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(54) **TREATMENT OF LEATHER INCLUDING EMPLOYING PECTIN**

BEHANDLUNG VON LEDER, BEINHALTEND DIE ANWENDUNG VON PEKTIN

TRAITEMENT DU CUIR COMPRENANT L'APPLICATION DE LA PECTINE

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EP 3 775 293 B1

Description**Field of the invention**

5 [0001] The present invention is in the field of leather manufacturing.

Background of the invention

10 [0002] Leather is a versatile material for many applications. Leather manufacturers are concerned with tailoring the leather towards this great variety of applications. Moreover, the raw hides that form the basis for leather manufacturing are from natural origin and therefore contain defects and natural variations. There also lies a challenge to valorize these raw materials to the maximum, despite these defects and natural variation. Moreover, as consumer preferences are constantly under development, there is also a need to apply or develop new colors, appearances and textures.

15 [0003] To meet these demands, leather manufacturing comprises a process with many possibilities to tailor the product. Variations in raw hides, processing and choice of chemicals enable the leather manufacturer to produce a great variety in end products. Although the process of leather production is versatile, the essence of leather making lies in preserving skins or pelts from putrefaction and further adjustments to meet the demands of the end-users. To do so, pre-treated hides are tanned, predominantly with metal ions such as chromium (III) ions but several alternatives (including vegetable tanning and synthetic reactive tanning using aldehydes) are also applied. The tanning agents interact with the skin collagen, wherein different classes of tanning agent provide different mechanisms of interaction.

20 [0004] The tanned leather is often not yet suitable for its end application; the uniformity, organoleptic, mechanical and/or other physical properties still need to be adjusted and optimized. Usually several treatment stages after tanning are employed to modify and further differentiate the leather and make the leather suitable for its end-use. These treatment stages include the employment of chemicals that may result in polluted waste-water streams and undesirable emissions during leather's lifecycle.

25 [0005] One group of chemicals that is regularly used in leather processing is synthetic petro-based compounds, such as vinyl polymers. With these compounds being synthetic, toxicity and environmental issues are largely associated with a combination of their petro-chemical nature and manufacturing process. Their carbon footprint is considerable and toxic monomers are used for their manufacturing. Moreover, as generally these polymer compounds are largely not biodegradable, they are undesirable compounds in the waste streams of leather manufacturing plants and may cause emission problems during leather's life-cycle.

30 [0006] In EP 2110446 A1 a method for retanning hides and skins with cider apple waste is described.

Summary of the invention

35 [0007] There is a continuous need for providing more sustainable manufacturing processes. There is also a need to make leather and leather production more sustainable, to lower the environmental impact of leather and the leather manufacturing process and to reduce the usage of toxic compounds during leather manufacturing and to reduce the amount of toxic emissions from the leather.

40 [0008] There is a continuous need for providing compounds that can be used to optimize leather performance.

[0009] There is also a need to replace synthetic petro-based compounds employed for leather manufacturing with compounds with lower environmental impact and lower toxic burden.

[0010] There is also a need to replace synthetic petro-based compounds employed for leather manufacturing with compounds with improved properties towards leather performance.

45 [0011] The inventors now surprisingly found that the above needs can be met by employing pectin in the leather manufacturing process and in the leather intermediate and end product. It was surprisingly found that through employing pectin in the leather manufacturing process, leather end products can be obtained having surprisingly good organoleptic properties and/or mechanical and/or other physical properties. Especially the grain appearance, evenness of dyeing, dyeing intensity, grain tightness, softness, fullness, milling pattern and evenness of milling grain can be optimized towards specific needs. Moreover tear strength can be improved. Also excellent levels of light fastness, heat yellowing and fogging can be obtained. Pectin is also found suitable for the manufacturing of waterproof articles.

50 [0012] It was also found that pectin can replace synthetic petro-based compounds such as vinyl polymers during leather manufacturing and in the leather intermediate and end product. In this way chemicals with a high environmental impact and which need toxic chemicals for producing are replaced with a natural and biodegradable material. Moreover in this way leather products comprising less poorly degradable chemicals can be produced; as can be deduced from biochemical oxygen demand (BOD) measurements. The leather product benefits related to the synthetic petro-based compounds, which are in the area of organoleptic and/or mechanical and/or other physical leather properties, can be realized by replacing these compounds with pectin. Pectin is also found suitable for the manufacturing of waterproof

articles.

[0013] Next to that it was found that replacing vinyl polymers with pectin even result in improved leather performance, for example in grain appearance, evenness of dyeing, dyeing intensity, grain tightness, softness, fullness, milling pattern and evenness of milling grain.

[0014] Also it was found that the chemical oxygen demand (COD) of waste water streams during leather manufacturing can be reduced while the biological oxygen demand (BOD) of waste water streams can be increased resulting in improvements in BOD/COD in comparison to values obtained from the use of vinyl polymers, so rendering a better quality waste water and giving an improved uptake in the leather. Pectin derivatives also do not contribute to emission problems of leather itself such as formaldehyde emission.

[0015] Moreover, as the pectin does not need to be food-grade to be applied in leather and leather manufacturing, the invention provides the possibility to valorize currently low-value pectin-rich waste streams, as for example the pectin-rich beet pulp waste stream of sugar production from sugar beets or the pectin-rich coffee pulp waste stream. As such waste streams may be relatively cheap, the invention also may provide a more cost efficient alternative for vinyl polymer compounds in leather manufacturing.

[0016] To obtain these benefits pectin is employed as an aqueous solution during post-tanning.

Detailed description of the invention

[0017] The invention concerns a method for treatment of leather, comprising providing leather and contacting the leather with an aqueous phase comprising pectin, wherein the leather is tanned leather, and wherein the pectin has a peak molecular weight from 1 to 300 kDa, wherein the peak molecular weight is the molecular weight of the highest peak in the molecular weight distribution.

[0018] The invention also concerns leather comprising pectin, preferably leather impregnated with pectin, wherein the pectin has a peak molecular weight from 1 to 300 kDa, wherein the peak molecular weight is the molecular weight of the highest peak in the molecular weight distribution.

[0019] Furthermore the invention concern a treated leather obtained by the method for treatment of leather. Also the invention concerns a product, such as a shoe, car upholstery, furniture upholstery, bag, garment and/or accessories comprising the treated leather or the leather comprising pectin.

Pectin

[0020] Pectins are complex polysaccharides which are found in every plant, in which their function is to give strength to the cell walls, and to adhere the cells together. Pectins belong to the class of acid oligosaccharides, which are polysaccharides comprising at least one acidic group selected from the group consisting of N-acetylneuraminic acid, N-glycolylneuraminic acid, free or esterified carboxylic acid, sulfuric acid group and phosphoric acid group.

[0021] The primary structure of pectin is homogalacturonan (HG), which is a linear chain of α -(1,4)-linked D-galacturonic acid (GalA) residues. Branches of neutral mono-, oligo- and/or polysaccharides are present on the HG backbone. The linear backbone may be intermittent with rhamnogalacturonan type I (RG-I), a copolymer of rhamnose and α -(1,4)-linked D-galacturonic acid, resulting in a alternating block copolymer structure comprising RG-I and HG. Also RG-I may comprise branches of neutral mono-, oligo- and/or polysaccharides. As there is a large variety in pectins, pectin is characterized as all oligosaccharides and polysaccharides with more than 40 % w/w GalA based on saccharide monomer units. Hence the invention concerns the use of oligosaccharides and polysaccharides with more than 40 % w/w GalA based on saccharide monomer units.

[0022] Pectin can be extracted from various types of plants. When the word pectin is used in this document, pectin refers to extracted pectin. Extracted pectin is to be distinguished from modified pectin, which is chemically, physically or enzymatically modified to alter its properties after extraction. Extracted pectin is also to be distinguished from native pectin, which is pectin before extraction. Typical modifications are methoxylation or de-methoxylation, amidation or (partial) depolymerization.

[0023] During extraction the native pectin may be altered, for example because the extraction is performed under acidic or caustic conditions. In the context of the current invention, these alterations during extraction do not result in modified pectin; upon extraction extracted pectin is obtained. As known in the art extraction commonly comprises one or more solid/liquid separation steps, filtration steps and/or water removal steps and/or combinations thereof. These steps (further) separate the pectin from the plant materials and concentrate the pectin.

[0024] Pectin is commercially mainly extracted from citrus fruit, apples or sugar beet, which yields citrus pectin, apple pectin or sugar beet pectin. On commercial scale pectin is also known to be extracted from sunflower head residues, mango peel, yellow passion fruit rind, coffee pulp and cashew apple pomace, which yields sunflower pectin, mango pectin, yellow passion fruit pectin, coffee pectin and cashew apple pectin. Preferably according to the present invention, the pectin is selected from the group of citrus pectin, sugar beet pectin, apple pectin, sunflower pectin, mango pectin,

yellow passion fruit pectin, coffee pectin and cashew apple pectin; more preferably the pectin is selected from the group of citrus pectin, sugar beet pectin and apple pectin even more preferably from the group of citrus pectin and sugar beet pectin, most preferably the pectin is sugar beet pectin. Also mixtures of pectin from different origin may be used. Origin of pectin in the context of this document refers to the plant the pectin is extracted from. In one embodiment a combination of two or more different pectins is applied selected from the group of citrus pectin, sugar beet pectin, apple pectin, sunflower pectin, mango pectin, yellow passion fruit pectin, and cashew apple pectin.

[0025] Preferably according to the present invention the pectin is not fruit pectin, more preferably the pectin is not apple pectin, most preferably the pectin is not derived from cider apples.

[0026] Pectin can be divided into two main categories: high methoxylated pectin (HM), which is characterized by a degree of methoxylation above 50% and low methoxylated pectin (LM) having a degree of methoxylation below 50%. As used herein, "degree of methoxylation" (also referred to as DE or "degree of esterification") is intended to mean the extent to which free carboxylic acid groups contained in the homogalacturonan chain have been esterified (e.g. by methoxylation or ethoxylation).

[0027] Under certain circumstances and in one embodiment according to the present invention the pectin is preferably high methoxylated pectin (HM). However, under different circumstances and in another embodiment according to the present invention the pectin is preferably low methoxylated pectin (LM). In one embodiment the pectin is preferably characterized by a degree of methoxylation above 20%, preferably above 35%, more preferably above 50%, even more preferable above 60% most preferably above 75%. In one embodiment the pectin is preferably characterized by a degree of methoxylation below 75%, preferably below 65%, more preferably below 50%, even more preferable below 35% most preferably below 25%. In one embodiment the pectin is preferably characterized by a degree of methoxylation from 10% to 90%, preferably from 25% to 75%, more preferably from 35% to 65%, even more preferable from 50% to 65%.

[0028] Methoxylation affects the charge on the pectin and may therefore influence leather penetration and interaction with the collagen. High methoxylated pectin therefore may diffuse more rapidly in the leather matrix resulting in higher uptake, shorter processing times and optimal organoleptic and mechanical properties. Moreover, due to the lower electrostatic interaction high methoxylated pectin may be better suitable as a filler and for use during fatliquoring. Low methoxylated pectin on the other hand, may interact to a higher extent with the collagen and therefore induce improved mechanical and organoleptic properties.

[0029] The pectin may also be amidated giving pectin with a certain "degree of amidation" or amidated pectin. During amidation galacturonic acid is converted with ammonia to carboxylic acid amide. As used herein, "degree of amidation" (also referred to as DA) is intended to mean the extent to which free carboxylic acid groups contained in the homogalacturonan chain have been amidated.

[0030] Under certain circumstances and in one embodiment according to the present invention the pectin is preferably amidated. However, under different circumstances and in another embodiment according to the present invention the pectin is preferably not amidated. In one embodiment the pectin is preferably characterized by a degree of amidation above 10%, preferably above 20%, more preferably above 30%. In one embodiment the pectin is preferably characterized by a degree of amidation below 40%, preferably below 30%, more preferably below 20%, most preferably below 10%. In one embodiment the pectin is preferably characterized by a degree of amidation from 5% to 50%, preferably from 10% to 40%, more preferably from 15% to 30%, even more preferably from 15% to 25%.

[0031] Amidation provides additional possibilities in tuning the charge or charge density on pectin and thus its interactions with collagen accordingly. In this way organoleptic and mechanical properties can be optimized. Moreover amidation can be especially advantageous for reduction of reducing the effluent COD.

[0032] Pectin has a molecular weight distribution. A molecular weight distribution describes the relationship between the number of moles of each polymer species (N_i) and the molar mass (M_i) of that species. The molecular weight distribution can be measured by chromatography as size exclusion chromatography. Representative molecular weight values as the weight-average molecular weight (M_w), number average molecular weight (M_n), minimum molecular weight, maximum molecular weight, molecular weight range and/or peak molecular weight can be derived from the molecular weight distribution. The representative molecular weight may be expressed in Da (Dalton) or in kg/mol (kilogram / mol). The peak molecular weight is the molecular weight of the highest peak in the molecular weight distribution. The molecular weight range is the range from the minimum molecular weight to the maximum molecular weight.

[0033] According to the present invention, the pectin has a peak molecular weight lower than 300 kDa, preferably lower than 200 kDa, more preferably lower than 100 kDa, even more preferably lower than 50 kDa, even more preferably lower than 25 kDa most preferably lower than 10 kDa. In one embodiment according to the present invention, the pectin preferably has a peak molecular weight higher than 2.5 kDa, more preferably higher than 10 kDa, even more preferably higher than 25 kDa, even more preferably higher than 50 kDa most preferably higher than 100 kDa. In one embodiment according to the present invention, the pectin has a peak molecular weight from 2.5 kDa to 300 kDa, more preferably from 5 kDa to 200 kDa, even more preferably from 10 kDa to 150 kDa, even more preferably from 10 kDa to 100 kDa most preferably from 25 kDa to 50 kDa.

[0034] According to the present invention in another embodiment, the pectin preferably has a molecular weight range

from 250 Da to 1000 kDa, more preferably from 500 Da to 750 kDa, even more preferably from 500 Da to 500 kDa, even more preferably from 750 Da to 250 kDa, even more preferably from 1000 Da to 150 kDa.

[0035] A relatively low molecular weight may improve diffusion into the leather, resulting in higher uptake, shorter processing times and optimal leather properties as mechanical strength and organoleptic properties. A relatively high molecular weight may improve the binding to the collagen, inducing optimal leather properties as mechanical strength and organoleptic properties. Moreover a relatively high molecular weight may improve the filling properties, and therefore in that way improve the organoleptic properties of the leather.

[0036] The pectin may also be partially depolymerized pectin. By partially depolymerizing, molecular weight of the extracted pectin is reduced by cleaving part of the glycosidic linkages. The molecular weight distribution will change upon partially depolymerizing, represented by a lower weight-average molecular weight (Mw), lower number average molecular weight (Mn), lower peak molecular weight, lower minimum molecular weight and/or lower maximum molecular weight. Partial depolymerization may be induced by enzymatic treatment, acid hydrolysis, hydrothermal processing, high shear processing and/or by photo-chemical reactions.

[0037] Opposite to the other mentioned types of depolymerization, enzymatic depolymerization is very specific in the sense that enzymes only target specific bonds. So by enzymatic partial depolymerization the depolymerization can be optimally controlled. For example endo polygalacturonase only breaks the GalA - GalA bond in the homogalacturonan backbone.

[0038] Also opposite to the other mentioned types of depolymerization, enzymatic depolymerization generally induce no other reactions (as for example de-methoxylation) except for the desired cleavage of the glycosidic linkage, so apart from the partial depolymerization the pectin stays intact and possible undesired side-reactions are prevented. Moreover enzymatic depolymerization generally takes place under mild conditions. In general, the non-enzymatic methods results in either high amounts of chemical waste (acid/salt), substantial energy consumption, unspecific degradation of polysaccharides and partial breakdown of monosaccharides released. Therefore, non-enzymatic processes are usually undesired. Typical enzymes for partially depolymerizing pectins are pectinesterase, polygalacturonase, pectate lyase, pectin acetylsterase, β -galactosidase and arabinosidase, resulting in partially depolymerized pectin by pectinesterase, polygalacturonase, pectate lyase, pectin acetylsterase, β -galactosidase and/or arabinosidase. The enzymatically partially depolymerization may target a specific part of the pectin, for example the homogalacturonan (HG) backbone. Depending on the specific enzyme the glycosidic linkages of the pectin may be hydrolyzed or may undergo beta-elimination. A partially enzymatically depolymerized pectin for which the glycosidic linkages are hydrolyzed is a partially enzymatically hydrolyzed pectin.

[0039] In one embodiment, the pectin preferably is partially depolymerized pectin. Preferably for this embodiment the pectin is partially depolymerized pectin with a molecular weight as defined in one of the preceding paragraphs. In one embodiment, preferably the pectin is partially depolymerized pectin selected from the group of partially acid hydrolyzed pectin, partially enzymatically depolymerized pectin, partially hydrothermally depolymerized pectin, partially high shear depolymerized pectin and partially photo-chemically depolymerized pectin, more preferably the pectin is selected from the group of partially acid hydrolyzed pectin and partially enzymatically depolymerized pectin, even more preferably the pectin is partially enzymatically depolymerized pectin. In one embodiment preferably the partially enzymatically depolymerized pectin is a partially enzymatically hydrolyzed pectin. In one embodiment preferably the partially enzymatically hydrolyzed pectin is a partially enzymatically hydrolyzed pectin by pectinesterase or polygalacturonase or both.

[0040] Partial depolymerizing results in pectin with a lower molecular weight and therefore may improve diffusion into the leather, making partially depolymerized pectin especially suitable for post tanning. A higher uptake, shorter processing times and optimal leather properties as mechanical strength and organoleptic properties are foreseeable as pectins with lower molecular weight diffuse more rapidly in the leather.

[0041] In one embodiment according to the present invention a combination of different pectins is applied. In one embodiment a combination of different pectins that differ in structure is applied, for example partially depolymerized pectin with amidated pectin.

[0042] It will be understood by the skilled person that depending on the circumstances, the preferred pectin may be HM pectin and amidated or LM pectin and amidated; the preferred pectin may also at the same time be partially depolymerized. It will also be understood by the skilled person that depending on the circumstances, the preferred pectin may also be characterized by a certain range of degree of methoxylation and a certain range of degree of amidation and a certain range of molecular weight. It will also be understood by the skilled person that depending on the circumstances, preferably a combination of the above pectins is used.

[0043] The pectin preferably is provided as an aqueous phase comprising pectin. Preferably the pectin is dissolved and/or emulsified and/or suspended and/or dispersed in the aqueous phase, resulting in an aqueous phase comprising dissolved pectin and/or an aqueous phase comprising emulsified pectin and/or an aqueous phase comprising suspended pectin and/or an aqueous phase comprising dispersed pectin or in other words resulting in dissolved pectin and/or emulsified pectin and/or suspended pectin and/or dispersed pectin.

[0044] Preferably no preservative is present in the aqueous phase, more preferably no preservative selected from the

group consisting of a biocide, a fungicide and a combination thereof is present in the aqueous phase.

[0045] In an embodiment of the invention the aqueous phase comprises from 0.1 to 10 wt.% pectin, preferably from 0.2 to 5 wt.%, more preferably from 0.4 to 2 wt.%. In an embodiment of the invention the weight ratio pectin to tanned leather ranges from 0.001 to 0.1, preferably from 0.002 to 0.05, more preferably from 0.004 to 0.02.

Compounds for leather manufacturing

[0046] In conventional leather manufacturing, usually vinyl polymers are employed. Vinyl polymers are characterized by that they are obtained from vinyl monomers through addition polymerization. Typical vinyl polymers employed for leather are homo- or co- polymers of polyacrylate and polymethacrylate. Various vinyl polymer compounds have been routinely used in leather post-tanning processes and are known to diffuse in the leather or to impregnate the leather. Vinyl polymers may be used in any of the post-tanning steps, moreover, in some case repetitive addition in different steps strengthens the effect of the vinyl polymer. Vinyl polymers may interact with the leather matrix through electrostatic interactions, which is generally particularly effective in the case of mineral tanned leather. When applied during post-tanning, vinyl polymers contribute amongst others to grain appearance, evenness of dyeing, dyeing intensity, grain tightness, softness, fullness, milling pattern, evenness of milling grain and thermal stability of the crust leather.

[0047] With the vinyl polymers being synthetic, toxicity and environmental issues are largely associated with a combination of their petro-chemical nature and manufacturing process. Also they are generally not biodegradable.

Leather manufacturing

[0048] Leather manufacturing starts with raw hides (or furs) and generally has four stages referred to as beamhouse, tanning, post-tanning and finishing. Each stage usually has several steps. After the tanning, tanned leather is obtained, after post-tanning crust leather is obtained and after finishing finished leather is obtained. During or at the end of each step the leather may be dried to a desirable moisture content. Crust leather does not necessarily always need to undergo finishing; for some applications crust leather is directly applied in an end-product. As leather manufacturing concerns turning raw hides into material resistant to putrefaction and tanning is the essential step for this transformation, leather as understood by the skilled person is tanned leather. So in the context of the current invention leather is tanned leather. Crust leather and finished leather are consequently a form of tanned leather.

[0049] Beamhouse operations prepares raw hides for tanning by removing all non-collagenous materials from the hides through a series of treatments that may include soaking, (green) fleshing, unhairing, liming, lime splitting, deliming, bating, degreasing and pickling. Tanning protects the hides from putrefaction when wet and improves the mechanical properties. Tanning transforms hides into tanned leather. During the tanning process tanning agents penetrate the hides and interact with collagen. Most commonly, hides are tanned with chromium salts, but several alternatives exist. Tanned leather tanned with chromium is often called wet-blue (WB) leather, whilst tanned leather tanned with aldehyde is often called wet-white (WW) leather.

[0050] In one embodiment of the invention the leather is wet-blue leather. In another embodiment of the invention the leather is wet-white leather. Leather is a product that is well-known in the art. Leather may also be understood to comprise man-made materials using tissue engineering and biotechnology to produce bio-materials with composition and properties similar to natural animal made leather as for example described in US 2014/0259439.

[0051] Tanned leather is sorted and mechanically processed (e.g. split, shaved), before post-tanning starts. During post-tanning leather's organoleptic properties are significantly improved and largely defined. The above mentioned post-tanning, like tanning, is a wet process in which leather is submerged in an aqueous phase and specific components penetrate in the leather and alter its properties. In other words, the leather is impregnated with the specific components. Post-tanning comprises several steps that are sequentially or (partially) simultaneously performed. Since post-tanning is specifically aimed to tailor the final leather properties and there is a need of a wide variety of properties, and since there is a large variety in tanned leather and each variant of tanned leather may need a specific post-tanning treatment the leather manufacturer makes a selection of the steps to be carried out, the types of chemicals used during these steps and the specific conditions as well as order of the steps.

[0052] Typically during post-tanning, or during post-tanning steps, different (combinations of) chemicals are sequentially added to the aqueous phase at specific time intervals. If needed the aqueous phase is drained and fresh water or a new aqueous phase is added. The following post-tanning steps are commonly applied:

Neutralizing: during neutralizing the pH of the tanned leather is adjusted.

(continued)

Retanning: During retanning one or more compounds are added that diffuse in the leather and interact with collagen. Retanning among others (further) strengthens the collagen structure; improves the overall organoleptic properties such as softness and fullness; fills the loose and empty parts of the leather thus improve the evenness and general cutting value; improves buffing properties and grain appearance. Mineral retanning such as rechroming is a retanning step.

Dyeing: During dyeing a dye is added which penetrates the leather and gives the leather a uniform shade of color.

Fatliquoring: during fatliquoring an oil or fat emulsion is provided, the oil or fat penetrates the leather and interacts with the collagen fibers. Fatliquoring aims at lubricating collagen fibers, preventing the fiber structure sticking together during drying, and to render specific characteristics (e.g. organoleptic, mechanical and/or waterproof properties).

[0053] These steps may also be combined, for example neutralizing and retanning, neutralizing and dyeing, neutralizing and fatliquoring, retanning and dyeing, retanning and fatliquoring, dyeing and fatliquoring, retanning and dyeing and fatliquoring or neutralizing and retanning and dyeing and fatliquoring. These steps may also be repeated, for example retanning and/or dyeing may be performed more than one time.

[0054] After the post-tanning the tanned leather is named crust leather. The crust leather may undergo surface treatments called finishing. Finishing not only renders leather grain protection against water and soiling, but also determines the appearance of the final surface of the leather and the surface properties such as flexibility and handle and/or permeability. Mechanical operations as well as coatings can be applied through common application methods such as padding, spray coating, roller coating or curtain coating.

[0055] In the context of the present invention, contacting the leather with an aqueous phase can be understood as submerging the leather in an aqueous phase.

[0056] In an embodiment of the invention contacting the leather with an aqueous phase comprising pectin is carried out for a time period that ranges from 10 to 1500 minutes, preferably from 20 to 500 minutes, more preferably from 20 to 250 minutes. In an embodiment contacting the leather with an aqueous phase comprising pectin is carried out at a temperature that ranges from 10 to 95 °C, preferably from 20 to 75 °C, more preferably from 25 to 55 °C. In an embodiment contacting the leather with an aqueous phase comprising pectin is carried out during one or more selected from the group consisting of neutralization, retanning, dyeing and fatliquoring.

[0057] The organoleptic and mechanical properties of the leather can be tailored by applying pectin at a specific post-tanning step, at a specific temperature or during a specific time period.

[0058] During post-tanning leather is in contact with an aqueous phase. Chemicals (among which polymers such as vinyl polymers and pectin) dissolved in the aqueous phase diffuse into the leather and interact with the collagen changing the leathers properties. Grain appearance, evenness of dyeing, dyeing intensity, grain tightness, softness, fullness amongst others may be altered. These organoleptic properties relate to the collagen structure and can only be altered by chemicals that diffuse into the leather. Also mechanical parameters such as tensile strength may be affected by chemicals that diffuse into the leather. As these mechanical parameters concern bulk properties of the leather, inevitably they only are altered when chemicals diffuse into the leather. Presence of chemicals in the leather can be demonstrated through commonly known methods as selective staining of a cross section and subsequent visual identification or through extraction from leather and chemical identification. Also a mass balance can be established over one or more post-tanning steps to establish impregnation of the leather by determining the concentration in the waste water and the total amount of waste water and comparing this with the amount added. Concentrations of organic material in the waste water may be established through COD or BOD measurement and may be related to uptake, as for example is described by Von Behr (Universal Journal of Materials Science, 6(1), 20-26, 2018). In the context of the present invention it is understood that leather is impregnated with a specific chemical when a specific chemical, for example pectin is present along a cross-section of a piece of leather. In an embodiment of the invention leather is impregnated with pectin if pectin is present at a length perpendicular to the surface of a cross section of the leather of more than 5% (length/length) of the total length of the cross section measured from the surface of the cross section, more preferably 10%, even more preferably 30%. In an embodiment of the invention the leather comprising pectin comprises at least 0.1 wt.% pectin, more preferably at least 0.2 wt.% pectin, even more preferably at least 0.4 wt.% pectin, most preferably at least 0.8 wt.% pectin, wherein the wt.% is calculated based on the weight of the leather.

Characterization

[0059] Leather can be characterized by its organoleptic properties, its mechanical properties and its physical properties.

For all of these properties the measurement methods are known in the art ('Tanning Chemistry: the Science of Leather' (Covington), RSC Publishing (2009), 'Pocket Book for the Leather Technologist' (Heidemann), BASF 4th edition, 'Fundamentals of Leather Manufacture', Eduard Roether KG (1993)). Also several standardized measurement methods are common in the art. Typical organoleptic properties are grain appearance, evenness of dyeing, dyeing intensity, grain tightness, softness, fullness, milling pattern and evenness of milling grain. Typical mechanical properties are the maximum force (F max (N)), tensile strength (Tn (N/mm²)) and elongation at break (Eb (%)). Typical physical properties are fogging behavior, formaldehyde emission, light fastness, heat yellowing and waterproofness.

[0060] Leather or leather chemicals may also be assessed for their biodegradability by for example BOD measurement. Waste water generated during leather processing may be analyzed for chemical oxygen demand (COD), which is a measure for all organic material in the waste water. Waste water generated during leather processing may also be analyzed for biological oxygen demand (BOD), which is a measure for all biodegradable organic material in the waste water. A high ratio of BOD/COD is desired, since in that case more of the organic material in the waste stream will be biodegradable.

Examples

Materials and methods

Pectins

[0061] Two commercial citrus pectins, CT 01 (low methoxyl) and CT 02 (amidated), and one sugar beet pectin SB 01 (high methoxyl) were obtained. All of these pectins were extracted and processed at the supplier. The pectins were not enzymatically treated at the supplier. For the leather application tests, these pectins were used without modification (unmodified pectin) and with modification (enzymatic hydrolysis and/or de-methoxylation) resulting in partially enzymatically hydrolyzed pectin, de-methoxylated pectin or partially enzymatically hydrolyzed de-methoxylated pectin.

Table 1: Unmodified pectin samples used in this study.

Pectin	Source	Degree of methoxylation [%]	Degree of amidation [%]	remarks
CT 01	citrus	37-38	-	low methoxyl
CT 02	citrus	29-30	21	amidated
SB 01	sugar beet	54-65	-	high methoxyl

Enzymes

[0062] Endo-polygalacturonase M2 (*Aspergillus aculeatus*), a pectin hydrolysing enzyme, was obtained from Megazyme. Novoshape (Novozymes) was used for the de-methoxylation of pectin.

Pectin hydrolysis

[0063] 2.5% solution of pectin CT 01 and 5% (w/w) solutions of the samples CT 02 and SB 01 were prepared and subjected to hydrolysis at 40°C by endo polygalacturonase (26 µL of ~ 650U/mL) at pH 5.5 for 2 hours, after which the enzyme was deactivated by heating the solution for 5 minutes at 95°C.

De-methoxylation of hydrolyzed sugar beet pectin

[0064] After the above hydrolysis step, Novoshape is used for further de-methoxylation of sugar beet pectin SB 01 to achieve methoxylation degrees of -50% and -100% relative to the initial degree of methoxylation. Starting from a 10 wt. % partially enzymatically hydrolyzed pectin solution of 1500 mL, 6 mL (for 100% de-methoxylation) or 100 µL (for 50% de-methoxylation) of Novoshape was added respectively. The reaction is carried out at 40°C while NaOH (2M) is used to maintain the pH at 5.2. 100% de-methoxylation is determined when no more NaOH is needed for pH adjustment any more, where 50% methoxylation is determined when 50% of the above consumed volume for 100% de-methoxylation has been added.

Mw determination

[0065] Samples were analyzed for molecular weight distribution using a Dionex UltiMate 3000 HPLC system (ThermoFisher Scientific, Breda, The Netherlands) equipped with three columns connected in series: TosoH Bioscience TSK-GEL AW4000, TosoH Bioscience TSK-GEL AW3000 and TosoH Bioscience TSK-GEL AW2500 (all 6 × 150 mm). The columns were preceded with a guard column (TosoH Bioscience TSK AW-L (4.6 × 35 mm)). The columns were conditioned at 55 °C. Sodium nitrate (0.2 M) was used as eluent at a flow rate of 0.6 mL/min and the injection volume was 20 µL. An UV-VIS detector operating at 260, 280 and 310 nm was used together with a refractive index detector (2414R, Waters).

Table 2: Molecular weights of the pectins used.

Pectin	Mw native pectin (Da)		Mw hydrolyzed pectin (Da)	
	<i>peak</i>	<i>range</i>	<i>peak</i>	<i>range</i>
CT 01	90k	2k-200k	5k	600-30k
CT 02	-	-	18k	1k-90k
SB 01	110k	700-700k	40k	-

Organoleptic analysis

[0066] Leather samples were assessed by a trained panel of at least 4 panelists. The leather was assessed for grain appearance, evenness of dyeing, dyeing intensity, grain tightness, fullness and softness. To do so, the leather samples were compared with a reference piece and scored. A positive value (+, ++ or +++) represents an improved performance for the leather sample on a specific parameter compared to the reference piece, a negative value (-, --, or ---) represents lower performance; a '+' represents an equal performance. '+' is a higher score than '-', '++' is a higher score than '+', '+++ is a higher score than '++'. '-' is a lower score than '+', '--' is a lower score than '-', '---' is a lower score than '--'.

Waste water analysis

[0067] Waste water streams of the relevant post-tanning treatments were analyzed for chemical oxygen demand (COD) according to the method ISO 15075/ISO 6060 Tubes: Macherey - Nagel.

[0068] The uptake/exhaustion of chemicals have been checked after the relevant application step(s) in each leather application example according to method described in D. von Behr, "Method for Determining the Optimized Exhaustion of Fatliquors to Minimize the ETP-in flow", Universal Journal of Materials Science, 6(1), 20-26, 2018. All COD values from the leather application examples in this document indicate sufficient uptake of pectins, which is comparable to that of the reference(s).

Biodegradability

[0069] The biodegradability of pectin SB 01 has been measured in a manometric respirometry test according to the method OECD 301F on a 50.0 mg/L sample over a 28-day period. The sample was found to be ready and completely biodegradable and not toxic to activated sludge at the tested concentration.

*Leather application examples*Example 1

[0070] Wet-blue (WB) bovine leather (thickness 1-2mm) is treated according to the basic recipe according to table 3, where 1.5 % (based on shaved weight of WB) of either unmodified citrus pectin CT 02, unmodified sugar beet pectin SB 01 or a synthetic derivate (Syntan RS 540 from Smit&zoon) is applied after mineral retanning and neutralization during the retanning process, just before the addition of phenolic retanning agents and dyestuff.

Table 3: Post-tanning recipe of example 1.

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight tanned leather</i>		°C	<i>minutes</i>	-

EP 3 775 293 B1

(continued)

step	Wt. %	Compounds	Temp.	Drum Time	pH
5	150	water	25		
	0.1	Formic acid (85%)		20	
10	200	water	35		
	3	Chrome 26/33		30	
	1	Sodium formate		60	
	100	water	40	10	
15					
	150	water	35		
	1.5	sodium formate		10	
20	x**	sodium bicarbonate		60	4.9-5.2
	300	water	35	10	
25	80	water	30		
	1.5	<i>Pectin or RS 540</i>		20	
	4	Phenolic syntan (Syntan SA)			
30	3	dyestuff		60	
	100	water	50	10	
	x**	Formic acid (85%)		10	3.8-4.0
35					
	300	water		10	
40	150	water	50		
	8-10	Natural oil based fatliquor		60	
	x**	Formic acid (85%)		30	3.4-3.6
45	300	water	20	10	
	300	water	20	10	
50	* Supplier Smit & Zoon** component is added to reach the define pH				

[0071] The resulting crust leather samples were compared to the reference, being either the crust leather sample that was treated according to table 3 with Syntan RS 540 instead of pectin or that was treated without the addition of pectin or RS 540 (blank). The results are listed in table 4. Both samples contribute to improvements in dyeing intensity and fullness. Softness performances vary.

Table 4: *Organoleptic assessment for example 1 (leather treated with CT 02 assessed against blank and leather treated with SB 01 against leather treated with reference Syntan RS 540).*

	CT 02 (blank leather as the reference)	SB 01 (leather treated with RS 540 as the reference)
Grain appearance	-	+-
Evenness of dyeing	-	-
Dyeing intensity	+	++
Grain tightness	+-	+-
softness	-	--
fullness	++	+-

Example 2

[0072] Wet-blue (WB)bovine leather (thickness 1-2 mm) is treated according to the recipe of table 3 modified for a shoe-upper article, where 1-2% (active matter, based on shaved weight of WB) of either partially enzymatically hydrolyzed citrus pectin CT 01 (H-CT 01), partially enzymatically hydrolyzed sugar beet pectin SB 01 (H-SB 01), or a synthetic derivate (Syntan RS 540 from Smit&Zoon) is applied after mineral retanning, after neutralization and during the retanning process just before the addition of phenolic retanning agents and dyestuff.

Table 5: *Organoleptic assessment for example 2 (all samples against reference WB treated with Syntan RS 540).*

	H-CT 01	H-SB 01
Grain appearance	+-	+-
Evenness of dyeing	-	-
Dyeing intensity	+++	+++
Grain tightness	+	+-
softness	+	-
fullness	-	+-

[0073] The resulting crust leather samples were compared to the reference, being the crust leather sample that was treated analogues to the test samples but with Synthan RS 540 instead of pectin. The results are listed in table 5. Both H-CT 01 and H-SB 01 render leather with interesting organoleptic properties in terms of great improvement in dyeing intensity while maintaining or improving the desired grain tightness, softness and fullness.

Example 3

[0074] Wet-White (WW) bovine leather (thickness 1-2mm) was treated according to the following recipe, where 1-2% (active matter, based on shaved weight of WW) of either partially enzymatically hydrolyzed, amidated citrus pectin CT 02 (H-CT 02), or an amphoteric acrylic copolymer retanning agent (reference) is applied at the beginning of retanning. The COD values after retanning and fatliquoring steps are collected to evaluate the performance of the product in reducing waste water treatment load.

Table 6: *Post-tanning recipe of example 3.*

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight tanned leather</i>		°C	<i>minutes</i>	-
wash	300	water	30	10	
drain					

EP 3 775 293 B1

(continued)

step	Wt. %	Compounds	Temp.	Drum Time	pH
neutralizing	100	water	30		
	1.5	sodium formate		30	
	x**	sodium bicarbonate		60	5.0-5.2
retanning	1.5	Sample/reference		60	
	7.5	Phenolic syntan (Syntan SF 156)			
	20	SDF syntan (Syntan SL 868)		60	
	7.5	Phenolic syntan (Syntan SF 156)			
	20	SDF syntan (Syntan SL 868)			
	3	dyestuff		120	
fatliquoring	150	water	50	10	
	10-14	Combination of various fatliquors			
				45	
				15	
	1.8	Formic acid (1:10)		30	
	x**	Formic acid (1:10)		60	3.4-3.6, COD1
drain					
wash	300	water	25	10	COD2
drain					
*Supplier Smit & Zoon** component is added to reach the define pH					

[0075] In order to evaluate the effluent treatment load, COD samples are taken after applying all wet-end chemicals and after washing (table 6). As references, blank samples corresponding to effluent from WW leather treatment with the same process but without the participation of the specific components (acrylic copolymer reference or H-CT 02) are also taken. A blank sample is linked to a specific treated samples since it is cut from the same hide and is even a neighboring piece of the treated piece of leather.

[0076] Compared to the reference acrylic copolymer, H-CT 02 appears to be more effective in reducing the effluent CODs.

Table 7: COD values for example 3.

	Blank H-CT 02	H-CT 02	difference
COD1 (mg/L)	25,600	20,200	-5400
COD2 (mg/L)	37,000	32,900	-4100
	Blank reference acrylic copolymer	reference acrylic copolymer	
COD1 (mg/L)	17,300	28,000	+10700
COD2 (mg/L)	28,800	34,000	+5200

Example 4

[0077] Wet-blue (WB) bovine leather (thickness 1-2mm) was treated according to the basic recipe used for example 1 (table 3), where 1.5% (active matter, based on shaved weight of WB) of a combination of partially enzymatically

EP 3 775 293 B1

hydrolyzed citrus pectin CT 01 and partially enzymatically hydrolyzed sugar beet pectin SB 01 with varying ratios (1:1 and 1:2) or a synthetic derivate (Syntan RS 540 from Smit&zoon) is applied after mineral retanning and neutralization during the retanning process just before the addition of phenolic retanning agents and dyestuff.

Table 8: Organoleptic assessments for example 4 (all samples against reference WB treated with Syntan RS 540).

	H-CT 01 + H-SB 01 (1:1)	H-CT 01 + H-SB 01 (1:2)
Grain appearance	+-	+-
Evenness of dyeing	+-	+-
Dyeing intensity	++	++
Grain tightness	+-	+-
softness	+	+
fullness	-	-

[0078] Both combination tested gives consistent result on leather's organoleptic properties as compared to leather treated with the reference synthetic derivate with improved dyeing intensity and softness. A different result is obtained compared to SB 01 of example 1 and example 2 on evenness of dyeing, softness and fullness.

Example 5

[0079] Wet-blue (WB) bovine leather (thickness 1-2mm) was treated according to the basic recipe of table 3, where 1.5% (active matter, based on shaved weight of WB) of either partially enzymatically hydrolyzed sugar beet pectin SB 01 without any de-methoxylation, or SB 01 which was subjected to a de-methoxylation treatment resulting in SB 01 with a degree of methoxylation of-50% or-100% relative to the initial degree of methoxylation, or a synthetic derivative (Syntan RS 540 from Smit&zoon) is applied after mineral retanning and neutralization during the retanning process just before the addition of phenolic retanning agents and dyestuff.

Table 9: Organoleptic assessments for example 5 (all samples against reference Syntan RS 540).

	H-SB 01	H-SB 01 (-50% methoxylated)	H-SB 01 (-100% methoxylated)
Grain appearance	+-	+-	+-
Evenness of dyeing	-	-	-
Dyeing intensity	++	++	++
Grain tightness	+-	+	+-
softness	-	-	-
fullness	+	+	+

[0080] The degree of methoxylation appears to have a minor effect on the organoleptic properties of the final crust leather. A different result is obtained compared to SB 01 of example 1 on softness and fullness.

Table 10: Mechanical properties for example 5 (all samples against reference WB treated with Syntan RS 540, test method ISO 3376).

		H-SB 01	Ref H-SB 01	H-SB 01 (50% dem.)	Ref H-SB 01 (50% dem.)	H-SB 01 (100% dem.)	Ref H-SB 01 (100% dem.)
F max (N)	Parallel	116	143	150	134	128	151
	Perpendicular	106	116	120	134	132	134

EP 3 775 293 B1

(continued)

		H-SB 01	Ref H-SB 01	H-SB 01 (50% dem.)	Ref H-SB 01 (50% dem.)	H-SB 01 (100% dem.)	Ref H-SB 01 (100% dem.)
T _n (N/mm ²)	Parallel	9.2	10	11.2	10.1	9.4	11.2
	Perpendiculair	8.2	8.5	9.5	10.6	10.5	9.8
Eb (%)	Parallel	68.7	80.6	74.9	74.9	61.2	80.6
	Perpendiculair	76.9	78	101.7	86.2	67.5	79.7

[0081] For mechanical properties similar to example 3 neighboring pieces are compared (for example H-SB 01 and ref H-SB 01). The mechanical properties of crust leather treated with pectin derivatives are comparable to the reference leather treated with traditional synthetic derivatives. Changes in pectins degree of methoxylation do not seem to have big impacts on leather's mechanical properties.

Example 6

[0082] Wet-blue (WB) and wet-white (WW) bovine leather (thickness 1-2 mm) were treated according to the following two recipes respectively, where 1.6% (active matter, based on shaved weight of WB) of partially enzymatically hydrolyzed sugar beet pectin SB 01 is applied; the same treatment is applied without SB 01 (Blank, as a reference). Fogging and formaldehyde tests were performed. Results are shown below:

Table 11: Post-tanning recipe example 6, wet-blue.

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight wet-blue</i>		°C	minutes	-
wetting back	200	water	30		
	0.2	Formic acid (85%)		15	
drain					
neutralizing	150	water	30		
	3	sodium formate		10	
	x**	sodium bicarbonate		60	5.6-5.8
drain					
	300	water	35	10	
drain					
treatment	100	water	50		
	1.6	<i>Pectin H-SB 01</i>		60	
	50	water	50	10	
	0.5	Formic acid (85%)		20	
	x**	Formic acid (85%)		20	
drain					
wash	300	water		10	
drain					
* Supplier Smit & Zoon **component is added to reach the define pH					

Table 12: Post-tanning recipe example 6, wet-white.

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight wet-white</i>		°C	<i>minutes</i>	-
neutralizing	200	water	35		
	2	sodium formate		45	4.6
drain					
	300	water	35	10	
drain					
treatment	100	water	35		
	1.6	<i>Pectin H-SB 01</i>		180	
	10	water	50		
	1	Formic acid (85%)		30	
	x**	Formic acid (85%)		60	
drain					
wash	300	water	20	10	
drain					
* Supplier Smit & Zoon ** component is added to reach the define pH					

Table 13: Formaldehyde emission and fogging, example 6

Fogging reflectometric			
Sample	Result 1	Result 2	Method
WB blank	93%	95%	ISO 17071 A 6 hours @ 75°C
WB with H-SB 01	93%	94%	ISO 17071 A 6 hours @ 75°C
WW blank	67%	63%	ISO 17071 A 6 hours @ 75°C
WW with H-SB 01	63%	58%	ISO 17071 A 6 hours @ 75°C
Fogging gravimetric			
Sample	Result 1	Result 2	Method
WB blank	1.0 mg	1.3 mg	ISO 17071 B 16 hours @ 100°C
WB with H-SB 01	1.4 mg	1.4 mg	ISO 17071 B 16 hours @ 100°C
WW blank	6.0 mg	5.5 mg	ISO 17071 B 16 hours @ 100°C
WW with H-SB 01	5.8 mg	5.7 mg	ISO 17071 B 16 hours @ 100°C
Formaldehyde emission			
Sample	Result		Method
WB blank	4.2 ppm		ISO 17226-3
WB with H-SB 01	4.4 ppm		ISO 17226-3
WW blank	2.6 ppm		ISO 17226-3
WW with H-SB 01	2.5 ppm		ISO 17226-3

[0083] It can be seen in table 13 that the addition of H-SB 01 does not contribute to additional formaldehyde emission and fogging results remains more or less the same.

[0084] Light fastness and heat yellowing tests were carried out based on a Smit & zoon in-house method adapted from ISO 105B02. Results show that Gray Scale (GS) changes of both WB and WW crust leather treated with H-SB 01 are in the optimal range of 4-5.

Example 7

[0085] For a waterproof shoe-upper article, wet-blue (WB) bovine leather (thickness 1-2mm) was treated according to the basic recipe of table 3 for which the retanning step was modified. Instead of adding pectin or RS 540, phenolic syntan (Syntan SA) and dyestuff, a combination of vegetable tannin (e.g. Chesnut KPN), a water-proof retanning agent (Syntan MW 005 from Smit & zoon) and a dyestuff is applied before the application of either 0.5 - 1 wt. % (based on shaved weight of WB) of partially enzymatically hydrolyzed sugar beet pectin SB 01 or a synthetic derivate (Syntan RS 540 from Smit & Zoon). The application of waterproof fatliquors (e.g. a combination of Synthol DS 600 and Syncotan TL from Smit & zoon) is carried out in the following fatliquoring step instead of the natural oil based fat liquor before end-capping with chrome salt.

Table 14: Organoleptic assessments for example 7 (against reference WB treated with Syntan RS 540).

	H-SB 01
Grain appearance	+/-
Evenness of dyeing	+/-
Dyeing intensity	+
Grain tightness	-
softness	+/-
fullness	-

[0086] Organoleptic properties of obtained crust leather has some differences compared the reference leather obtained from treatment with traditional synthetic derivatives.

[0087] The average Maeser value (standard measurement for water-proofness according to ASTM D-2099/ISO 5403-2) of crust leather treated with H-SB 01 according to this example is above 75.000, lower than that from leather treated with traditional synthetic derivatives (which is above 130.000) but much higher than general requirements of 20.000.

Example 8

[0088] For a milled furniture upholstery article, wet-blue (WB)bovine leather (thickness 1-2 mm) was treated according to a modified recipe used for Example 1 with different syntan/fatliquor combinations, where either 0.8 wt. % (based on shaved weight of WB) of partially enzymatically hydrolyzed sugar beet pectin SB 01 or a synthetic derivate as reference (Syntan RS 540 from Smit&Zoon) is applied at the end of fatliquoring and just before the final pH adjustment using formic acid.

Table 15: Organoleptic assessments for example 8 (against reference WB treated with Syntan RS 540).

	H-SB 01
Grain appearance	+/-
Evenness of dyeing	+/-
Dyeing intensity	-
softness	+
fullness	-
milling pattern	+/-
Evenness of milling grain	+/-

[0089] Above assessment shows that hydrolyzed pectin is also suitable for use in milling articles. Moreover, the different

way of application (after fatliquoring instead of earlier in the application process) also provides an alternative in tuning the organoleptic properties, which is comparable or better than those of leathers treated with traditional synthetic derivatives.

5 Example 9

10 **[0090]** For an automotive upholstery article, wet-blue (WB) tanned bovine leather (thickness 1-2 mm) was treated according to the following recipe, where either 1 wt. % (based on shaved weight of WB) of partially enzymatically hydrolyzed sugar beet pectin SB 01 or a synthetic derivate (Syntan RS 540 from Smit&zoon) is applied before mineral retanning.

Table 16: Post-tanning recipe example 9.

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight tanned leather</i>		°C	<i>minutes</i>	-
wetting-back	150	water	30		
	0.5	Electrolyte stable fatliquor (e. g. Synthol PF 991)		45	>5
drain					
retanning	70	water	30		
	1	<i>Pectin or RS 540</i>		30	
	1	Formic acid (1:10)		20	2.8
	2.5	Chrome-free mineral (re)tanning agent (e.g. Syntan ZLR 100)		45	
neutralizing	2	Sodium formate			
	0.25	sodium bicarbonate		30	
	2	Neutralizing agent (e.g. Syntan NN 555)			
	1.5	Sodium formate			
	x**	sodium bicarbonate		60	4.6-4.8
drain					
wash	200	water	30	10	
drain					
Retanning & fatliquoring	50	water	30		
	~10	Combination of various fatliquors		45	
	~11	Combination of various syntans		30	
	3	dyestuff		60	
	150	water	60	10	
	~2.5	Combination of various fatliquors		45	
	x**	formic acid (1:10)		45	3.6-3.8
	0.5	Chrome-free mineral (re)tanning agent (e.g. Syntan ZLR 100)			
	x**	formic acid (1:10)		30	3.4-3.6
drain					
wash					

EP 3 775 293 B1

(continued)

step	Wt. %	Compounds	Temp.	Drum Time	pH
* Supplier Smit & Zoon ** component is added to reach the define pH					

[0091] When comparing the results of example 9 (table 17) with results from the above example 8, it is clearly seen that the organoleptic properties (especially dyeing intensity and softness) can be tuned by changing the position where the pectin material is applied in the post-tanning processes.

Table 17: Organoleptic assessments for example 9 (against reference WB treated with Syntan RS 540).

	H-SB 01
Grain appearance	+
Evenness of dyeing	-
Dyeing intensity	+++
Grain tightness	-
softness	+/-
fullness	-
milling patterns	+

Example 10

[0092] For an automotive upholstery article, wet-white (WW)bovine leather (thickness 1-2 mm) was treated according to the following recipe (table 18). The leather was treated with and without partially enzymatically hydrolyzed sugar beet pectin SB 01 (0.6 wt. % based on shaved weight of WW) and is applied at the beginning of retanning (sample 1) or at the end of fatliquoring (sample 2).

Table 18: Post-tanning recipe example 10.

step	Wt. %	Compounds	Temp.	Drum Time	pH
	<i>based on weight tanned leather</i>		°C	<i>minutes</i>	-
wash	300	water	25		
	2	Neutralizing agent (Syntan NN 555)		30	
	0.5	Sodium bicarbonate		60	5.0-5.2
drain					
Retanning	200	water	30		
<i>Sample 1</i>	<i>0.6</i>	<i>Pectin or water (blank)</i>			
	1.5	Sulfited fatliquor (Synthol CP 996)		45	
	18	Combination of various phenolic syntans		40	
	2.5	Combination of fatliquors		15	
	12	Combination of phenolic syntan, vegetable tannin and resin retan		60	
	3	dyestuff		30	
Next day, fatliquoring	150	water	50	10	

(continued)

step	Wt. %	Compounds	Temp.	Drum Time	pH
	1+7	Combination of various fatliquors		20	
				60	
Sample 2	0.6	Pectin or water (blank)		20	
	1	Formic acid (1:10)		15	
				45	
				60	3.4-3.6
drain					
wash	300	water	25	10	
drain					
* Supplier Smit & Zoon ** component is added to reach the define pH					

[0093] When comparing the results of sample 1 and 2, it is clearly seen that the organoleptic properties (especially grain appearance, grain tightness and fullness) can be tuned by changing the position where the pectin material is applied in the post-tanning processes, see table 19.

Table 19: Organoleptic assessments for example 10 (against reference without the addition of H-SB 01).

	H-SB 01 sample 1 (beginning of retanning)	H-SB 01 sample 2 (end of fatliquoring)
Grain appearance	+-	-
Evenness of dyeing	+-	+-
Dyeing intensity	+	+
Grain tightness	-	+-
softness	+-	+-
fullness	+	++

Claims

1. A method for treatment of leather, comprising providing leather and contacting the leather with an aqueous phase comprising pectin, wherein the leather is tanned leather, and wherein the pectin has a peak molecular weight from 1 to 300 kDa, wherein the peak molecular weight is the molecular weight of the highest peak in the molecular weight distribution.
2. The method according to claim 1, wherein contacting the leather with an aqueous phase comprising pectin is carried out for a time period that ranges from 10 to 1500 minutes, preferably from 20 to 500 minutes, more preferably from 20 to 250 minutes and or wherein contacting the leather with an aqueous phase comprising pectin is carried out at a temperature that ranges from 10 to 95 °C, preferably from 20 to 75 °C, more preferably from 25 to 55 °C.
3. The method according to claims 1 or 2, wherein contacting the leather with an aqueous phase comprising pectin is carried out during one or more selected from the group consisting of neutralization, retanning, dyeing and fatliquoring.
4. The method according to any one of claims 1-3, wherein the aqueous phase comprises from 0.1 to 10 wt.% pectin, preferably from 0.2 to 5 wt.%, more preferably from 0.4 to 2 wt.%, and/or wherein the weight ratio of pectin to tanned leather ranges from 0.001 to 0.1, preferably from 0.002 to 0.05, more preferably from 0.004 to 0.02.

5. The method according to any one of claims 1-4, wherein the pectin has a peak molecular weight-from 2.5 to 200 kDa, even more preferably from 5 to 150 kDa, most preferably from 10 to 100 kDa.
- 5 6. The method according to any one of claims 1-5, wherein the pectin has a degree of methoxylation above 20%, preferably above 35%, more preferably above 50%, even more preferable above 60%, and/or wherein the pectin has a degree of methoxylation below 65%, more preferably below 50%, even more preferable below 35% most preferably below 25%.
- 10 7. The method according to any of one claims 1-6, wherein the pectin has a degree of amidation from 5 to 50%, preferably from 10% to 40%, more preferably from 15% to 30%, even more preferably from 15% to 25%.
- 15 8. The method according to any one of claims 1-7, wherein the pectin is a partially depolymerized pectin, preferably selected from the group of partially acid hydrolyzed pectin and partially enzymatically depolymerized pectin even more preferably partially enzymatically hydrolyzed pectin.
- 20 9. The method according to any one of claims 1-8, wherein the pectin is selected from the group consisting of citrus pectin, sugar beet pectin and apple pectin, preferably the pectin is selected from the group consisting of citrus pectin and sugar beet pectin.
- 25 10. Leather comprising pectin, preferably leather impregnated with pectin, wherein the pectin has a peak molecular weight from 1 to 300 kDa, wherein the peak molecular weight is the molecular weight of the highest peak in the molecular weight distribution, preferably wherein the pectin has a peak molecular weight-from 2.5 to 200 kDa, even more preferably from 5 to 150 kDa, most preferably from 10 to 100 kDa.
- 30 11. The leather according to claim 10, wherein the pectin has a degree of methoxylation above 20%, preferably above 35%, more preferably above 50%, even more preferable above 60%, and/or wherein the pectin has a degree of methoxylation below 65%, more preferably below 50%, even more preferable below 35% most preferably below 25%.
- 35 12. The leather according to claim 10 or 11, wherein the pectin is a partially depolymerized pectin, preferably selected from the group of partially acid hydrolyzed pectin and partially enzymatically depolymerized pectin even more preferably partially enzymatically hydrolyzed pectin.
- 40 13. The leather according to any one of claims 10-12, wherein the pectin is selected from the group consisting of citrus pectin, sugar beet pectin and apple pectin, preferably the pectin is selected from the group consisting of citrus pectin and sugar beet pectin.
- 45 14. The leather according to any one of claims 10-13, wherein the leather comprises at least 0.1 wt.% pectin, wherein the wt.% is calculated based on the weight of the leather.
- 50 15. A treated leather obtained by the method of any of claims 1-9.
- 55 16. A product, such as a shoe, car upholstery, furniture upholstery, bag, garment, accessories comprising the treated leather according to claim 15 or the leather according to any of claims 1-14.

Patentansprüche

1. Verfahren zur Behandlung von Leder, das das Bereitstellen von Leder und das Inkontaktbringen des Leders mit einer wässrigen Phase umfasst, die Pektin umfasst, wobei das Leder gegerbtes Leder ist und wobei das Pektin ein Peak-Molekulargewicht von 1 bis 300 kDa hat, wobei das Peak-Molekulargewicht das Molekulargewicht des höchsten Peaks in der Molekulargewichtsverteilung ist.
2. Verfahren nach Anspruch 1, wobei das Inkontaktbringen des Leders mit einer wässrigen Phase, die Pektin umfasst, über einen Zeitraum ausgeführt wird, der in einem Bereich von 10 bis 1500 Minuten, vorzugsweise von 20 bis 500 Minuten, besonders bevorzugt von 20 bis 250 Minuten liegt und/oder wobei das Inkontaktbringen des Leder mit einer wässrigen Phase, die Pektin umfasst, bei einer Temperatur ausgeführt wird, die in einem Bereich von 10 bis 95 °C, vorzugsweise von 20 bis 75 °C, besonders bevorzugt von 25 bis 55 °C liegt.

3. Verfahren nach Anspruch 1 oder 2, wobei das Inkontaktbringen des Leders mit einer wässrigen Phase, die Pektin umfasst, während einer oder mehrerer ausgeführt wird, die aus der Gruppe ausgewählt sind, die aus Neutralisation, Nachgerben, Färben und Fetten besteht.
- 5 4. Verfahren nach einem der Ansprüche 1-3, wobei die wässrige Phase 0,1 bis 10 Gew.-%, vorzugsweise 0,2 bis 5 Gew.-%, besonders bevorzugt 0,4 bis 2 Gew.-% Pektin umfasst und/oder wobei das Gewichtsverhältnis von Pektin zu gegerbtem Leder in einem Bereich von 0,001 bis 0,1, vorzugsweise von 0,002 bis 0,05, noch bevorzugter von 0,004 bis 0,02 liegt.
- 10 5. Verfahren nach einem der Ansprüche 1-4, wobei das Pektin ein Peak-Molekulargewicht von 2,5 bis 200 kDa, noch bevorzugter von 5 bis 150 kDa, am bevorzugtesten von 10 bis 100 kDa hat.
6. Verfahren nach einem der Ansprüche 1-5, wobei das Pektin einen Methoxylierungsgrad von über 20 %, vorzugsweise von über 35 %, besonders bevorzugt von über 50 %, noch bevorzugter von über 60 % hat und/oder wobei das Pektin einen Methoxylierungsgrad von unter 65 %, besonders bevorzugt von unter 50 %, noch bevorzugter von unter 35 %, am bevorzugtesten von unter 25 % hat.
- 15 7. Verfahren nach einem der Ansprüche 1-6, wobei das Pektin einen Amidierungsgrad von 5 bis 50 %, vorzugsweise von 10 % bis 40 %, besonders bevorzugt von 15 % bis 30 %, noch bevorzugter von 15 % bis 25 % hat.
- 20 8. Verfahren nach einem der Ansprüche 1-7, wobei das Pektin ein teilweise depolymerisiertes Pektin ist, vorzugsweise ausgewählt aus der Gruppe von teilweise säurehydrolysiertem Pektin und teilweise enzymatisch depolymerisiertem Pektin, noch bevorzugter teilweise enzymatisch hydrolysiertem Pektin.
- 25 9. Verfahren nach einem der Ansprüche 1-8, wobei das Pektin aus der Gruppe ausgewählt ist, die aus Zitruspektin, Zuckerrübenpektin und Apfelpektin besteht, wobei das Pektin vorzugsweise aus der Gruppe ausgewählt ist, die aus Zitruspektin und Zuckerrübenpektin besteht.
- 30 10. Leder, das Pektin umfasst, vorzugsweise Leder, das mit Pektin imprägniert ist, wobei das Pektin ein Peak-Molekulargewicht von 1 bis 300 kDa hat, wobei das Peak-Molekulargewicht das Molekulargewicht des höchsten Peaks in der Molekulargewichtsverteilung ist, wobei das Pektin vorzugsweise ein Peak-Molekulargewicht von 2,5 bis 200 kDa, noch bevorzugter von 5 bis 150 kDa, am bevorzugtesten von 10 bis 100 kDa hat.
- 35 11. Leder nach Anspruch 10, wobei das Pektin einen Methoxylierungsgrad von über 20 %, vorzugsweise von über 35 %, besonders bevorzugt von über 50 %, noch bevorzugter von über 60 % hat und/oder wobei das Pektin einen Methoxylierungsgrad von unter 65 %, besonders bevorzugt von unter 50 %, noch bevorzugter von unter 35 %, am bevorzugtesten von unter 25 % hat.
- 40 12. Leder nach Anspruch 10 oder 11, wobei das Pektin ein teilweise depolymerisiertes Pektin ist, vorzugsweise ausgewählt aus der Gruppe von teilweise säurehydrolysiertem Pektin und teilweise enzymatisch depolymerisiertem Pektin, noch bevorzugter teilweise enzymatisch hydrolysiertem Pektin.
- 45 13. Leder nach einem der Ansprüche 10-12, wobei das Pektin aus der Gruppe ausgewählt ist, die aus Zitruspektin, Zuckerrübenpektin und Apfelpektin besteht, wobei das Pektin vorzugsweise aus der Gruppe ausgewählt ist, die aus Zitruspektin und Zuckerrübenpektin besteht.
14. Leder nach einem der Ansprüche 10-13, wobei das Leder mindestens 0,1 Gew.-% Pektin umfasst, wobei das Gew.-% basierend auf dem Gewicht des Leders berechnet wird.
- 50 15. Behandeltes Leder, das durch das Verfahren nach einem der Ansprüche 1-9 erhalten wird.
16. Produkt, wie z. B. ein Schuh, eine Autopolsterung, eine Möbelpolsterung, eine Tasche, ein Kleidungsstück, Zubehörteile, das das behandelte Leder nach Anspruch 15 oder das Leder nach einem der Ansprüche 1-14 umfasst.

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Revendications

1. Procédé pour le traitement du cuir, comprenant la fourniture de cuir et la mise en contact du cuir avec une phase

EP 3 775 293 B1

aqueuse comprenant de la pectine, où le cuir est du cuir tanné, et où la pectine a un poids moléculaire de pic de 1 à 300 kDa, où le poids moléculaire de pic est le poids moléculaire du pic le plus haut dans la distribution de poids moléculaire.

- 5 **2.** Procédé selon la revendication 1, où la mise en contact du cuir avec une phase aqueuse comprenant de la pectine est effectuée pendant une période de temps comprise entre 10 et 1500 minutes, de préférence entre 20 et 500 minutes, plus préférablement de 20 à 250 minutes et/ou où la mise en contact du cuir avec une phase aqueuse comprenant de la pectine est effectuée à une température comprise entre 10 et 95 °C, de préférence entre 20 et 75 °C, plus préférablement entre 25 et 55 °C.
- 10 **3.** Procédé selon les revendications 1 ou 2, où la mise en contact du cuir avec une phase aqueuse comprenant de la pectine est effectuée pendant un ou plusieurs sélections du groupe consistant en neutralisation, retannage, teinture et mise en bain.
- 15 **4.** Procédé selon l'une quelconque des revendications 1 à 3, où la phase aqueuse comprend de 0,1 à 10 % en poids de pectine, de préférence de 0,2 à 5 % en poids, plus préférablement de 0,4 à 2 % en poids, et/ou où le rapport pondéral de la pectine au cuir tanné est compris entre 0,001 et 0,1, de préférence entre 0,002 et 0,05, plus préférablement entre 0,004 et 0,02.
- 20 **5.** Procédé selon l'une quelconque des revendications 1 à 4, où la pectine a un poids moléculaire de pic de 2,5 à 200 kDa, encore plus préférablement de 5 à 150 kDa, le plus préférablement de 10 à 100 kDa.
- 25 **6.** Procédé selon l'une quelconque des revendications 1 à 5, où la pectine a un degré de méthoxylation supérieur à 20 %, de préférence supérieur à 35 %, plus préférablement supérieur à 50 %, encore plus préférable supérieur à 60 %, et/ou où la pectine a un degré de méthoxylation inférieur à 65 %, plus préférablement inférieur à 50 %, encore plus préférable inférieur à 35 % le plus préférablement inférieur à 25 %.
- 30 **7.** Procédé selon l'une quelconque des revendications 1 à 6, où la pectine a un degré d'amidation de 5 % à 50 %, de préférence de 10 % à 40 %, plus préférablement de 15 % à 30 %, encore plus préférablement de 15 % à 25 %.
- 35 **8.** Procédé selon l'une quelconque des revendications 1 à 7, où la pectine est une pectine partiellement dépolymérisée, de préférence sélectionnée du groupe de la pectine partiellement hydrolysée à l'acide et de la pectine partiellement dépolymérisée enzymatiquement encore plus préférablement pectine partiellement hydrolysée enzymatiquement.
- 40 **9.** Procédé selon l'une quelconque des revendications 1 à 8, où la pectine est sélectionnée du groupe consistant en pectine d'agrumes, pectine de betterave sucrière et pectine de pomme, de préférence la pectine est sélectionnée du groupe consistant en pectine d'agrumes et pectine de betterave sucrière.
- 45 **10.** Cuir comprenant de la pectine, de préférence cuir imprégné avec de la pectine, où la pectine a un poids moléculaire de pic de 1 à 300 kDa, où le poids moléculaire de pic est le poids moléculaire du pic le plus haut dans la distribution de poids moléculaire, où de préférence la pectine a un poids moléculaire de pic de 2,5 à 200 kDa, encore plus préférablement de 5 à 150 kDa, le plus préférablement de 10 à 100 kDa.
- 50 **11.** Cuir selon la revendication 10, où la pectine a un degré de méthoxylation supérieur à 20 %, de préférence supérieur à 35 %, plus préférablement supérieur à 50 %, encore plus préférable supérieur à 60 %, et/ou où la pectine a un degré de méthoxylation inférieur à 65 %, plus préférablement inférieur à 50 %, encore plus préférablement inférieur à 35 %, le plus préférablement inférieur à 25 %.
- 55 **12.** Cuir selon la revendication 10 ou 11, où la pectine est une pectine partiellement dépolymérisée, de préférence sélectionnée du groupe de la pectine partiellement hydrolysée à l'acide et de la pectine partiellement dépolymérisée enzymatiquement, encore plus préférablement pectine partiellement hydrolysée enzymatiquement.
- 13.** Cuir selon l'une quelconque des revendications 10 à 12, où la pectine est sélectionnée du groupe consistant en pectine d'agrumes, pectine de betterave sucrière et pectine de pomme, de préférence la pectine est sélectionnée du groupe consistant en pectine d'agrumes et pectine de betterave sucrière.
- 14.** Cuir selon l'une quelconque des revendications 10 à 13, où le cuir comprend au moins 0,1 % en poids de pectine, où le % en poids est calculé sur la base du poids du cuir.

EP 3 775 293 B1

15. Cuir traité obtenu par le procédé de l'une quelconque des revendications 1 à 9.

16. Produit, comme une chaussure, rembourrage de voiture, rembourrage de meubles, un sac, un vêtement, des accessoires comprenant le cuir traité selon la revendication 15 ou le cuir selon l'une quelconque des revendications 1 à 14.

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REFERENCES CITED IN THE DESCRIPTION

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