# Studies on Tara-phosphonium Combination Tannage: Approach Towards A Metal Free Eco-benign Tanning System

*by*

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## Abstract

One of the important criteria determining the sustainability of an industrial activity is the ecological acceptability of the processing methods. Tanners throughout the world are looking for alternative eco friendly tanning systems. In the present work, metal free tanning system using a combination of Tetrakis Hydroxymethyl Phosphonium Sulphate (THPS) and Tara has been developed. This combination tanning is expected to be an effective eco-friendly mineral free tanning. The shrinkage temperature of the leathers obtained is 88°C. The tanning system is versatile in terms of processing both upper and garment leathers. The physical strength characteristics and organoleptic properties of the leathers obtained are comparable to that of chrome tanned leather. Environmental impact assessment shows that there is reduction in total solids when compared to control chrome tanning. Tara as a combination tanning agent not only improves the leather properties but also can act as a scavenger of free formaldehyde present in THPS tanned leather.

## Introduction

Any alternative tanning system should result in leathers with good hydrothermal stability, strength characteristics, organoleptic properties and very importantly eco-friendlier.[1] In line with the resurgence of natural product dominance in the global market, leather industry is also re-looking at the possibility of increased use of organic materials. In this scenario, vegetable tanning could play a dominant role in the future leather industry.

Tara is the name commonly given for a fairly well known material, which consists of the dried pods of *Caesalpinia spinosa*, a tree or shrub widely distributed in North Western South America. The tannin content varies from 30-35%. It is a hydrolysable type of tannin.[2] It contains practically no coloring substances therefore permits very bright and light-resistant leathers. Tara gives leather fullness and softness and at the same time a fine, closed grain. In leathers tanned with tara, the grain resistance to breaking load is higher than that achieved with any other vegetable tannin. Vegetable tannin as solo tanning agent may not be effective for the manufacture of leather with all required properties. Hence, suitable adjuncts need to be used to attain required characteristics.

Tetrakis Hydoxymethyl Phosphonium Sulphate (THPS) is an organic tanning agent, which interacts with the amino groups of collagen and results in tanning. The main advantages of the THPS tanning include, metal-free tanning, easier to recycle/dispose, white appearance, excellent strength properties, easy to handle and apply in the drum, low toxicity, rapid breakdown in the environment and no bioaccumulation. (THPS) as tanning agent has been explored previously by prior research at this laboratory and by other researchers.[3-8]

In the present study, a combination tanning based on Tara and THPS has been developed. The tanning and the post tanning system have been optimized for producing both upper and garment leathers.

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## MATERIALS AND METHODS

Pickled goat and sheep skins were taken as raw material for making upper and garment leathers, respectively. All other chemicals used for leather processing were of commercial grade. The chemicals used for analysis were of laboratory grade.

**Determination of Shrinkage Temperature**

The shrinkage temperature, which is a measure of hydrothermal stability of leather, was determined using a Theis shrinkage meter.[9] Each value reported is an average of three experiments with a standard deviation of ±1.

**THPS Tara Combination Tanning**

The pickled skins at a pH of 2.8 were taken for both control and experimental tanning system. Eight pickled skins were taken. Two skins were used for each trial. Pickled skins were treated with 50% pickle liquor, 1.5% of THPS[4,5] and drummed for 45 min. The drum was flooded with 50% water and run for 10 min. Fixation of the tanning agents was initiated by the

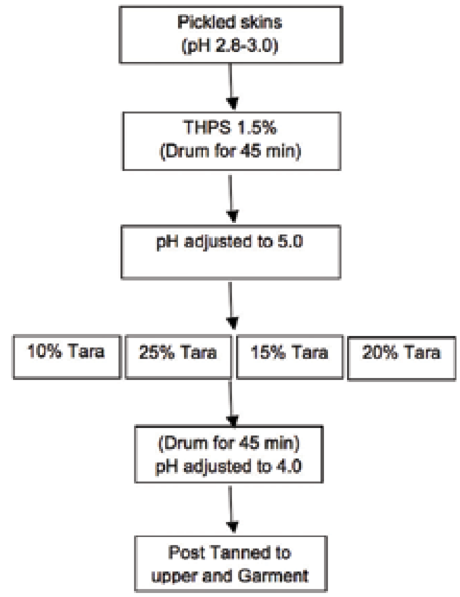


Figure 1. Flow chart representing experimental trails of THPS Tara tanning system.

**TABLE I**
**Post tanning recipe for Upper leather manufacture.**

Tanned goat leathers were sammed and shaved to a thickness of 1.0 -1.1 mm

| Process | Chemical | % | Duration | Remarks |
|---|---|---|---|---|
| Neutralisation | Water | 150 | | |
| | Sodium formate | 1 | | |
| | Sodium bicarbonate | 0.75 | 3 x 20+30 | pH - 5.0 -5.2 D/O wash |
| Retanning, dyeing & fatliquoring | Water | 150 | | |
| | Acrylic resin | 2 | | |
| | Melamine formaldehyde syntan | 5 | 40 | |
| | Phenolic replacement syntan | 5 | | |
| | Dye levelling agent | 1 | | |
| | Acid black dye | 2 | 40 | Check penetration |
| | Synthetic fatliquor | 6 | | |
| | Waxy synthetic fatliquor | 6 | 30 | |
| | Phenolic replacement syntan | 3 | 20 | |
| Fixing | Formic acid | 2 | 3 x10 + 30 | D/W, pile O/N |

Setting, hook to dry, staking, trimming and buffing.

**TABLE II**
**Post tanning recipe for garment leather manufacture.**

Tanned sheep leathers were sammed and shaved to a thickness of 0.7- 0.8 mm

| Process | Chemical | % | Duration | Remarks |
|---|---|---|---|---|
| Neutralisation | Water | 150 | | |
| | Sodium formate | 1 | | |
| | Gluteraldehyde based syntan | 2 | | |
| | Sodium bicarbonate | 1.0 | 3 x 20+30 | pH - 5.5<br>D/O wash |
| Retanning, dyeing & fatliquoring | Water | 150 | | |
| | Waxy synthetic fatliquor | 10 | | |
| | Phosphoric ester based fatliquor | 8 | | |
| | Lecithin based fatliquor | 2 | 40 | |
| | Melamine formaldehyde based synthan | 3 | | |
| | Phenolic replacement syntan | 3 | | |
| | Dye levelling agent | 1 | | |
| | Acid black dye | 2 | 30 | Check penetration |
| | Phenolic syntan | 2 | 20 | |
| Fixing | Formic acid | 2 | 3 x10 + 30 | D/W, pile O/N |

Setting, hook to dry, staking, trimming and buffing.

addition of 0.5% sodium formate, drummed for 15 min and 1.0-1.2% sodium bicarbonate (1:10 dilution and given in 3 feeds with 10 min interval). Finally, the drum was run for 2 hrs and the pH was checked to be 5.0. Different percentages of tara viz., 10, 15, 20 and 25% were then offered and the drum was run for another 60 min. Fixation of the tanning agent was carried out by adding 0.5-0.75% formic acid and drummed for 15 min. Finally, the drum was run for 1 hr and the pH was checked to be 4.0. Then the leathers were piled over night. The flowchart of the process employed is given in Fig. 1. Next day, hydrothermal stability of tanned leathers was measured using a shrinkage tester.

The optimized tanning process was followed for three goatskins and three sheepskins to make THPS-Tara tanned upper and garment leathers, respectively. Control chrome tanned (3 goatskins and 3 sheepskins) leathers were obtained following the conventional chrome tanning process.[5] Then the leathers were piled overnight. Next day, the hydrothermal stability of the tanned leather was measured using a shrinkage tester.

**Post Tanning Process**

Tanned leathers from goatskins were shaved to a uniform thickness of 1.0-1.1 mm and post tanned into upper crust leathers following the recipe given in Table I for both control and experimental leathers. Tanned leathers from sheepskins were shaved to a uniform thickness of 0.7-0.8 mm and post tanned to obtain garment crust leathers using the recipe described in Table II for both control and experimental leathers. After post tanning operations, the leathers were piled overnight. Next day, the leathers were sammed, set, hooked to dry, staked and buffed.

**Objective Assessment of Softness Through Compressibility**

The leathers made from control and experimental THPS-Tara combination processes were taken for softness measurements and the samples (three) were cut from the official sampling position.[10] The leather samples were conditioned at 20±2°C and 65±4% R.H. for 48 hours. The softness of the leathers was measured using ST 300D leather softness tester as per IUP 36 method.[11] The softness tester measures the deflection of leather by a fixed diameter plunger (35 mm) when a force (500 g) is applied to it.

**Physical Testing and Hand Evaluation of Leathers**
Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures for upper and garment leathers (both experimental and control).[12-14] Each value reported is an average of three (2 along the backbone, 2 across the backbone) measurements with standard deviation. Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness, fluffiness and general appearance by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property.

**Color Measurement**
Reflectance measurements were made for tara-THPS tanned upper leathers using Gretagmacbeth Spectrolino 21 hand held spectrophotometer. The L, a, b and c values were calculated. 'L' indicates the lightness, 'a' represents red and green axis, 'b' represents yellow and blue axis and 'c' represents chromacity. The values reported are average of three values.

**Environmental Impact Assessment**
Spent tan liquors from control and experimental leather processing were collected and analyzed for chemical oxygen demand (COD) and total solids (TS) (dried at 103-105°C for 1 hr) as per the standard procedure.[15] The values reported are average of 3 experiments along with their standard deviations.

## RESULTS AND DISCUSSION

**THPS-Tara Combination Tanning: Optimization of Offer of Tara**
The amount of THPS was kept constant at 1.5% and the amount of tara was varied from 10 to 25%. The results are provided in Table III. From the table, it could be observed that shrinkage temperatures of leathers tanned using THPS-Tara combination tannings with various offer of Tara (E1, E2, E3 and E4) are comparable at around 89±1°C. The tensile strength, tear strength and elongation at break of E1 were found to be better than other three systems (E2, E3 and E4). The grain smoothness, tightness, roundness of the leathers tanned with the system E1 is better when compared to E2, E3 and E4. Though, the systems E2, E3 and E4 show comparable properties to that of E1, the amount of Tara used in these experiments is higher. Increase in Tara usage will result in higher pollution load and will also affect the cost of the leather. The strength properties of upper leather made from THPS-Tara combination tanning were comparable to that of chrome tanned upper leather. Thus, the system E1, which uses least amount of Tara (10%) is optimized for further tanning experiments.

**TABLE III**
**Shrinkage temperature, strength properties and hand evaluation* of leather tanned with various offer of Tara.**

| | E1 | E2 | E3 | E4 | Control (Cr tanned leather) |
|---|---|---|---|---|---|
| $T_s$ (°C) | 88±0.5 | 88.5±0.5 | 89.0±0.5 | 89±1 | 110±2 |
| Tensile strength (kg/cm$^2$) | 255±10 | 241±6 | 241±6 | 243±5 | 233±5 |
| Tear strength (kg/cm) | 69±3 | 52±3 | 55±2 | 49±2 | 50±2 |
| Elongation at break (%) | 60±1.5 | 58±1.5 | 55±2 | 50±2 | 53±3 |
| Smoothness* | 9±0.5 | 7±1 | 6±2 | 6±2 | 8±1 |
| Tightness* | 8±1 | 8±0.5 | 8±1 | 8±0.5 | 8±1 |
| Roundness* | 8±1 | 7±1 | 7±1 | 8±0.5 | 8±1 |

E1– THPS (1.5%) and Tara (10%); E2– THPS (1.5%) and Tara (15%);
E3– THPS (1.5%) and Tara (20%); E4– THPS (1.5%) and Tara (25%)

*Hand evaluation of upper leathers after final crusting following the process in Table I

**Optimization of Order of Addition of Tanning Agents (THPS and Tara)**

Using optimized quantities of the tanning agent, two tanning methods with difference in order of addition of Tara and THPS have been carried out. It was found that the shrinkage temperature of THPS-Tara tanned leather seems to be comparatively higher than that of Tara-THPS tanned leather. Similar results were found in the leathers evaluated by experienced tanners and the results are provided in Table IV. One can observe from the table that the grain smoothness and tightness is better in THPS-Tara tanned leathers. The leathers tanned with THPS-Tara were found to have better handling properties than Tara-THPS tanned leathers. Based on the strength properties and hand evaluation, THPS-Tara combination tanning (THPS offer of 1.5% and Tara offer of 10%) was chosen for further tanning experiments.

**Preparation of Garment Leathers**

Optimized order of addition of THPS and Tara and optimized offer of THPS (1.5%) and Tara (10%) was used for the preparation of garment leathers. The prepared garment leathers were converted in to crust leathers employing process provided in Table II. The strength properties and organoleptic properties of garment leathers are shown in Table V. The strength properties of the leather were found to be better and the leather seems to have improved organoleptic properties to suit the garment requirements. Thus by employing the optimized tanning and post tanning system, good quality garment leather can be manufactured.

**Color Measurements**

The Lightness factor L, a, b, hue, chromaticity values are assessed for both upper and garment leathers tanned using the optimised combination tanning system and the values are shown in Table VI. From the table it could be observed that the lightness factor is around 25 for upper and garment leathers manufactured, which indicates the richness in color could be obtained by using only 2% dye. The control samples for both upper and garment leathers (chrome tanned) also showed similar color values as that of the experimental leathers.

**TABLE IV**
**Shrinkage temperature and Hand evaluation* of leathers processed using two tanning methods.**

| Samples | $T_s$ (°C) | Fullness | Roundness | Smoothness | Softness | Tightness |
|---|---|---|---|---|---|---|
| Tara-THPS | 85±0.5 | 6±1 | 7±1 | 7±1 | 6±1 | 6±1 |
| THPS-Tara | 88.5±0.5 | 8±1 | 8±1 | 9±0.5 | 7±1 | 8±1 |

*Hand evaluation of upper leathers after final crusting following the process in Table I

**TABLE V**
**Strength properties and hand evaluation* of the garment leather.**

| Parameters | Optimised combination tanning system | Control (Cr tanned leather) |
|---|---|---|
| Shrinkage temperature | 88±1 | 110±2 |
| Tensile strength (kg/cm$^2$) | 165±5 | 167±5 |
| Tear strength (kg/cm) | 29±2 | 28±2 |
| Elongation at break (%) | 58±2 | 57±5 |
| Grain smoothness* | 9±0.5 | 9±0.5 |
| Softness* | 9±0.5 | 9±0.5 |
| Fluffiness* | 8±0.5 | 8±0.5 |

*Hand evaluation of upper leathers after final crusting following the process in Table II

**Softness Measurements**

The softness of the upper and garment leathers developed using the optimized combination tanning system is assessed through digital leather softness tester and the values are shown in Table VII. The softness of the upper crust leathers both control and experimental were on par. Similarly, the softness of the garment crust leathers is also on par and higher than that of upper leathers. This indicates that the developed tanning system can be used for the development of garment leathers, which is also in accordance with the observations made from the hand evaluation properties. Further, combination tanning system results in softer leather indicating that the fiber structure is not affected.

**TABLE VI**
**L*, a*, b*, hue* and chromaticity* of the upper and garment leathers tanned using optimized combination tanning system.**

| Leather | L | a | b | Hue | Chromaticity |
|---|---|---|---|---|---|
| Upper Control | 26.71 | 0.02 | 6.64 | 91.84 | 3.5 |
| Upper Experiment | 24.36 | -0.10 | 4.04 | 90.45 | 4.037 |
| Garment Control | 24.44 | 0.06 | 4.6 | 90.47 | 4.3 |
| Garment Experiment | 28.13 | -0.11 | 5.17 | 90.15 | 5.07 |

*L, a, b, hue and chromaticity values are evaluated after final crusting

**TABLE VII**
**Softness of the upper and garment leathers tanned using optimized combination tanning system.**

| Leather | Softness | |
|---|---|---|
| | Experimental Leather | Control Leather (Chrome tanned) |
| Upper leather | 3.59 | 3.74 |
| Garment leather | 6.77 | 7.24 |

**TABLE VIII**
**Environmental characteristics of spent tan liquor from optimized leather process.**

| Parameter | Experiment (THPS-Tara) | Control (Cr tanned) |
|---|---|---|
| Chemical oxygen demand (COD) (mg/L) | 16834±55 | 2600±60 |
| Total solids (TS) (mg/L) | 47362±13 | 48090±20 |

**TABLE IX**
**Free formaldehyde content* in the experimental and control leathers.**

| Leather samples | Formaldehyde[a] (ppm) | Free formaldehyde due to THPS[c] |
|---|---|---|
| THPS alone | 147±2 | 119±2 |
| THPS->Tara (10%) | 30±3 | – |
| Tara (10%) ->THPS | 33±1 | 4±1 |
| Chrome tanned | 29±2[b] | – |

*Free formaldehyde determination was done after final crusting
a = Total free formaldehyde present in leather
b = Free formaldehyde caused by post tanning chemicals
c = Free formaldehyde caused due to THPS alone (a-b)

**Environmental Impact of THPS – Tara Combination Tanning System**

The chemical oxygen demand (COD) and total solids (TS) were determined for the spent tan liquors from optimized combination tanning and control chrome tanning and the values are provided in Table VIII. It could be observed from the table that total solids are less than that of control chrome tanning system, whereas the COD value is higher. This could be due to the organic nature of both the tanning materials employed in this study. Though, the COD is higher, the wastewater can be easily treated employing simple treatment methods such as aeration, ozonization or aerobic biological treatment methods. The total solids content can be reduced by simple sedimentation or settling techniques.

**Role of Tara in Scavenging of Free Formaldehyde Formed Due to THPS**

THPS, chrome, THPS-Tara and Tara-THPS tanned leather were subjected to formaldehyde determination.[16] The results are shown in Table IX. It could be observed that the chrome tanned leather crust showed free formaldehyde concentration of about 29 mg/L. This could be due to free formaldehyde formed during post tanning process. THPS alone tanned leather crust showed free formaldehyde concentration of about 147 ppm. This is a cumulative of free formaldehyde formed due to THPS as well as during post tanning process. Hence, the amount of free formaldehyde formed due to THPS is only approximately 118 ppm. Similar calculation has been carried out for Tara-THPS and THPS-Tara tanned crust leathers. It is clearly observed from table that both the THPS-Tara and Tara-THPS tanned leathers showed almost 99% scavenging of free formaldehyde formed due to THPS. Also, it was observed that the % offer of Tara had no significant effect on the scavenging of free formaldehyde. But, based on the hand evaluation, 10% Tara was essential to provide the leathers with better characteristics. This is an added advantage of this optimized combination tanning system.

## CONCLUSIONS

A new combination tanning system based on THPS and Tara has been developed. It has been found that both upper and garment leathers, which have physical and organoleptic properties on par with chrome tanned leathers, could be made using this new combination tanning system. From an environment impact assessment, it has been found that TS values are much less compared to chrome tanning system. The increase in COD may be attributed to the presence of unfixed THPS and Tara. The combination tanning system using Tara and THPS results in leathers with reduced or absence of free formaldehyde in crust stage when compared to leathers tanned with THPS alone. Thus, Tara-THPS combination tanned leathers can meet the mandatory and voluntary requirements in terms of permissible limits of formaldehyde set by the EPA. The Tara-THPS combination tanning system is not only a mineral free, environmentally friendly tanning system, but also a commercially viable process.

## ACKNOWLEDGMENT

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