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2,906,591

## METHOD OF DEHYDRATING WITH ORGANIC SOLVENT AND THEN VEGETABLE TANNING UNTANNED SKINS

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No Drawing. Application June 21, 1954  
Serial No. 438,319

8 Claims. (Cl. 8—94.18)

This invention consists in a vegetable tanning process carried out entirely under non-aqueous conditions, and provides a process which may be carried out far more rapidly than prior art processes as well as one in which superior control over the leather is afforded.

Vegetable tanning as generally practiced consists in immersing the skins under carefully controlled conditions in aqueous vegetable tannin solutions of gradually increasing strength until the desired amount of tannin has been incorporated in the skin. The skin is thereafter dried carefully with frequent mechanical manipulation to produce the finally tanned leather. The process is time-consuming, generally requiring several weeks for the introduction of the tannin, and several days for drying.

The advantages of treating skins in systems utilizing inert water miscible organic solvent instead of water have long been appreciated. A primary advantage is that the tannin may be introduced into the skin rapidly, generally in the time required for the solution to penetrate the skin. It has, however, not been possible prior to this invention to complete the tanning operations under non-aqueous conditions. Prior art processes of vegetable tanning using inert organic solvent solutions of tannins have all included the steps of wetting the skins in water after they have been impregnated with the tannin solution. The reports on these processes indicate that a final water treatment is necessary to fix properly the tannin in the skin.

Thus, while prior art reports indicate that the time consuming operations of depositing tannin in the skin may be avoided by treating the skin with an organic solvent solution of tannin, the step of rewetting in water makes it necessary to dry the skin slowly and under carefully controlled conditions. Furthermore, rewetting of the solvent wet skin in water after treatment with the organic tannin solution renders solvent recovery difficult because of the formation of a solvent-water mixture.

A process of vegetable tanning which may be carried out completely under non-aqueous conditions is disclosed in applicant's copending applications Serial No. 100,965 filed June 23, 1949, now abandoned, and Serial No. 263,129, filed December 24, 1951, now Patent No. 2,781,241, of which this application is a continuation-in-part. This invention is based in part on the discovery that the tannin may be deposited in the skin from an organic solvent solution by altering the solubility of the tannin or the affinity of the skin for the tannin, and that a finally and completely tanned skin may be obtained if the skin is finally acidified, which may be performed either before or after the skin is finally dried.

Accordingly, the process of this invention consists in general of extracting and replacing the water of an ordinary water-wet untanned skin with an inert organic water-miscible solvent, then impregnating the skin with an organic solvent solution of a vegetable tannin and causing the tannin to be deposited in the skin. The skin is then

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finally tanned by acidifying and drying, in the manner indicated.

The initial step of extracting and replacing the water in the water-wet untanned skin to solvent dehydrate it may be performed by repeatedly immersing the skin in the inert water-miscible organic solvent until substantially all of the water is extracted, as may be determined by measuring the water content of the water-solvent mixture in equilibrium with the skin. Alternatively, the solvent may be forced through the skin under an applied fluid pressure differential, conveniently in the manner and by the process described and claimed in applicant's copending application, Serial No. 233,924, filed June 27, 1951, now Patent No. 2,702,229. The skin is thereafter treated under substantially non-aqueous conditions until finally tanned, and may be dried of solvent prior to further treatment. When dried the solvent dehydrated skin exhibits much of the softness, flexibility and texture of tanned skins, and may accordingly be inspected and graded prior to being tanned. A further advantage of drying the solvent dehydrated skin accrues from the rapidity with which the tannin solution penetrates a dry skin during the subsequent step of immersing or otherwise treating the skin with an organic solvent solution of a vegetable tannin.

The tannin solution may consist of any of numerous well-known vegetable tannins, such as quebracho, cutch, sumac, wattle and hemlock, to name but a few, dissolved in a suitable inert organic solvent, such as acetone or methanol. Preferably, the solvent is made acidic to increase the solubility of the tannin and to permit introduction of the tanning solution into the skin without causing deposition of the tannin on the skin fibers and consequent clogging.

In this connection it has been observed with respect to inert organic solvent solutions of vegetable tannins, that under acidic conditions the tannin tends to remain in solution, and that the solubility decreases as the solution is made more basic. It further appears that as the skin is made more basic its affinity for the tannin increases. Thus, in introducing the tannin into the skin and causing it to be deposited it is preferred that the skin and solution be initially quite acidic (e.g. an acidity equivalent to a pH of below about 2.0) to permit complete and thorough penetration of the tannin, and that the tannin be thereafter deposited in the skin as by introducing a basic material into the solvent wet skin, as by immersing the skin in an organic solvent solution of a base or by exposing the skin to vapors of a base.

It has been observed, however, that in the acidity-basicity range equivalent to a pH range of about 2.0—6.0, as determined by color indicators (e.g. Bromphenyl blue and Methyl red), tannin from an organic solvent solution will penetrate the skin and become deposited therein to some extent, and the skin may accordingly be at least partially tanned by immersing it in an organic solvent solution of a tannin at acidity-basicity conditions equivalent to a pH of about 2.0—6.0 and drying it without adding additional base to the skin. If the solvent dehydrated skin is treated with the tannin solution under conditions more basic than this, the tannin will tend to deposit in greater amounts in the skin as the solution penetrates, with the result that the outer regions of the skin will initially pick up tannin to the exclusion of the interior, and complete penetration of the skin with tannin will require greater time. But nevertheless, even with such limitations, the tannin may be introduced into the skin under slightly basic conditions. Preferably, however, as indicated above, the tannin is introduced while the skin and solution have an acidity equivalent to a pH of below about 2.0 and the tannin is then caused to become deposited by reducing the acidity to correspond to a pH of above 6.0, prior to final acidification and drying.

After the tannin has been deposited in the skin, the skin may be dried and further treated as required, or alternatively the skin may be treated as required prior to drying.

With the tannin deposited in the skin, the skin should be acidic to bring it to its finally tanned condition. A subsequent acidification step may not be necessary if the skin is already acidic, as pointed out above. If, however, deposition of the tannin has involved adding a base to the skin, further treatment to make it acidic is preferred. Accordingly, the skin may be immersed or otherwise treated with an organic solvent solution of an acid, which may be done without redissolving or otherwise adversely affecting the tannin deposited therein, apparently because the rate of solution of vegetable tannins is slow. Alternatively, the skin may be exposed to acid vapors after the tannin has been deposited in it, and either before or after the skin is dried. When the acidified skin is finally dried, it will be found to be fully tanned and equal or superior as leather to that produced by conventional vegetable tanning processes. An effect achieved by this process which is not achieved readily by aqueous vegetable tannage is a uniform distribution of tannin throughout the cross-section of the skin.

Suitable solvents for carrying out the process include generally any inert water-miscible organic solvent, such as acetone, methanol, ethanol, isopropyl alcohol, methyl acetate, dioxane to name but a few of the more common ones. It is obviously desirable to carry the process through in the presence of a single solvent to prevent intermixing of solvents and the resulting necessity of separating the solvents.

In acidifying the skin and the organic solvent solution of the vegetable tannin prior to incorporation of the tannin solution into the skin, hydrochloric acid is preferred although other mineral and organic acids may be used. It has been found that in organic systems a skin will adsorb very large amounts of strong mineral acids, such as HCl, much in the manner of an anion exchange resin, but only moderate amounts of weak organic acids such as acetic acid. Thus, because hydrochloric acid is volatile and may escape from the skin when it is dried, it is preferred over other mineral acids, as sulfuric, which would remain in the skin after drying and would require subsequent treatment for removal, and is preferred over weak acids because desirably large amounts may be adsorbed by the skin.

In the final acidification the skin need be made only moderately acidic. Thus, if the final acidification involves treating the skin with an organic solvent solution of an acid, a weaker acid, such as acetic acid, is preferred, because smaller amounts are adsorbed by the skin than when a strong mineral acid is used, although the latter may be used satisfactorily. If acidification is done by exposing the dried skin to acid vapors, any volatile acid is satisfactory, such as acetic or hydrochloric, the latter being preferred.

Under preferred conditions, the skin during impregnation with the tannin solution is maintained at an acidity equivalent to a pH of about 2.0 or lower, but is acidified during the final acidification such that when dried the acidity is equivalent to a pH of between about 2.0 and 6.0, preferably about 2.5 to 4.0.

Suitable bases for treating the skin during processing according to this invention include ammonia, either in solution or as a gas, trimethylamine, also either in solution or as a gas, as well as such other well-known basic materials as sodium hydroxide or sodium carbonate. In adding a base to the skin, the skin may be immersed in a basic solution or it may be exposed to the vapors of a basic material.

The foregoing description is presented as a general outline of the invention, and limited to the essential steps. Other conventional tanning operations may be included, if desired, such as fat-liquoring which is conveniently per-

formed in the manner described in my copending application, Ser. No. 426,151, filed April 28, 1954, after the tannin has been deposited in the skin and preferably before the skin has ever been dried of solvent.

In general, the several steps may be performed by immersing or drumming the skins in appropriate solutions until the desired condition is attained, or, where there is no danger of the tannin migrating from the skin, by forcing the treating solution through the skin under a fluid pressure differential, as by the apparatus and process described in applicant's copending application, Serial No. 233,924, filed June 27, 1951, now Patent No. 2,702,229. A convenient method of determining when the condition desired by any step has been attained in the skin consists in cutting a sample of the skin to obtain a fresh cross-section, to which may be applied color indicators to determine the degree and distribution of acids or bases through the skin. Similarly, by obtaining a fresh cross-section of a skin the distribution of tannin through it may be readily determined.

In describing this invention, reference is made to the acidity of the skin in terms of an equivalent pH value, by which is meant the pH as determined by applying a color indicator to the skin, and comparing the resultant color with standardized samples of known pH.

The following examples have been selected as illustrative of preferred embodiments of this invention.

#### Example I

A water-wet pickled sheepskin is washed in water to remove excess salt and then solvent dehydrated by drumming in successive baths of acetone until the acetone-water mixture in equilibrium with the skin is no more than 0.792 at 70° F. The skin is then drummed in five times its wet weight of acetone to which has been added about one fifth its wet weight of concentrated commercial hydrochloric acid (22° Bé.). Drumming is continued until the skin is acidified throughout to an acidity equivalent to a pH of less than 2.0. This may be determined by taking a sample of the skin, rinsing it in acetone to remove excess acid, then cutting it to expose a cross-section and applying a color indicator, e.g., thymol blue, to the fresh section. Initially the acid will be adsorbed at the surfaces while the interior remains at a low acidity and this will be readily apparent by the color of the indicator. When the skin is thoroughly acidified, as evidenced by an acid reaction with the indicator through the entire cross-section of the skin, the skin is removed from the acidified acetone, rinsed in acetone to remove excess acid and then dried of acetone.

The dried skin is then immersed in a methanol solution of quebracho formed by combining

|                                       |           |      |
|---------------------------------------|-----------|------|
| Quebracho extract, cold water soluble | --grams-- | 600  |
| Methanol                              | -----cc-- | 2400 |
| Hydrochloric acid, conc. commercial   | -----cc-- | 20   |

then tumbling the mixture for 24 hours and filtering out undissolved quebracho (about 54 grams).

After the skin is thoroughly impregnated with the quebracho solution, it is removed and immersed in about four times its wet weight of methanol to which is added ammonia, either as a gas, as its concentrated aqueous solution or as a methanol solution, in an amount at least sufficient to neutralize the acid in the skin. In this example, 5% of the wet weight of the skin of ammonia gas, or 15% of the wet weight of the skin of concentrated aqueous ammonia (28%), added to the methanol is sufficient. The skin is kept in the ammonia bath until it is uniformly basic throughout as may be determined by removing a sample, rinsing it in methanol, then cutting a fresh cross-section to which is applied a color indicator such as Bromthymol blue. Generally one to two hours in the ammonia solution is required, and preferably the neutralization is carried out in two stages, by changing to a fresh ammonia solution about halfway

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through the neutralization, each solution containing about half the total ammonia required.

After the skin is neutralized, and the quebracho has been deposited in the skin, the skin is acidified, conveniently by drying the skin and then exposing it in an atmosphere of hydrogen chloride until the skin indicates acidity uniformly throughout which may be determined by applying a color indicator to a freshly cut cross-section. The time required will depend on such factors as the concentration of hydrogen chloride and the porosity and thickness of the skin, but will generally require in an atmosphere in equilibrium with concentrated hydrochloric acid at room temperature, an exposure period of between 30 seconds and five minutes.

*Example II*

In this procedure, the skin is treated in the manner described in Example I to and including the neutralization in the ammonia solution. Instead of being dried the skin is finally acidified by immersing it in five times its wet weight of methanol containing sufficient acid, such as acetic or hydrochloric, to render the skin acidic (equivalent to a pH between about 2.5 and 4.0) throughout.

Preferably acetic acid is used because of the lower adsorptive capacity of the skin for it, as compared with hydrochloric acid, with the result that the acid penetrates the skin rapidly. When the skin shows an acidity throughout its cross-section equivalent to a pH of 2.5-4.0, as may be determined by Bromphenol blue or Bromcresol green, it is removed and dried.

If the acidifying acid is a strong mineral acid such as HCl, it will be adsorbed by the skin initially at its outer surfaces and will penetrate inwardly only as the adsorptive capacity of the outer regions is satisfied. Thus, before there is total penetration by the acid, more than enough to bring about the necessary acidification will have been adsorbed. Ordinarily the skin will have adsorbed sufficient hydrochloric acid when the acid has penetrated from each side a distance of about one-third the thickness of the skin, as may be determined by applying an indicator such as thymol blue to a cross-section of the skin. If the skin is then dried, the acid at the outer regions will thoroughly permeate the skin and bring about proper acidification throughout such that the dried skin is well tanned.

*Example III*

A pickled sheep skin is drummed repeatedly in methanol until the specific gravity of the equilibrium solution is below 0.805 at 70° F., and is then drummed in its weight of methanol to which has been added 2% of the weight of the skin of 22° Bé. hydrochloric acid. The skin is then dried and drummed in a quebracho solution formed by combining

Quebracho extract -----grams-- 400  
Methanol to make up -----cc-- 2000

and tumbling the mixture for 24 hours then filtering out undissolved quebracho fractions, adding to the filtrate 290 cc. of a solution of ammonia gas in methanol having a specific gravity of 0.777 at 70° F., then boiling the ammoniated mixture under reflux for three hours, and finally cooling it prior to introduction of the skin.

After the skin is thoroughly penetrated by the quebracho solution, during which time quebracho will be deposited in the skin, the skin is immersed and tumbled in its own wet weight of carbon tetrachloride to which has been added 1% of its wet weight of acetic acid, until thoroughly penetrated, and the skin is then dried.

In this example the tannin solution was made basic by the addition of ammonia, and as a result the tannin deposited on the skin during immersion of the skin in the tannin solution and without subsequent treatment. The finally dried skin is a fully tanned leather of high quality.

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*Example IV*

A wet depickled cowhide weighing 750 grams is washed in water to remove excess salt and is then drummed repeatedly in acetone until the acetone in equilibrium with the skin has reached a specific gravity of less than 0.792 at 70° F. The skin is then made basic by drumming in a solution consisting of:

Cc.  
Ammonium hydroxide (conc. commercial) ----- 50  
Acetone ----- 1000

until uniformly permeated as determined by a color indicator such as thymol blue applied to a freshly cut cross-section, and is then rinsed in acetone to remove excess base.

A piece of the skin weighing 464 grams is then drummed in a quebracho solution consisting of:

Cc.  
Quebracho solution as described in Example I above ----- 928  
Ammonium hydroxide, conc. commercial ----- 3.1

until thoroughly impregnated with the tannin, and then rinsed in acetone until the washings are clear.

A piece of this skin weighing 240 grams is finally tumbled in an acid solution consisting of:

Cc.  
Acetone ----- 1000  
Glacial acetic acid ----- 4.8

until uniformly acid throughout a cross-section, and is finally rinsed of excess acid in acetone and dried.

*Example V*

A pickled sheep skin is washed in water to remove excess salt, and is then solvent dehydrated by tumbling repeatedly in methanol until the liquid in equilibrium with the skin has a specific gravity of less than 0.805 at 70° F. The skin is then removed and drummed in its weight of a methanol solution of ammonia having a specific gravity of 0.777 at 70° F., until thoroughly penetrated as determined by applying a color indicator to a freshly cut cross-section. The skin is then drummed in twice its weight of methanol to which has been added 0.4% of sodium hydroxide based on the wet weight of the skin, until equilibrium is reached. After the skin is rinsed in methanol it is drummed in twice its wet weight of a tannin solution consisting of:

Parts by vol.  
Quebracho solution of Example III ----- 1  
Methanol ----- 4

until thoroughly penetrated with the tannin. The skin is then acidified by drumming in twice its weight of carbon tetrachloride to which is added 5% of the wet weight of the skin of glacial acetic acid, until uniformly acidified, and is finally dried.

The leather produced in each of the foregoing examples is in all respects fully tanned such that it may be wet in water and dried without becoming hard or horny and will have a shrinkage temperature generally well in excess of 150° F. In addition to producing fine leather, the process has the advantages of being rapid and lacking the critical control of conditions characterizing vegetable tanning processes carried out under aqueous conditions. In this connection it has been found that the concentrations of the various treating solutions are not particularly critical so long as sufficient treating reagent is present to achieve the desired condition, and in carrying out the various steps it is contemplated that one skilled in the art will be able to formulate treating solutions suitable for performing the step on the basis of the teachings of this specification and without resorting to experimentation amounting to invention.

It is also contemplated that modifications to the process described will occur to those skilled in the art and that

such may be made without departing from the scope of this invention. In particular, other well-known vegetable tanning agents may be used with entirely satisfactory results as may certain synthetic materials known to behave as vegetable tanning agents. One such is benzoquinone which has been used, as a solution in methanol prepared by adding to 2500 cc. of a saturated (at room temperature) solution of benzoquinone in methanol, 2500 cc. of methanol and 40 cc. of a 10% solution of sodium hydroxide in water, as the tanning agent in the procedure of Example V.

Similarly, the tanning agents derived from sulfite waste liquors, e.g. sodium ligno sulphonate, commercially available as Maratan, and other synthetic tanning materials, such as naphthalen sulfonic acid-formaldehyde condensation product (available as Leukanol N.D.) and the sodium salt thereof (sold as Tamol) are generally suitable in the practice of this invention. It is also contemplated that chemically similar materials, not soluble in water and hence not presently used as tanning agents, but soluble in suitable organic solvents may also be used with very satisfactory results in the practice of this invention.

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

1. A method of tanning skins under substantially, non-aqueous conditions consisting essentially of contacting an untanned water-wet skin with an inert water-miscible organic solvent until substantially all the water from the skin is extracted and replaced by said solvent, then processing the skin in the absence of water with the steps of impregnating the skin with an inert organic solvent solution of a vegetable tanning at an acidity of the skin such that the tannin is introduced into the skin, controlling the acidity of the skin until the tannin impregnated skin is brought to an acidity corresponding to a pH of more than 6, the tannin is distributed through the skin and the skin remains essentially untanned, then finally adding an acidic reagent to the skin to bring the final acidity of the skin to correspond to a pH of between 2.0 and 6.0 and drying the skin to remove organic solvent so that the skin is tanned.

2. A method of tanning skins under substantially non-aqueous conditions consisting essentially of contacting an untanned water-wet skin with an inert water-miscible organic solvent until substantially all the water from the skin is extracted and replaced by said solvent, then processing the skin in the absence of water with the steps of impregnating the skin with an inert organic solvent solution of a vegetable tannin at an acidity of the skin such that the tannin is introduced into the skin, controlling the acidity of the skin until the tannin impregnated skin is brought to an acidity corresponding to a pH of more than 6, the tannin is distributed through the skin and the skin remains essentially untanned, then finally adding an acidic reagent to the skin to bring the final acidity of the skin to correspond to a pH of between 2.5 and 4.0 and drying the skin to remove organic solvent so that the skin is tanned.

3. A method of tanning skins under substantially non-aqueous conditions consisting essentially of contacting an untanned water-wet skin with an inert water-miscible organic solvent until substantially all the water from the skin is extracted and replaced by said solvent, then processing the skin in the absence of water with the steps of impregnating the skin with an inert organic solvent solution of a vegetable tannin under conditions such that the acidity of the skin corresponds to a pH of less than 2.0, then reducing the acidity of the skin until the tannin impregnated skin is brought to a pH of more than 6, the tannin is distributed through the skin and the skin remains essentially untanned, then finally adding an acidic reagent to the skin to bring the final acidity of the skin to correspond to a pH of between 2.0 and 6.0 and drying the skin to remove organic solvent so that the skin is tanned.

4. A method of tanning skins under substantially non-aqueous conditions consisting essentially of contacting an untanned water-wet skin with an inert water-miscible organic solvent until substantially all the water from the skin is extracted and replaced by said solvent, then processing the skin in the absence of water with the steps of impregnating the skin with an inert organic solvent solution of a vegetable tannin under conditions such that the acidity of the skin corresponds to a pH of less than 2.0, then reducing the acidity of the skin until the tannin impregnated skin is brought to a pH of more than 6, the tannin is distributed through the skin and the skin remains essentially untanned, then finally adding an acidic reagent to the skin to bring the final acidity of the skin to correspond to a pH of between 2.5 and 4.0 and drying the skin to remove organic solvent so that the skin is tanned.

5. The method defined by claim 4 wherein the acid added in the final steps is in solution in an organic solvent.

6. The method defined by claim 5 wherein the acid added in the final steps is acetic acid.

7. The method defined by claim 4 wherein the acid added to the skin to bring the final acidity of the skin to correspond to a pH of between 2.5 and 4.0 is added by exposing the skin to vapors of a volatile acid.

8. The method defined by claim 7 wherein the skin is dried before acid is added to the skin to bring the final acidity of the skin to correspond to a pH of between 2.5 and 4.0 and the skin is thereafter exposed to the vapors of a volatile acid.

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