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(54) Title: LEATHER TANNING

(57) Abstract: A condensate formed by the reaction of THP with a dialdehyde such as glutaraldehyde is effective as a tanning agent for leather.

LEATHER TANNING

The present invention relates to a novel process for tanning leather.

Tanning is a process for the preservation of skins, by which is meant the collagen-containing integuments of vertebrates including mammals (e.g. cows, pigs, deer, goats, sheep, seals, antelope, mink, stoats and camels), fish, (e.g. sharks), reptiles (e.g. snakes, lizards and crocodiles), and birds (e.g. ostrich). Skins comprise a layer of collagen, and tanning entails reacting the collagen with a cross linking, or tanning, agent to cross link reactive sites within the collagen molecule. The product of the cross linking is leather, which is substantially less susceptible than skin to bacterial degradation.

A consequence of the cross linking is an increase in the minimum temperature at which the wet leather tends to shrink. This shrink temperature is often used as an indication of the degree of tanning.

The collagen layer of the skin is separated from fats, connective tissue and other subcutaneous protein, and optionally from the outer keratinous layer, by a combination of chemical and physical steps. The former may include liming, bating, pickling and/or degreasing.

The skin is then subjected to treatment in one or more stages with various tanning agents selected to give the desired end properties.

The main types of tannage are:- vegetable tannage, based on tannin as the active cross linking agent; mineral tannage using various polyvalent metal salts, especially salts of chromium, aluminium, iron, or zirconium; and synthetic tanning agents, referred to as "syntans". Syntans include replacement syntans which are active tanning agents capable of tanning leather when used as the sole tannage e.g. by reacting with collagen at two or more sites to form cross links, and auxiliary syntans

which are added to other tannages to modify the character of the leather but which are not in themselves active tanning agents. Auxiliary syntans are absorbed by the leather or may react with collagen at one site only. Syntans include various polymers and copolymers, such as those obtained by condensing formaldehyde with, for example, phenols and/or aryl sulphonates, and acrylate, methacrylate, acrylamide and/or acrylonitrile homopolymers and copolymers. Formaldehyde itself and dialdehydes such as glutaraldehyde are also used in tanning, usually in combination with other tannages.

For centuries the production of leather was based on the vegetable tannages which produce the characteristic brown colour traditionally associated with leather. One of the first mineral tannages was alum, but currently the most widely used tanning agent is chrome, usually in the form of basic chromium sulphate, which produces a blue grey leather with high shrink temperatures. However mineral tannages in general, and chrome tannages in particular are under pressure on environmental grounds. Syntans are less environmentally harmful than mineral tanning agents. However, many syntans are derived from formaldehyde, which may be released during tanning. Formaldehyde and difunctional aldehydes present a health hazard and are unpleasant to handle.

Tetrakis (hydroxymethyl) phosphonium salts which will be referred to generically herein as THP salts have long been used as fire-retardants for textiles and have been applied to the keratinous (fur) side of skins for this purpose. The salts may be applied directly to the fabric or in the form of precondensates which are water soluble or sparingly water soluble copolymers of THP with organic nitrogen compounds such as urea or an amine and which are referred to herein as "THP condensates". THP salts have also been known as possible ingredients of tanning liquors for more than thirty six years. US. 2 992 879 referred to THP chloride (THPC) as an unsatisfactory tanning agent on its own, and recommended a combination of THPC and a phenol such as resorcinol speculating that the two react together to form an effective tanning agent when the pH is raised. In fact THP salts do copolymerise with phenols such as resorcinol (see, for example, Textile Research Journal, December 1982, P743). US 3

104 151 describes the use of such THPC phenol copolymers as light pretannages for leather in which the main tannage is vegetable or mineral. GB 2 287 953 describes the use of THP salts as cross linkers in conjunction with melamine formaldehyde or urea formaldehyde prepolymers, in order to form a copolymeric tanning agent in situ in the tanning liquor. EP 0 559 867 describes the use of phosphonium salts such as THP sulphate (THPS) on raw or cured skin prior to tanning e.g. in acid degreasing. EP 0 681 030 describes the use of THPS as a cross linker for casein finishes applied to leather after tanning. GB 2 314 342 describes the use of hydroxyalkyl phosphines and phosphonium salts as tanning agents in conjunction with aromatic anionic syntans and EP O 808 908 describes the use of THP salts with condensable nitrogen compounds.

THP salts are stable under acidic conditions in the absence of air or oxidising agents. At pH above 3 and in the absence of oxidising agents they are gradually converted to the parent base, tris(hydroxymethyl)phosphine herein referred to as THP. Conversion is rapid and substantially complete between pH of about 4 and 6. Above pH 7, or in the presence of oxidising agents THP salts or THP are converted to tris(hydroxymethyl)phosphine oxide (THPO), conversion being rapid and substantially complete at pH above about 10, e.g. 12. It has been stated, e.g. in US 2 993 744, that THPO is the effective tanning agent in THP based tannages.

Contrary to statements in the art, THPO is not effective as a tanning agent for leather, and THP salts are also ineffective as tannages. Moreover THP used in conjunction with co-condensable monomers or polymers provides complex systems which are difficult to control to obtain consistent results. However THP on its own is an effective main tanning agent. THP is usually most effective when formed in situ by first impregnating the leather with a THP salt, in the substantial absence of monomers or prepolymers which react or copolymerise with THP and raising the pH above 4 and preferably above 5.

In addition to THP, compounds of the formula R $P(CH_2OH)_2$, referred to herein as THP analogues, where R is an organic group which does not react chemically with

collagen, such as a C_{1-20} alkyl, alkenyl, aryl, aralkyl, alkaryl, polyalkyleneoxy, alkylpolyalkyleneoxy or polyalkyleneoxy alkyl group are highly effective tanning agents.

For convenience "THP" will be used herein, where the context permits, to refer generically to THP, THP salts, THP condensates and THP analogues.

The steps required to produce leather including the pickling and degreasing which usually precede tanning, remove most of the natural oils and fats from leather. These are normally at least partially replaced after tanning by fat liquoring, which entails contacting the leather with an aqueous emulsion of oils and fats which soften and lubricate the finished leather. It has been found that leather which has been tanned with THP does not readily absorb fat liquor. THP generally gives a tight leather. It would be useful to be able to obtain the advantages of THP, but prepare a less tight and more easily fat liquored leather.

One object of the present invention is to provide tannages which exhibit the advantages of THP but which are less tight and/or more readily fat liquored.

Mixtures of THP with various aldehydes, and in particular dialdehydes such as glutaraldehyde, succinaldehyde and glyoxal are described in EP O 385 801 as being useful synergistic biocides. We have found that the synergism is at least in part due to acetal-like condensates formed when THP reacts with dicarbonyl compounds.

A further object of the invention which is achieved by the use of THP and carbonyl compounds is a reduction in the levels of formaldehyde in the finished leather. Levels below 20ppm have been attained.

We have now discovered that the reaction products of THP with dicarbonyl compounds having up to fifteen carbon atoms are very effective tanning agents which achieve at least in part the aforesaid object of the invention.

The invention provides a method of tanning leather which comprises reacting collagen with a compound of the type produced when THP reacts with a water soluble compound having at least one carbonyl group and at least one other group selected from carbonyl and carboxyl and especially one having up to fifteen carbon atoms.

The carbonyl compound is preferably a dialdehyde but may alternatively be a diketone or ketoaldehyde, or a compound with three or more carbonyl groups.

The dialdehyde may for example be a compound of the formula $OHC(CH_2)_nCHO$ where n is from 0 to 12, especially to 0 to 10, e.g. succinaldehyde or glutaraldehyde. Alternatively the dialdehyde may comprise an aryl or alicyclic structure such as benzadial or cyclohexadial. Suitable diketones include orthoquinone and 5, 5-dimethyl-1,3-cyclohexadione, polymeric carbonyl compounds such as polymers or copolymers of acrolein, e.g. with acrylic acid, have been found highly effective, as has 1,3-dimethyl acetone dicarboxylate.

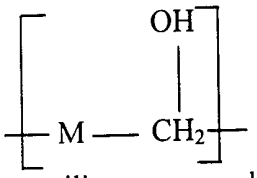
The compound may optionally be substituted e.g. by one or more hydroxyl groups.

The reaction product which may resemble an acetal or ketal will be referred to generally herein as "the acetal". It may for example be formed by mixing an aqueous solution of trishydroxymethylphosphine or a THP analogue with the carbonyl compound. The reaction occurs at ambient temperature, but optionally the mixture may be warmed e.g. to temperatures between 30 and 100°C, typically 35 to 80°C. The reaction occurs most readily at pH in the range 3 to 8, e.g. 4 to 7, especially 5 to 6. The THP and carbonyl compound may be used in substantially equimolar proportions. However a molar excess of either component, especially the THP, may be present, e.g. up to a 10 fold molar excess.

The acetal may be prepared in situ by adding THP or a THP salt and a dicarbonyl compound to basified skin or to acidic skin and basifying with alkali such as sodium carbonate.

The acetal may be used in conjunction with syntans, e.g. by treating the skin with a mixture of the acetal and syntan (preferably a syntan which does not react with THP or the acetal under normal tanning conditions) and/or by treating the skin in a plurality of stages at least one of which entails treatment with syntan and at least one other of which entails treatment with the acetal.

For the purpose of this specification "syntan" is used to refer to replacement syntans which are synthetic organic compounds capable of reacting with collagen at two or more sites to form cross links and also to auxiliary syntans which do not in themselves contribute substantially to the cross linking but which are physically absorbed by the leather or react at no more than one site so as to modify the physical properties of the leather. For example the term includes any water soluble polymer prepared by copolymerising formaldehyde, which is capable of increasing the shrink resistance of collagen and which comprises at least two units of the formula



where each M is an aryl group such as a phenyl, naphthyl or aniline group substituted with one or more hydroxyl and/or sulphate, sulphone or sulphonimide groups or a urea or melamine residue. As used herein the term "syntan" also includes resin syntans which are homopolymers and copolymers of unsaturated carboxylic acids or their salts, esters, amides or nitriles, e.g. acrylic acid, methacrylic acid, acrylamide, acrylonitrile, maleic acid, fumaric acid, itaconic acid, aconitic acid, crotonic acid, isocrotonic acid, citraconic acid, mesaconic acid, angelic acid, tiglic acid and cinnamic acid. The copolymers may also comprise other vinylic comonomers such as styrene. Also included are acetone condensates with, for example sulphones and sulphonamides. Resin syntan may modify such properties as dye levelling, filling, grain appearance, break, grain strength, buffing nap, softness and tensile or tear strength.

The acetal tends to react with nitrogen containing syntans and with other nitrogenous compounds and also to some extent with aromatic syntans. Such reactions may compete with cross linking reactions of both the acetal and the syntan resulting in

chaotic behaviour when the two are used together. Such systems are so highly sensitive to the conditions of use that it may be difficult or impossible to control them so as to obtain the consistent results required for a viable commercial process.

For these reasons we prefer not to use the acetal in a mixture with such compounds. However it is possible to precondense the acetal with, for example, cocondensable nitrogenous compounds such as urea, melamine, dicyandiamide and/or aliphatic amines to form condensates comprising two or more phosphorus atoms and having at least two hydroxymethyl groups. Such condensates are useful tanning agents which constitute a further aspect of the invention.

The acetal may optionally be used in conjuction with mineral tannages. Mixtures of the acetal with, e.g. chrome zirconium or aluminium are highly effective. The latter tanning agents can be used in lower concentrations, when used in conjunction with the acetals, than are usually required for mineral tannage alone, but can give better shrink temperatures compared with the acetal alone.

High pH is preferably avoided because it converts the phosphine group to phosphine oxide, which is substantially ineffective as a tanning agent. We prefer that acetal solutions for use according to our invention should have a pH less than 10, more preferably less than 9, especially less than 8, typically less than 7.5, most preferably 4.5 to 7. We prefer that the acetal contains less than 15%, more preferably less than 10%, e.g. less than 9% of THPO based on the weight thereof. Generally the less THPO present the better.

The acetal is preferably used in a total concentration of from 0.01 to 20% by weight based on the total weight of the tanning liquor, more preferably 0.5 to 10%, e.g. 1 to 5%, most preferably 1.5 to 4%. The total proportion of the acetal used is preferably from 0.3 to 20% by weight based on the weight of wet skin, more preferably 1 to 15%, especially 1.5 to 10%, most preferably 2 to 5%.

We particularly prefer processes in which skins are treated with an auxiliary syntan prior to tanning with the acetal.

When the acetal is used in combination with a syntan, the latter is preferably a polyacrylate, polymethacrylate, or copolymer of acrylic and/or methacrylic acid with acrylonitrile and/or acrylamide. Typically the polymer has a molecular weight in the range 1,000 to 200,000, more usually 3,000 to 100,000.

The syntan is preferably present at a concentration of from 0.5 to 35% by weight of the tanning liquor. e.g. 1 to 20%, more preferably 2 to 10% especially 3 to 6%. The total proportion of syntan used is preferably from 1 to 20% by weight based on the wet weight of skins, e.g. 2 to 10% especially 3 to 5%.

The proportion by weight of acetal to syntan may typically be from 1:10 to 10:1, preferably 1:5 to 2:1, especially 1:2 to 1:1. The total proportion of tannages used is preferably from 2 to 20% active weight based on the wet weight of skins, e.g. 3 to 10%, especially 4 to 8%. The total tannage used preferably comprises more than 80% by weight, more preferably more than 90% by weight, e.g. more than 95% of the acetal and syntan. Where white leather is required, we prefer that the total tannages consist essentially of the acetal and syntan. In particular we prefer the leather is not tanned with vegetable or mineral tannage.

The acetal is preferably applied in the substantial absence of monomers or prepolymers capable of copolymerising with the acetal such as phenol, urea, melamine or their precondensates with formaldehyde. For the purposes of this specification, "the substantial absence of monomers or prepolymers" means less than the minimum that would be capable of reacting or copolymerising with 50% of the acetal, more preferably less than the minimum that would be required to react or copolymerise with 20%, e.g. less than 5% by weight based on the weight of acetal, most preferably less than 2%, especially less than 1%.

The acetal may be applied as a first tanning step with a syntan as a retan. Preferably the acetal is applied to acidified skins following aqueous degreasing. E.g. the initial pH is typically below 5, e.g. below 4. We prefer that the pH be raised above 5 and preferably maintained above 6 for the main duration of the tanning process.

The skins are preferably agitated in the tanning liquor for a sufficient time to raise the shrink temperature above 75°C, more preferably above 80°C, most preferably above 85°C.

The tanned skins are typically washed with warm water and fat liquored using a suitable oil or blend of oils. Fat liquoring is normally carried out after dyeing.

The invention will be illustrated by the following examples.

Example 1

Equimolar proportions of THP (as a 70% by wt aqueous solution) and glutaraldehyde (as a 33% by wt aqueous solution) were mixed and allowed to stand. The concentration of the acetal was monitored by ^{31}P nmr. The acetal gave distinctive peaks at a shift of between 18 and 20 ppm. After 10 minutes 53.5% of the total phosphorus had reacted to form the acetal. After 2 hours the proportion had risen to 60.2%. The acetal solution was applied to skins in a rotary drum at a concentration of 1.5% based on the wet weight of skin and at a pH of 5.1 and a temperature of 25°C. The pH was raised progressively to 6.5 over 4 hours by additions of sodium carbonate, giving a shrinkage temperature of 78°C. The leather was drained and washed. The product was of good quality and had a fuller texture from leather tanned with THP alone.

Example 2

Example 1 was repeated using dimedone (5,5-dimethyl-1,3 cyclohexadione) in place of glutaraldehyde with similar results.

Example 3

A tannage was carried out on a pickled, wool-off ovine pelt, to produce a soft, full, mellow-handle leather having a high shrinkage temperature at low pH.

The following formation was made up:

1000g pickled pelt;
8% (by weight of pelt) sodium chloride } to give a s.g.
2% (by weight of pelt) sodium formate } of 6 to 8° Baumier;
0.1% (by weight of pelt) phosphonate sequestering agent, available as BRIQUEST® 301-50A;
100% float (i.e. 100% by weight of water, relative to the pelt).

After 10 minutes' rotation, the pH of the float was found to be in the range 3.8 to 4.2,

2% of a 75% active THP sulphate (available as ALBRITE ® AD75E) and 2% of a copolymer of acrolein and acrylic acid were mixed together to form a slurry, using the minimum volume of water necessary to solubilise. This mixture was added to the rotation drum via the axle, the contents of the drum then being subjected to a further 90 minutes' rotation. The pH of the float after this time was found to be 4.1 and the shrinkage temperature of the treated pelt was 70°C.

After the addition of 0.5% (by weight of pelt) of sodium bicarbonate and a further 30 minutes' rotation, the pH of the float was 4.8 and the shrinkage temperature 77°C.

A further 0.5% sodium bicarbonate was added and rotation continued for another 30 minutes. The pH of the float was found to be 5.5 and the shrinkage temperature 84°C.

Further addition of sodium bicarbonate did not result in any further elevation of the shrinkage temperature.

The tanned leather was found to have a free formaldehyde level of 843ppm, compared to a control tannage (copolymer omitted) which had a free formaldehyde level of 1134ppm.

Example 4

Example 3 was repeated, except that the THP sulphate was replaced by a 4:1 THPS /urea condensate, available as ALBRITE ® CS4.

The float pH values and corresponding shrinkage temperatures were as follows:

PH	Shrinkage Temp (^{o}C)
4.2	72
4.8	83
5.5	86

No further elevation of the shrinkage temperature occurred after further addition of sodium bicarbonate.

The tanned leather was found to have a free formaldehyde level of 565 ppm. The leather was soft and full with a mellow handle, the handle being slightly fuller than that of the leather of Example 3.

CLAIMS

1. A method of tanning leather which comprises the step of reacting collagen with a compound of the type produced when THP reacts with a water soluble compound having at least one carbonyl group and at least one other group selected from carbonyl and carboxyl.

2. A method according to claim 1 wherein the carbonyl compound is a dialdehyde of the formula $OHC(CH_2)_nCHO$, where n is from 0 to 12.

3. A method according to claim 2 wherein the dialdehyde is glutaraldehyde.

4. A method according to claim 1 wherein the dicarbonyl compound is 5,5 dimethyl-1,3-cyclohexadione or orthoquinone.

5. A method according to any foregoing claim wherein the collagen is also reacted with a syntan or mineral tannage before, during or after said step.

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 00/02018

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C14C3/08

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)
IPC 7 C14C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 104 151 A (WINDUS W. ET AL) 17 September 1963 (1963-09-17) cited in the application column 2, line 7 - line 40 claims 15,16; examples 12,15	1-3
X	EP 0 808 908 A (SUEDLEDER GMBH & CO) 26 November 1997 (1997-11-26) cited in the application page 2, line 35 -page 3, line 27 example 2	1-3
A	US 3 734 684 A (DONALDSON D ET AL) 22 May 1973 (1973-05-22) example 1	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2000	13/09/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Int\ \ ional Application No
PCT/GB 00/02018

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 385 801 A (ALBRIGHT & WILSON) 5 September 1990 (1990-09-05) cited in the application example 2 -----	1-3

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte .ional Application No
PC./GB 00/02018

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