590 are at least the following:

The leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather is stronger than leather obtained by applying the conventional process or by applying the composition and procedure described in US-A-6,033,590. This improvement in strength is measured both in respect of tensile and tear strength. Particularly, the leather of the present invention has a single edge tear strength,
determined by ISO 3377-1:2002 (RH 40-45%; T = 22 °C), of at least 25 N, but in fact at least 40 N and even at least 50 N. In addition, it has a double edge tear strength, determined by ISO 3377-2:2003 (RH 40-45%; T = 22 °C), of at least 60 N, but in fact at least 70 N and even at least 80 N. In addition, it has a maximum load in the tensile strength, determined by ISO 3376:2002 (RH 40-45%; T = 22 °C), of at least 100 N, but in fact at least 120 N, and even at least 140 N.

The leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather has swollen much less than leather obtained by applying the conventional process or by applying the composition and procedure described in US-A-6,033,590, Compared to US-A-6,033,590, the leather obtained is softer (or the method of said US Patent requires more fatliquoring agent). An additional advantage of the leather preparation process of the present invention over the conventional step-wise retanning and fatliquoring process and the process described in US-A-6,033,590 is that it does not require so much time. The leather obtained by applying the composition of the present invention in the preparation of leather from pre-tanned leather is obtained in a much shorter processing time than in the conventional process, while also compared to the process of US-A-6,033,590 a time gain is obtained. Moreover, savings in amounts of water and energy are obtained.

Incidently, it is taught in US-A-2007/021552 that specific fatliquoring dispersions based on a natural lipoid, at least one (meth)acrylic acid polymer, and an emulsifier composition containing a C6-i7 -alkanol alkoxylated with up to 12 alkylene oxide units or a mixture of two or more such alkanols and a C12-24-fatty alcohol mixture alkoxylated with at least 15 alkylene oxide units may give softness.

Further, it is described in an article of Baskar et al. in The Journal of the American Leather Chemists Association 86(1991). 159-165 that modified
castor oil-based fat liquor emulsions can be used to prepare softy types of lightweight leathers.

As indicated herein-above, the composition of the present invention requires the presence of 30-80 wt.% retanning agent.

The retanning agents to be used in the present invention can be of natural or synthetic origin.

Suitable examples are the commonly used compounds such as vegetable tanning agents, aromatic syntans, resin tanning agents, reactive tanning agents and polymeric tanning agents. Preferred retanning agents are those that are solid at ambient temperature and pressure.

Examples of suitable vegetable tanning agents are those tanning agents, preferably but not necessarily those that are solid at ambient temperature, obtained from vegetable sources and belonging to the classes consisting of the condensed tanning agents or hydrolysable tanning agents, such as chestnut extract, mimosa, oak, tara or quebracho.

Examples of suitable aromatic syntans are those compounds, preferably but not necessarily those that are solid at ambient temperature, which are obtainable by condensation of sulfonated aromatic compounds with formaldehyde and/or urea.

Examples of aromatic compounds suitable for this purpose are naphthalene, biphenyl, terphenyl, phenols, cresols, 4,4'-dihydroxydiphenyl sulfone, β-naphthol, dihydroxybenzenes, resorcinol, 2,2-bis(hydroxyphenyl) propane and diaryl ethers, such as diphenyl ethers and ditolyl ethers, which may have been sulfonated.

Particularly suitable anionic aromatic syntans are the following compounds: (I) condensation products of sulfonated phenol or cresol and formaldehyde, (II) condensation products of naphthalene sulfonic acid and formaldehyde, (III) formaldehyde condensation products of 4,4'-dihydroxydiphenyl sulfones with arylsulfonic acids or (hydroxy)aryl sulfonic acids, (IV) formaldehyde condensation products of sulfo-containing aromatic hydroxy
compounds with aralkyl halides, (V) urea-formaldehyde condensation products of phenols and phenolsulfonic acids, (VI) reaction products of phenol and a sulfonating agent, where the molar ratio (phenol):(SO₃) is (1):(1.1-2.2), (VII) condensation products of sulfonated diaryl ethers and formaldehyde, (VIII) condensation products of sulfonated bi- or terphenyls and formaldehyde, (IX) condensation products of 4,4'-dihydroxydiphenyl sulfone and sulfonated 4,4'-dihydroxydiphenyl sulfone with formaldehyde, (X) formaldehyde condensation products of diaryl ether sulfonic acid and 4,4'-dihydroxydiphenyl sulfone, and (XI) formaldehyde condensation products of phenol with arylsulfonic acids or hydroxyarylsulfonic acids.

These condensation products are in the form of the free acids, such as in the form of the sulfonic acids, or as salts, especially ammonium, lithium, potassium or, in particular, sodium salts.

Examples of suitable resin tanning agents are those cationic condensation products of nitrogen-containing organic compounds, that are preferably but not necessarily solid at ambient temperature, such as urea, thiourea, dicyandiamide or melamine, with formaldehyde or other simple oxo-compounds.

Other suitable resin tanning agents are those anionic compounds, preferably but not necessarily those that are solid at ambient temperature, that are obtained when condensation products of nitrogen-containing organic compounds, for example urea, thiourea, dicyandiamide or melamine, are condensed with formaldehyde or other simple oxo-compounds and with anionic compounds, for example phenols, alkali metal salts of aromatic sulfonic acids, sulfonamides, ligninsulfonates, sulfite or hydrogen sulfite.

Particularly preferred resin tanning agents that are solid at ambient temperature are the condensation products of urea with formaldehyde, and dicyandiamide-based resin tanning agents.

Examples of suitable reactive tanning agents are those reactive tanning agents, that are preferably but not necessarily solid at ambient
temperature, such as polyfunctional isocyanates, alkyl sulfochlorides, relatively high molecular mass alkylsulfonates and also monomeric vinyl derivatives and acrylic derivatives and polymers thereof.

Examples of the polymeric retanning agents are polyacrylates, copolymers comprising acrylates, polyurethanes or polybutadienes that are preferably but not necessarily solid at ambient temperature.

The above-mentioned retanning agents are known to the skilled man and to a large extent available commercially.

In addition to the retanning agent, the compositions of the present invention comprise 10-50 wt.%, and preferably 15-40 wt.%, drawn to the total composition of a fathquoring agent comprising at least 50 wt.% (drawn to the weight of the fathquoring agent) of phospholipid, preferably at least 60 wt.%, more preferably at least 70 wt.%, up to 100 wt.% of phospholipid.

Preferred fathquoring agents are those that are solid at ambient temperature and pressure.

Suitable phospholipids for use in fathquoring agents encompass those phospholipids, preferably but not necessarily solid at ambient conditions, selected from the group of fatty esters of phosphorylcholine and fatty esters of a mixture of a polyol, a fatty acid and phosphorylcholine in which the polyol is a triol, a diol or an erythrytol.

Examples of suitable phospholipids are 1-hexadecanoyl-3-glycerophosphorylcholine, N,N,N-trimethyl-2-(phosphonoxy)ethylchloride, choline-glycerophosphate, 1,2-dimyristoyl-3-lecithine, disodium phosphorylcholine, phosphorylcholine-calcium chloride, dipalmitoyl-lecithine, dilauroyl-phosphatidylcholine, dioleyl-lecithine, distearoylfosfocholine, palmitoyl-oleyl-phosphorylcholine, sphingomyelines, ceramides, and so on.

Preferred examples of these fathquoring agents encompass or are natural or synthetic phospholipids, dialkylphosphorylcholines, phosphatidylethanolamine, phosphatidylinositol and lecithines.
If applicable, the balance of the fatliquoring agents is formed by customarily used fatliquoring agents, such as fatliquoring agents based on animal fats such as fish oil, neat's-foot oil, wool fat or lard oil; fatliquoring agents based on vegetable fats such as castor oil, coconut oil or olive oil; synthetic fatliquoring agents such as products of the chlorination and sulfochlorination of paraffinic hydrocarbons, synthetic fatty acid esters and ester oils; and mineral oils and other petrochemical products.

These fatliquoring agents are preferably employed in powder form.

The balance of the composition of the present invention is - as said - formed by other crusting chemicals not being retanning agents and fatliquoring agents. These crusting chemicals (c) may be selected from the same neutralizing agents and additives as taught in US-A-6,033,590, but also encompass inert filling materials and traces of moisture. Suitable materials of these other crusting chemicals not being retanning agents and fatliquoring agents are carriers, colorants, impregnants, dressing agents and dressing auxiliaries, alkali metal salts of inorganic and organic weak acids, aromatic sulfonic acids and aliphatic mono- or dicarboxylic acids. Preferably, the other crusting chemicals not being retanning agents and fatliquoring agents are selected from the group consisting of complexation agents, carriers, conventional dyes, surfactants, and stabilisers. In yet a further preferred embodiment, these optional other components (c) are solid at ambient conditions.

More in detail, suitable such other components (c) may comprise complexation agents, carriers, conventional dyes, surfactants, stabilisers; preferably in solid form.

Examples of such complexation agents are polyphosphate, sodium citrate, sodium potassium tartrate and sodium oxalate.

Examples of such carriers are sodium chloride, Glauber salt, sodium bicarbonate, sodium formate, protein powders, starch, kaolin, polysaccharides, glucose or gelatin.
Examples of such dyes are acridine dyes, anthraquinone dyes, diarylmethane dyes, triarylmethane dyes, azo dyes, diazonium dyes, metal complex dyes, nitro dyes, nitroso dyes, phthalocyanine dyes, quinone-imine dyes, azin dyes, eurhodin dyes, safranin dyes, indophenol dyes, oxazin dyes, oxazone dyes, thiazin dyes, thiazole dyes, xanthene dyes, fluorene dyes, pyronin dyes, fluorone dyes and rhodamine dyes.

Examples of such stabilisers are anti-oxidants, light stabilisers and heat stabilisers.

These other components are preferably employed in powder form, as well.

The compositions for the retanning and fatliquoring of pre-tanned leather are prepared by simple mixing of the separate components into one mixture. Although this can be in a solvent or solvent mixture, preferably the components are mixed when these are in solid form. Mixing may take place at ambient temperatures, i.e. between about 10°C and 40°C and may use all kinds of available equipment.

The compositions for the retanning and fatliquoring of pre-tanned leather are suitable for the preparation of different types of leather and pelts. Using these compositions it is possible to prepare leathers for all applications, for example shoe, furniture, car, clothing and bag leathers.

The compositions can be used for the preparation of leathers in all conventional machines that are used for the wet dressing of leather.

Leathers can be prepared using the compositions by, for example, putting a piece of wet-white leather in a vat with 100-200 wt.% water with a temperature of 10-40°C - drawn to the dry weight of the leather - then adding 5-50 wt.% of the composition of the invention - drawn to the dry weight of the leather - and, subsequently soaking the mixture for 30-100 minutes at 10-40°C. This step is followed by the addition of 100-300% water of 30-70°C - drawn to the dry weight of the leather - and after 2-10 minutes 0.5-3% of a (conventional) fixation agent, such as formic acid or acetic acid, is added,
followed after 2-30 minutes by another 1-3% of a fixation agent. After 10-60 minutes the liquor is drained and the leather is subsequently washed with 100-400% of cold water.

After this preparation step, the leather is dried and finished as desired.

The present invention will be further elaborated by the following non-limiting working examples. Parts and percentages of components referred to in these working examples are drawn to the weight of the total composition wherein these components are present, like in the other parts of the description and claims, unless otherwise indicated.

Example 1

50 parts by weight of urea-formaldehyde condensation product of phenolsulfonic acid (Renektan D® ex Stahl Europe B.V., The Netherlands) as retanning agent in powder form, 25 parts by weight of solid lecithin in powder form, 5 parts by weight of sodium bicarbonate as carrier in powder form and 20 parts by weight of kaolin as carrier in powder form were mixed at room temperature to obtain Composition A.

Example 2

A piece of wet-white leather with a thickness of 1.5 mm based on shaved weight was put in a suitable vat with 150% water with a temperature of 25°C, drawn to the weight of the wet-white leather, and 25 wt.% of Composition A from Example 1, drawn to the weight of the wet-white leather, was added and the mixture was soaked for 50 minutes at 25°C. Then, 200 wt.% water of 50°C was added and after 5 minutes 1.5 wt.% of formic acid was added, followed after 10 minutes by another 1.5 wt.% of formic acid. After 30 minutes the bath was drained and the leather was subsequently washed with
200 wt.% of cold water. The resulting leather was subsequently horsed up and toggled or vacuum dried.

The total processing time in the vat was only about 2 hours. The leather obtained had a thickness of 1.6 mm. The thickness of the leather has thus increased from 1.5 mm to 1.6 mm during the process. The leather had a soft touch.

Example 3 (comparative example illustrating a conventional crusting process)

A piece of wet-white leather with thickness of 1.3 mm based on shaved weight of the same type as used in Example 2 was put in a vat with 200 wt.% water with a temperature of 30°C. After 10 minutes the bath was drained. Subsequently, 100 wt.% of water with a temperature of 30°C was added, followed by 1.5 wt.% of glutaraldehyde, and after another 20 minutes followed by 5 wt.% of urea-formaldehyde condensation product of phenolsulfonic acid as syntan (Renektan D®) and followed after another 30 minutes by 3 wt.% of fish oil as fatliquor. After 20 minutes the float was drained. Then, 100 wt.% of water was added together with 1 wt.% of sodium formate, after 20 minutes followed by 0.5 wt.% of sodium bicarbonate, after 60 minutes followed by 3 wt.% of a polyester dispersion in water that also contains some vegetable oils (Corilene CP-MF®, ex Stahl Europe B.V. The Netherlands), after 20 minutes followed by 8 wt.% of the same fatliquor, after 15 minutes followed by 20 wt.% of urea-formaldehyde condensation product of phenolsulfonic acid as syntan (Renektan D®) followed after 20 minutes by 2 wt.% of an azo dye, after 50 minutes followed by 3 wt.% of the same fatliquor, after 30 minutes followed by 6 wt.% of urea-formaldehyde condensation product of phenolsulfonic acid as syntan (Renektan D®) and after 10 minutes followed by 4 wt.% of tara.
After 60 minutes of treatment, 50 wt.% of water with a temperature of 50°C was added. The mixture was heated to 45°C and after 10 minutes 10 wt.% of the same fatliquor was added, after 60 minutes 1.5 wt.% of formic acid was added, followed after 10 minutes by another 1.5 wt.% of formic acid. After 30 minutes the bath was drained and the leather was subsequently washed with 200 wt.% of cold water, after 10 minutes followed by the addition of 1 wt.% of formic acid as fixation agent. After 20 minutes, the liquor was drained and the leather was subsequently washed with 200 wt.% of cold water. The resulting leather was subsequently horsed up, toggled and milled.

The total processing time in the vat was about 11 hours. The leather obtained has a thickness of 1.7 mm. The thickness of the leather has thus increased from 1.3 mm to 1.7 mm during the process. The leather had a similar softness as the leather of Example 2.

Example 4 (comparative example illustrating US-A-6,033,590)

A piece of wet-white leather with thickness of 1.3 mm based on shaved weight of the same type as used in Example 2 was treated using the composition as essentially described in example 7 of US-A-6,033,590. The piece of wet-white leather was put in a suitable vat with 150% water with a temperature of 25°C, drawn to the weight of the wet-white leather, 25 wt.% of the composition of US-A-6,033,590, drawn to the weight of the wet-white leather, was added and the mixture was soaked for 50 minutes at 25°C. Then, 200 wt.% water of 50°C was added and after 5 minutes 1.5 wt.% of formic acid was added, followed after 10 minutes by another 1.5 wt.% of formic acid. After 30 minutes the bath was drained and the leather was subsequently washed with 200 wt.% of cold water. The resulting leather was subsequently horsed up and toggled or vacuum dried.

Since the resulting leather felt considerable harder than the material obtained in Examples 2 and 3, additional fatliquoring agent had to be added to
obtain leather with a similar softness as obtained in Example 2 and Example 3. The total processing time in the vat was about 2.5 to 3 hours. The leather obtained has a thickness of 1.7 mm. The thickness of the leather has thus increased from 1.3 mm to 1.7 mm during the process.

Example 5

Samples of pieces of leather obtained in Example 2, Example 3 and Example 4 were subjected to a number of evaluative tests after conditioning for 48 hours at 23°C and 50% relative humidity, according to DIN50014.

The tensile strength was measured according to ISO 3376:2002 (RH = 40-45%; T = 22 °C) and for leather from Example 2 with a thickness of 1.63 mm the maximum load for the tensile strength was 240 N, the mean tensile strength was 8.2 N/mm², and mean elongation was 57%, whereas for leathers from Example 3 and 4 with thicknesses of 1.63 mm the maximum loads for the tensile strengths were 180 N, the mean tensile strengths were 5.6 N/mm² and mean elongations were 41%.

The single edge tear strength was measured according to ISO 3377-1:2002 (RH = 40-45%; T = 22 °C) and the single edge tear strength for leather from Example 2 with a thickness of 1.7 mm was 57 N, whereas the single edge tear strengths for leathers from Example 3 and Example 4 with thicknesses of 1.6 mm were 32 N.

The double edge tear strength was measured according to ISO 3377-2:2003 (RH = 40-45%; T = 22 °C) and the double edge tear strengths for leather from Example 2 with a thickness of 1.63 mm were 82 N and 92 N for pieces cut perpendicular and parallel to the backbone, respectively, resulting in an average double edge tear strength of 87 N, whereas the double edge tear strengths for leathers from Example 3 and Example 4 with thicknesses of 1.63 mm were 50 N and 58 N for pieces cut perpendicular and parallel to the
backbone, respectively, resulting in an average double edge tear strength of 54 N.

The leather obtained in Example 2 is stronger than the leathers obtained in Example 3 and Example 4.
Claims

1. A composition for the retanning and fatliquoring of pre-tanned leather, comprising:
   (a) 30-80 wt.% drawn to the total composition of a retanning agent;
   (b) 10-50 wt.% drawn to the total composition of a fatliquoring agent comprising at least 50 wt.% (drawn to the weight of the fatliquoring agent) of phospholipid, preferably at least 60 wt.%, more preferably at least 70 wt.%, up to 100 wt.% of phospholipid; and
   (c) optionally other crusting chemicals not being retanning agents and fatliquoring agents balancing to 100 wt.% of the total composition.

2. The composition according to claim 1, wherein the phospholipids used as (part of) the fatliquoring agent are solid at ambient conditions (atmospheric pressure and a temperature of 25°C).

3. The composition according to claim 1 or claim 2, wherein the total fatliquoring agent used is solid at ambient conditions.

4. The composition according to any one of the previous claims, in solid form, preferably in powder form, at ambient conditions.

5. The composition according to any one of the previous claims, wherein the retanning agent is present in an amount of 30-70 wt.%, and wherein the fatliquoring agent is present in an amount of 15-40 wt.%. 

6. The composition according to any one of the previous claims, wherein the retanning agent is selected from the group of vegetable tanning agents, aromatic syntans, resin tanning agents, reactive tanning agents and polymeric tanning agents.

7. The composition according to any one of the previous claims, wherein the fatliquoring agent comprises a phospholipid selected from the group of fatty esters of phosphorylcholine, fatty esters of a mixture of a polyol,
a fatty acid and phosphorylcholine in which the polyol is a triol, a diol or an erythrytol.

8. The composition according to any one of the previous claims, wherein the fathquoring agent comprises or is a phospholipid selected from the group of natural or synthetic phospholipids, dialkylphosphorylcholines, phosphatidylethanolamine, phosphatidylinositol, lecithines, or mixtures of one or more of these phospholipids.

9. The composition according to any one of the previous claims, wherein the fathquoring agent consists entirely of phospholipids.

10. A process for preparing the composition of any one of the previous claims, comprising mixing the various ingredients.

11. The process according to claim 10, wherein the respective ingredients are solid at ambient conditions and are mixed in solid form.

12. Use of the composition according to any one of claims 1-9 for retanning and fathquoring of pre-tanned leather, pelts, skins, hides, leather intermediate products or non-finished leather.

13. A process for retanning or fathquoring of pre-tanned leather, pelts, skins, hides, leather intermediate products or non-finished leather comprising a one-step treatment with a composition according to any one of claims 1-9 in a suitable solvent and preferably in water.

14. The process of claim 13, comprising the steps of putting a piece of pre-tanned leather in a suitable container with 100-200 wt.% water with a temperature of 10-40°C - drawn to the dry weight of the leather - then adding 5-50 wt.% of the composition of any one of claims 1-9 - drawn to the dry weight of the leather - and, subsequently soaking the mixture for 30-100 minutes at 10-40°C; adding 100-300% water of 30-70°C - drawn to the dry weight of the leather - and after 2-10 minutes adding 0.5-3 wt.% of a fixation agent, followed after 2-30 minutes by the addition of another 1-3 wt.% of the same or another fixation agent; after 10-60 minutes draining the liquor and washing the leather with water.
15. The leather, preferably obtainable by the process of claim 13 or claim 14, having a soft touch and/or having a high tear strength and high tensile strength.
## INTERNATIONAL SEARCH REPORT

### A. CLASSIFICATION OF SUBJECT MATTER

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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

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

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Date of the actual completion of the international search: 3 June 2013

Date of mailing of the international search report: 13/05/2013

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Neugebauer, Ute

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