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COMBINATION TANNAGE WITH TETRAKIS (HYDROXY-METHYL) PHOSPHONIUM CHLORIDE AND A PHENOL

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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 hides and skins, these terms including all animal skins that are tanned commercially.

This application is a continuation-in-part of co-pending application Serial No. 842,535, filed September 25, 1959, now Patent No. 2,992,879.

In our co-pending application Serial No. 842,535 we described the tanning of skins with an aqueous solution containing tetrakis (hydroxymethyl) phosphonium chloride, hereafter referred to as THPC, and a phenol or phenol acid to produce leathers having excellent physical properties. A deterring factor to more widespread use of that process is that the best tannages are obtained with a concentration of more than 3% THPC, based on drained weight of skin, and about 2% of phenol or phenol acid.

We have now discovered that the beneficial features of the THPC-phenol tannage are obtained with only small quantities of these tanning agents when combined with other tanning agents such as those of mineral, vegetable, or synthetic organic composition.

The preferred molar ratio of THPC to phenol in the tanning liquor is about one to one, although higher or lower ratios may be used. The amount of THPC, based on wet, drained weight of pickled skin may range about from 0.4 to 2%, preferably in the range of about from 0.75 to 1%, and the amount of phenol or phenol acid from about 0.25 to 1% on same basis.

The amounts of THPC, a phenol or phenol acid, and another tanning agent such as a mineral tanning agent or organic (natural or synthetic) tanning agent, employed in the combination tannage will vary with the properties desired in the finished leather and with making optimum use of tanning materials added to the tanning solution but, for any desired product, are considered to represent a considerable saving in time, materials, and cost over tannage with larger amounts of just one of the elements in the combination. For instance, an excellent leather was obtained in Example 1 using about one-fourth the amounts of THPC-resorcinol recommended for a good tannage and only about one-half the amount of chromium salt conventionally employed in a chrome tannage.

In a tannage such as described in Example 1, and in many of the other examples, it is convenient to use the terms "tanning" and "retanning" to differentiate the treatment with two tanning solutions. Tanning does occur in the first solution, as shown by considerable increase in shrink temperature and by other tanning action to the skin, but exhaustion of the tanning agent takes place before maximum tannage of the skin has occurred and the result at this stage could, as an alternative description, be termed a partial tanning of the skin.

Tannage and retannage of skins by the processes of this invention are very rapid. Although the examples include tanning one day followed by retannage the next day, this is more a matter of convenience than a require-

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ment of the process. The tannage is usually substantially complete in 4 to 5 hours and the retannage is complete in another 2 to 4 hours, as indicated by shrink temperatures. Simultaneous tannages by the processes of this invention are usually complete in 6 to 7 hours, as indicated by shrink temperatures.

In general, according to the present invention, skins are tanned by a process in which a THPC-phenol tannage, preferably the THPC-resorcinol tannage employing less than about 2% THPC and less than about 1% resorcinol based on wet drained weight of pickled skin, is combined with (a) a tannage by a mineral tanning agent, such as the chromium, zirconium or aluminum salts conventionally employed by tanneries, with (b) a tannage with a vegetable tanning agent, or (c) a tannage with an aldehyde tanning agent such as dialdehyde starch, glutaraldehyde, formaldehyde, or a condensation product of formaldehyde and melamine.

By one process of the present invention skins are tanned by impregnating with an aqueous solution containing THPC and a phenol, such as resorcinol, 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 partially tanned, washing, acidifying to a pH of about 2.5 to 5.0, and retanning with a mineral such as chromium, zirconium, or aluminum, or with a vegetable tannin such as quebracho, wattle, or canaigre, or with an organic compound such as formaldehyde or trimethylolmelamine, under conditions of pH, concentration, time and temperature which are favorable for tannage by the agent being used.

By another process of the present invention the skins are simultaneously tanned by impregnating with an aqueous solution containing THPC and a phenol, such as resorcinol, and another tanning agent such as glutaraldehyde or dialdehyde starch, 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.

In a third process of the present invention skins are tanned by impregnating with an aqueous solution of a tanning agent such as trimethylolmelamine, basic aluminum acetate, or basic chromium sulfate, the solution having a pH of about 2.5 to 5.0 depending on the tanning agent used, until the skins are partially tanned, washing, retanning with an aqueous solution containing THPC and a phenol, such as resorcinol, the solution having an initial pH below about 4.5, and adjusting the pH of the solution during the retanning operation to a final pH in the range of about 8.5 to 9.5, until the skins are retanned.

Various combinations of tannages are illustrated in the examples, but the scope of the invention is not intended to be limited to the particular combinations and conditions recited.

Examples 1 to 4 are combination tannages in which tanning with the THPC-phenol is followed by a chromium retannage to give excellent leathers.

In these examples (1 to 4) the THPC-phenol tannage was conducted with solutions containing from 0.43% THPC and 0.25% resorcinol (Example 4) to 1.73% THPC and 1% resorcinol (Example 2). Although the chrome retannage was performed with 3 or 4%, based on wet, drained weight of pickled skin, of commercial basic chromium sulfate (only a fraction of the amount usually used in chrome tannages), the tanned skins had shrink temperatures of about 100° C. or higher, and in other characteristics were rated as good to excellent leather.

As demonstrated in Example 5, a satisfactory tannage was obtained by reversing the order of impregnating the skins with the tanning agents of Examples 1 to 4, although

the shrink temperature was somewhat lower than in Examples 1 to 4.

Combination tannages in which skins pretanned with 0.87% THPC and 0.5% resorcinol were retanned with vegetable, mineral or trimethylolmelamine tanning agents are demonstrated in Examples 6 to 10. Examples 11 to 16 illustrate combinations of the THPC-phenol tannage with aldehydes such as dialdehyde starch, glutaraldehyde and formaldehyde. The simultaneous tannages of Examples 12 and 15 are particularly interesting because of compatibility of pH conditions at which the tanning agents are effective and because of the efficient utilization of the tanning agents.

Example 1.—Chromium Retannage

Three pickled Iran goatskins were horsed, thoroughly drained, and weighed. The combined weight, 2,112 grams, was used as 100% to calculate the composition of the tanning solution, using the following percentages: water, 100%; sodium sulfate (anhydrous), 5%; sodium acetate (anhydrous), 1%; tetrakis (hydroxymethyl) phosphonium chloride (THPC), 0.87%; and resorcinol, 0.5%.

The pickled skins were placed in a laboratory churn in the above solution and drummed for one and one-half hours at room temperature, 80° F. At this time the solution pH was 3.9 sodium carbonate (monohydrate), 42 grams (2.0%) was added, bringing the pH of the tanning liquor to 5.5 after another one and one-half hours drumming. Then another 42 grams (2.0%) sodium carbonate (monohydrate) were added and drumming continued one and one-half hours. At this time the solution pH was 8.8 and the shrink temperature of the skins was 78° C. The churn was steamed for 1 minute to raise the temperature of the tanning liquor to 88° F. After another one and one-half hours of drumming (six hours' total tanning time) the solution temperature was 88° F., the pH 8.9, the shrink temperature was 78° C. The skins were washed 30 minutes, acidified to pH 4.0 with a solution of formic and sulfuric acids for 30 minutes, washed 30 minutes and horsed.

The above three THPC-resorcinol tanned skins were retanned in a laboratory churn at 84 to 96° F. with the following chromium solution, calculated from the drained, pickled skin weight: water, 100%; a commercial basic chromium sulfate, 3.0%. The chromium salt was dissolved in about 17% of the water by heating. One-half of the chromium salt solution was added at the start of the retannage and the remainder one-half hour later. After three and a half hours the retannage was complete; the solution pH was 3.9 and the shrinkage temperature 100° C. The skins were washed, wrung, dyed, fat-liquored and finished as grain leather. The finished leather was full, well-tanned and had a good textured grain appearance with a small, pebbled pattern.

Example 2.—Chromium Retannage

Three pickled New Zealand sheepskins were horsed, thoroughly drained, weighed and tanned with 0.87% THPC and 0.5% resorcinol (calculated from the drained, pickled weight) as described under Example 1. The shrink temperature of the acidified skins was 81° C.

The above three THPC-resorcinol tanned skins were retanned in a laboratory churn at 90 to 104° F. with the following chromium solution, calculated from the drained, pickled weight: water, 100%; a commercial basic chromium sulfate, 4.0%. The chromium was dissolved in about 20% of the water by heating. One-half of the chromium was added at the start of the retannage and the remainder one-half hour later. After four hours the retannage was complete; the solution pH was 3.8 and the shrink temperature above 100° C. (no shrinkage after 5 minutes boiling). The skins were washed, wrung, dyed, fat-liquored and finished as suede leather. The finished leather was full, mellow and well tanned; the nap was somewhat coarse because the skins were large sheep.

Example 3.—Chromium Retannage

Three pickled, domestic sheepskins were horsed, thoroughly drained, weighed and tanned with 1.73% THPC and 1.0% resorcinol (calculated from the drained pickled weight) as described under Example 1. The shrink temperature of the acidified skins was 83° C.

The above three THPC-resorcinol tanned skins were retanned with a commercial basic chromium sulfate, 4.0% on the drained, pickled weight, by the procedure described under Example 2. The shrink temperature was above 100° C. (no shrinkage after 5 minutes boiling). The skins were washed, wrung, dyed, fat-liquored and finished. The finished skins were full, well-tanned work glove leather.

Example 4.—Chromium Retannage

Three pickled, Syrian sheepskins were horsed, thoroughly drained, weighed and tanned with 0.43% THPC and 0.25% resorcinol (calculated from the drained, pickled weight) as described under Example 1. The shrink temperature of the acidified skins was 66 to 68° C.

The above three THPC-resorcinol tanned skins were retanned in a laboratory churn at 80 to 84° F. with the following chromium solution, calculated from the drained, pickled weight: water, 150%; a commercial basic chromium sulfate, 4.0%. The chromium was dissolved in about 20% of the water by heating. One-half of the chromium was added at the start of the retannage and the remainder one-half hour later. After six hours the retannage was complete; the solution pH was 3.98 and the shrink temperature 97 to 98° C. The skins were washed, wrung, dyed, fat-liquored and finished as glove leather. The finished leather was full, mellow and well-tanned.

Example 5.—Chromium Tannage, THPC-Resorcinol Retannage

Three pickled New Zealand lambskins were horsed, thoroughly drained and weighed. The combined weight, 1,852 grams, was used to calculate the composition of the tanning solution, using the following percentages: water, 200%; sodium chloride, 6%; a commercial basic chromium sulfate, 4%. One-half of the chromium was added at the start of the tannage and the remainder one-half hour later. After another hour the solution temperature was 90° F., the solution pH 3.5; sodium bicarbonate 0.5% (9.3 grams) was added. The churn was steamed at intervals to raise the solution temperature. The tannage was complete after a total of 3 hours, solution temperature 91° F., solution pH 3.90; shrink temperature 85° C. The skins were washed with warm (95° F.) water for 5 minutes and horsed for 10 minutes.

The above three chromium tanned skins were retanned in a laboratory churn at 86° F. with the following solution: water, 200%; sodium sulfate (anhydrous), 5%; THPC, 0.87%; and resorcinol, 0.5%. After 1½ hours the pH was 4.1; sodium carbonate (monohydrate), 37 grams (2%) was added and drumming continued for one hour. At this time the solution pH was 7.4 and the shrink temperature 91° C.; sodium carbonate (monohydrate), 37 grams (2%) was added and drumming continued. The retannage was completed after a total of 3½ hours; solution temperature 86° F.; solution pH 9.02; shrink temperature 88° C. The tanning solution was acidified by addition of 62 grams concentrated (97%) sulfuric acid and drummed for one hour; the solution pH was 3.6 and the skins about pH 4.0, shrink temperature 93° C. The skins were washed for 30 minutes and wrung. The skins had a well-tanned appearance and feel and the shrink temperature showed that the tannage was adequate.

Example 6.—Wattle Retannage

Six comparable pickled New Zealand lambskins were horsed, thoroughly drained, and weighed. The combined weight, 3,775 grams, was used to calculate the composi-

tion of the tanning solution, using the following percentages: water, 100%; sodium sulfate (anhydrous), 5%; sodium acetate (anhydrous), 2%; THPC, 0.87%; and resorcinol, 0.5%.

The pickled skins were placed in a laboratory churn in the above solution and drummed for 1½ hours at room temperature, 82° F. At this time the solution pH was 4.2; sodium carbonate (monohydrate), 75.5 grams (2%) was added, bringing the pH of the tanning liquor to 6.4 after another 1½ hours of drumming. Then another 75.5 grams (2%) sodium carbonate were added and drumming continued 1¾ hours. At this time the solution pH was 9.0 and the shrink temperature of the skins was 77° C. The churn was steamed for one minute to raise the temperature of the tanning liquor. After another 1¾ hours of drumming (6 hours' total tanning time) the solution temperature was 92° F., the pH 9.3, and a resorcinol test was negative; the shrink temperature was 80° C. The skins were washed 30 minutes, acidified to pH 4.1 with a solution of formic and sulfuric acids, washed and horsed.

After acidifying the shrink temperature was 82° C. One of the above THPC-resorcinol tanned skins was retanned in a small laboratory drum at 88° F. with the following wattle solution, calculated from the drained, pickled skin weight: water, 200%; wattle extract (67.7% tannin, 78% purity), 6.0%. The wattle was dissolved in about 50% of the water by heating, then the pH was adjusted to 3.9 with lactic acid. After 1½ hours retanning the pH was 4.3; 5 ml. lactic acid were added. After another hour the wattle liquor was completely exhausted and the retannage stopped. The liquor pH was 3.8 and the shrink temperature 82° C. The skin was washed, wrung, dyed, fat-liquored, and finished as suede leather. The finished leather was full, mellow, good color; the nap was slightly harsh and coarse with a dry feel typical of a vegetable tannage.

Example 7.—Canaigre Retannage

One of the above THPC-resorcinol tanned skins (Example 6) was retanned in a small laboratory drum at 90° F. with the following canaigre solution, calculated from the drained, pickled skin weight: water, 200%; canaigre extract (60.8% tannin, 63.6% purity), 6.0%. The canaigre was dissolved in about 50% of the water by heating, then the pH was adjusted to 3.8 with lactic acid. After 2¼ hours retanning the pH was 4.2; 5 ml. lactic acid were added. After another hour the canaigre liquor was completely exhausted and the retannage stopped. The liquor pH was 3.7 and the shrink temperature 81° C. The skin was washed, wrung, dyed, fat-liquored, and finished as suede leather. The finished leather was full, mellow, good color; the nap was slightly coarse, typical of vegetable tannage, but had a better feel than the wattle (Example 6).

Example 8.—Trimethylolmelamine Retannage

Another of the THPC-resorcinol tanned New Zealand sheepskins (Example 6) was retanned in a small laboratory drum at 90° F. with the following trimethylolmelamine solution, calculated from the drained, pickled skin weight: water, 200%; trimethylolmelamine, 3.43% (melamine, 2.0%; formaldehyde (36.6% by weight), 3.91%). The melamine and formaldehyde were added to about 10% of the water and heated to 80° C. on a steam bath until a clear solution was obtained, then cooled quickly to room temperature. One-half of the methylolmelamine was added at the start of the retannage and the remainder after one hour. After drumming another hour, the pH was 5.2. Lactic acid (8.0 ml.) was added and drumming continued another 3½ hours. At this time the pH was 4.1 and the shrink temperature 83° C. The skin was immersed in the tanning solution over a 3-day weekend, then drummed for one hour. The solution pH was 3.9 and the shrink temperature 86° C. The skin was washed, wrung, dyed, fat-liquored and finished as suede leather.

The finished leather was full, slightly firm and had a good color and nap.

Example 9.—Zirconium Retannage

Three comparable pickled New Zealand lambskins were horsed, thoroughly drained, weighed and tanned with 0.87% THPC and 0.5% resorcinol as described under Example 1. The shrink temperature of the acidified skins was 82° C.

One of the above THPC-resorcinol tanned skins was retanned in a small laboratory drum at 90 to 95° F. with the following zirconium solution, calculated from the drained, pickled skin weight: water, 200%; a commercial basic zirconium sulfate (32% ZrO_2), 10%. One-half of the zirconium was added at the start of the retannage and the remainder after one hour. After drumming another 2½ hours, the pH was 2.4. Sodium bicarbonate, 8.13 grams (1.7%) was added and drumming continued for 2 hours. At this time the solution pH was 4.0 and the shrink temperature 89° C. The skin was washed, wrung, dyed, fat-liquored and finished as suede leather. The finished leather was full and mellow, and had a good color and nap.

Example 10.—Aluminum Retannage

Three comparable pickled New Zealand lambskins were horsed, thoroughly drained, weighed and tanned with 0.87% THPC and 0.5% resorcinol as described under Example 1. The shrink temperature of the acidified skins was 77° C.

One of the above THPC-resorcinol tanned skins was retanned in a small laboratory drum at 90° F. with the following aluminum acetate solution, calculated from the drained, pickled skin weight: water, 200%; a commercial basic aluminum acetate (40.42% Al_2O_3), 7.42%, equivalent to 3.0% Al_2O_3 . The aluminum acetate was dissolved in about 50% of the water by heating. One-half of the aluminum acetate was added at the start of the retannage and the remainder one hour later. The retannage was stopped after a total of 5½ hours; the solution pH was 4.8 and the shrink temperature 92° C. The skin was washed, wrung, dyed, fat-liquored and finished as suede leather. The finished leather was full, mellow, good color, although darker than the zirconium retanned leathers (Example 9); the nap was slightly coarse.

Example 11.—Resorcinol-THPC Tannage, Dialdehyde Starch Retannage

Nine pickled, domestic sheepskins were horsed, thoroughly drained and weighed. The combined weight, 8,514 grams, was used to calculate the composition of the tanning solution, using the following percentages: water 150%; sodium sulfate (anhydrous), 5% (on solution basis); sodium acetate (anhydrous), 2%; THPC, 1.73%; resorcinol, 1.0%. The skins were tanned in a laboratory churn at 82 to 84° F. and pH 4.2 for 1½ hours; sodium carbonate (monohydrate), 213 grams (2.5%) was added and drumming continued for 1½ hours. At this time the solution pH was 6.88. Sodium carbonate (monohydrate), 213 grams (2.5%) was added and drumming continued for 3 hours. The solution pH was 8.9 and the shrink temperature 82° C. The skins were washed for 40 minutes then horsed overnight.

Three of the above resorcinol-THPC tanned skins, 2,727 grams pickled weight, were retanned in a laboratory churn at 76 to 86° F. with the following solution: water 200%, sodium sulfate (anhydrous), 5.0% (on solution basis); dialdehyde starch, 5.0%; borax, 9.0%. The dialdehyde starch was heated on the steam bath at about 70° C. with the borax and 1,750 ml. of the water until the dialdehyde starch was completely dissolved. The entire dialdehyde starch was added at the start of the retannage. After 4 hours drumming the solution pH was 8.3 and the shrinkage temperature 84° C. The retannage was completed after a total of 23½ hours. The solu-

tion pH was 8.3 and the shrinkage temperature 85° C. The skins were washed for 30 minutes, acidified to about pH 4.0 with a solution of formic and sulfuric acids, washed 30 minutes and horsed. The skins had a well-tanned appearance and feel and the shrinkage temperature was adequate.

Example 12.—THPC-Resorcinol-Dialdehyde Starch Simultaneous Tannage

Three comparable pickled New Zealand lambskins were horsed, thoroughly drained, weighed and tanned with THPC, resorcinol and dialdehyde starch (DAS) simultaneously. The combined weight, 1,917 grams, was used to calculate the composition of the tanning solution, using the following percentages: water, 150%; sodium sulfate (anhydrous), 5.0%; sodium acetate (anhydrous), 2.0%; THPC, 1.73%; resorcinol, 1.0%; and dialdehyde starch, 5.0%.

The pickled skins were tanned in a laboratory churn for 1½ hours at pH 4.2. Thirty-eight grams (2.0%) sodium carbonate (monohydrate) were added and drumming continued 1½ hours with solution at pH 6.0. Thirty-eight grams (2.0%) sodium carbonate (monohydrate) were added and drumming continued 2 hours with solution at pH 8.2. The pH was adjusted to 8.7 with 11.5 grams (0.6%) sodium carbonate (monohydrate) and the skins drummed for one hour. At this time (6 hours' treatment) the leather had a shrink temperature of 84° C. The skins were washed, acidified to pH 3.9 with formic and sulfuric acids, washed, wrung, dyed, fat-liquored and finished as suede leather. The finished leather was full, round, mellow and had a good nap.

Example 13.—Resorcinol-THPC Tannage, Glutaraldehyde Retannage

Three of the domestic sheepskins tanned with 1.73% THPC and 1.0% resorcinol (Example 11), having a shrink temperature of 82° C., were retanned in a laboratory churn at 76 to 78° F. with the following solution, based on the pickled skin weight (2,970 grams): water 150%; sodium sulfate (anhydrous), 5.0% (on solution basis); glutaraldehyde (25%), 4.0%. All of the glutaraldehyde was added at the start of the retannage. After one hour drumming the solution pH was 8.3. The retannage was completed after a total of 4½ hours. The solution pH was 8.2 and the shrinkage temperature 85° C. The skins were washed for 30 minutes, acidified to about pH 4.0 with a solution of formic and sulfuric acids, washed 30 minutes and horsed. The skins had a well-tanned appearance and feel.

Example 14.—Glutaraldehyde Tannage, THPC-Resorcinol Retannage

Three comparable pickled New Zealand lambskins were horsed, thoroughly drained, weighed and tanned with glutaraldehyde. The combined weight, 2,017 grams, was used to calculate the composition of the tanning solution, using the following percentages: water, 200%; sodium sulfate (anhydrous), 5%; sodium acetate (anhydrous), 2%; glutaraldehyde (25%), 5%.

The pickled skins were drummed in the above solution in a laboratory churn for one hour at 88° F. At this time the solution pH was 4.4. Sodium carbonate (monohydrate) 40.3 grams (2%) was added and drumming continued for one hour at pH 7.2. Sodium carbonate (monohydrate) 40.3 grams (2%) was added and drumming continued for another hour at pH 9.6. The shrink temperature at this time (3 hours) was 75° C. The THPC, 17.5 grams (0.87%) and resorcinol, 10.1 grams (0.5%) were added to the tanning solution and drumming was continued another 3 hours. The solution pH was 8.8, the shrink temperature 81° C. and a test for resorcinol was negative. The skins were washed for 30 minutes, acidified to pH 4.0 with a solution of formic and sulfuric acids for 30 minutes, washed, wrung, dyed, fat-

liquored and finished as grain leather. The finished leather was exceptionally soft, clothly and somewhat pipey.

Example 15.—THPC-Resorcinol-Glutaraldehyde Simultaneous Tannage

Three comparable pickled New Zealand lambskins were horsed, thoroughly drained, weighed and tanned with THPC, resorcinol and glutaraldehyde simultaneously. The combined weight, 1,525 grams, was used to calculate the composition of the tanning solution, using the following percentages: water, 100%; sodium sulfate (anhydrous), 5.0%; sodium acetate (anhydrous), 2.0%; THPC, 0.87%; resorcinol, 0.5%; and glutaraldehyde (25%), 4.0%.

The pickled skins were tanned in a laboratory churn for 1½ hours at pH 4.2. Thirty-one grams (2.0%) sodium carbonate (monohydrate) were added and drumming continued 1½ hours with solution at pH 6.3. Thirty-one grams (2.0%) sodium carbonate (monohydrate) were added and drumming continued 2 hours with the solution at pH 9.1. The churn was steamed at intervals to raise the tanning liquor temperature from 73° to 104° F. The skins were drummed for 2 more hours. At this time (7 hours' treatment) the liquor pH was 9.0 and the shrink temperature 81° C.; a test for resorcinol was negative. The skins were washed, acidified to pH 4.0 with formic and sulfuric acids, washed, wrung, dyed, fat-liquored and finished as suede leather. The finished leather was full, mellow, good color, and had a very good nap.

Example 16.—Resorcinol-THPC Tannage, Formaldehyde Retannage

Three of the domestic sheepskins tanned with 1.73% THPC and 1.0% resorcinol (Example 11), having a shrink temperature of 82° C., were retanned in a laboratory churn at 82 to 86° F. with the following solution, based on the pickled skin weight (2,817 grams): water, 150%; sodium sulfate (anhydrous), 5.0% (on solution basis); formaldehyde (37%), 5.0%. All of the formaldehyde was added at the start of the retannage. After 30 minutes' drumming the solution pH was 7.5. Sodium carbonate (monohydrate), 1.0% (28.2 grams) was added and drumming continued at pH 9.0. The retannage was completed after a total of 4½ hours. The solution pH was 8.9 and the shrink temperature 87° C. The skins were washed for 30 minutes, acidified with a solution of formic and sulfuric acids, washed 30 minutes and horsed. The skins had a well-tanned appearance and feel.

We claim:

1. A process for tanning skins comprising impregnating a skin with an aqueous solution containing about from 0.4 to 2% of tetrakis (hydroxymethyl) phosphonium chloride and about from 0.2 to 1% of a phenol in combination with a tanning agent selected from the group consisting of a mineral tanning agent, a vegetable tannin and a synthetic organic tanning agent, said percentages being based on the wet drained weight of the pickled skins.

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

3. The process of claim 2 in which the tanning solution contains about from 0.4 to 2% tetrakis (hydroxymethyl) phosphonium chloride and about from 0.25 to 1% resorcinol, based on the wet drained weight of the pickled skins.

4. A process for tanning skins comprising impregnating a skin with a first aqueous tanning solution at pH in the range of about 4.0 to 4.5 containing about from 0.4 to 2% tetrakis (hydroxymethyl) phosphonium chloride and about from 0.25 to 1% of resorcinol, said percentages being based on the wet drained weight of the pickled skins, adjusting the pH of the solution during the tanning operation to a maximum pH in the range of about 8.5 to

9.5, separating the skin from said first solution, washing the skin with water, acidifying the washed skin to a pH in the range of about 2.5 to 5.0 and impregnating the skin with a second solution at a pH in the range of about 2.5 to 5.0 containing a tanning agent selected from the group consisting of a mineral tanning agent, a vegetable tanning agent and trimethylolmelamine.

5 5. The process of claim 4 in which the tanning agent of the second solution is a chromium compound.

6. The process of claim 4 in which the tanning agent of the second solution is a zirconium compound.

7. The process of claim 4 in which the tanning agent of the second solution is quebracho.

8. The process of claim 4 in which the tanning agent of the second solution is wattle.

9. The process of claim 4 in which the tanning agent of the second solution is trimethylolmelamine.

10. A process for tanning skins comprising impregnating a skin with a first aqueous solution at a pH in the range of about 2.5 to 5.0 containing a tanning agent selected from the group consisting of a mineral tanning agent, a vegetable tanning agent and trimethylolmelamine, separating the skin from said first solution, washing the skin with water, impregnating the washed skin with a second aqueous solution at a pH in the range of about 4.0 to 4.5 containing about from 0.4 to 2% tetrakis (hydroxymethyl) phosphonium chloride and about from 0.25 to 1% of resorcinol, said percentages being based on the wet drained weight of the pickled skins, and adjusting the pH of the second solution during the tanning operation to a maximum pH in the range of about 8.5 to 9.5.

11. The process of claim 10 in which the tanning agent of the first solution is a mineral tanning agent.

12. The process of claim 11 in which the mineral tanning agent is a chromium compound.

13. The process of claim 11 in which the mineral tanning agent is a zirconium compound.

14. The process of claim 11 in which the mineral tanning agent is an aluminum compound.

15. A process for tanning skins comprising impregnating a skin with an aqueous solution at pH in the range of about 4.0 to 4.5 containing about from 0.4 to 2% tetrakis (hydroxymethyl) phosphonium chloride, about from 0.25 to 1% of resorcinol, and about from 3.0 to 5.0% of dialdehyde starch, 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, said percentages being based on the wet drained weight of the pickled skins.

16. A process for tanning skins comprising impregnating a skin with an aqueous solution at pH in the range of about 4.0 to 4.5 containing about from 0.4 to 2% tetrakis (hydroxymethyl) phosphonium chloride, about from 0.25 to 1% of resorcinol, and about from 3.0 to 5.0% of glutaraldehyde, 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, said percentages being based on the wet drained weight of the pickled skins.

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