VEGETABLE TANNING PROCESS

8 Claims. (Cl. S—94.32)

This invention relates to vegetable tanning and comprises a novel process of tanning skins and the like to produce high quality vegetable tanned leather rapidly and inexpensively.

Vegetable tanning, as generally practiced, consists in treating the skin under acidic conditions with successive tanning solutions of increasing strength until the necessary amount of tannin has been deposited in the skin, and the skin is thereafter further processed and dried under carefully controlled conditions so that its flexibility and softness are retained in the final leather. The process is time-consuming and generally requires several weeks for completion.

Attempts to use stronger tanning solutions to accelerate the process have not been successful, largely because under acidic conditions, the affinity of the skin for tannin is so great that tannin from strong solutions deposits rapidly in the surface regions and clogs them so that little or no tannin reaches the interior. Dilute solutions of successively increasing strength have accordingly been considered necessary to assure complete penetration of the tannin into and throughout the skin.

The present invention overcomes the limitations to vegetable tanning occasioned by the necessity of so treating the skin as to avoid too rapid a depositing of the tannin in the skin, and thereby providing a rapid and economical vegetable tanning process. The process of this invention has, moreover, the advantage of permitting controlled amounts of tannin to be deposited uniformly throughout the skin, as compared to prior art processes in which the tannin concentration in the skin is generally higher near the surface than at the center. In this connection, by this invention vegetable tanning may be accomplished with a uniform tannin concentration as low as 8 percent by weight, whereas it is generally acknowledged that a vegetable tannin content of 20 percent by weight is required before the skin is tanned.

In general, the process consists in treating the skin under basic conditions with an aqueous solution of the vegetable tannin, until the skin is thoroughly penetrated by the tanning solution. By so treating a skin, the tannin rapidly permeates the skin completely with little or no depositing of the tannin on the skin protein. The skin is thereafter acidified, with the result that the tannin, already present throughout the skin, becomes deposited in the skin, and final drying of the skin is done by extracting and replacing the water with an inert water-miscible organic solvent, which is then dried from the skin.

By treating the skin under basic conditions, preferably at a pH above about 9 and below about 12, there is avoided the necessity of using successive tanning baths of gradually increasing strength, for the affinity between the skin and tannin is apparently low under basic conditions. The tannin solution may accordingly be boiled down to the amount of tannin it is desired to have present in the skin; if desired, concentrated tannin solutions may be used. The subsequent acidification, to within the pH range normally employed in vegetable tanning, that is between about pH 2 and pH 6, produces what would normally be considered a burned or case hardened skin, apparently as a result of suddenly increasing the affinity between the tannin and skin to cause a sudden depositing of the tannin in the skin. If the skin were at this stage dried by evaporating the water it would be hard and brittle and of a dark brown color. However, by drying the skin by extracting and replacing the water with an inert water-miscible organic solvent, the skin may be dried rapidly without showing signs of case hardening.

It is believed that the effect of this solvent dehydration is to decrease temporarily the affinity between the skin and tannin and thus partially detan the skin and redisperse the tannin particles, for it is known that vegetable tannins become increasingly soluble in the water-miscible organic solvents as the acidity increases, whereas the contrary is true of aqueous solutions of vegetable tannins.

A prior investigator (Pawlowitsch British Patent 302,408) has described a vegetable tanning process in which the skin is initially treated with a vegetable tanning solution having a pH of 6–12 to cause the tannin to be introduced into the skin without becoming bound to it. The skin is then gradually acidified to lower the pH to 5–2 to cause the tannin to coagulate on the skin fibers. He reports that acidification carried out over a period of several days, preferably in an acid tanning bath, produces leather of quality comparable to that obtained by conventional practices. Applicant's process is different in that it utilizes a solvent dehydration step to prevent hardening of the skin, and thereby makes it possible to acidify the skin much more rapidly but in a manner such that the skin after acidification becomes hard and brittle upon drying. Whereas the prior process requires several days for the acidification step, applicant's entire process requires only a few hours. The process is accordingly characterized by the addition of acid to the skin at a rate sufficiently rapid to cause the skin to be in such condition that it would become hard and brittle upon drying after the acid is added, as may be determined by air drying a portion of the skin, and then extracting the water from the acidified skin by means of the solvent to cause the skin to be in condition that it may be dried without becoming hard and brittle.

The process of this invention may be carried out with ordinary vegetable tanning agents such as quinacrine (either ordinary or sulfite), wattle, chestnut, cutch, and also with synthetic vegetable tanning agents such as the lignosulfonates (commonly referred to as "sulphite cellulose extract"), spruce extract and the like. Solutions of these materials in water may be used in various concentrations, it being only necessary that the amount of solution absorbed by the skin contain the desired amount of tannin dissolved therein. Adjusting the pH of the tannin solution to within the desired range of 9–12 is conveniently accomplished by adding a water-soluble base, such as sodium hydroxide or sodium carbonate, to the tannin solution until the desired pH, as conveniently measured by a Beckman glass electrode or by a color indicator, is reached.

The skin is treated with the tannin solution as by drumming it in the solution, until uniformly permeated which usually requires 1–2 hours. The treatment may be carried out at room temperature but is accelerated if the solution is heated to a temperature preferably about 20 Fahrenheit degrees below the shrinking temperature of the skin. During this treatment, the pH should be maintained within the 9–12 range and the addition of a base may be required, particularly if the skin was in-
lately acid. After the skin has been permeated with the tannin solution, it is acidified preferably after rinsing off residual tannin solution and by immersing it in an aqueous solution having an acidity to neutralize the base within the skin and to bring the final pH between about 2 and preferably between about 3 and 4.5.

This may be done by calculating from the amount of tannin solution absorbed and the concentration of base in the skin by well-known stoichiometric methods the amount of acid required to neutralize the base in the skin, and adding this to an aqueous solution having a pH of the desired final value. Alternatively, the skin may be immersed in water and acid added slowly until a final and constant pH of the desired value is attained.

Acidification may also be carried out in non-aqueous systems, for instance in a solution of an inert water-miscible organic solvent, e.g. acetone or methanol, by adding the required amount of acid to the solvent and immersing the skin therein. In this modification, acidification occurs simultaneously with at least part of the subsequent solvent dehydration step. It should here be noted that inasmuch as acidification of the basic skin results in the formation of salts frequently insoluble in the organic solvent, acidification in an organic solvent solution usually leads to salt retention in the skin.

Materials suitable for acidification include such acids as hydrochloric, sulfuric, and acetic and other acidic materials having no deleterious effect on the skin.

The final step of extracting and replacing the water with a water-miscible organic solvent may be accomplished by immersing or drumming the skin in the solvent repeatedly until it is substantially dehydrated. Alternatively, the solvent may be forced through the skin under a fluid pressure differential, conveniently by the method and apparatus described in applicant's United States Patent No. 2,702,229. Suitable solvents include alcohols such as methyl or ethanol, ketones such as acetone or methyl ethyl ketone and other well-known inert water-miscible organic solvents, preferably volatile solvents of low viscosity.

Following the extraction of the water, the skin is dried of solvent advantageously under conditions permitting solvent recovery, but may beforehand be fat-liquored or curried by immersing the skin in, or applying to it, a fatting composition such as oleic acid, cod liver oil, neats-foot oil, castor oil, mineral oil, or other suitable oil or grease compositions.

While raw, bated or pickled skins may be tanned as described above with entirely satisfactory results, it is preferred that the skin be pretreated to increase its permeability and to stabilize it against swelling when treated with the basic tannin solution. A suitable pretreatment is disclosed in applicant's copending application, Serial No. 613,338, filed October 1, 1956, now U.S. Patent 3,066,714 (which was a continuation-in-part of Serial No. 481,999, filed January 17, 1955, now abandoned, which in turn was a continuation-in-part of application Serial No. 330,067, filed January 7, 1953, now abandoned) and consists in a treatment with formaldehyde. In a preferred embodiment, the skin is pretreated by immersing it in an aqueous formaldehyde solution having a pH between 2.0 and 5.0, preferably in the range of 3.0-4.5, and containing at least 2.0-4.0 percent salt (based on weight of solution), and at least 0.5 percent formaldehyde based on the wet weight of the skin, preferably at a concentration level of 1-40 percent by weight. The skin is drumming in the pretreating solution until its shrinkage temperature has reached about 150° F. or higher and is then removed and rinsed of the pretreating solution. To accelerate the pretreatment, it is advantageous to heat the solution as the shrinkage temperature rises, but while maintaining the temperature no higher than about 15-20 Fahrenheit degrees below the shrinkage temperature of the skin.

After pretreatment the skin is acidic and should be 75% equilibrated to the pH range of the tanning bath, as by drumming the skin in a basic aqueous solution to raise the pH to the 9-12 range, but if desired, the additional amount of base required to neutralize the acid in the pretreated skin may be added to the tanning solution, and the acid skin added directly without preliminary equilibration.

The process of this invention may also be used to tan or retan skins previously treated with other tanning agents, such as chrome tanned skins.

A typical and preferred process embodying and representative of this invention is described in detail below.

A pickled water-wet sheepskin having a pH of about 3.8 and weighing about 3 lbs. is drummed in five gallons of a pretreating solution consisting of:

<table>
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<th>Parts by weight</th>
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<tr>
<td>Formaldehyde (aqueous 40%)</td>
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<tr>
<td>Salt (NaCl)</td>
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<tr>
<td>Sulfuric acid—to adjust the pH to 3.8.</td>
</tr>
<tr>
<td>Water—to make up 100 parts by weight.</td>
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The shrinkage temperature from samples cut from the skin is determined initially and at 45 minute intervals, and at each determination the bath temperature is raised to 20 Fahrenheit degrees beyond the shrinkage temperature, and held there. After the shrinkage temperature has reached about 180° F. (generally after about 1/4-1/2 hours) the skin is removed and washed with water.

The skin is then drummed in about twice its wet weight of an aqueous solution to which sodium hydroxide in an amount sufficient to raise the equilibrium pH to a constant value of about 11 is added (about 1-2 percent NaOH on the wet weight of the skin), and after equilibrium at pH 11 has been attained, the skin is removed and immersed in twice its wet weight of the tanning solution.

A typical tanning solution consists of a concentrated aqueous solution of quebracho (containing about 33 percent solids by weight) to which sodium hydroxide has been added to bring the pH to about 11. The skin is drummed in the tanning solution until thoroughly penetrated as may be determined by cutting a fresh cross-section in the skin and noting from the color the degree of penetration.

The skin permeated with the tanning solution is then removed from the tanning bath, rinsed quickly in water to remove excess tanning solution and then drummed in twice its wet weight of an aqueous solution to which hydrochloric acid has been added in an amount sufficient to neutralize the base in the tanning solution absorbed by the skin and bring the final equilibrium final pH to about 3.8. Conveniently, the acid is added slowly while the pH is measured until the desired pH is maintained at a constant value.

After acidification the skin is removed from the acidifying bath and drummed repeatedly in acetone until the acetone-water solution in equilibrium with the skin has attained a constant specific gravity of 0.910 (20° C.), which corresponds to a water content in the acetone of about 7 percent by weight.

The skin is then immersed in a 10 percent solution of oleic acid and acetone, and finally dried.

The skin thus treated is completely tanned throughout, and is soft and pliable and in all respects a leather of high quality.

It will be understood that the foregoing example is presented to describe the preferred method of practicing this invention, and modifications readily occurring to those skilled in the science of tanning may be made without departing from the spirit and scope of this invention. For instance, the pretreating treatment in formaldehyde may be eliminated if desired, or may be replaced by a pre-tanning step in a chrome tanning solution or in other pre-tanning baths. Also, other vegetable tanning agents may be used, and other solvents for extraction of the water are entirely satisfactory, and the concentrations and other
conditions of the treatment may be varied within the limits established.

From the foregoing disclosure, it is believed apparent that the process of this invention represents a substantial advance in the art of vegetable tanning, particularly in the speed with which it may be carried out, in the degree of control over the deposition and uniformity of distribution of the tannin in the skin, and in the ease with which the skin may be finally dried.

This application is a continuation-in-part of applicant's copending application Serial No. 467,207, filed November 5, 1954, now abandoned.

Having thus disclosed my invention and described in detail the preferred embodiments thereof, I claim and desire to secure by Letters Patent:

1. A vegetable tanning process comprising impregnating a skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, contacting said skin having a pH between about 9 and 12 with an aqueous acid solution containing sufficient acid to bring the pH in the skin to between about 2 and 6 thereby to acidify the skin at a rate so rapid as to cause the skin to be in such condition that it would become hard and brittle if air dried to remove the water after said acid is added, extracting the water from the skin by contacting the skin with acetone thereby causing the skin to be in condition to be dried without becoming hard and brittle as aforesaid, and drying the skin to remove the acetone, thereby tanning the skin.

2. A vegetable tanning process comprising impregnating a skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, adding acid to the skin in an amount to bring the pH in the skin to between about 2 and 6 by contacting the skin with a solution of an acid in an inert, water-miscible organic solvent thereby causing the skin to be in condition to be dried and brittle if air dried to remove the water after said acid is added, extracting the water from the skin by contacting the skin with acetone thereby causing the skin to be in condition to be dried without becoming hard and brittle, and drying the skin to remove the solvent, thereby tanning the skin.

3. A vegetable tanning process comprising contacting a skin with an aqueous solution of formaldehyde having a pH of between about 2 and 5 at least until the shrinkage temperature of the skin has reached 150°F, impregnating the skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, contacting said skin having a pH between about 9 and 12 with an aqueous acid solution containing sufficient acid to bring the pH in the skin to between about 2 and 6 thereby to acidify the skin at a rate so rapid as to cause the skin to be in such condition that it would become hard and brittle if air dried to remove the water after said acid is added, extracting the water from the skin by contacting the skin with acetone thereby causing the skin to be in condition to be dried without becoming hard and brittle as aforesaid, and drying the skin to remove the solvent, thereby tanning the skin.

4. A vegetable tanning process comprising impregnating a skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, contacting said skin having a pH between about 9 and 12 with an aqueous acid solution containing sufficient acid to bring the pH in the skin to between about 2 and 6 thereby to acidify the skin at a rate so rapid as to cause the skin to be in such condition that it would become hard and brittle if air dried to remove the water after said acid is added, extracting the water from the skin by contacting the skin with acetone thereby causing the skin to be in condition to be dried without becoming hard and brittle as aforesaid, and drying the skin to remove the acetone, thereby tanning the skin.

5. A vegetable tanning process comprising contacting a skin with an aqueous solution of formaldehyde having a pH of between about 2 and 5 at least until the shrinkage temperature of the skin has reached 150°F, impregnating the skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, contacting said skin having a pH between about 9 and 12 with an aqueous acid solution containing sufficient acid to bring the pH in the skin to between about 2 and 6 thereby to acidify the skin at a rate so rapid as to cause the skin to be in such condition that it would become hard and brittle if air dried to remove the water after said acid is added, extracting the water from the skin by contacting the skin with acetone thereby causing the skin to be in condition to be dried without becoming hard and brittle as aforesaid, and drying the skin to remove the acetone, thereby tanning the skin.

6. A vegetable tanning process comprising impregnating a skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, removing said skin having a pH between about 9 and 12 from said aqueous solution and contacting the skin with an acidic solution until the pH in the skin is between about 2 and 6, extracting the water from the skin by contacting the skin with an inert, volatile, water-miscible organic solvent and drying the skin to remove the solvent, thereby tanning the skin.

7. A vegetable tanning process comprising contacting a skin with an aqueous solution of formaldehyde having a pH of between about 2 and 5 at least until the shrinkage temperature of the skin has reached 150°F, impregnating the skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, removing said skin having a pH between about 9 and 12 from said aqueous solution and contacting the skin with an acidic solution until the pH in the skin is between about 2 and 6, extracting the water from the skin by contacting the skin with an inert, volatile, water-miscible organic solvent and drying the skin to remove the solvent, thereby tanning the skin.

8. A vegetable tanning process comprising contacting a skin with an aqueous solution of formaldehyde having a pH of between about 2 and 5 at least until the shrinkage temperature of the skin has reached 150°F, impregnating the skin with an aqueous solution of a vegetable tanning agent at a pH in the skin of between about 9 and 12, removing said skin having a pH between about 9 and 12 from said aqueous solution and contacting the skin with an acidic solution until the pH in the skin is between about 2 and 6, extracting the water from the skin by contacting the skin with acetone, and drying the skin to remove the acetone, thereby tanning the skin.

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