(57) Abstract: The invention relates to a composition for wet retanning and lubricating of pelts, skins, hides, leather intermediate products or non-finished leather, consisting of (A) a reaction product of an ethylenically unsaturated \( C_2\)\(_2\)-dicarboxylic anhydride with \( C_2\)\(_2\)-alpha-olefins, followed by partial or total neutralisation with a base, (B) a reaction product of ethylenically unsaturated \( C_\text{ar}\)\(_2\)-dicarboxylic anhydrides with \( C_{10}\)\(_{18}\)_\text{fatty acids} or \( C_2\)\(_2\)-polycarboxylic acids or \( C\)\(_{10}\)\(_{18}\)_\text{fatty alcohols} or \( \text{o xo-alcohols} or glycols or polyglycols or \( C_2\)\(_2\)-organic amines all being saturated or unsaturated, linear or branched and the fatty acids being ethoxylated and/or propoxylated and/or having been reacted with polyglycols or glycols, and the \( C_2\)\(_2\)-polycarboxylic acids being ethoxylated and/or propoxylated and/or having been reacted with polyglycols or glycols at least with one carboxylic group, and (C) a reaction product of (B) with bisulphite or metabisulphite or sulphite or sulphuric acid or oleum preferably neutralised with a base where the base is an alkali or earth alkali hydroxide, ammonia or an organic amine.
RETANNING AND FATLIQUORING AGENT FOR LEATHER

The invention relates to a composition for wet retanning and fatliquoring of pelts, skins, hides, leather intermediate products or non-finished leather and to its production and use.

For wet retanning and fatliquoring the leather industry is using different compounds, especially polymeric compounds have been proposed for obtaining soft and firm leather types.

US 5,279,613 discloses copolymers which are obtainable by free radical copolymerization of (a) Cs-C^+-monoolefins with (b) ethylenically unsaturated C_4-C_s-dicarboxylic anhydrides by mass polymerization at from 80°C to 300°C to give copolymers having molecular weights of from 500 to 20,000 g/mol, subsequent solvolysis of the anhydride groups of the copolymers and partial or complete neutralization of the carboxyl groups formed during the solvolysis, in an aqueous medium by means of a base, and which are present in the form of aqueous dispersions or solutions, which are used as agents for rendering leathers and skins water-repellent.

US 5,575,939 discloses a process for the fatliquoring/softening of leathers and furs by treatment with an aqueous dispersion of a copolymer obtainable by polymerization of a) maleic anhydride, b) C_{12}-C_{30} alpha-olefins, esters of (meth)acrylic acid and/or maleic acid with C_{12}-C_{30} alcohols and c) optionally, further hydrophilic, ethylenically unsaturated monomers which are copolymerizable with a) and b), reaction of the anhydride groups with monovalent alcohols comprising at least one ether functionality, and partial neutralization or hydrolysis of the residual acid or anhydride groups and manufacture of a flowable dispersion having an active substance content of at least 40%-wt.

Nevertheless there is always a need for compounds with even better properties.

It has now surprisingly been found that with the below defined composition, there can be achieved in wet retanning and fatliquoring of pelts, skins, hides, leather intermediate
products or non-finished leather an outstanding and highly satisfactory retanning and fatliquoring of the substrates.

Therefore an object of the instant invention is a composition consisting of the components (A), (B) and (C) wherein:

(A) is a reaction product of an ethylenically unsaturated C^4Cs-dicarboxylic anhydride with C3-C40-alpha-olefins, used in acid form or preferably followed by partial or total neutralisation with a base in aqueous dispersion with or without solvents, optionally part of the anhydride groups are reacted with alcohols, polyalcohols, glycols or organic amines,

(B) is a reaction product of ethylenically unsaturated C^4Cs-dicarboxylic anhydrides with C_{10}^-C_{40} fatty acids or C4-C30 polycarboxylic acids or C_{10}^-C_{40} fatty alcohols or oxo-alcohols or glycols or polyglycols or C3-C20 organic amines, all being saturated or unsaturated, linear or branched and the fatty acids being ethoxylated and/or propoxylated or having been reacted with polyglycols or glycols, and the polycarboxylic acids being ethoxylated and/or propoxylated or having been reacted with polyglycols or glycols at least with one carboxylic group, whereas the fatty alcohols or oxo-alcohols and the fatty amines can optionally be ethoxylated and/or propoxylated, and

(C) is a reaction product of (B) with bisulphite or metabisulphite or sulphite or sulphuric acid or oleum preferably neutralised with a base where the base is an alkali or earth alkali hydroxide, ammonia or an organic amine in aqueous dispersion with or without solvents.

In the component (B) the glycols or polyglycols can be reacted with other carboxylic acids or C4-C30 polycarboxylic acids or derivates of carboxylic or polycarboxylic acids.

This composition provides excellent softening and retanning properties which can make further treatment with retanning and lubricating agents unnecessary. It confers outstanding chemical and physical properties to the leathers: excellent fogging values, good light and heat stability, no spue problems, ecological advantage: low COD in the bath, no phenol or formaldehyde in the bath as well as in the leather (usually present in bath and leather after treatments with common retanning agents), properties which
otherwise are very difficult to reach with the standard fatliquoring and retanning agents already available on the market.

Preferred are compositions wherein

in the component (A) the dicarboxylic anhydride is maleic anhydride and the alpha-olefins have a chain length of 12 to 30 C-atoms and the base is ammonia, an amine or an alkali or earth alkali hydroxide in aqueous dispersion with or without solvents,

in the component (B) the dicarboxylic anhydride is maleic anhydride, and the fatty acids or fatty alcohols or oxo-alcohols have a chain length of 12 to 30 C-atoms and are ethoxylated/propoxylated with 2-25 mol of EO/PO (ethylene oxide/propylene oxide) or the fatty acids are reacted with polyglycols 100 - 1200,

the component (C) is a reaction product of (B) with sodium bisulphite carried out in aqueous dispersion.

Especially good properties show compositions wherein

in the component (A) the alpha-olefins have a chain length of 18 to 24 C-atoms and the base is NaOH,

in the component (B) the fatty acids or fatty alcohols or oxo-alcohols have a chain length of 12 to 20 C-atoms and have one or more double bonds, and the fatty acids and fatty alcohols or oxo-alcohols have been ethoxylated and optionally the fatty acids have been reacted prior to the reaction with maleic anhydride with polyethylene glycols or glycols.

Examples of said fatty acids used for (B) are lauroleic acid, miristoleic acid, palmitoleic acid, oleic acid, linoleic acid, or alpha-linolenic acid. Preferred are oleic acid and linoleic acid or mixtures thereof, and especially preferred is oleic acid.

Preferred examples of said alcohols used for (B) are oleyl alcohol, linoleyl alcohol, cetyloleylalcohols or mixtures thereof as well as branched alcohols from oxo-synthesis like C9, Cio, Cn, C_{12}, C_{13} - C_{14}, C_{15} oxo-alcohols or mixtures thereof.
Especially preferred compositions are those wherein

in the component (A) the alpha-olefins have a chain length of 20 to 22 C-atoms,

in the component (B) the fatty acid is oleic acid and wherein the polyethylene

 glycol is a polyethylene glycol of the formula \( HO(CH_2CH_2O)_nH \) with an

average number of \( n \) from 2 to 25 (like for example „polyglycol 100 -

1200“).

The alpha-olefins used are commercial products. A chain length of 20 to 22 C-atoms
does not exclude smaller amounts (up to 10 mol-%) of \( C_{18} \) or shorter and \( C_{24} \) or longer.

The oleic acid used is a commercial product from natural sources, that means mixture

of fatty acids \( C_{12} - C_{18} \) whereas the percentage of oleic acid is > 60%.

The instant compositions in general have a molar ratio of \( (A):[(B) + (C)] \) of from 5:100
to 100:5 and a molar ratio of \( (B):(C) \) of from 5:100 to 100:5.

Preferred are compositions wherein the molar ratio of \( (A):[(B) + (C)] \) is from 50:100 to

100:50, more preferably from 70:100 to 100:70 and the molar ratio from \( (B):(C) \) is from

20:100 to 100:20, more preferably from 60:100 to 100:60.

The instant compositions may further comprise amides and esters of \( (A) \) as described in

US 5,279,613. Details of these amidation and esterification reactions are found in this

prior art.

The instant compositions may further comprise at least one formulation additive \( (S) \) e.g.

for adjusting the physical aspect of the composition and/or its use properties and may be

selected from water or an organic solvent or a solubiliser or mixtures thereof, said

additives being miscible with or soluble in \( (A) \) and \( (B) \) and \( (C) \) or in which \( (A) \) and \( (B) \)

and \( (C) \) are soluble. Furthermore at least one of the following additives or mixtures

thereof may be contained: defoamers, natural or mineral oils, surfactants, lecithines,

biocides.

\( (S) \) may in particular comprise one or more solvents and/or solubilisers and/or a
defoamer and/or one or more surfactants and/or mineral or natural oil and/or a biocide. Preferably (S) is selected from the group comprising (S1) water, (S2) an organic solvent or mixture of organic solvents and/or a solubiliser or mixture of solubilisers, miscible with or soluble in (A) and (B) and (C) or in which (A) and (B) and (C) are soluble,

(S3) a defoamer and/or (S4) a surfactant and/or (S5) a mineral or natural oil and/or (S6) synthetic or natural lecithine and/or (S7) a biocide.

Preferably (S2) is an organic solvent miscible with water, which is aliphatic and contains at least one oxygen and no other heteroatoms, or a mixture of two or more of such solvents. More preferably (S2) is selected from the group consisting of aliphatic mono- or oligofunctional alcohols and mono- or di-(C1-C4-alkyl)-ethers thereof. (S2) may include water-miscible, saturated aliphatic solvents of ether and/or alcohol character. As (S2) there may in particular be employed a C3-C4-alkanol, a diol which is a C2-C6-alkylene glycol or a higher diol e.g. with 6 carbon atoms mainly 2-methyl-2,4-pentanediol (hexylene glycol), dipropylene glycol or a di-, tri- or tetraethylene glycol, and mono- or di-(C1-C4-alkyl)-ethers thereof, or glycerol. Particularly preferred solvents or solubilisers (S2) include e.g.: isopropanol, mono- or dipropylene glycol, mono-, di-, tri- or tetraethylene glycol, hexylene glycol, mono- or dipropylene glycol monomethylether, ethylene glycol monobutylether and methyl, ethyl, isopropyl or butyl mono- or diethers of di-, tri- or tetraethylene glycol.

As solvents/solubilisers in (S) there may be employed water (S1) alone, solvent or solubiliser (S2) alone or a mixture of water (S1) and solvent or solubiliser (S2).

As defoamers (S3) there may be employed known products in the commercially available forms, like, for example, silicones, silica, paraffins, paraffin oil, mineral oil or trialkylphosphates (e.g. triisopropyl-phosphate or tributylphosphate), ethers, alkoxylated fatty esters, alkoxylated fatty acids, in an efficient concentration, e.g. below 0.2 % by weight, preferably below 0.1 % by weight, referred to the dry content of (A)+(B)+(C).

Mostly a defoamer (S3) is not necessary and is not added.

As surfactants (S4) there may be employed any conventional non ionic or anionic surfactants in particular with emulsifier character.
As non ionic surfactants are preferably employed alkoxylated, mainly ethoxylated, alcohols. As alkoxylated alcohols can also be employed some alkoxylated, preferably ethoxylated oxo-alcohols.

As anionic surfactant preferably emulsifiers contain a sulpho group, optionally a phosphorus group. Preferably anionic surfactant (S4) are employed arilaliphatic or more preferably aliphatic sulphonates, which may contain a heteroatomic bridge in the aliphatic chain (e.g. an ester, amine, amide or preferably ether bridge) and which contain a lipophilic hydrocarbon radical e.g. with 7 to 24 carbon atoms, more preferably sulphuric acid monoesters of fatty alcohols or of ethoxylated (e.g. mono- to oligo-ethoxylated) fatty alcohols or fatty amine with e.g. 12 to 24 carbon atoms in the fatty hydrocarbon radical. Among these the sulphuric acid esters of ethoxylated fatty alcohols are preferred. Optionally as anionic surfactant are employed arilaliphatic or more preferably aliphatic mono- or di-phosphoric acid esters or mixture thereof. Among these the phosphoric acid esters of ethoxylated fatty alcohols are preferred.

The anionic surfactants (S4) are preferably in the form of alkali metal salts, more preferably sodium or potassium salts.

As mineral or natural oils (S5) may be employed hydrocarbons fluid got by distillation of the oil, paraffinic hydrocarbons and / or natural or synthetic waxes or vegetable or animal tryglycerides.

If desired to modify the applicative properties may be employed synthetic or natural lecithine (S6). Mostly the lecithine is not necessary and is not added.

As biocide (S7) there may be employed known products in the commercially available forms, e.g. biocide based on 1,2-benzoisotiazolin-3-one and 1,2-dibromo-2,4-dicianobutano, biocide based on chloro or chloro free isotiazolinoni, based on bronopol, based on 2-(tiocianometiltilio)-benzotiazolo or based on p-cloro-m- cresol. These products can be employed alone or in mixture.
The polymers (A) are basically known products and are for example described in US 5,279,613, US 5,575,939 or DE 3 730 885. Details of their preparation are also disclosed in these documents.

The instant compound (B) is not a polymerization product where a radical polymerization takes place and therefore still contains double bonds, in contrast to the product of US 5,575,939 where a radical polymerization takes place.

Component B can be obtained by heating the mentioned starting compounds at a temperature in the range 80 - 160 °C, with water distillation if required, optionally under vacuum for 2 - 6 hours and in the presence of an organic solvent, if necessary.

The ethoxylated products or ethoxylated and propoxylated products (fatty acids, fatty alcohols, oxo-alcohols) are known or may be produced in a manner conventional per se by addition reaction of ethylene oxide or of ethylene oxide and propylene oxide to the mixtures of fatty acids, fatty alcohols, oxo-alcohols, or organic amines.

As ethoxylation there is meant herein the addition reaction of ethylene oxide (also known as oxyethylation). As propoxylation there is meant herein the addition reaction of propylene oxide (also known as oxypropylation).

The addition reaction may be carried out under reaction conditions known per se, preferably in the presence of an alkali metal hydroxide, e.g. sodium hydroxide or potassium hydroxide, with heating, e.g. at a temperature in the range of 90 to 240 °C, preferably 130 to 220 °C in a closed vessel, in the presence of an inert gas, e.g. nitrogen. If propylene oxide is also reacted, it is preferably reacted first, followed by the reaction of ethylene oxide. Propylene oxide, if used, is employed in a minor proportion, preferably in this case there being added 1 to 2 moles of propylene oxide per mole of fatty acids or fatty alcohols or oxo-alcohols or organic amines mixture; more preferably no propylene oxide is added, but the mixture of fatty acids or fatty alcohols or oxo-alcohols or organic amines is reacted only with ethylene oxide. The molar proportion of ethylene oxide referred to fatty acids or fatty alcohols or oxo-alcohols or organic amines or mixtures thereof is in the range of 2 to 25, preferably 6 to 14.
The reaction of fatty acids with polyglycols can be carried out at a temperature in the range of 80-160°C for 2-6 hours optionally under vacuum (like for example 50-70 mm Hg), preferably with an acid catalyst like methansulfonic acid, as example.

Parts of component (B) are further reacted to synthesize (C) with sodium bisulphite at a temperature in the range of 60-120°C for 2-10 hours in the presence of water, earth alkali hydroxides and, if necessary, organic solvents (like for example 2-propanol). The preferable pH range during the reaction is 5-8.

The compositions of the invention may be produced in a manner conventional per se, e.g. by mixing the components (A), (B) and (C) and any formulation additive (S).

The admixing of (A) with (B) and (C) and any (S) may be carried out e.g. at a temperature in the range of 15 to 70°C.

More preferably the corresponding mixture of (B) and (C) is prepared in a reactor with the required addition of sulphite or bisulphite or sulphuric acid or oleum agent to (B) and follows the neutralization with a base in the presence of water and, if necessary, organic solvents, and then (A) is added and (S) is added, if desired, at a temperature in the range of 15 to 70°C.

Of course, it is also possible to add the mixture of (B) and (C) to the component (A) that can already be added with (S), if desired, mixing all the components at a temperature in the range of 15 to 70°C.

It is also possible to add the mixture of (B) and (C) to the component (A) and then (S) is added, if desired, mixing all the components at a temperature in the range of 15 to 70°C.

The so produced compositions are ready for use. They are of satisfactory stability to storage and transportation. They are readily dilutable with water resulting in an aqueous dispersion and may e.g. be directly dosed into the treatment bath.
The aqueous dispersions thus obtainable are stable and have a long shelf life. They are very suitable for treating leathers and skins because they have a particularly pronounced action in fatliquoring and retanning. In many cases no additional fatliquoring agents based on natural or synthetic fatliquoring oils are required. The dispersions impart to the product good body and high tensile strength and tear strength, so that additional treatment with commercial retanning agents, for example with vegetable tanning agents or synthetic organic tanning agents (syntans) based on phenolsulfonic acid/phenol/formaldehyde condensates, is no longer necessary in most cases.

The dispersions described above are suitable for the treatment of all conventional tanned hides, in particular hides tanned with mineral tanning agents, such as chromium(III) salts.

The invention further provides a process for wet retanning and fatliquoring of tanned pelts, skins, hides, leather intermediate products or non-finished leather (crusted leather) or pelts, characterised in that a composition as defined above is employed as a retanning and fatliquoring agent.

In particular the invention provides a process for the production of leather, pelts or furskins, comprising in their production at least a wet degreasing treatment, a tannage, a retanning, a fatliquoring and a dyeing or finishing treatment, wherein retanning and fatliquoring can be carried out in one step with the instant composition or completed, if desired, with other commercial fatliquoring and retanning products.

As a substrate according to the invention there may be employed any hides, skins or pelts as conventionally processed in the beamhouse, tanned conventionally to get a wet blue or wet white leathers. There may e.g. be mentioned pelts, hides or skins from cow, sheep, goat, swine, cattle and other animals (e.g. horse, colt, reptiles - e.g. snake, lizards, water reptiles -, doe, deer, ostrich, poultry, dromedary, camel and camel-like animals - e.g. lama or alpaca -), and woolled skins (mainly from sheep or goat) and furskins.

Retanning and fatliquoring according to the invention may also be applied to leather
intermediate products or non-finished leather (crusted leather). Thus if the substrate has already been tanned or retanned, the instant composition may be used before dyeing, mostly in order to improve dyeability e.g. uniform dispersion and distribution of the dye, or after dyeing to confer a fuller and deeper dyeing, or before finishing in order to prepare the substrate for a particular uniform link of the finishing.

To the retanning and fatliquoring bath there may e.g. be added one or more anionic surfactants (G) and/or a water miscible solvent (H).

As surfactants (G) of anionic character there may be employed any conventional surfactants, preferably those containing a sulpho group, e.g. aliphatic or arylaliphatic sulphates (Gi) or sulphonates (Gj), which may contain a heteroatomic bridge in the aliphatic chain (e.g. an ester, ether or preferably amide, bridge, an ether bridge being with particular preference part of a glycol ether chain) and which contain a lipophilic hydrocarbon radical e.g. with 7 to 24 carbon atoms. They are preferably in the form of alkali metal salts, more preferably sodium or potassium salts.

Suitable sulphates (Gi) are e.g.:

(Gi) sulphuric acid monoesters of fatty alcohols or of ethoxylated (e.g. mono- to oligo-ethoxylated) fatty alcohols or fatty amine with e.g. 12 to 24 carbon atoms in the fatty hydrocarbon radical,

(Gi") sulphuric acid esters of fatty acid monoglycerides with e.g. 12 to 24 carbon atoms in the fatty acid radical,

(Gi")' products of sulphation of unsaturated fatty acids or unsaturated oils (fatty acid triglycerides) with e.g. 18 to 22 carbon atoms in the unsaturated fatty acid radical or of ricinoleic acid or castor oil.

Suitable sulphonates (Gj) are e.g.

(Gj) fatty alkyl sulphonates and isothionates, with e.g. 12 to 24 carbon atoms in the fatty hydrocarbon radical, petroleum sulphonate (mainly secondary sulphonates with e.g. 10 to 15, usually 12 to 13, carbon atoms in the aliphatic chain),

(Gj") fatty acid taurides and N-methyltaurides with e.g. 12 to 24 carbon atoms
in the fatty acid radical,

\( (G'') \) products of sulphitation of unsaturated fatty acids or unsaturated oils (fatty acid triglycerides) with e.g. 16 to 24 carbon atoms in the unsaturated fatty acid radical,

\( (G'_2'') \) mono- and di-alkyl-benzene sulphonates with e.g. a total of 1 to 12 carbon atoms in the alkyl substitution, e.g. with 4 to 12 carbon atoms in the alkyl chain, or short chain alkyl-benzene sulphonates with 1 to 3 carbon atoms in the alkyl radical and in the total alkyl substitution.

As mono- to oligo-ethoxylated in \( (G_1') \) there is meant the addition product of 1 to 10 moles of ethylene oxide to one mole of fatty alcohol. As examples of \( (G_i) \) there may be mentioned in particular lauryl sulphate, stearyl sulphate, and the sulphates of the addition product of 1 to 6 moles of ethylene oxide to one mole of lauryl or stearyl alcohol. As examples of \( (G_2) \) there may be mentioned in particular toluene-, xylene- or cumene-sulphonic acids, and fatty acid taurides or N-methyl taurides with on average 16 to 20 carbon atoms in the fatty acid radical. They are preferably in the form of potassium salts or more preferably sodium salts.

The solvents \( (H) \) are water-miscible, organic, preferably aliphatic solvents containing at least two linked oxygen atoms per molecule in the form of aliphatic hydroxy groups and/or ether bridges, and are in particular exempt of other heteroatoms than oxygen. There may in particular be mentioned saturated aliphatic compounds of ether and/or alcohol character, mainly mono-, di-, tri- and/or tetra-alkylene glycols and their mono- or di-(C\(_{1-4}\)-alkyl) ethers, preferably with \( \geq 4 \) carbon atoms in the molecule, more preferably with \( \geq 6 \) carbon atoms, e.g. butane-2,3- or -1,4-diol, dipropylene glycol, monomethyl ether of mono- or dipropylene glycol, and methyl-, ethyl-, isopropyl- or butyl-ethers of mono-, di-, or Methylene glycol, among which the monoalkylethers are preferred, especially diethylene glycol mono-butyl ether.

According to one feature of the invention one or more anionic surfactants \( (G) \) and/or a water miscible solvent \( (H) \) can be added to the instant composition.

Wet retanning and fatliquoring with the instant composition may be carried out
analogously to methods known per se, expediently in a treatment drum or in a rotated aqueous bath e.g. in the range of 3 to 100 %, preferably 5 to 40 %, more preferably 5 to 15 % by weight referred to the wet shaved weight of the substrate for tanned leathers (wet blue leather or wet white leathers) and to the dry weight of the substrate for crusted leathers.

The temperature $T$ of the retanning and fatliquoring bath advantageously is in the range of 20 to 60°C, preferably 30 to 60°C. The pH may be as desidered and advantageously is in the range 3.0 - 6.5.

Retanning and fatliquoring may be carried out in one or more stages, and in each stage it may be carried out in one or more steps, preferably two, even if one is already sufficient to get a good penetration and an homogeneous dispersion of the agents. If it is carried out in two steps, one step may be regarded as the main step for the retanning and fatliquoring, while the second step may be regarded as a follow-up step for improving the effects and the substrate properties.

According to one feature of the invention, the instant composition may be used alone or if desired in the presence of one or more further retanning or other fatliquoring products especially if leathers are manufactured to get particular articles, like automotive upholstery leathers.

According to one feature of the invention at least a part of said composition may be combined with other retanning or fatliquoring products. Preferably, however, any or at least the major required proportion of other retanning or fatliquoring agents are added separately to the bath, as desired and as suitable in the concerned treatment stage and/or step.

For retanning and fatliquoring of tanned substrates it is of advantage to use for the setting of bath and also for rinsing from 100-400 % of water and of an organic acid like formic acid, acetic acid etc., e.g. of a concentration in the scope from 0.1 to 5 %, preferably 0.1 to 0.5 % by weight and 0.2 - 3.0 % of a common wetting agent (a single component or a formulation) referred to the wet shaved weight of the substrate.
As wetting agent can be employed one or more anionic surfactants and one or more non ionic surfactants, preferably is employed one of more formulations of these surfactants present on the market for this scope.

Then the substrate is drained, the bath is added with water from 50 to 300 %, the pH is increased by addition of conventional bases or buffer salts such as sodium acetate, sodium formiate from 1.0 to 4.0 % or sodium bicarbonate from 0.5 to 3.0 % or other products having neutralising/buffering properties.

The bath is drained, again well washed with water from 50 to 400 % and drained again.

The retanning and fatliquoring treatment of the invention may be carried out for a duration as conventional per se for retanning and fatliquoring e.g. in the range of 1 to 4 hours, preferably 40 - 70 minutes for every treatment stage (in one or two steps).

For retanning and fatliquoring of crusted substrates it is of advantage to use for the setting of bath and also for rinsing from 200-800 % of water and of an organic acid like formic acid or acetic acid, e.g. of a concentration in the scope from 0.2 to 5 %, preferably 0.2 to 2.0 % by weight and 0.2 - 4.0 % of a wetting agent (alone or in formulation as many are available on the market) referred to the dry weight of the substrate.

As wetting agent can be employed one or more anionic surfactants and one or more non ionic surfactants, preferably is employed one of more formulations of these surfactants present on the market for this scope.

Then the substrate is drained, the bath is added with water from 100 to 600 %, the pH is increased by addition of conventional bases or buffer salts such as sodium acetate, sodium formiate from 2.0 to 8.0 % or sodium bicarbonate from 1.0 to 6.0 % or other products having neutralising/buffering properties.

The substrate is drained, again well washed with water from 100 to 800 % and drained
The retanning and fatliquoring treatment of the invention may be carried out for a duration as conventional per se for retanning and fatliquoring e.g. in the range of 1 to 4 hours, preferably 40 - 70 minutes for every treatment stage (in one or two steps).

After completion of the retanning and fatliquoring treatment, which preferably is followed by adjustments of pH or washing, the substrate may be directly further processed in the foreseen sequence of treatments for the production of the leather or pelt as desired. If desired, the retanning and fatliquoring substrates may even be washed, eventually added with biocides, drained and dried, for being e.g. stored or shipped in order to be further treated at a later stage. Preferably, however, the treatment sequence is not interrupted after retanning and fatliquoring, but the substrate is further treated in the same apparatus. The substrate retanned and fatliquored according to the invention is readily and optimally suitable for each of the subsequent treatments.

By the process of the invention there may be achieved an outstanding degree of retanning and fatliquoring of the substrate at once. In particular may be achieved a surprisingly good retanning and fatliquoring, without impairing other characteristic properties of the substrate, such as quality of the leather structure (especially the grain structure), handle, dyeability, light fastness, heat fastness, fogging of the finished leathers while a subsequent treatment with any chemicals finds in the substrate retanned and fatliquored according to the invention a substrate of high suitability for even distribution of the applied products, e.g., filling agents, other (re)tanning agents, dyestuffs, pigments, leather softeners, so that dyed and/or finished leathers and pelts of optimum quality are obtainable with a high yield of the corresponding applied products.
EXEMPLARY
The following examples shall explain the instant invention in more detail. If not indicated otherwise, parts and percentages are by weight and in the Application Examples the percentages refer to the wet shaved weight of the substrate, if not otherwise indicated. The starting materials employed in Examples and the additives employed in the Application Examples further to the retanning and fatliquoring agent, are commercially available products. The water used is a soft-middle hard water (max. 13-14 °F of hardness).

I.U.C. standards mentioned in the Application Examples are international standards in leather testing as recommended in IULTCS (International Union of Leather Technologists and Chemists Societies)

PREPARATION EXAMPLES

EXAMPLE 1

196 g of oleic acid are charged in a reactor and, under stirring, 139.0 g of polyglycol 200 are added and 1.3 g methan sulfonic acid are added. The mixture is heated up to 90-105 °C under vacuum (residual pressure of 50-70 mm Hg in reactor) and maintained at that temperature for 3-4 hours distilling water (water to be destilled: 12.5 g).

323.8 g of reaction mass is cooled down to 80-90 °C and added with 34.1 g of maleic anhydride. A weak exothermic reaction takes place. Then the reaction mass is heated up to 88 - 92 °C and kept at 88 - 92 °C for 30-40 minutes.

Then within 2-3 hours the temperature of the mass is increased to 100 - 110 °C under vacuum (residual pressure in reactor is 50-60 mmHg): condensation water is destilled.

The reaction mass is then heated up to 120 - 130 °C and kept at 120 - 130 °C for 2-3 hours, destilling water. Amount of water to be destilled: 6.3 g of water.

Yield of reaction: 351.6 g
EXAMPLE 2
351.6 g of product prepared as indicated in example 1 are charged in reactor and heated to 80-90 °C and added with an aqueous solution of sodium metabisulphite and NaOH, prepared by mixing 88 parts of water with 33 parts of metabisulphite and 27.5 parts of NaOH sol. 30%.

The mixture is heated up to 85-98 °C for 2-3 hours.

EXAMPLE 3
745 g of α-olefine are charged in a dry reactor and heated up to 148-152 °C. At 140-145°C 36 g of ditert-butylperoxide are added. Then during one hour, 275 g of maleic anhydride, melted at 80-90°C, are added under nitrogen flow and at a temperature of 150-165°C. When the addition is finished the mixture is heated three hours at 155-165°C. At the end of the reaction, the polymerization product is poured into an aqueous solution pre-heated at 80°C of 320g of water and 475 g of sodium hydroxide 30% sol. The mixture is stirred one hour at 88-92°C and then cooled at 30-35°C.

EXAMPLE 4
472 g prepared as indicated in example 2 are heated at 40-50 °C and mixed with 500 g of the product obtained in example 3.

APPLICATION EXAMPLES

APPLICATION EXAMPLE A
Retanning and fatliquoring of wet blue cow leathers, thickness: 1.5-1.6 mm
(percentages are based on the shaved weight).

Wet Blue leathers (half of a leather) are given into a drum and 300 % of water at 40°C are added, followed by 0.2 % of formic acid and the drum is rotated for 15 minutes. The bath is drained. Then 150 % of water and 2 % of sodium formate and 1 % of sodium bicarbonate are added and drumming is continued for 60 minutes at 35-40 °C. The pH is increased to 5.0. The bath is drained. 200 % of water at 35°C is added and the goods are
washed for 10 minutes, then the bath is drained. 100 % of water at 40 °C, 10 % of the
instant retanning and lubricating composition are added and the drum is rotated for 60
minutes at this temperature. 0.5 % of formic acid is added and the drum is rotated for 10
minutes at 40 °C. Other 0.5 % of formic acid is added and the drum is rotated for 20
minutes 40 °C : pH is 3.6.

The bath is drained. 300 % of water at 25°C is added and the goods are washed for 10
minutes, then the bath is drained and leathers are discharged, horseh up and dried with
one of the conventionally dry system (samm/sett out/vac dry/Hang
dry/condition/stake/air off), staked for assessing the properties of the leathers and the
light, heat fastness as well as the fogging.

The leather is retanned and fatliquored very regularly, is firm, tight, soft and is
optimally suitable for further processing in the tannery. Light and heat resistances are
good, fogging values are excellent.

**APPLICATION EXAMPLE B**

Retanning and fatliquoring of wet blue cow leathers, thickness 1.1 - 1.2 mm
(percentages are based on the shaved weight).

Wet Blue leathers (half of a leather) are given into a drum and 300 % of water at 40°C
are added, followed by 0.2 % of formic acid and the drum is rotated for 20 minutes. The
bath is drained. Then 100 % of water, 2 % of a neutralising Syntan (like Tanicor AS 6),
1.5 % of sodium bicarbonate and 3.0 % of the instant composition are added and
drumming is continued for 75 minutes at 35 - 40 °C. The bath is drained. 300 % of
water at 40°C is added and the goods are washed for 10 minutes, then the bath is
drained. 100 % of water at 40 °C, 3 % of the instant retanning and lubricating
composition are added and drumming is continued for 20 minutes, 3 % of a polyacrylate
30 % sol (like Tergotan PR) is added and drumming is continued for 20 minutes, 4.0 %
of a phenol/cresol synthan (like Sandotan SG powder) and 4.0 % of TARA powder
(vegetable tanning agent) are added and drumming is continued for 30 minutes, 3 % of
Dye (Melioderm Deep Brown F) is added and drumming is continued for 60 minutes,
0.5 % of formic acid are added and the drum is rotated for 15 minutes at this
temperature, 1.0 % of formic acid is added and the drum is rotated for 30 minutes at 35 -40 °C.

The bath is drained. 200 % of water at 60 °C is added and the goods are washed for 10 minutes, then the bath is drained. 150 % of water is added and 8.0 % of the instant retanning and lubricating composition is added and the drum is rotated for 60 minutes at 60 °C. 0.5% of formic acid is added and the drum is rotated.

Then the bath is drained and leathers are discharged, horsed up and dried with one of the conventionally dry systems (samm/sett out/vac dry/Hang dry/condition/stake/air off), staked, for assessing the properties of the leathers.

The leather is retanned and fatliquored very regularly, is firm, tight, very soft and is optimally suitable for further processing in the tannery.

**APPLICATION EXAMPLE C**

Retanning and fatliquoring of wet blue caw leathers, thickness 1.5 - 1.6 mm (percentages are based on the shaved weight).

Wet Blue leather (half of a leather) are given into a drum and 200 % of water at 30°C are added, followed by 1.0 % of a wetting agent (like Tergolix W 01) and 0.5 % of acetic acid and the drum is rotated for 30 minutes. The bath is drained. Then 50 % of water at 35 °C, 5 % of Baychrom F (Chrom basic sulphate) are added and drumming is continued for 90 minutes at 35 - 40 °C. The leather is left in the bath during the night.

At the morning pH is 3.5. 100 % of water of 7°Be at 50°C and 1 % of sodium formate are added and the drum is rotated for 30 minutes. pH is 4.8. The bath is drained. 100 % of water of 7°Be at 35 °C, 1 % of sodium formiate are added and rotated for 20 minutes, 1 % of sodium bicarbonate is added and rotated for 40 minutes. pH is 5.6-5.7 . The leathers are washed with 300 % of water. The bath is drained. 100 % of water at 40 °C, 20 % of a phenol synthan 50% sol (like Syncotan MRL ) are added and drumming for 60 minutes. 1% of formic acid is added and drum is rotated for 20 minutes. The bath is drained.
50% of water is added at 20 °C, 1% of Dye (Bruno Melioderm G) is added and drum is rotated for 30 minutes. 100% of water at 50 °C, 10% of the instant retanning and fatliquoring composition is added and the drum is rotated for 60 minutes. 1% of formic acid is added and the drum is rotated for 20 minutes. The bath is drained.

200% of water at 15 °C is added and the drum is rotated for 10 minutes. The bath is drained and the leathers are discharged and dried with one of the conventionally dry system (samm/sett out/vac dry/Hang dry/condition/stake/air off), staked, for assessing the properties of the leathers.

The leather is retanned and fatliquored very regularly, is firm, tight, soft and are optimally suitable for further processing in the tannery.
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Customer: Internal
Article: Upholstery - Automotive
Raw Material: Wet Blue
Origin: LGR
Tannage: Chrome
Date: 13.07.2006

Thickness: 1.1 - 1.2 mm
Method: Direct
Colour: Brown
% Based on: Shaved weight
Trial Number: 1201

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Samm/SET OUT/Toggle DRY/CONDITION/STAKE (7+7 twice through machine)/ASSESS/MILL 24 HRS/ ASSESS
CLAIMS

1. A composition consisting of the components (A), (B) and (C) wherein
   (A) is a reaction product of an ethylenically unsaturated C₄-Cs-
       dicarboxylic anhydride with C₃-C₄-o-alpha-olefins followed by partial
       or total neutralisation with a base, in aqueous dispersion with or
       without solvents,
   (B) is a reaction product of ethylenically unsaturated C₄-Cs-dicarboxylic
       anhydrides with C₁₀-C₄₀-fatty acids or C₄-C₃₀ polycarboxylic acids or
       C₁₀-C₄₀ fatty alcohols or oxo-alcohols or glycols or polyglycols or C₃-
       C₂₀ organic amines all being saturated or unsaturated, linear or
       branched and the fatty acids being ethoxylated and/or propoxylated or
       having been reacted with polyglycols or glycols, and the
       polycarboxylic acids being ethoxylated and/or propoxylated or having
       been reacted with polyglycols or glycols at least with one carboxylic
       group, and
   (C) is a reaction product of (B) with bisulphite or metabisulphite or
       sulphite or sulphuric acid or oleum, followed by partial or total
       neutralization with a base where the base is an alkali or earth alkali
       hydroxide, ammonia or an organic amine in aqueous dispersion with
       or without solvents.

2. Composition according to claim 1 wherein
   in the component (A) a part of the anhydride groups are reacted with alcohols,
   polyalcohols, glycols or organic amines, or ammonia
   in the component (B) the fatty alcohols or oxo-alcohols and the fatty amines have
   been ethoxylated and/or propoxylated, and the glycols or polyglycols have
   been reacted with other carboxylic acids or C₄-C₃₀ polycarboxylic acids or
   derivates of carboxylic or polycarboxylic acids.

3. Composition according to claim 1 or 2 wherein
   in the component (A) the dicarboxylic anhydride is maleic anhydride and the
   alpha-olefins have a chain length of 12 to 30 C-atoms and the base is
ammonia, an amine or an alkali or earth alkali hydroxide in aqueous dispersion with or without solvents,
in the component (B) the dicarboxylic anhydride is maleic anhydride, and the fatty acids or fatty alcohols or oxo-alcohols have a chain length of 12 to 30 C-atoms and are ethoxylated/propoxylated with 2-25 mol of EO/PO or the fatty acids are reacted with polyglycols 100-1200, and the component (C) is a reaction product of (B) with sodium bisulphite carried out in aqueous medium.

4. Composition according to claim 3 wherein
in the component (A) the alpha-olefins have a chain length of 18 to 24 C-atoms and the base is NaOH,
in the component (B) the fatty acids or fatty alcohols or oxo-alcohols have a chain length of 12 to 20 C-atoms and have one or more double bonds, and the fatty acids and fatty alcohols or oxo-alcohols have been ethoxylated.

5. Composition according to claim 4 wherein
in the component (B) the fatty acids have been reacted prior to the reaction with maleic anhydride with polyethylene glycols or glycols.

6. Composition according to claim 3 or 4 wherein
in the component (A) the alpha-olefins have a chain length of 20 to 22 C-atoms, in the component (B) the fatty acid is oleic acid and wherein the polyethylene glycol is a polyethylene glycol of the formula HO(CH₂CH₂O)ₙH with an average number of n from 2 to 25.

7. Composition according to any of the preceding claims wherein the molar ratio of (A):[(B) + (C)] is from 5:100 to 100:5 and the molar ratio from (B):(C) is from 5:100 to 100:5.

8. Composition according to claim 7 wherein the molar ratio of (A):[(B)+(C)] is from 50:100 to 100:50, and the molar ratio from (B):(C) is from 20:100 to 100:20.
9. Composition according to any of the preceding claims, further comprising amides and esters of the component (A).

10. Composition according to any of the preceding claims, further comprising at least one formulation additive (S) selected from

   • water or an organic solvent or mixture and/or solubiliser or mixture miscible with or soluble in (A) and (B) and (C) or in which (A) and (B) and (C) are soluble,
   • a defoamer,
   • a natural or mineral oil,
   • a surfactant,
   • a lecithine and
   • a biocide.

11. Process for producing a composition according to claim 1 by mixing the components (A), (B) and (C) and optionally adding any formulation additive (S).

12. Use of a composition according to claims 1 to 10 for retanning and fatliquoring of pelts, skins, hides, leather intermediate products or non-finished leather.

13. A process for retanning or fatliquoring of pelts, skins, hides, leather intermediate products or non-finished leather comprising a treatment with a composition according to any of claims 1 to 10.
A. CLASSIFICATION OF SUBJECT MATTER
INV. C14C9/02 C14C3/28

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 CIOL

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C

See patent family annex

Special categories of cited documents
'A' document defining the general state of the art which is not considered to be of particular relevance
'E' earlier document but published on or after the international filing date
'L' document which may throw doubts on novelty claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
'O' document referring to an oral disclosure, use, exhibition or other means
'P' document published prior to the international filing date but later than the priority date claimed
'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
'X' document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
'Y' document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
'Z' document member of the same patent family

Date of the actual completion of the international search
17 March 2009

Date of mailing of the international search report
30/03/2009

Name and mailing address of the ISA/A
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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