

1

3,482,925

PROCESS FOR THE RAPID TANNING OF LEATHER

Helmut Schmid and Wolfhard Luck, Leverkusen, Ernst Loderhose, Stuttgart, Bruno Zinz, Cologne-Flittard, and Ernst Komarek, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany
No Drawing, Filed Feb. 8, 1966, Ser. No. 525,864
Claims priority, application Germany, June 5, 1965, F 46,273

Int. Cl. C14c 1/00, 1/08

U.S. Cl. 8—94.17

8 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in the acidification step of rapid tanning processes for delimed or non-delimed pelts, which comprises the steps of (1) acidification, (2) chrome pretanning, and (3) tanning, by conducting the acidification with mixtures of (1) mineral acid or acidic mineral acid salts and (2) salts of naphthalene sulfonic acids. Preferably, the acidification mixture contains a mineral acid and ammonium salts of naphthalene sulfonic acids or alkali metal salts of naphthalene sulfonic acids and an ammonium salt. Salts of sulfurous acid and neutral inorganic salts can also be added. The acidification mixture is of a concentration to produce pelts having a pH below about 6.5. This process can be carried out in the same drum with all three steps in the absence of liquor.

DISCLOSURE

A number of rapid tanning processes for the production of vegetable-tanned leather are known, in which the pelts are pretreated with acids in the form of a pickle before the final tanning with vegetable tannins. If mineral acids or lower fatty acids are used for this purpose, the addition of neutral salts, e.g. sodium chloride, is necessary to prevent an undesired swelling of the pelts. Such a pretreatment by pickling is customary, especially in those cases where the pelts are pre-tanned with chromium tanning agent before the final tanning.

It has already been proposed to use organic acids which have no swelling action, particularly naphthalene-sulphonic acids, for acidifying the pelts before the tanning with vegetable tannins. When these acids are used, the addition of salts is not necessary and there is also achieved an accelerated penetration of tannin with the vegetable tannins and a brightening of the leather.

To acidify the pelts, a specific amount of acid is required which is comparatively high for organic acids without swelling action, due to their high equivalent weight. In comparison with mineral acids, such as sulphuric acid, these organic acids are moreover only obtained at a relatively high price, and their practical use is therefore limited for economic reasons. When naphthalene-sulphonic acids are used as acidifying agent, it must also be taken into account that these acids which have, moreover, a strong corrosive effect on metals, are highly hygroscopic and are only available in the form of pastes or blocks which are difficult to handle. It is therefore expedient to dissolve these acids in water before application. Consequently, they are not very suitable to be used for the acidification of pelts in the drum without a liquor.

A rapid tanning process has now been found in which the pelts are acidified with mixtures of mineral acids or salts having a mineral acid reaction in aqueous solution, and of salts of naphthalene-sulphonic acids, pre-tanned with chromium tanning agent, and then finally tanned with vegetable tannin and/or syntans. Compared with the

2

use of free naphthalene-sulphonic acids for acidification, the mixtures which are considerably easier to handle lead to an at least equally rapid tannin penetration in the final tanning process with vegetable tannins. It has also been found that this new process which is the object of the present application, can be carried out with particular advantage without a liquor.

According to the new process, the pelts which may be delimed and wetted in the usual manner are acidified with mineral acids or salts having a mineral acid reaction in aqueous solution and with salts of naphthalene-sulphonic acids, possibly in the presence of water-soluble inorganic neutral salts or carboxylic acids. The acids are used in such an amount that at the end of the treatment the pelts exhibit a pH value below 6.5, preferably of 3.0–3.6, throughout their cross-section. The acidified pelts are then pre-tanned in known manner with (1) chromium tanning agents or (2) chromium complex tanning agents or (3) mixtures of chromium tanning agents and (a) syntans and/or (b) naphthalene-sulphonic acids and/or (c) condensation products of naphthalene-sulphonic acids and formaldehyde and/or (d) sulphite waste liquor, and finally tanned with vegetable tannins and/or syntans. The chromium tanning agents (1)–(3) can be used by themselves or as mixtures.

When non-delimed pelts are used as starting material, the alkaline pelts are acidified with mineral acids and salts of naphthalene-sulphonic acid, the ammonium or alkali metal salts being preferably used as salts of naphthalene-sulphonic acid. If alkali metal salts of naphthalene-sulphonic acid are used, it is advantageous that salts of sulphurous acid or carboxylic acids, and optionally other water-soluble inorganic neutral salts, besides the ammonium salts, are present.

As salts of naphthalene-sulphonic acids there are preferably used the alkali metal or ammonium salts of β -naphthalene-sulphonic acid or of technical mixtures substantially containing β -naphthalene-sulphonic acid. Salts of α -naphthalene-sulphonic acid, 1,5- or 1,6-naphthalene-disulphonic acid or 1,3,6- or 1,3,7-naphthalene-trisulphonic acid are also suitable. Furthermore, neutralised technical mixtures which are obtained in the production of naphthalene-disulphonic acids as a by-product and mainly consist of sulphuric acid and naphthalene-disulphonic acids can be used with particular advantage. The amounts of such salts of naphthalene-sulphonic acids employed, in general, lie at about 0.5–10%, preferably 1–6%, referred to the pelt weight.

As mineral acids, sulphuric acids, hydrochloric acid or phosphoric acid are especially suitable. It is also possible to use salts having a mineral acid reaction in aqueous solution, such as sodium or potassium bisulphate. The amount of mineral acids to be used depends on the pH value which the pelts are to have at the end of the treatment.

Examples of water-soluble inorganic neutral salts are, inter alia, sodium sulphate, sodium chloride, potassium sulphate, potassium chloride, ammonium sulphate, ammonium chloride, and other known water-soluble inorganic salts of neutral reaction. These salts are generally used in amounts of about 0.5–10%, referred to the pelt weight.

Carboxylic acids which are especially suitable for being used for the present process are those of the aliphatic series, such as formic acid, acetic acid, propionic acid, adipic acid, glutaric acid, oxalic acid and hydroxycarboxylic acids, such as lactic acid, as well as citric acid. As examples of the aromatic series, there may be mentioned: sulphophthalic acid and sulphosalicylic acid. Mixtures of carboxylic acids can also be used. The carboxylic acids are normally used in quantities of 0.5–2% formic acid or

of an equivalent amount of another carboxylic acid, referred to the pelt weight.

Ammonium salts of acids other than naphthalene-sulphonic acids, which can be concurrently used are, inter alia, water-soluble ammonium salts of inorganic acids, such as ammonium sulphate and ammonium chloride, or water-soluble ammonium salts of organic acids, such as ammonium acetate, ammonium formate and ammonium phthalate. Mixtures of such ammonium salts are also frequently employed with advantage.

By the concurrent use of ammonium salts and carboxylic acids there is achieved a more uniform and faster acidification of the pelts. The addition of salts of sulphurous acid removes the hydrogen sulphide liberated in the acidification of the alkaline pelts.

It was not to be foreseen that it would be possible to achieve with the mixtures of mineral acids and salts of naphthalene-sulphonic acids according to the invention and at least equally satisfactory acceleration of the tanning agent penetration in the final tanning with vegetable tannins, as can be obtained with free naphthalene-sulphonic acid. It has hitherto generally been assumed that only the free acids which have no swelling action have these advantageous effects when used as salt-free pickle. Compared with the free naphthalene-sulphonic acids, the salts thereof have the advantage of being considerably easier to handle. Any detrimental effect on the final tanning with vegetable tannins, caused by the neutral salts introduced during acidification of the pelts with the mixtures according to the invention can be obviated by rinsing the pelts after pre-tanning with chromium tanning agents, without the specific effect of the acidification according to the invention being lost.

According to an advantageous method of carrying out the new process, the pelts which may be delimed and wetted are acidified with mixtures of mineral acids and salts of naphthalene-sulphonic acids, possibly in the presence of water-soluble inorganic neutral salts and carboxylic acids, without a liquor, then pre-tanned in the usual manner with chromium tanning agents, and finally tanned with vegetable tannins and/or syntans.

Suitable agents for the acidification of pelts without a liquor are, in particular, powdered mixtures of salts of naphthalene-sulphonic acids with sodium and/or potassium bisulphate. It is equally advantageous to use spray-dried alkali metal or ammonium salts of technical mixtures containing naphthalene-disulphonic acids and possibly naphthalene-trisulphonic acids, such as are obtained as by-product in the production of naphthalene-disulphonic acids, in admixture with bisulphates, as powdered agents for the acidification of pelts.

The pre-tanning with chromium tanning agents or chromium complex tanning agents or mixtures of chromium tanning agents and the components (a) to (d) mentioned above is carried out by known methods. As a rule, amounts of chromium tanning agents are employed which would be insufficient for complete tanning. Pre-tanning according to the process described in U.S. Patent No. 2,997,857 is especially suitable. Pre-tanning without a liquor can be carried out with particular advantage according to U.S. Patent 3,254,937.

In this process 100 kg. of unsplit cow butt is treated with a spray dried mixture of 225 pts. of waste sulfite liquor, 300 pts. H_2O , 300 pts. basic chromium sulfate and 150-320 pts. of a condensate from the reaction by formaldehyde with phenol with or without crude cresols with solid NaOH as a catalyst and with SO_2 blown in after condensation.

A dry mixture of chrome tanning agent with naphthalene SO_3Na or 33% basic chrome tanning salt with 3% formic acid can also be used to pretan.

Suitable chromium pre-tanning agents are chromic sulphates ready for tanning which are directly placed into the tanning drum in powdered form. The powdered chromium tanning agents which are the object of U.S.

Patent No. 3,174,817 wherein hides are chrome tanned with powdered dried chromic sulfate or basic chrome sulfate, which has been masked with acetic acid are particularly suitable. Chromium complex tanning agents obtained by mixing chromic salts with syntans prepared by sulphomethylation of phenol/formaldehyde condensation products are especially useful. Data regarding the synthesis of such tanning agents can be found in U.S. Patent No. 2,997,857.

Mixtures of chromic salts with naphthalene-sulphonic acids or with condensation products of naphthalene-sulphonic acids and formaldehyde, especially with sodium salts of such condensation products, or mixtures with sulphite waste liquor, especially with sodium salts of delimed sulphite waste liquors, are also very advantageous.

The pre-tanning agents (1) to (3) are preferably used in such amounts that the finished leather has a chromium oxide content of less than 1.5% Cr_2O_3 , preferably less than 0.6% Cr_2O_3 .

Final tanning is carried out with vegetable tannins and/or syntans in known manner.

It has proved to be particularly advantageous that according to the new process the final tanning can be performed without a liquor. Even when working on an industrial scale, the risk of case-hardening or of an undesirable strong formation of drawn grain does not occur.

A preferred method of carrying out the new process consists in that the acidification of the pelts as well as the pre-tanning with chromium tanning agents or chromium-containing tanning agents and also the final tanning with vegetable tannins and/or syntans are carried out without a liquor. This offers the advantageous possibility of continuously processing the material from the alkaline pelts to the finished leather in a single operation in one and the same drum. It is expedient to rinse the pelts before the final tanning in order to remove the salts introduced by the alkaline pelts and, after discharging the rinsing liquors, to carry out the final tanning with vegetable tannins and/or syntans in the same drum without a liquor.

Compared with the process of U.S. Patent 3,254,937, the new process provides a simple method of operation, a faster tanning agent penetration and, particularly when carried out on an industrial scale, leather with noticeably less drawn grain or with none at all.

In the preferred method of carrying out the new process, in which the acidification as well as the pre-tanning and the final tanning are performed without a liquor, it has proved advantageous to initiate the final tanning with powdered syntans. As described in the process of U.S. Patent No. 3,253,879, this patent shows a chrome tanning salt or basic chrome tanning agent mixed with a syntan produced by condensing a phenol, an aldehyde and a sulfite or a bisulfate. This chromed syntan is applied to a delimed hide. It is possible to use for this purpose those syntans which have a good dispersing action, are readily soluble, and have themselves a good tanning action. In particular U.S. Patent 3,253,879 describes a process for the rapid tanning of medium and heavy leathers consisting essentially of

(A) pretanning delimed hides with a normal or basic tanning chromium salt and a syntan obtained by the condensation of a phenol with an aliphatic aldehyde and with a member selected from the group consisting of a sulfite and a bisulfite;

(B) drumming the pretanned hides before final tanning with a powdered well dispersing and readily soluble exchange tanning agent; and

(C) finally tanning the hides by drumming with an effective amount of a powdered vegetable tanning extract only.

Other syntans of this type are e.g. exchange syntans such as are described in U.S. Patent 1,901,536 and are

made by condensing naphthalenes or tetrahydronaphthalenes sulfonated at 140–160° C., and condensing the sulfonated naphthalene with formaldehyde and dihydroxy diphenylsulfones. Sulfur chloride can also be used in the condensation. Even more suitable for initiating the final tanning without a liquor are auxiliary syntans and/or sulphite waste liquor, possibly used together with up to 50% of exchange syntans, referred to the amount of pre-tanning agent used. The final tanning without a liquor is advantageously carried out with those condensation products of naphthalene-sulphonic acids and formaldehyde and/or with those sulphite waste liquors which are adjusted to an acid number of at least 30, preferably 50 to 120, with inorganic or organic acids and which may also contain 5–20% of their weight of water-soluble inorganic neutral salts.

The term "acidification or tanning without a liquor" in the meaning of the present invention comprises those processes in which the agents for acidification or tanning are caused to act on the pelt material or the leather in the wet state but without water or substantial amounts of water. Any alkaline swollen pelt yields water in the course of the acidification. As a rule, this amounts to about 15–25%, referred to the pelt weight, that is to say that in the case of the acidification without a liquor as preferred according to the present invention, a corresponding amount of liquor accumulates in the course of the operation. This liquor can be discharged before the pre-tanning with chromium tanning agents or chromium-containing tanning agents. Within the scope of the present invention, however, pre-tanning in the presence of this liquor separated during acidification is also possible without disadvantage. When operating without a liquor, the products are normally used in powdered form, but the use of solid products, e.g. in block form, or of highly concentrated extracts, is also possible. Acidification and tanning without a liquor are mainly performed by milling the pelt or leather with the acidifying agents or tanning agents in a rotating drum.

The new process is particularly suitable for the production of split hides, welting leather, insole leather, sole leather, sole leather splits and water-proof leather.

In the following Examples which are given for the purpose of illustrating the invention, the parts by weight stand for kilograms. The percentages are referred to the weight of the pelt.

Example 1

Split hide pelts (splitting substance 2 mm.) which have been delimed and bated in the usual manner are pickled with 60% water at 20° C., 0.8% sulphuric acid (66° Bé.), 1.5% calcium formate and 4% sodium β -naphthalene-sulphonate. After a drumming time of about 2 hours, the pelts are evenly acidified. Pre-tanning is then carried out in the pickling liquor with 2.5% of a powdered 33% basic chromium sulphate (content of chromium oxide 25%). After a drumming time of about 2 hours, the pelts are evenly tanned. The tanning liquor is drained off and the pre-tanned pelts are rinsed.

The pre-tanned leather is finally tanned in the drum with a vegetable tanning liquor of 5° Bé. The tanning liquor employed consists of 35 parts by weight pure tannin of mimosa, 50 parts by weight pure tannin of a sulphited quebracho extract and 15 parts by weight pure tanning agents of a soft-tanning synthetic exchange tanning agent as is obtainable from 1 mol 4,4'-dihydroxydiphenyl-sulphone, 0.85 mol β -naphthalene-sulphonic acid and 1 mol formaldehyde.

The leather is completely tanned after a tanning time of about 2 days. A smooth leather with a gentle feel is obtained after the usual finishing.

The pre-tanned leather can also be finally tanned in a series of suspenders with 5 pits of 2–6° Bé. In this case a tannin mixture of sulphited quebracho and mimosa is used in a ratio of equal parts by weight of pure tan-

nin. The leather is completely tanned after a tanning time of about 1 week and finished in the usual manner. A smooth and plump leather is obtained.

Example 2

Split hide pelts which are suitable for the production of split hides are delimed and bated in the usual manner. The pelts are then drummed without a liquor with 5% of a powdered mixture of 50 parts by weight sodium or potassium bisulphate, 25 parts by weight ammonium sulphate or ammonium chloride and 25 parts by weight sodium β -naphthalene-sulphonate with the concurrent use of 0.9% of 85% formic acid (diluted with water 1:1). After a treatment time of about 1½ to 2 hours, the pelts have a pH value of about 3.2 to 3.4 throughout their cross-section.

The liquor formed by the elimination of water from the pelts during acidification is left in the drum and 4% of a powdered chromium complex tanning agent as described in Example 1 of U.S. Patent 3,254,937 are added. The acidified pelts are drummed without the addition of water, until the whole cross-section of the pelts is tanned through. This is normally achieved after a tanning time of 1½ to 2 hours. The pre-tanned pelts are subsequently rinsed.

After discharging the rinsing liquor, the pre-tanned pelts are further drummed in the same drum with 8% of a powdered precursory tanning agent. The precursory tanning agent consists of 80 parts by weight of a spray-dried condensation product which is obtained from a technical naphthalene-sulphonation mixture chiefly containing β -naphthalene-sulphonic acid, and present in the form of the ammonium salt, and 0.65 mol formaldehyde per mol naphthalene-sulphonic acid, 10 parts by weight sodium sulphate and 10 parts by weight adipic acid. After a drumming time of 2–3 hours, the pelts are evenly tanned through.

For final tanning the pelts are first drummed in the same drum with 10% pure tannin of a powdered sulphited quebracho extract without a liquor for 1 hour. Then there are added 4% pure tannin of a powdered sweetened chestnut wood extract, 2% of the same powdered quebracho extract and 2% of a commercial soft-tanning synthetic exchange tanning agent, as is obtainable from 1 mol 4,4'-dihydroxydiphenyl-sulphone, 0.9 mol β -naphthalene-sulphonic acid and 1 mol formaldehyde.

After a total tanning time of about 4–5 hours, the leather is completely tanned and is greased and finished in the usual manner. A light-coloured leather of level shade is obtained, which exhibits only a negligible drawn grain or none at all.

Example 3

To produce case leather, 500 parts of split hide pelts (splitting substance 3 mm.) prepared in the usual manner in the lime house, are treated in the drum in one operation, from the alkaline limed pelt to the completely tanned leather, without previous scudding, with 5% of the powdered mixture described below, 0.2% sodium metabisulphite, 0.8% of 85% formic acid diluted with water 1:1 and 0.2% acetic or lactic acid. No liquor is added. After 30 minutes to one hour, the pelts are evenly acidified and have a pH value of about 3.2 to 3.4 in the cross-section. The small amount of liquor formed (about 15 to 20%) is discharged.

The powdered mixture used for acidification of the pelts consists of 50 parts by weight sodium bisulphate and 50 parts by weight of a technical mixture neutralised with ammonia and spray-dried and containing about 65% sulphuric acid, about 35%, 1,5- and 1,6-naphthalenedisulphonic acid, and small amounts of 1,3,6- and 1,3,7-naphthalene-trisulphonic acid.

The acidified pelts are subsequently further drummed in the same drum with 4% powdered pre-tanning agent.

The pre-tanning agent consists of 50 parts by weight

of a 33% basic chromium sulphate (chromium oxide content 25%) and 50 parts by weight of a condensation product present in the form of the sodium salt and obtained from β -naphthalene-sulphonic acid and formaldehyde (molar ratio 1:0.65 mol).

After a drumming time of 2 hours, the pelts are evenly tanned through. The leather is subsequently washed for 10 minutes and rinsed at 30° C. for 5 minutes. The rinsing liquor is completely discharged.

The leather is then further drummed without a liquor with 6% of a powdered synthetic precursory tanning agent.

The precursory tanning agent consists of 70 parts by weight of a spray-dried condensation product present in the form of the ammonium salt and obtained from a technical naphthalene-sulphonation mixture mainly consisting of β -naphthalene-sulphonic acid and formaldehyde in a molar ratio of 1 mol naphthalene-sulphonic acid to 0.9 mol formaldehyde, which has been adjusted to an acid number of 120 by the addition of glutaric acid and also contains 30 parts by weight of a purified and delimed sulphite waste liquor.

After a drumming time of 2 hours, the leather is evenly tanned through. Final tanning is subsequently carried out in the same drum by the addition of 7% of a powdered sulphited quebracho extract and 7% of a powdered mimosa extract. After a treatment of 3-4 hours the leather is completely tanned, then greased and finished in the usual manner. A smooth leather is obtained which exhibits only a negligible drawn grain or none at all.

Example 4

500 parts of alkaline cow butt pelts prepared in the beam house by the methods customary for the production of sole leather are levelled (thickness 4.2 mm.) and treated in the drum, without the addition of water, with 5% of the powdered mixture described below, 0.2% sodium metabisulphite and 1.2-1.5% of 85% formic acid for about 3-4 hours. The liquor emerging from the alkaline swollen pelts has a pH value of about 3.2-3.5. The pelts are evenly acidified throughout their cross-section.

The powdered mixture consists of 50 parts by weight sodium bisulphate, 25 parts by weight ammonium sulphate and 25 parts by weight of a technical naphthalene-sulphonation mixture present in the form of the ammonium salt and mainly consisting of β -naphthalene-sulphonic acid.

After discharging the separated liquor, pre-tanning is carried out with 4% of a powdered chromium-containing synthetic tanning agent.

The pre-tanning agent consists of 60 parts by weight chromic sulphate and 40 parts by weight of a condensation product present in the form of the sodium salt and obtained from β -naphthalene-sulphonic acid and formaldehyde in a molar ratio of 1:0.65.

After a drumming time of 2-3 hours, the pelts are completely penetrated. The pre-tanned leather is washed at 30° C. for 10 minutes and subsequently rinsed for 10 minutes.

After draining the rinsing liquor, drumming is continued with 10% of the powdered precursory tanning agent described below. After a treatment time of about 4 hours the pelts are evenly tanned through.

As precursory tanning agent there is used a spray-dried condensation product present in the form of the ammonium salt, obtained from 1 mol β -naphthalene-sulphonic acid and 0.7 mol formaldehyde, and adjusted to an acid number of 110 by the addition of glutaric or oxalic acid.

The leather is then finally tanned with 16% pure tannin of quebracho extract, 6% pure tannin of mimosa extract and 3% pure tannin of chestnut wood extract, all in powdered form. To avoid chafe marks, it is expedient to add about 0.5% of a sulphited castor oil to-

gether with 1% water simultaneously with the tannin. Depending on the type of raw material employed, the leather is completely tanned after a total tanning time of 24-30 hours. The leather is then finished in the usual manner. A smooth firm sole leather is obtained, which exhibits a negligible drawn grain or none at all.

Example 5

An unsplit cow butt pelt which has been limed in the beam house in the manner customary for sole leather is divided into pieces of 8 by 30 cm. The pieces are treated overnight in the drum in 300% water, 2% ammonium sulphate, 1.5% sodium metabisulphate and 0.5% of 85% formic acid. After discharging the liquor (pH value about 6), one part of the completely delimed pelt pieces the cross-section of which is coloured in a level yellow to yellow-green shade according to the indicator bromothymol blue, are pickled with 100% water and 4.8% of a technical naphthalene-sulphonation mixture mainly containing β -naphthalene-sulphonic acid (acid number 370).

The other part of the comparable pelt pieces are pickled with 100% water, 3.8% sodium bisulphate and 7% sodium β -naphthalene-sulphonate.

The pickled pieces are then individually pre-tanned without a liquor, in a drumming machine as has been described by E. Komarek and G. Mauthe in "Das Leder" 12 (1961), pages 285-289, particularly page 287, with 2.25% of a powdered 33% basic chromic sulphate (chromium oxide content 25%), until the whole cross-section of the pelt is tanned through. The pre-tanned leather is then rinsed with water at 35° C. and the pieces are finally tanned, again individually, in the drumming machine without a liquor with 30% of a powdered sulphited quebracho extract.

To test the rate of tanning agent penetration, the tanning in the drumming machine is interrupted and the leather is cut. The pelt pieces which have been pickled with the sodium salt of naphthalene-sulphonic acid are tanned through more rapidly than the control samples pickled with naphthalene-sulphonic acid. A comparison of the rate of tanning agent penetration with that of pelts which have been pickled with sulphuric acid and sodium chloride only, also shows that the rate of tanning agent penetration is noticeably faster in the case of the pelts pickled with sodium-naphthalene-sulphonate and sodium bisulphate.

Example 6

Bellies suitable for the preparation of case leather are soaked and limed in the customary manner. After short rinsing with water the pelts are delimed and bated in the drum with 200% (referred to the weight of the pelts) of water of 25 to 30° C., 1% of ammonium sulphate, 0.2% of sodium metabisulphite and 0.5% of a customary bating agent. The pelts are then rinsed and pickled with 100% of water, 1.2% of sulphuric acid (66° Bé.), 3% of β -naphthalene sulphonic acid in form of its sodium salt, 3% of sodium sulphate or potassium sulphate and 0.5% of 85% formic acid. After a drumming time of 2 hours the pelts are evenly acidified and exhibit a pH of 3.5 through the entire cross-section.

The pelts are then pretanned in the pickle liquor with 10% of a powdered mixture of 80 parts by weight of 33% basic chromium sulphate (Cr_2O_3 content 25%) and 20 parts by weight of a delimed purified sulphite waste liquor in form of its sodium salt. After a tanning time of 30 minutes the liquor is buffered by the addition of sodium sulphite and sodium carbonate so that at the end of the chrome tannage the liquor exhibits a pH of 3.8.

The evenly tanned leather is rinsed with water, neutralised and drummed without liquor with 6% of a powdered precursory tanning agent. The precursory tanning agent consists of 50 parts by weight of a neutralised condensation product of a technical naphthalene sulphonic acid which essentially contains β -naphthalene sulphonic

acid, and formaldehyde (molar ratio 1:0.65), in form of its sodium salt, and 50 parts by weight of a synthetic exchange tanning agent prepared by condensation of β -naphthalene sulphonic acid and 4,4'-dihydroxy-diphenylsulphone.

After a drumming time of about 2 hours 7% of a pure tannin of a sulphited quebracho extract in powdered form and 7% of a pure tannin of a mimosa extract in powdered form are added. The final tannage is finished after about 4 hours. The leathers obtained are sammed, ret out and finished in the customary manner. Smooth leathers are obtained which exhibit no drawn grain at all or only negligible drawn grain.

Example 7

In Example 6 the chromium pretanning agent is replaced by 10% of a powdered mixture of 60 parts by weight of a 33% basic chromium sulphate tannin (Cr_2O_3 content 25%) and 40 parts by weight of β -naphthalene sulphonic acid (Na-salt). As precursory agent a mixture of 25 parts by weight of a condensation product of β -naphthalene sulphonic acid and formaldehyde (molar ratio 1:1), in form of its sodium salt and spray-dried, 25 parts by weight of a delimed sulphite waste liquor, in form of its sodium salt, and 50 parts by weight of a synthetic exchange tanning agent is employed.

As exchange tanning agent the reaction product of 1 mol of phenol sulphonic acid with 1.2 mol of urea and 1.7 mol of formaldehyde, after-treated with 0.75 mol of phenol and 0.56 mol of formaldehyde, neutralised with ammonia, spray-dried and adjusted to an acid number of 120 by means of glutaric acid is used.

If otherwise proceeded as described in Example 6 smooth leathers are obtained which exhibit no drawn grain at all and which show a full and round handle.

Example 8

Pelt butts suitable for the preparation of sole leather splits are soaked and limed in the customary manner. The pelts are then drummed with about 200% (referred to the weight of the pelt) of water of 28 to 30° C. and 0.2% of hydrochloric acid for 10 minutes. 1.5% of ammonium chloride and 1% of sodium metabisulphite are then added. After a drumming time of 1.5 to 2 hours the pelts are evenly acidified through the entire cross-section. If necessary, 0.2 to 0.3% of hydrochloric acid or formic acid are further added. The pelts shall exhibit a pH of 5.5 to 6 through the cross-section.

The liquor is completely removed and after short rinsing 100% of water, 1.2% of sulphuric acid, 3% of the ammonium salt of β -naphthalene sulphonic acid and 3% of potassium chloride are added. After further drumming for 2 hours 4% of a chromium-containing pretanning agent in powdered form are added. This pretanning agent consists of equal parts by weight of a 33% basic chromium sulphate tanning agent (Cr_2O_3 content 25%) and a spray-dried condensation product of 1 mol of phenol sulphonic acid and 1 mol of urea and 1.55 mol of formaldehyde, in form of its sodium salt. After a tanning time of 3 hours the pelts are evenly tanned through.

The pretanned leathers are washed at 30° C. for 10 minutes and subsequently rinsed with water of 30° C. for 10 minutes. The rinsing liquor is discharged and 10% of a powdered precursory tanning agent as described below added and the drumming continued. As precursory tanning agent a spray-dried sodium salt of a neutral condensation product of 1 mol of β -naphthalene sulphonic acid, 0.5 mol of o-chlorophenol and 0.85 mol of formaldehyde which is adjusted to an acid number of 110 by means of glutaric acid is employed. The preparation of a precursory

tanning agent of this kind is described in U.S. Patent No. 2,829,122.

After a tanning time of 4 hours 26% of a pure tannin of sulphited quebracho extract in powdered form are added without further addition of liquor. The final tannage is complete after a total tannage of 24 to 30 hours. The leathers obtained are finished in the customary manner and represent valuable sole leathers.

We claim:

1. In a process for the rapid tanning of medium-weight and heavy leather, comprising the steps of treating delimed or non-delimed pelts by:

- (1) acidification;
- (2) pretanning with a material selected from the group consisting of
 - (a) inorganic chromium tanning agents; and
 - (b) complexes or mixtures of inorganic chromium tanning agents with at least one material selected from the group consisting of syntans and sulphite waste liquor; and

(3) tanning with a material selected from the group consisting of vegetable tannins, syntans, and mixtures thereof;

the improvement comprising preparing an acidifying agent by mixing:

- (A) mineral acid or salts of mineral acids giving an acid reaction in aqueous solution;
- (B) salts of naphthalene sulfonic acids; and
- (C) salts or the free acid form of the lower alkyl mono-, or hydroxy-carboxylic acid, sulfosalicylic acid or sulfophthalic acid;

at least one of (A), (B), and (C) being an ammonium salt; and by conducting said acidification step (1) thereby; said acidifying agent being used in such amount to produce a pH below about 6.5 throughout the cross-section of said pelts.

2. The process of claim 1 in which said acidifying agent comprises, in addition, a salt of sulfurous acid.

3. The process of claim 1 in which the acidification is conducted to produce a pH of 3.0 to 3.6 in said pelts.

4. The process of claim 1 in which said acidifying agent is a mixture of mineral acid and salts of naphthalene sulfonic acids, said salts of naphthalene sulfonic acids selected from the group consisting of ammonium salts and mixtures of ammonium and alkali metal salts.

5. The process of claim 1 in which said acidifying agent contains, in addition, (D) a neutral salt different from (A), (B), or (C).

6. The process of claim 1 in which the acidification is conducted without substantial amounts of water.

7. The process of claim 1 in which said steps of (2) pretanning and (3) tanning are conducted without substantial amounts of water.

8. The process of claim 7 in which step (1) acidification is also conducted without substantial amounts of water.

References Cited

Otto: Das Leder, November 1963, pages 205-209, TS 940 S.
Progress in Leather Science, 1920-1945, pages 181 and 195-197, Pub. by Brit. Lea. Mfg. Res. Assoc., London, Eng. TS 965 B 75.

GEORGE F. LESMES, Primary Examiner

D. LEVY, Assistant Examiner

U.S. Cl. X.R.

8-94.18, 94.26, 94.27, 94.32