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DRY CHROME PRETANNAGE AND DRY SYNTAN OR VEGETABLE TANNAGE

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7 Claims. (Cl. 8—94.26)

The present invention relates to and has as its objects a new and surprising tanning procedure without the use of tanning liquors but by using solid tannins directly, especially for the preparations of heavy and medium heavy leathers.

The object of copending U.S. patent application Ser. No. 207,418, filed July 3, 1963, is a process for tanning medium heavy and heavy leather which is characterized in that the hides prepared in the usual way in the lime house are pretanned by mixtures of normal or basic tanning chromic salts with synthetic tanning substances which are produced according to known processes either from phenols by condensation with sulphites and/or bisulphites and aldehydes or from methylol compounds of the phenols by condensation with sulphites and/or bisulphites optionally in the presence of ketones or aldehydes (e.g. according to the instructions of U.S.-Patent No. 2,997,364) and the thus pretreated pelt material is tanned in the drum with powdered vegetable tanning extracts without liquor.

In the above tanning process the pretanning takes place with a dissolved pretanning agent in conventional manner whether stationary in the pits or by moving in the drum, whereupon the actual tanning in the drum takes place with powdered tanning agent without liquor.

It has now been found that a further simplification of the above described process can be performed in that the pretanning also takes place with powdered chrome-containing tanning agents without liquor in the drum. This pretanning can be immediately followed by the main tanning in the hitherto usual way or by adding synthetic and/or vegetable powder extracts without liquor in the drum.

As suitable pretanning agents for the new process of the invention the following tanning agents may be considered in the first place:

(1) Chromic sulphates ready for tanning, added to the tanning directly in powder form. Especially the powdered chromium sulphate compounds forming the object of copending application Serial No. 148,245 are suitable.

(2) Chrome complex tanning agents, which are obtained by mixing chromic salts with synthetic tanning agents produced by sulphomethylation of phenol formaldehyde condensation products. More details of the formation of such chrome complex tanning materials are e.g. to be found in U.S.-Patent No. 2,997,364).

(3) Mixtures of chromic salts with synthetic tanning agents or with naphthalene sulphonic acid or with condensation products of naphthalene sulphonic acid and formaldehyde or with sulphite waste liquors.

(4) Mixtures of the chrome-containing pretanning agents described under 1–3, with each other.

The pretanning agents are preferably applied in an amount which corresponds to a chromium content of the finished vegetable tanned leather of less than about 0.6% chromic oxide. The pretanning agents penetrate the delimed pelts surprisingly very rapidly and impart to the whole cross-section an acid reaction. They lead to a strongly marked grain firmness and improve the

penetration and fixing of the powdered tanning agent in rapid tanning. This simple and effective type of pretanning is valuable not only in all modern rapid tanning processes but can also be applied with good result in the hitherto usual tanning methods according to the counter-current process. The new process is distinguished by an extraordinary simplicity. Since in this pretanning process there is no need to get rid of chrome containing effluent water, the process of the invention is furthermore technically valuable and an advance.

In contrast to a usual chrome pretanning with a pickle and tanning chromic salts, the new process is distinguished by its surprising simplicity, moreover the leather pretreated according to the invention possesses only a small content of chromic oxide (less than about 0.6% of chromic oxide, mainly about 0.3%) which in no way detrimentally affects the properties of the sole leather. It is known that the properties of the combined tanned leather produced according to this process are disadvantageously influenced by higher amounts of chromic oxide, as are present in the customary pretanning with chrome tanning materials, and by salts imported in the pickle.

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

Example 1

100 kg. of unsplit cow butts are pretreated with 4% of the subsequently described powdered chrome complex tanning agent in the drum following the lime house procedure usual for sole leather.

225 parts by weight of the condensation product produced according to Example 1 of German patent specification No. 1,053,517, which may be obtained as follows:

(a) 150 parts by weight of crude cresol and 50 parts by weight of phenol are condensed with 245 parts by volume of 30% formaldehyde in the presence of 112 parts by weight of 50% sodium hydroxide at about 70° C for 3 hours. Sulfur dioxide is blown into the precondensate thus obtained until neutral reaction of the mixture is reached (pH 6–7). After one further hour the product can be dissolved clear in dilute acids (Example 1 of German Patent 1,053,517).

(b) In accordance with the method given under (a) 200 parts by weight of crude cresol are condensed with 200 parts by volume of 37% formaldehyde in the presence of 52 parts by weight of solid sodium hydroxide at 85° C. within 3 hours. After sulfur dioxide has been blown into the precondensate formed the sulfitation reaction is carried out at a temperature of 95° C. for one hour. (Example 3.)

(c) 300 parts by weight of phenol are mixed with 96 parts by weight of 45% soda-lye and 300 parts by volume of 30% formaldehyde added with stirring. The mixture is refluxed for one and a half hours and then sulfur dioxide blown into the mixture until neutral reaction is reached. The condensation product is soluble in water. After 30 minutes further reaction it is acidified with acetic acid.

(d) 320 parts by weight of technical cresol (composed of about 20% phenol, 62% o-cresol, 5% m-cresol and 8% p-cresol) are mixed with 161 parts by weight of 45% soda-lye and condensed with 350 parts by volume of 30% formaldehyde. The condensation reaction is carried out at 98° C. within 35 minutes and subsequently sulfur dioxide blown into the mixture until the reaction is weakly acid. After further 90 minutes reaction time a clearly soluble product is obtained which is acidified with acetic acid. (Example 5.)

The above product is mixed with a solution of 225 parts by weight of purified sulphite waste liquor and a solution of 300 parts by weight of O-basic chromium sulphate in 300 parts by weight of hot water and dried by a spray drying process.

The duration of the pretanning with this chromium complex tanning agent amounts with thick materials to about 3 hours. The tanning out with vegetable synthetic tanning agents follows immediately upon the pretanning. This pretanning is especially suitable for the rapid tanning in the drum with powdered extracts, without liquor. The total tanning time amounts even with very thick hide materials to not more than 24 hours.

Example 2

500 kg. of split hide are pretreated according to the usual preparation in the lime house in the drum with 4% of the following powdered chrome mixed tanning agent.

200 parts by weight of a tanning chromic salt are mixed intimately with 150 parts by weight of the sodium salt of β-napthalene sulphonic acid.

The duration of the pretanning amounts to one and a half hours. The tanning out can proceed in the usual way with vegetable tanning agents. The pretanning according to the invention is especially suitable for the rapid tanning in the drum with powdered synthetic and/or vegetable tanning agents in the drum without liquor. The total tanning time amounts to about 6–8 hours.

Example 3

1000 kg. of split cow butts are drummed for three hours with 3% of a 4/12 basic chrome tanning salt and with 0.3% formic acid in the drum without liquor. Tanning is then carried out with a powdered synthetic and vegetable tanning agent. Total tanning time about 18 hours. The split cow butts are finished directly after tanning, in the usual way.

We claim:

1. A process for tanning vegetable leather consisting essentially of pretanning hide from the lime house by applying directly thereto a dry powdered chrome-tanning agent in the drum in the absence of liquor and thereafter finally tanning by drumming the hide with an effective amount of a member selected from the group consisting of (a) dry synthetic tanning agent and (b) vegetable powder extracts only.

2. A process of claim **1** wherein the pretanning agent is a member selected from the group consisting of

A. chromic sulphate tanning agent;

B. chrome complex tanning mixture of chrome-tanning agent with a syntan consisting of the sulphomethylation product of pheol-aldehyde condensation product; and

C. a mixture of chromic salts with a member selected from the group consisting of (1) a synthetic tanning agent, (2) naphthalene sulfonic acid, (3) a condensation product of naphthalene sulfonic acid with formaldehyde, and (4) sulfite waste liquor.

3. The process of claim **1** wherein hide from the lime house is pretanned in the drum with about 4% by weight of a powdered chrome complex tanning agent obtained by mixing (a) O-basic chromium sulphate, (b) purified sulphite waste liquor, and (c) a condensation product of cresol and phenol with formaldehyde, the ratio of a:b:c being about 3:2:2 parts by weight.

4. The process of claim **1** wherein hide from the lime house is pretanned in the drum with about 4% by weight of a powdered chrome complex tanning agent obtained by mixing (a) O-basic chromium sulphate, (b) purified sulphite waste liquor, and (c) a condensation product of cresol with formaldehyde, the ratio of a:b:c being about 3:2:2 parts by weight.

5. The process of claim **1** wherein hide from the lime house is pretanned in the drum with about 4% by weight of a powdered chrome complex tanning agent obtained by mixing (a) O-basic chromium sulphate, (b) purified sulphite waste liquor, and (c) a condensation product of phenol and formaldehyde, the ratio of a:b:c being about 3:2:2 parts by weight.

6. The process of claim **1** wherein hide from the lime house is pretreated in the drum with about 4% by weight of a powdered chrome mixed tanning agent obtained by mixing (a) a tanning chromic salt with (b) a salt of β-naphthalene sulphonic acid at a ratio of about 2:1.5 parts by weight.

7. The process of claim **1** wherein hide from the lime house is pretreated in the drum with about 3% by weight of a 4/12 basic chrome tanning salt and about .3% formic acid.

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