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[54] **TANNING WITH TRIS(HYDROXYMETHYL)**
NITROMETHANE AND A POLYHYDRIC PHENOL
11 Claims, No Drawings

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ABSTRACT: A process for tanning skins in which skins are first impregnated and drummed at a pH range of 4.5 to 4.7 in a buffered aqueous solution containing tris(hydroxymethyl)nitromethane and a polyhydric phenol such as resorcinol, catechol, hydroquinone, pyrogallol and phloroglucinol. During the operation the pH of the tanning solution is adjusted to the range of 8.0 to 8.5 and the skins drummed until tanned. Skins tanned by the above process can be retanned with any other tanning material.

TANNING WITH TRIS(HYDROXYMETHYL)NITROMETHANE AND A POLYHYDRIC PHENOL

A nonexclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to the tanning of skins and hides. More particularly, it relates to a new in situ tanning process using tris(hydroxymethyl)nitromethane [2-(hydroxymethyl)-2-nitro-1,3-propanediol] hereafter referred to as THNM, and free phenols under controlled conditions.

THNM by itself is a very poor tanning agent and cannot be used to produce an acceptable leather. Free and initially uncombined phenols are also very limited in tanning applications. In fact, many phenols such as resorcinol have no tanning ability per se. Even mixtures of phenols and aldehydes are not generally applicable as combination tanning agents. For instance, of the dihydric phenols, the ortho- and paraderivatives, catechol and hydroquinone, exhibited no tanning power when combined with formaldehyde. Although the meta derivative, resorcinol, gave a satisfactory tannage, the leathers were unstable to light and darkened with ageing even in the absence of light.

Since THNM and resorcinol are both extremely poor tanning agents, it was highly unexpected that the combination would be useful in a process to produce high quality leather. Sheepskins tanned with THNM at pH levels of about 1.5, 4.5 and 8.0 to 8.6 had the appearance and feel of raw skin. The highest shrinkage temperature was obtained after 8 days of tanning at 64° C. and at a pH of 8.0 to 8.6. Addition of resorcinol and further tannage for 24 hours produced a soft, flexible well filled leather having a shrinkage temperature of 92° C.

One object of the present invention is to provide a process for making good quality leather, one that is full and mellow, with good temper, strength and appearance and one that is saleable.

Another object is to produce a leather having perspiration resistant properties and a moderately high shrinkage temperature.

Still another object is to provide a relatively short term tanning process which can be completed within 8 hours.

A further object is to provide a tanning process in which the tanning agent contains a chemical group which, when combined with a skin, hide or collagen, can be detected in such substance and measured by physical or chemical means.

According to the present invention the above objects are accomplished by a process in which the skin, hide or collagen to be tanned is impregnated with an aqueous solution buffered to a pH range of 4.5 to 4.7 and containing tris(hydroxymethyl) nitromethane and a polyhydric phenol and then adjusting the pH of the tanning solution to and maintaining it at about 8.0 to 8.5 until the skin, hide or collagen is tanned.

The adjustment of the pH of the tanning liquor is an essential feature of the process. Maintenance of the tanning liquor at an acid pH for the entire process as shown in examples 4 and 5 as set forth later resulted in only partial utilization of the tanning agents. At a pH level of 4.5 or below very little tanning took place and a hide or skin so treated had the appearance of raw hide or skin and showed no appreciable change in shrinkage temperature. Maintenance of the tanning liquor at a pH of about 6.7 for the entire process resulted in a flat and tinny leather having a shrinkage temperature of about 74°-77° C.

Tanning by the process of this invention consistently produces a strong, soft, mellow, good appearing leather with a shrinkage temperature of between 85° and 95° C. Although the ratio of THNM to phenol can vary over a substantial range, a one to one ratio is preferred.

Hides, skins or collagen tanned by the process of this invention can be retanned with any other tanning material. Leather tanned by the process of this invention has been retanned with basic chromium sulfate, with glutaraldehyde and with vegetable tannins consisting of chestnut, bisulfited quebracho and wattle. All retannages have produced high-quality leathers.

The process of this invention differs from the prior art in that the activity of the tris(hydroxymethyl)nitromethane depends upon electron withdrawal by the nitro group. This is the first time that electron withdrawal has been used to activate a molecule to react with resorcinol in dilute aqueous solution at room temperature to produce tanning molecules.

This invention is exemplified by the following experimental data:

EXAMPLES 1-3

Each of three 50.0 g. samples of pickled Iran sheepskin was placed in an individual tanning solution containing the following components: water, 100.0 g.; sodium sulfate (anhydrous) 10.0 g.; sodium acetate, 1.5 g.; THNM, 5.0 g. After tumbling for 1.5 hours the pH of each solution was in the range of 4.5 to 4.6. Sufficient H₂SO₄ was then added to example 1 and sufficient Na₂CO₃ was added to example 3 to adjust the pH of each solution to 1.7 and 8.5, respectively. The three skin samples in their respective tanning solutions at the above pH levels were then tumbled continuously for a total time of about 9 days. Each skin was then sampled and shrinkage temperature determined. The shrinkage temperatures for each skin was as follows: example 1, 43° C.; example 2, 56° C.; example 3, 65° C. None of the examples had the appearance or feel of a tanned skin.

At this stage 3.6 g. of resorcinol was added to each solution and the skins were given a final tumbling for about 1 more day. Shrinkage temperatures were then determined to be as follows: example 1, 41° C.; example 2, 57° C.; and example 3, 90° C.

Example 3 which was beige colored at this stage was removed from the tanning solution and treated as follows: washed with water, immersed in a solution acidified with an amount of H₂SO₄ adequate to adjust the pH of the skin to 4.0, removed from the acid solution, washed again with water to remove excess acid, fatliquored with a mixture of 1.5 g. raw neatsfoot oil and 3.0 g. sulfated neatsfoot oil and then dried. The dried leather was a good quality leather, full, soft, supple and mellow and had a shrinkage temperature of 95° C.

Examples 1 and 2 were tumbled one additional day, removed from their respective tanning solutions and treated in the manner described for example 3. The results in both cases were entirely unsatisfactory; the shrinkage temperatures, 41° C. for example 1 and 55° C. for example 2, were low and the dried skins were hard, stiff, horny, exhibited blackened areas and resembled dried raw untreated skin.

EXAMPLES 4-7

Each of four 50.0 g. samples of pickled Iran sheepskin was placed in an individual tanning solution containing the following components: water, 100.0 g.; sodium sulfate (anhydrous), 10.0 g.; sodium acetate, 1.5 g.; THNM, 5.0 g.; resorcinol, 3.6 g. After tumbling for 1.5 hours, the pH of each solution was in the range of 4.6 to 4.7. Sufficient H₂SO₄ was then added to example 4 and sufficient Na₂CO₃ was added to examples 6 and 7 to adjust the pH of each solution to 1.7, 7.1 and 8.0, respectively, after which the samples were tumbled for about 24 hours. The pH of each solution at this point was as follows: example 4, 1.7; example 5, 4.7; example 6; 7.3; and example 7, 8.0. Each skin was then removed from the tanning solution and treated in the following manner: washed with water, immersed in a solution containing an adequate amount of either H₂SO₄ or Na₂CO₃ to adjust the pH of the skin to 3.9, washed again with water and then drained. A small segment of each skin was fatliquored with a mixture made of 1.5 g. of raw neatsfoot oil and 3.0 g. of sulfated neatsfoot oil. The segments were dried and the shrinkage temperature of each determined to be as follows: example 4, 56° C.; example 5, 59° C., example 6, 79° C., example 7, 88° C. Example 7 was soft and full and the best leather. Example 6 was not as soft and full as example 7 and had a light beige color. Examples 4 and 5 had a parchment like appearance and resembled dried raw skin.

EXAMPLE 8

A 50 g. sample of pickled Iran sheepskin was placed in a tanning solution containing the following components: water, 100 g.; sodium sulfate (anhydrous), 10.0 g.; sodium acetate 1.5 g.; THNM, 5.0 g.; resorcinol, 3.6 g. After tumbling for 1.5 hours the pH of the solution was 4.6. Then 1.0 g. of anhydrous sodium carbonate was added and drumming continued for two hours after which the pH was 7.1. An additional 0.5 g. of anhydrous sodium carbonate was added and the drumming continued for about 24 hours. The pH was then 7.9. The skin was removed from the tanning solution, washed, acidified to a pH of about 4.0, washed again and fatliquored. The dried leather was full, mellow, soft and strong. The shrinkage temperature of the finished leather was 84° C.

EXAMPLE 9

A 50 g. sample of pickled Iran sheepskin was placed in a tanning solution the same as used in example 8 and treated in a similar manner except that after tumbling for 1.5 hours, only one addition of 4.0 g. of sodium carbonate (anhydrous) was made to raise the pH from 4.6 to 8.0. The leather obtained was strong, soft, mellow and full and had a shrinkage temperature of 86° C.

EXAMPLE 10

A 50 gram sample of pickled Iran sheepskin was placed in a tanning solution containing the following components: water, 100 g.; sodium sulfate (anhydrous), 10.0 g.; sodium acetate 1.5 g.; THNM, 10.0 g.; and resorcinol, 7.2 g. After tumbling for 1.5 hours the pH was 4.6. Enough sodium carbonate (anhydrous) was added in two separate portions to raise the pH to 8.0 and tumbling was continued for about another 24 hours. The sample was removed from the tanning solution and then acidified to about a pH of 4.0, washed again, fatliquored and dried. The dried leather had a shrinkage temperature of 84° C. and was strong, soft, mellow and full.

EXAMPLE 11

A 50 gram sample of pickled Iran sheepskin was placed in a tanning solution containing the following components: water, 100 g.; sodium sulfate (anhydrous) 10.0 g.; sodium acetate, 1.5 g.; THNM, 1.25 g.; and resorcinol, 0.9 g. After tumbling for 1.5 hours the pH was 4.7. Enough sodium carbonate (anhydrous) was added in one portion to raise the pH to 8.0 and tumbling was continued for about another 24 hours. The sample was removed from the tanning solution and then washed, acidified to about pH 4.0, washed again, fatliquored and dried. The dried leather had a shrinkage temperature of 83° C. and was strong and of good quality, but was not quite as full as skins tanned with larger amounts of THNM and resorcinol.

EXAMPLE 12

Three pickled cabretta skins, 1,230 g. wet, drained weight, were tanned in a small laboratory drum at about 75° to 80° F. using the following solution: water, 2,460 g.; sodium sulfate (anhydrous), 246 g.; sodium acetate, 37 g.; THNM, 123 g.; and resorcinol 37 g. The skins were drummed 1.5 hours at pH 4.6. Forty-nine grams (4%) of anhydrous sodium carbonate was added and the drumming continued at a pH of 8.3. After 7.5 hours of tanning the shrink temperature was 88° C. Drumming was continued overnight for a total tanning time of 24 hours. The final pH was 8.3 and the shrink temperature was 93° C. The skins were washed, acidified to a pH of 4.0 with H₂SO₄, washed again, wrung, fatliquored and processed into finished leather in a tannery. A good quality leather was obtained.

EXAMPLE 13

Three pickled cabretta skins, 1,435 g. wet, drained weight, were tanned in a small laboratory drum at about 80° to 85° F.

using the following solution: water, 2,870 g.; sodium sulfate (anhydrous), 287 g.; sodium acetate, 43 g.; THNM, 144 g.; and resorcinol, 103 g. After drumming for 30 minutes, the pH was 4.7. Twenty-nine grams of anhydrous sodium carbonate was added and the skins drummed for an additional hour. The pH was now 6.7. Fifteen grams of anhydrous sodium carbonate was added raising the pH to 8.3 and the skins were drummed again for a total tanning time of 7.5 hours after which the shrinkage temperature of the skins was 91° C. The skins were washed and drained overnight and then acidified to a pH of 4.0 with H₂SO₄, washed again, wrung, fatliquored and processed into finished leather. A good quality leather was obtained.

EXAMPLE 14

Three pickled domestic sheepskins, 2,790 g. wet, drained weight, were tanned in a small laboratory drum at about 80° F. using the following solution: water, 5,580 g.; sodium sulfate (anhydrous), 558 g.; sodium acetate, 84 g.; THNM, 279 g.; and resorcinol, 199 g. The skins were drummed for 1.5 hours at a pH of 4.6. One hundred twenty-six grams of Na₂CO₃H₂O was added, the skins were again drummed until the total tanning time was 24 hours. At this time the pH was 8.2 and the shrinkage temperature of the leather was 89 to 91° C. The skins were then washed, acidified to pH 3.9 with H₂SO₄, washed again, fatliquored, paste dried and finished for shoe lining leather in a tannery. The leather finished well as shoe lining leather and the temper, appearance and tensile strength were adequate for this use as judged by a tanner.

EXAMPLES 15 and 16

Two fifty gram samples of Iran sheepskin, drained pickled weight, were tanned in solutions containing 100 g. water, 10 g. sodium sulfate (anhydrous), 1.5 g. of sodium acetate, 5.0 g. THNM and 3.6 g. of a phenol, catechol in example 15 and hydroquinone in example 16. Each sample was drummed in its respective solution for about 1.5 at a pH of 4.5 to 4.7. Sodium carbonate was added to adjust the pH to about 8.0 and drumming was continued for a total tanning time of 24 hours. The shrinkage temperatures were 78° C. and 80° C. respectively. Each skin was washed, acidified to pH 4.0 with H₂SO₄, washed again, fatliquored and dried. Satisfactory leather was obtained in each case.

EXAMPLES 17 and 18

Two fifty gram samples of Iran sheepskin, drained pickled weight, were tanned in solutions containing 100 g. water (example 17) or 150 g. water (example 18). 10 grams of sodium sulfate (anhydrous), 1.5 g. of sodium acetate, 5.0 g. of THNM and 4.2 g. of a phenol, pyrogallol in example 17 and phloroglucinol in example 18. Each sample was drummed in its respective solution for about 1.5 hours at a pH of 4.6. Sodium carbonate was added to adjust the pH to about 8.0 and drumming continued for a total tanning time of 24 hours. The shrinkage temperatures of the leathers were 89° C. and 92° C. respectively. Each skin was washed, acidified to pH about 4.0 with H₂SO₄, washed again, fatliquored and dried. Satisfactory leather was obtained in each case.

EXAMPLE 19

A sample of pickled cattlehide belly, 100 g. drained, wet weight was tanned in the following solution: 200 g. water, 20 g. of sodium sulfate (anhydrous), 3.0 g. of sodium acetate, 10 g. of THNM and 7.2 g. of resorcinol. The solution was drummed for 6 hours at a pH of 4.6. Enough sodium carbonate was added to raise the pH to 5.4 and drumming was continued for about 17 hours. The pH was then adjusted to 6.9 with sodium carbonate and the drumming continued for about another 6 hours. The pH was again raised to 7.5 and the drumming continued for about another 24 hours. The shrinkage temperature was 88° C. The sample was then allowed to

soak in the tanning solution for about 64 hours at the end of which time the pH was about 7.4 and the shrinkage temperature was 93° C. The tanning solution was then adjusted to pH 4.0 with H₂SO₄ after which the shrinkage temperature was 95° C. The hide was washed with water, fatliquored and dried. Satisfactory leather was obtained. The tannage had completely penetrated and tanned the hide to make a soft, flexible full-thickness leather.

We claim:

1. A process for tanning skins comprising impregnating and drumming skins with an aqueous solution buffered to a pH in the range of 4.5 to 4.7 containing tris(hydroxymethyl)nitromethane and a polyhydric phenol, and adjusting the pH of the solution during the tanning operation to and maintaining it in the range of about 8.0 to 8.5 until the skins were tanned.

2. The process of claim 1 in which the polyhydric phenol is resorcinol.

3. The process of claim 1 in which the polyhydric phenol is catechol.

4. The process of claim 1 in which the polyhydric phenol is hydroquinone.

5. The process of claim 1 in which the polyhydric phenol is pyrogallol.

6. The process of claim 1 in which the polyhydric phenol is

phloroglucinol.

7. A process for tanning skins comprising impregnating and drumming skins for about 1.5 hours with an aqueous solution buffered to a pH in the range of 4.5 to 4.7 containing tris(hydroxymethyl)nitromethane and a polyhydric phenol, adjusting the pH of the solution to a range of about 6.5 to 7.0, drumming the skins at this pH level for about 1 hour, readjusting the pH of the solution to a range of about 8.0 to 8.5 and drumming the skins at this pH level until said skins are tanned.

8. A process for tanning skins comprising impregnating and drumming skins with an aqueous solution buffered to a pH in the range of 4.5 to 4.7 containing tris(hydroxymethyl)nitromethane and a polyhydric phenol, adjusting the pH of the solution during the tanning operation to and maintaining it in the range of about 8.0 to 8.5 until the skins are tanned and then retanning said tanned skin with a second tanning agent.

9. The process of claim 8 in which the second tanning agent is basic chromium sulfate.

10. The process of claim 8 in which the second tanning agent is glutaraldehyde.

11. The process of claim 8 in which the second tanning agent is a blend of vegetable tannins consisting of chestnut, bisulfited quebracho and wattle.

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