PROCESS FOR THE RAPID TANNING OF MEDIUM-WEIGHT AND HEAVY LEATHER

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U.S. Cl. 8—942.6

4 Claims

ABSTRACT OF THE DISCLOSURE

Process for rapid tanning of leather by pretreating the leather with chromium-containing tanning agents, chromium complex tanning agents, or mixtures of chromium-containing tanning agents with syndans, naphthalene-sulfonic acids, condensates of naphthalene-sulfonic acids, and formaldehyde, or sulfit waste liquor followed by a final tanning in the absence of a liquor, the final tanning being initiated by a condensation product of naphthalene-sulfonic acids and formaldehyde, a sulfit waste liquor, or a mixture thereof, these initiating agents having been adjusted to an acid number of at least 30, and finishing the final tanning with powdered synthetic or vegetable tanning agents.

Processes for the rapid tanning of medium-weight and heavy leathers, in which the tanning or a substantial part of it is carried out without a liquor are known from U.S. Pat. Nos. 3,253,879 and 3,254,937. According to U.S. Pat. No. 3,253,879 the hides which have been prepared in the lime house in the usual manner are pretanned with chromium complex tanning agents and the tanning is then finished in the drum with powdered vegetable and synthetic (syntan) tanning agents without a liquor. For pretanning there may be used, for example, the chromium complex tanning agents known from U.S. Pat. No. 2,997,364, which consist of a mixture of chromic tanning salts and synthetic tanning agents which are prepared (x) from mono- or polyvalent phenols or both types of phenols, or also polynuclear phenols or phenol resins, by condensation with sulphites and/or bisulphites and with aldehydes and/or ketones, or (β) from methylol compounds of the said phenols with sulphot and/or bisulphites, possibly in the presence of aldehydes and/or ketones and/or alcohols.

According to a special method of carrying out this known process, the final tanning of the pretanned hides with powdered vegetable tanning agents is initiated by means of powdered synthetic tanning agents without a liquor. For this purpose so-called exchange tanning agents are used which have a good dispersing action, are readily soluble, and have themselves a good tanning effect. These so-called precursor tanning agents improve the rate of tanning through and the uniform dispersion of the tanning agent.

According to U.S. Pat. No. 3,254,937 chromium tanning agents or known chromium complex tanning agents or mixtures or chromium tanning agents with synthetic tanning agents and/or naphthalene-sulfonic acids and/or condensation products of naphthalene-sulfonic acids and formaldehyde and/or sulphite waste liquor, are used in powdered form for pretanning without liquor in the drum. The final tanning is subsequently carried out with powdered synthetic tanning agent and/or vegetable tannins.

Depending on the type of raw material used, there frequently appears on the leather a drawn grain in these rapid tanning processes during the tanning which is carried out without liquor in the drum. By a suitable mechanical pressing of the wet leather, such a drawn grain can be removed in many cases to such an extent that it is no longer visible on the finished leather.

In accordance with the demands of the market, the producers of leather are, however, often compelled or desirous to process a sensitive raw material which tends to form a drawn grain. The drawn grain in the leather is in rapid tanning can frequently not be removed by mechanical means to a sufficient extent and remains visible on the finished leather. The formation of drawn grain has therefore become a problem of considerable importance.

Furthermore, the complainant is frequently made that the leathers produced by these methods with the aid of chromiun-containing preservative tanning agents have a green tint caused by the type of preservative tanning agents employed.

It has now been found that in the rapid tanning of medium-weight and heavy leathers by pretreating with chromium tanning agents or chromium complex tanning agents or mixtures of chromium tanning agents and (a) synthetic tanning agents and/or (b) naphthalene-sulfonic acids and/or (c) condensation products of naphthalene-sulfonic acids and formaldehyde and/or (d) sulphite waste liquors, in a liquor or without a liquor, followed by final tanning with powdered synthetic tanning agent and/or vegetable tannins without a liquor, the formation of a drawn grain can substantially be reduced or completely prevented, if the final tanning without liquor is initiated with those condensation products of naphthalene-sulfonic acids and formaldehyde and/or with those sulphite waste liquors ("preservative tanning agents") which contain inorganic or organic acids in an amount sufficient for the condensation products or sulphite waste liquors to have an acid number of at least 30, preferably 50 to 120, and which may also contain 5—20% of their weight of water-soluble inorganic neutral salts, and if the final tanning is subsequently carried out in the usual manner with powdered synthetic tanning agent and/or vegetable tannins without liquor. By the term "acid number" there is to be understood the consumption of mg. KOH for neutralizing 1 g. of dry substance of the tanning agent to be titrated, i.e., in the present case of the preservative tanning agent. The undesirable drawn grain is reduced or completely prevented by this process. Moreover, the greenish tint of the leather caused by the chromium-containing preservative tanning agents is reduced and a more reddish colour of the leather is obtained if the required acid number of preservative tanning agents is adjusted by using inorganic or organic acids the dissociation constant of which is equal to or greater than 10^-2.

The condensation products of naphthalene-sulfonic acids and formaldehyde to be used as preservative tanning agents can, by definition, be replaced completely or, more advantageously, in part, by sulphite waste liquors.

The naphthalene-sulfonic acid/formaldehyde condensation products to be used as preservative tannins are preferably those which can be prepared by known methods from technical naphthalene-sulphonation mixtures chiefly containing β-naphthalene-sulphonic acid. The molar ration of naphthalene-sulfonic acid to formaldehyde is about 1:06 to 1 mol. When the reaction is completed, the condensation products are usually converted into their alkali metal or ammonium salts and then dried. They contain alkali metal or ammonium sulphate originating from the sulphonic acid usually employed in excess for the sulphonation of naphthalene. It is also possible to use products freed from these neutral salts.

The term "sulphite waste liquor" is known to mean technical mixtures which contain, as the main compo.
nent lignin-sulphonic acid in the form of its salts, especially the sodium salts.

Suitable organic acids for adjusting the required acid number of the precursory tannins are chiefly aliphatic carboxylic acids, such as acetic acid, formic acid, glutaric acid or adipic acid. Liquid as well as solid acids can be admixed to the naphthalene-sulphonic acid condensation products or to the sulphite waste liquor (precursory tannins).

According to a variant of the process of the present invention it is also possible to proceed in such a manner that the hide material which has first been pre-tanned with chromium tannins or chromium complex tannins or mixtures of tannins and compounds (a) and/or (b) and/or (c) and/or (d) as defined above, is treated with a precursory tanning agent which is a condensation product of naphthalene-sulphonic acids and formaldehyde, or a sulphite waste liquor not yet adjusted to an acid number of at least 30, that the acid number of at least 30, referred to the amount of precursory tanning agent employed, is adjusted before or during this treatment with such a neutral or more weakly acidic precursory tanning agent by means of inorganic or organic acids, followed by the final tanning carried out in the usual manner, as mentioned above, with synthetic tanning agent and/or vegetable tannins. The amount of acid required for adjusting the acid number of the precursory tanning agent used for the precursory tanning can easily be determined also in this case, since the weight of the precursory tanning agent is known.

Suitable acids with a dissociation constant of 10⁻³ are, for example, sodium bisulphate, naphthalene-sulphonic acid, sulphuric acid or oxalic acid. It is also possible to use the naphthalene-sulphonic acid/formaldehyde condensation products to be employed as precursory tannins, in a partially neutralised form. This means that, after completion of the reaction, the reaction products are neutralised only to such an extent that they are still present in the form of free sulphonic acids in a quantity corresponding to the desired acid number.

Examples of water-soluble inorganic neutral salts are, inter alia, sodium sulphate, sodium chloride, potassium sulphate, potassium nitrate, ammonium sulphate, ammonium chloride and other known water-soluble inorganic salts of neutral reaction.

The term "tanning without liquor" in the meaning of the present invention comprises tanning processes in which the tanning agents are used without water or without substantial amounts of water. The precursory tannins are usually employed in a powdered form, but the use of solid products, e.g., in the form of blocks, or of highly concentrated syrups, is also possible. The tanning process itself is mainly carried out by milling the pelt or leather with the tanning agents in a rotating drum.

The precursory tannins to be used according to the present process are employed in amounts of about 5–20%, preferably 8–12%, referred to the pelt weight. As chrome tanning salts, vegetable tannins, synthetic tannins and exchange tanning agents there are used the agents known in leather technology, which need not be explained in greater detail, since they are known to the man skilled in the art and can be seen from the literature. Some of the suitable compounds are mentioned in the patent specifications given above.

The new process is particularly suitable for the production of sole leather, sole leather splits, inside sole leather, wetting leather, vachettes or upper leather tanned in combination.

According to the data of the aforesaid U.S. Pat. Nos. 3,253,879 and 3,254,937, it was not to be expected that the condensation products of naphthalene-sulphonic acids and formaldehyde or the sulphite waste liquors which have an acid number of at least 30, preferably 50 to 120, and have no good tanning action, would be especially suitable as precursory tanning agents for rapid tanning processes with and without liquor. It must be regarded as particularly surprising that the formation of a drawn grain is so strongly reduced by the use of these products which have themselves merely the property of an adjuvant. It was, in fact, to be assumed that only the use of exchange tannins with a good tanning action as precursory tannins would lead to an improved fixation of the grain layer of the leather and render it more resistant to the formation of a drawn grain.

The following examples are given for the purpose of illustrating the invention.

**EXAMPLE 1**

(a) After the lime-house processing customary for sole leather, 500 kg. unsplit cow pelts are pre-tanned in the pit with a chromium complex tanning agent according to Example 1 of U.S. Pat. No. 3,253,879.

The pre-tanned pelts are milled in the usual manner without a liquor in a drum preheated to about 30°C, with 10% (referred to the pelt weight) of a powdered precursory tanning agent as described below. After the treatment for about 3 to 4 hours, the pelts are evenly tanned through. 15% pure tannin of a sulphonated quebracho are then added in powdered form. It is expedient to add about 0.5% of a sulphonated castor oil together with about 1% water simultaneously with the tannin, in order to avoid chafe marks. After a further milling time of 90 minutes, 5% pure tannin of mimosa extract in powdered form and 5% pure tanning of sweetened chestnut nut extract are added in powdered form and tanning is continued (the percentages are referred to the weight of the pelt). Depending on the raw material used, the leather is completely tanned after a total tanning time in the drum of about 24 to 30 hours.

As precursory tanning agent there is used a condensation product obtained by condensation of a technical naphthalene-sulphonation mixture substantially containing β-naphthalene-sulphonic acid with 0.65 mol formaldehyde per mol naphthalene-sulphonic acid, which is present in the form of the sodium salt and has been adjusted to an acid number of 120 by the addition of glutaric acid.

(b) The process is the same as stated under (a) but, instead of the precursory tannin there mentioned, the same amount of a powdered exchange tanning agent is used, which had been obtained by condensation of 4,4'-dihydroxy-4-phenylsulphone, naphthalene-sulphonic acid and formaldehyde according to Example 1 of U.S. Pat. No. 1,901,536.

When comparing the leathers produced according to (a) and (b), respectively, it will be found that the leather (a) tanned with the precursory tanning agent according to the invention is noticeably smoother and exhibits substantially less drawn grain or none at all. This difference is still visible on the finished leather.

**EXAMPLE 2**

500 kilograms unsplit cow pelts are pre-tanned in the same manner as described in Example 1 and milled without a liquor in the drum with 13% (referred to the pelt weight) of one of the powdered precursory tannins described below. After tanning for 3 to 4 hours, two portions of 25% pure tannin (referred to the pelt weight) of a sulphonated quebracho extract in powdered form are added. After a total milling time in the drum of about 20 to 30 hours, the tanning is completed.

As precursory tanning agent there is used a condensation product of β-naphthalene-sulphonic acid and formaldehyde (molar ratio 1:1) which has been neutralised with ammonia and then adjusted to an acid number of 100 by the addition of oxalic acid.

The leather obtained after finishing in the usual manner has a reddish tint and little or no drawn grain.
EXAMPLE 3

After the usual preparation in the lime house, 500 kg. unsplit cow pelts which is suitable for the production of bag leather, are pickled in the usual manner and pretanned in the drum without a liquor with 4% (referred to the pelt weight) of the following powdered chromium complex tanning agent.

225 parts by weight of the condensation product prepared according to the instructions of Example 1 of U.S. Pat. No. 3,065,039 are mixed with a solution of 225 parts by weight of purified sulphite waste liquor, and a solution of 300 parts by weight 0 (nought)-based chromic sulphate in 300 parts by weight hot water, and subsequently spray-dried.

After a milling time of about 2 hours, the pelts are evenly tanned through. After briefly rinsing with warm water at about 30° C. and discharging the rinsing liquor, the leather is carried out without a liquor in the drum with 6% of a powdered synthetic precursory tanning agent as described below and 0.5% acetic acid (acid number 78%)

As synthetic precursory tanning agent there is used a mixture of 90 parts by weight of the sodium salt of a condensation product obtained from a technical naphthalene-sulphonation mixture substantially containing β-naphthalene-sulphonic acid, and 1 mol formaldehyde per mol naphthalene-sulphonic acid, and 10 parts by weight sodium sulphate.

After a milling time of about 2 hours, there are added 7% pure tannin (referred to the weight of the pretanned leather) of a sulphited quebracho extract in powdered form and 7% pure tannin of a mimosa extract in block form. The tanning is completed after a further milling time of about 4 hours. After piling, the leather is sanded, set out and finished in the usual manner. A smooth leather is obtained, which has only negligible drawn grain or none at all.

EXAMPLE 4

To produce a waterproof leather, 500 kg. of North German cow pelts are tanned, after the usual lime house processing, with a 33% basic chromium sulphate tanning agent in an amount corresponding to 1.5% Cr₂O₃ (referred to the pelt weight). After shaving to 2.5 mm, the leather is washed and neutralised in the usual manner so that the cut exhibits a level yellow-green coloration with the bromocresol green indicator. After brief rinsing, the leather is treated without a liquor in the drum with 8% (referred to the weight of the shaved leather) of a mixture of 70 parts by weight of the precursory tanning agent described in Example 1 and 30 parts by weight of a delimed sulphite waste liquor which is present in the form of its sodium salt. After a milling time of about one hour, there are added 7% pure tannin of a sulphited quebracho extract in powdered form, 7% pure tannin of a mimosa extract in powdered form, and 2% of pure tannin of a conventional soft-tanning synthetic exchange tanning agent in powdered form (the percentages are referred to the weight of the shaved leather). After a further tanning time of 1½ to 2 hours, the tanning is completed. The leather is seasoned, greased and finished in the usual manner.

When pretanning or final tanning is carried out without a liquor, the leather or pelt material is treated with the pretanning agent, the precursory tanning agent or the other tanning agents used for final tanning, in the wet state but without a liquor. The wet or dripping wet state of the material presupposes, strictly speaking, a certain amount of liquor, but this is generally less than 20%, referred to the weight of the leather or pelt, and is not regarded as a tanning liquor in the technical sense. The term "without liquor" as used in the present application is therefore to be understood to mean that the liquor originating, for example, from deliming or pretanning (with liquor), which normally amounts to many times the volume stated above, is completely drained, pumped off or removed in any other way, whereby, obviously small residual amounts of liquor remain between the pelts; the definition of the term "without liquor" also excludes the addition of larger amounts of liquor to the pelt or leather before pretanning or final tanning than are taken up by the pelt or leather until the wet or dripping wet state is reached.

EXAMPLE 5

For the manufacture of split hide cattle pelts are pickled and pretanned in the drum without liquor with 5% (referred to the pelt weight) of the following pre-tanning agent:

The pre-tanning agent consists of 50 parts by weight of a powdered 33% basic chromium sulphate tanning agent having a chromium oxide content of 25%, a tanning agent weight of a powdered sodium salt of the condensation product of β-naphthalene sulphonic acid and formaldehyde (condensation ratio 1:0.65).

After drumming for 1½ to 2 hours the pelts are evenly tanned through. The pre-tanned leathers are rinsed for a short time, the rinsing liquor completely discharged and the leathers then milled with 10% of the following precursory tanning agent:

The precursory tanning agent is a delimed sulphite waste liquor used in form of its sodium salt and containing as much acetic acid as the liquid product has an acid number of 20 referred to its content of dry substance.

After a milling time of about 2 hours there are added 7% pure tannin of a sulphited quebracho extract in powdered form, and 8% pure tannin of a mimosa extract in powdered form. The tanning is completed after a further tanning for 3 to 4 hours. The leather is finished in the usual manner and shows approximately no grain.

EXAMPLE 6

The process described in Example 5 can be varied in that instead of the precursory agent there is used the same amount of a powdered mixture of 45 parts by weight of the powdered ammonium salt of the condensation product of β-naphthalene sulphonic acid and formaldehyde (molar ratio 1:0.8), 30 parts by weight of a powdered delimed sulphite waste liquor in form of its sodium salt and 5 parts by weight of sodium chloride; the mixture contains as 20 parts by weight of adipic acid. After completion of the tannage the leather is finished in the customary manner; smooth leather having a full handle is obtained and having little or no drawn grain.

EXAMPLE 7

For manufacture of waterproof leather, North German cow butts are treated in the lime house in customary manner and then tanned with a chrome tanning agent which was prepared by reduction of bichromate with glucose in the presence of sulphuric acid and which is 35% basic and corresponds to 2% chromic oxide referred to the weight of the pelts. The chrome-tanned and shaved leather is rinsed with water and after complete discharge of the rinsing liquor pretanned with 5% (referred to the weight of the shaved leather) of the following precursory tanning agent:

The precursory tanning agent consists of 50% of a powdered sodium salt of a condensation product of a techinal naphthalene sulphonation mixture which essentially contains α- and β-naphthalene sulphonates (molar ratio between naphthalene and sulphuric acid 1:1, 2), 0.62 mol formaldehyde per mol naphthalene sulphonic acid, 30% (referred to 100 parts of the mixture) of anhydrous sodium sulphate and 20% (referred to 100 parts of the mixture) of anhydrous potassium or ammonium sulphate.

The pretanned leather is briefly rinsed, neutralised in the customary manner so that the cut exhibits a level yellow-green coloration with the bromo cresol green indicator. After brief rinsing and complete discharging of the
rinsing liquor the leather is tanned without liquor with 8% pure tanning of a sulphited quebracho extract in powdered form and 8% pure tannin of a mimosa extract in powdered form. After a tanning time of further 1 to 2 hours the tannage is completed. The leather is then finished in usual manner. One obtains smooth full and even leathers.

EXAMPLE 8

Leathers of similar properties are obtained if instead of the precusory agent of Example 7, 20% (referred to the weight of the pelts) of the following about 50% product are used:

A condensation product of a technical naphthalene sulphonation which essentially contains β-naphthalene sulfonic acid and 0.63 mol formaldehyde per mol naphthalene sulfonic acid is neutralised with as much ammonia as the mixture shows an acid number of 90 referred to the content of dry substance of the mixture. If necessary, water is added up to a dry substance content of 50%.

What is claimed is:

1. A process for the rapid tanning of medium-weight and heavyweight leather in which the leather is pretanned with:
   (a) chromium tanning agents or,
   (b) mixtures of chromium tanning agents and at least one member from the group consisting of:
   (1) synthetic tannings agents,
   (2) naphthalene-sulfonic acid, and
   (3) sulfite waste liquor, and thereafter subjected to a final tanning step without substantial amounts of water, with a powered form of another tanning agent, the improvement which comprises initiating the final tanning, without substantial amounts of water, with at least one material which has been adjusted by means of one or more inorganic acids to an acid number of 50–120, and is selected from the group consisting of:

8. (1) condensation products of only naphthalene-sulfonic acid and formaldehyde, and
   (2) sulfite waste liquor.

2. Process of claim 1, in which the said material employed in initiating the final tanning contains 5 to 20% by weight of water-soluble inorganic salts.

3. Process of claim 1, in which said inorganic acids or organic acids have a dissociation constant which is equal to or greater than 10⁻².

4. Process of claim 1, in which the final tanning is initiated by applying to the pretanned leather a material which is selected from the group consisting of (a) a condensation product of naphthalene-sulfonic acids and formaldehyde, and (b) a sulfite waste liquor, said material having an acid number of less than 30, and thereafter adjusting the acid number to about 50–120.

References Cited

UNITED STATES PATENTS
1,327,105 1/1920 Landmark ------------ 8—94.31
1,430,477 9/1922 Tullis -------------- 8—94.31
2,997,364 8/1961 Komarek et al. ------ 8—94.26
3,065,039 11/1962 Komarek ----------- 8—94.24
3,253,879 5/1966 Komarek et al. ----- 8—94.24 XR
3,254,937 6/1966 Komarek et al. ---- 8—94.24 XR

FOREIGN PATENTS
739,312 10/1955 Great Britain.

OTHER REFERENCES
Baum et al.: J. American Leather Chem. Assoc., 1951, pp. 269 and 270.

DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

8—94.24, 94.31.
**UNIVERSAL STATES PATENT OFFICE**

**CERTIFICATE OF CORRECTION**

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<th>Dated</th>
<th>July 7, 1970</th>
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<td>Inventor(s)</td>
<td>Wolfhard Luck, et al.</td>
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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

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Signed and sealed this 12th day of January 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. WILLIAM E. SCHUYLER, JR.
Attesting Officer Commissioner of Patents