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TANNING WITH TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE AND PHENOL

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This invention relates to the tanning of hides. More particularly, this invention relates to a new in situ polymeric tannage employing free tetrakis(hydroxymethyl)-phosphonium chloride and free phenols under carefully regulated conditions.

The term "skins," as used herein, includes all animal skins that are tanned commercially, such as cowhide, horsehide, calfskin, goatskin, sheepskin, pigskin and fur skins.

Leather obtained from tanning with tetrakis(hydroxymethyl)phosphonium chloride alone, hereafter abbreviated as THPC, has many of the disadvantages of formaldehyde tannage. With a weight gain of about 2.5% the result is a flat, firm leather.

The use of free and initially uncombined phenols in tanning has heretofore found only limited application. Many phenols, such as resorcinol, have no tanning ability per se. The use of phenols and aldehydes in combination tannages is not generally applicable; for instance, of the dihydric phenols the meta-derivative, resorcinol, gives satisfactory tanning in conjunction with formaldehyde, but catechol, the ortho-derivative, and hydroquinone, the para-derivative, did not tan hides. Moreover, the tanned hides produced by phenol-aldehyde tannages are very unstable to light and will darken with ageing even in the absence of light.

An object of the present invention is to provide a process for making a good quality leather, that is, a leather which is full and mellow, has good temper, and good appearance. A further object is to produce a good quality leather which has the added feature of a high shrink temperature. Another object is to provide a leather which has color stability. A further object is to provide a tanning process which is rapid, yet produces a leather having the properties described in the foregoing objectives. Other objects and a fuller understanding of the invention may be had by referring to the following description and claims.

According to the present invention skins are tanned by a process comprising impregnating skins with an aqueous solution containing tetrakis(hydroxymethyl)phosphonium chloride and a phenol, such as phenol, cresol, catechol, etc., or a phenol acid, such as gallic or gentisic acid, the solution having an initial pH below about 4.5, and adjusting the pH of the solution during the tanning operation to a final pH in the range of about 8.5 to 9.5, until the skins are tanned.

The adjustment of pH of the tanning liquor during the tanning process is a critical feature. The maintenance

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of an acid pH for the tanning solution for the entire time that the skin is being impregnated with the solution, as exemplified in Example 4, results in only partial utilization of the tanning materials. The tanned skin is difficult to fat-liquor and the result is a hard leather of poor appearance.

In view of the similarity of the results of Example 4, THPC and a phenol at a pH of about 4, and of THPC alone at about the same pH, it is apparent that little or no reaction occurs between the THPC and the phenol or the skin and the phenol under these acid conditions. This conclusion is supported by the qualitative test for phenol on the "spent" tanning liquor of Example 4 which showed unreacted and uncombined phenol present in large amounts. Finished leather from Example 4 and from a comparable tannage with THPC alone resulted in commercially unsatisfactory leather in both instances.

It is only when the pH is raised that the phenol disappears from the tanning liquor and good leather is produced. The results which occur at an alkaline pH are attributed to an in situ reaction between the THPC and the phenol to form a new tanning agent or agents. It is reasonable to assume that one or more of the four methylol groups in THPC react with the active hydrogens of the phenol to form a larger molecule which is then able to bridge across polypeptide chains to reach the necessary reactive groups available in the protein, thus tanning the skin. With excess methylol groups present in THPC it is likely that they are able to react with the epsilon amino groups of the lysine residue, with the elimination of water. Regardless of the particular mechanism involved in the tannage, a pH of 8 or above, preferably in the range of 8.5 to 9.5, in the last phase of the tanning operation results in a successful tannage of the skins.

A critical feature of the present process, however, is that the tannage be started in an acidic medium. The use of tanning solutions having an alkaline pH such as in the range of 8 to 9 during the entire time the skin is being impregnated with the solution causes a too-rapid formation and take-up of the tanning agents, resulting in a leather of drawn grain and having generally unsatisfactory leather qualities.

In a preferred embodiment of the present invention the skin is impregnated with the tanning solution containing THPC and a phenol or phenol acid at an acid pH, preferably in the range of 4.0 to 4.5, in order to set the grain, usually for a period of time of about 1 to 2 hours, the pH is then adjusted to about 5 to 7, preferably about 5.5 to 6.5, and maintained at about this range of pH for about another hour, and the tanning is then completed at a pH in the range of about 8.5 to 9.5. This procedure provides for a regulated taking-up and forming of the new tanning materials, resulting in a thorough and uniform, yet still rapid tannage of the skin, and, when the tanning materials are employed at the suggested concentrations, also results in maximum take-up, in many instances complete utilization, of the tanning materials. A practical, two- or three-step adjustment of the pH of the tanning solution is demonstrated in accompanying examples.

It is understood that the process can be started at a pH lower than 4.0 to 4.5, for example at the pH of the pickled skins, namely about pH 2.0 to 2.5, followed by gradual neutralization as described.

Although addition of sodium carbonate is a good

means of adjusting the solution to the desired pH, other means, such as sodium bicarbonate, ammonium bicarbonate, and borax, may be employed for this purpose.

Tannage of skins by the process of this invention is very rapid. Although most of the examples include intermittent drumming overnight as the final phase of the tanning process, this is more a matter of convenience than a requirement of the process. The tannage is usually substantially complete in 4 to 6 hours, as indicated by shrink temperatures, and as illustrated by Example 13.

The general applicability of phenols in the practice of this invention is demonstrated by the monohydric compounds, such as phenol; dihydric compounds, such as catechol, resorcinol and hydroquinone; and the trihydric phenols, such as pyrogallol and phloroglucinol. Phenol acids may also be used in the present invention as demonstrated, for example, by the dihydroxybenzoic acid, gentisic acid, and the trihydroxybenzoic acid, gallic acid.

The preferred molar ratio of THPC and the phenol or phenol acid in the tanning liquor is about one to one, although somewhat higher or lower ratios may be used.

The amount of THPC may range from 2 to 8%, based upon the wet, drained weight of pickled skin. Depending upon the phenol or phenol acid used with the THPC and the properties desired in the finished leather, a concentration of THPC of about 3.75 to 7.5% was the most useful range for obtaining an excellent tannage with optimum utilization of tanning materials in the tanning solution.

While most of the examples illustrating the invention describe combining THPC and the phenol or phenol acid in the starting tanning liquor, it may be advantageous in tanning certain types of skins to start the tannage with only THPC in the liquor and then add the phenol or phenol acid after about one hour of drumming. The purpose of this alternative procedure is as an additional precautionary step to avoid drawn grain in the tanned skin.

The critical effect of the pH of the solution during the tanning operation is illustrated in the following examples.

EXAMPLES 1 TO 4

Four comparable pickled domestic sheep skins were horsed, thoroughly drained, and weighed. The weight, about 1 kilogram, was used to calculate the composition of the tanning solutions, using the following percentages: water, 200%; sodium sulfate (anhydrous), 10%; sodium acetate, 3%; THPC, 3.75%; and resorcinol, 2.0%.

Each skin was placed in its respective solution and drummed for one hour. At this time the pH of the solutions is in the range of 4.0 to 4.4. Predetermined amounts of sodium carbonate were added to the solutions of Examples 1 to 3. The skins were drummed 4 hours, then intermittently overnight. The next morning the drumming was stopped. The final pH of each solution was determined, the values ranging from 9.2 for Example 1 to 4.3 for Example 4 to which no sodium carbonate was added. These values are included in Table I. The skins were washed, acidified in aqueous acetic acid at pH 3.9, washed again, drained, and wrung to remove excess water. Analogous sections of each skin were clipped for making shrink temperature determinations. The tanned skins were washed at 120° F., dyed (Rescotine Browns), formic acid to pH 3.6, washed again at 120° F. and fatliquored (5% soap type, 2.5% medium sulfated cod).

Only one of the skins, Example 1, was mellow enough for staking. The other three were wet back with wetting agent, washed, treated with an emulsifying agent, washed again and fatliquored with 6% non-ionic emulsified oil. Examples 2 and 3 had become softer and were staked. Example 4 was still hard and was too crusty to be staked.

The results are summarized in Table I.

Table I
EFFECT OF pH ON TANNING WITH SOLUTIONS CONTAINING 3.75% THPC AND 2.0 RESORCINOL

Example No.	pH of tanning solution		Ts, °C.	Leather	
	Initial	Final		Appearance	Temper
1.....	4.0	9.2	92	Excellent	Excellent.
2.....	4.2	8.9	89	Good	Fair.
3.....	4.4	6.5	79	Poor	Crusty.
4.....	4.0	4.3	78	do.	Very hard.

After the skins were removed from the tanning solutions, the solutions were tested for presence of phenols. The solutions of Examples 1 and 2 gave negative tests, but red precipitates, indicating incomplete up-take of the resorcinol, formed in the solutions of Examples 3 and 4.

The practice of this invention is further illustrated by the following examples.

EXAMPLE 5

A pickled cabretta sheep skin, 350 grams wet drained weight, was placed in a small laboratory drum containing the following solution: water, 700 ml.; sodium sulfate (anhydrous), 70 grams; sodium acetate (crystalline), 10.5 grams; and THPC, 26.3 grams (7.5%). The skin was drummed for one hour at room temperature, 85° F., then 14 grams (4%) of resorcinol added and the drumming continued (solution pH 4.2). After one hour, 7 grams sodium carbonate (anhydrous) was added to the solution and the drumming continued. The pH of the solution adjusted to 5.8. An hour later 13 grams of sodium carbonate was added, bringing the pH to 8.2. After another hour 1.2 grams of sodium carbonate was added and drumming continued for one more hour. The solution pH was now 8.6 and the leather had a shrink test of 94° C. The skin was drummed intermittently overnight, then stopped. Final pH of the solution was 8.7, and a qualitative resorcinol test on the solution was negative. The leather did not shrink after 5 minutes in boiling water.

The tanned skin was washed, acidified with acetic acid to pH 4.0, washed, wrung, dyed, fatliquored and finished. The finished leather was full, mellow, and strong. This process was rated an excellent tannage.

EXAMPLE 6

The general plan of Example 5 was followed using half the tanning materials, that is, 3.75% THPC and 2.0% resorcinol. The initial pH was 4.2, then adjusted in two additions of sodium carbonate to 6.2 and finally 8.5. Drumming consisted of 4 hours continuous and intermittent overnight. Final pH of the solution was 8.5 resorcinol test negative. The leather had a shrink test temperature of 94° C.

Post-tanning treatment was identical with the leather of Example 5. The finished leather was of excellent quality. Where the higher shrink temperature is not required this process would be preferable to that of Example 5, since a comparable leather is obtained at less cost.

EXAMPLE 7

A pickled cabretta skin, 406 grams wet drained weight, was tanned in a small laboratory drum at room temperature, about 80-85° C. Composition of the tanning liquor: water, 812 ml.; sodium sulfate (anhydrous), 81 grams; sodium acetate, 12.2 grams; gallic acid (technical)

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10.2 grams (2.5%); and THPC, 15.2 grams (3.75%). The skin was drummed one hour at pH 4.3. Eight grams sodium carbonate (anhydrous) were added and drumming continued one hour with solution at pH 5.4. The pH was adjusted to 8.2 with 13 grams sodium carbonate and the skin drummed for two hours. At this time (four hours treatment) the leather had a shrink temperature of 85° C. Addition of 1.5 grams sodium carbonate raised the pH to 8.5. Further drumming was one hour continuous and intermittent overnight. Final pH of the liquor was 8.1 and shrink temperature of the leather was 85° C.

The skin was washed, acidified to pH 3.8 with acetic acid, washed, wrung, dyed, fatliquored, and finished. The leather was well tanned, being full, mellow, and strong.

EXAMPLE 8

A pickled cabretta skin, 417 grams wet drained weight, was placed in a small laboratory drum with the following solution: water, 834 ml.; sodium sulfate (anhydrous), 83 grams; sodium acetate, 12.5 grams; pyrogallol (technical), 10.5 grams (2.5%); and THPC, 15.7 grams (3.75%). The skin was drummed one hour at pH 4.1. Ten grams sodium carbonate were added and the skin drummed one hour at pH 6.0. Adding 20 grams sodium carbonate brought the pH to 8.5. After drumming two more hours the leather had a shrink temperature of 81° C. The skin was drummed intermittently overnight.

The final pH of the tanning liquor was 8.2 and the leather had a shrink temperature of 87° C.

The skin was washed, acidified to pH 3.8 with acetic acid, washed, wrung, dyed, fatliquored, and finished. This was a very satisfactory tannage, the leather being full and mellow, though not as soft as the products of Examples 5 and 6.

EXAMPLE 9

A pickled cabretta skin, 398 grams wet drained weight, was tanned in a small laboratory drum at about 80 to 85° C. using the following solution: water, 796 ml.; sodium sulfate (anhydrous), 80 grams; sodium sulfite, 11.9 grams; catechol (technical), 13.3 grams (3.33%); and THPC, 19.9 grams (5.0%). The skin was drummed one hour at pH 4.6. Nine grams sodium carbonate (anhydrous) was added and the drumming continued for one hour at pH 7.8. Sixteen grams sodium carbonate brought the pH to 8.9 for the next hour of drumming. At this time the leather had a shrink temperature of 83° C. Drumming was continued intermittently overnight.

Final pH of the liquor was 8.7 and the shrink temperature was 83° C.

The skin was washed, acidified to pH 3.9 with acetic acid, washed again, wrung, dyed, fatliquored and finished. A good quality leather was obtained.

EXAMPLES 10 TO 12

Pieces of domestic sheep skin, 50 grams drained pickled weight, were tanned in solutions containing 100 ml. water, 5 grams sodium sulfate (anhydrous), 1.5 grams sodium acetate, 3.75 grams (7.5%) THPC and 2.5 grams (5%) of a phenol or phenol acid selected from phenol, hydroquinone, or gentisic acid. The general procedure was to drum each skin in its respective solution for about one hour (pH 4.0 to 4.5), add sodium carbonate to give an intermediate pH of about 7.0 with drumming for at least one hour, then raising the pH to about 8.5 to 9.0, drumming for two hours, followed by several hours intermittent drumming.

The tanned skins were washed, acidified with acetic acid to pH 3.9, washed, wrung, fatliquored and dried. The results are summarized in Table II.

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Table II

TANNAGE OF DOMESTIC SHEEP SKIN WITH THPC AND PHENOLS

Ex. No.	Agent combined with THPC	Final pH of tanning liquor	Ts, ° C.	Leather quality
10.....	Gentisic acid..	8.8	84	Satisfactory leathering.
11.....	Phenol.....	8.6	86	Do.
12.....	Hydroquinone.	8.6	81	Good tannage; full, mellow, tan colored leather.

EXAMPLE 13

A pickled domestic sheep skin, 1252 grams wet drained weight, was tanned in a small laboratory drum at 85° F. The skin was placed in the following solution: water, 2504 ml.; sodium sulfate (anhydrous), 250 grams; sodium acetate (crystalline), 37.6 grams; and THPC, 47 grams (3.75%). The skin was drummed in this solution for one hour, then 25 grams (2%) of resorcinol were added and the drumming continued for one hour. The solution pH was 4.2. Sodium carbonate, 29.3 grams, was added, bringing the pH of the tanning liquor to 6.1. After drumming one hour the skin had a shrink temperature of 83° C. Fifty-six more grams sodium carbonate were added and the skin drummed three hours at pH 9.2. The shrinkage temperature was 83° C. A resorcinol test of the tanning liquor was negative. The skin was washed, acidified to pH 3.9 with acetic acid, washed, wrung, dyed, fatliquored and finished. After acidifying the shrink temperature was 92° C. The finished leather was of excellent quality.

We claim:

1. A process for tanning skins comprising impregnating skins with a buffered aqueous solution at pH in the range of about 4.0 to 4.5 containing tetrakis(hydromethyl)phosphonium chloride and a compound selected from the group consisting of phenols and phenol acids, and adjusting the pH of the solution during the tanning operation to a maximum pH in the range of about 8.5 to 9.5.

2. A process for tanning skins comprising impregnating skins with a buffered aqueous solution at pH in the range of about 4.0 to 4.5 containing tetrakis(hydroxymethyl)phosphonium chloride and a compound selected from the group consisting of phenols and phenol acids for about 1 to 2 hours, adjusting the pH of the solution to about 5.5 to 6.5, maintaining the solution at this pH range for about 1 hour, readjusting the pH of the solution to about 8.5 to 9.5, and maintaining the solution at this pH range until the skins are tanned.

3. The process of claim 2 in which the compound is a phenol.

4. The process of claim 2 in which the compound is a phenol acid.

5. The process of claim 2 in which the phenol acid is gallic acid.

6. The process of claim 2 in which the phenol acid is gentisic acid.

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

8. The process of claim 3 in which the phenol is resorcinol.

9. The process of claim 3 in which the phenol is hydroquinone.

10. The process of claim 3 in which the phenol is pyrogallol.

11. The process of claim 3 in which the phenol is phloroglucinol.

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