Novel Titanium (IV) Tanning for Leathers with Superior Hydrothermal Stability

III. Study on Factors Affecting Titanium Tanning and an Eco-friendly Titanium Tanning Method

by

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Abstract

A novel eco-friendly titanium tanning system based on lactate-masked titanium sulfate solution as the tanning agent was developed. This approach offers enhanced tanning power, compared to previous system. The factors affecting this type of titanium tanning were investigated. The results showed that a conventional pickling process with high NaCl concentration was not suitable for titanium tanning while a pickle-less or salt-free pickling with titanium tanning increased shrinkage temperature (T_s) more than 10ºC. The optimum tanning conditions were 7.5%-10% TiO_2 offer (based on pelt weight with 65% moisture content), 30% titanium solution basicity and pH 3.5 tanning ending pH (basified by sodium bicarbonate or magnesium oxide). Proper pre-fatliquoring resulted in better titanium tanning agent penetration into the skin. But the pre- and post-treatment with multicarboxylates, acrylic resins and glyoxlic acid did not improve titanium combination with collagen. The shrinkage temperature of the leather was 102ºC. The white titanium tanned leather had better strength and fullness than the chrome tanned leather control. But the spongy feel of titanium tanned leather was inferior to chrome tanned leather but superior to aluminum and zirconium tanned leather. The titanium absorption rate was more than 99% and no sodium chloride and/or ammonium salt were discharged.

Resumen

Un sistema novedoso eco-amigable de curtición basado en una solución de sulfato de titanio enmascarada con lactatos como agente curtiente fue desarrollado. Esta investigación ofrece un poder curtiente realzado, comparado con sistemas anteriores. Los factores que afectan este tipo de curtición al titanio fueron investigados. Los resultados demostraron que un proceso de pickelado convencional con alta concentración del NaCl no es conveniente para curtir al titanio mientras que un pickelado con poca sal o sin ella en un curtido al titanio aumentó la temperatura de contracción (T_s) más de 10ºC. Las condiciones de curtición óptimas se obtuvieron con una oferta de 7.5%-10% TiO_2 (basada en peso de la piel con un contenido de agua del 65%), basicidad de la solución de titanio de 30% y pH al final de curtido de 3.5 (basificado con bicarbonato de sodio u óxido de magnesio). Un pre-engrase apropiado dio lugar a una mejor penetración del agente curtiente titanio en la piel. Pero los pre y post-tratamientos con polycarboxylados, resinas acrílicas y el ácido glicólico no mejoró la combinación del titanio con el colágeno. La temperatura de contracción del cuero fue 102ºC. El cuero blanco curtido al titanio tuvo mejores resistencias y plenitud que el cuero curtido al cromo usado como control. Pero el toque esponjoso del cuero curtido al titanio fue inferior al cuero curtido al cromo, pero superior a los cueros curtidos al aluminio y al zirconio. El grado de absorción del titanio fue mayor al 99% y no fueron descargados ni cloruro de sodio ni sales de amonio.

Introduction

Previous work on titanium tanning mainly based on using ammonium titanyl sulfate and citrate-masked basic titanium sulfate as tanning agents.[1-3] Although much about improving the tanning power of titanium tanning has been done, almost no truly satisfactory result has been obtained, so far. Titanium

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tanning using ammonium titanyl sulfate as a tanning agent obtained very firm leather, but its shrinkage temperature was below 90ºC. The shrinkage temperature of the leather tanned by basic titanium sulfate masked with citrate was only 85ºC.[4] Ts of the leather tanned by the Ti-Al combination tanning agent developed and patented by Covington was also 85ºC.[5] So it has been accepted that the shrinkage temperature of titanium tanned leather is not as high as that of zirconium tanned leather, no higher than 90ºC.[6]

Our previous research in this series postulated that the tanning power of Ti(IV) should be higher than zirconium tanning, in other words, traditional titanium tanning did not achieve its theoretical tanning power.7 Traditional titanium tanning has to start in a very acidic medium with the pelt strongly pickled in the presence of salt. Using ammonium titanyl sulfate as the tanning agent, the traditional titanium tanning discharges not only NaCl but also ammonium, which seriously pollute environment. Basic titanium sulfate masked by citrate is not an ideal tanning agent in terms of its tanning power. So, conventional titanium tanning agents and tanning methods can not meet the practical requirements. A novel titanium tanning system for substituting chrome tanning should not only have higher tanning effects, better leather performance, as well as be eco-friendly. Our previous research also showed that lactate-masked titanium sulfate solution at the mole ratio of lactate to Ti^{4+} of 0.40 to 0.5 to 1 has the highest tanning power among the common masking agents, because lactate has small molecule-volume and moderate and suitable coordination ability with Ti^{4+}. The shrinkage temperature of the leather tanned by Lactate-Ti solution is more than 10ºC higher compared with citrate-Ti solution.[7] So, Lactate-masked titanium sulfate solution provides an important basis of tanning agent for further researching a novel, eco-friendly titanium tanning system with high tanning power.

In the present study, the factors affecting titanium tanning, such as tanning medium, dosage of titanium tanning agent, tanning ending pH, tanning solution basicity, basifying agent and pre- and post-treating methods, are investigated based on using the lactate-masked titanium sulfate solution as a tanning agent. The aim of this study is to construct a novel eco-friendly titanium tanning process for leathers with superior hydrothermal stability and performances.

Experimental

Materials

Titanium sulfate was analytical grade from Shanghai Experimental Reagent Company, China. Standard white hide powder was also analytical grade and from Chinese Academy of Forestry. All chemicals used for leather processing were commercial grade and other reagents were analytical grade.

Titanium Tanning Solution

Cit-Ti tanning solution: Titanium sulfate solution was masked with citrate at the mole ratio (citrate to Ti) of 0.30:1.0.
Lact-Ti tanning solution: Titanium sulfate solution was masked with lactate at the mole ratio (lactate to Ti) of 0.40:1.0. Titanium concentration of tanning solutions was 80g/L TiO_2; and basicities were 30%, 50%, 65% and 75%.

Tanned Matrixes

White hide powder (17.2% moisture content) and depickled goat skins were used as tanning matrixes in this study. Pickled goat pelts were made as per conventional wet-salted goatskins leather making processes. Depickled goat pelts were obtained by neutralizing pickled goat pelts (pH 2.5) to pH 6.5 with $NaHCO_3$ solution in 8% salt solution and the depickled pelts were thoroughly washed to remove salts. After being squeezed and hung for 2h, the pelts were cut into small pieces (10g/piece). The moisture content at this stage was 65% and the chemical dosages percentages in the following experiments were based on the weight of these depickled skin pieces.

Titanium Tanning Procedures

Tanning hide powder

1.5g white hide powder (17.2% moisture content) was soaked in a conical flask with 20ml distilled water and stirred overnight at 25ºC in an incubator. Titanium tanning liquor (Lact-Ti or Cit-Ti) was added to the conical flask at different offer levels. After 2 hours of stirring, the tanning bath was slowly basified to different ending pH with 100g/L $NaHCO_3$ solution. Then the hide powder was continuously stirred for another six hours at 35ºC. The total tanning time was 24 hours. Spent tanning liquor was collected and the titanium concentration was determined. The tanned hide powder was washed with distilled water until no SO_4^{2-} ion was detected in the washings. The titanium content of the dry tanned hide powder was also tested.

Tanning depickled goat pelts

Two pieces of depickled goat pelt (20g) were put into a conical flask with 40ml different tanning medium solutions, such as H_2O; 2.5%, 5.0%, 7.5% and 10% (w/w) NaCl solution; 5% and 10% (w/w) Na_2SO_4 solution; 4% (w/w) Selletan P (a salt-free pickling auxiliary from TFL Company) solution and a pickling solution (pH 2.5, 6% (w/w) NaCl). The flask was stirred for 30min at 25 in an incubator then a titanium tanning liquor (Cit-Ti or Lact-Ti) of different basicity (30%, 50%, 65% or 75%) was added into the flask with varying amounts (2.5%-20% TiO_2 offer levels). After 2 hours stirring, the tanning bath was slowly basified to varying pH (2.0-7.0) with 100g/L $NaHCO_3$ solution or other alkali solutions, and then the flask was continuously stirred for another 6 hours at 35ºC. Total tanning time was 24 hours. Spent tanning liquors were collected and the titanium concentration was analyzed. The leathers were split into 3 layers and TiO_2 content of each layer was determined. The Ts of leathers were also tested.

Pre- and Post-treatment of Titanium Tanning

Pretreatment: Depickled goat skin was treated for 12 hours at pH 7.0 and 25ºC with 2.0% fatliqours or 5% phthalate, benzene-tetracarboxylate, salicylate, quinol, pyrogallol and glyoxylic acid, respectively. Then these pretreated skins were tanned by Lact-Ti solution as the following conditions: 50% titanium solution basicity, 7.5% TiO_2 dosage, and 3.5 ending pH.

TABLE I
Influence of Tanning Medium on Titanium Tanning

Tanning medium	Absorbed Ti Rate (%)	T_S after tanning (°C)	T_S after washing (°C)	TiO_2 content in leather (%)
pickling liquor	54.30	84	85	8.64
free-salt pickling	96.52	92	92	14.92
H_2O	98.26	94	93	15.35
2.5% NaCl	78.35	90	90	12.42
5.0% NaCl	66.37	83	85	11.20
7.5% NaCl	56.37	75	78	8.85
10.0% NaCl	52.97	73	72	7.87
5.0% Na_2SO_4	90.23	90	89	13.94
10.0% Na_2SO_4	74.40	88	87	11.57

Depickled goat pelts was tanned by Lact-Ti tanning solution of 50% basicity with 7.5% TiO_2 offer; the ending pH was 3.5; the concentration is w/w.

TABLE II
Influence of NaCl Concentration on pH and Precipitate Point pH of Titanium Solution (0.05M Lact-Ti solution of 50% basicity)

NaCl concentration (M)	0	0.5	1.0	1.5	2.0
Ti solution pH	1.80	1.70	1.60	1.50	1.40
precipitation pH	5.80	6.00	5.20	5.00	4.80

TABLE III
Ti-distribution Uniformity in Leathers Tanned with Lact-Ti Solution at Different Dosages (%)

TiO2 dosage (%	5.0	7.5	10.0	15.0	20.0
5% NaCl medium	95.22	93.20	83.91	83.57	83.82
water medium	75.61	91.10	88.86	85.35	--

Treatment during basifying: Depickled goat skins were tanned with 7.5% TiO_2 offer of Lact-Ti solution (50% basicity) in water. Tanning bath was basified to pH 3.5, then different chemicals, such as 5% Relugan RF, 5% Implenal DC (from BASF Company), 5% phthalate, oxalate or gluconate at 1:1 mole ratio to titanium, were added, respectively. The treatment time was 12 hours.

Post-treatment: Ti-tanned leather was treated with 5% phthalate, benzene-tetracarboxylate, salicylate, quinol or pyrogallol, respectively. T_s of the leathers before and after treated were tested.

Trial of Titanium Tanning at Pilot Plant

Eleven bated goat skins were taken, which were obtained using a conventional leather making processes. Several skins were titanium tanned as per the following procedures; another batch of bated skins was chrome tanned as a control.

The titanium tanned and chrome-tanned leathers were processed by sammying, shaving, neutralization, dying, fatliquoring, drying and milling as per conventional goat garment leather recipes.

Determination of Shrinkage Temperature

Shrinkage temperature of leather was determined using a SW-1 leather shrinkage temperature meter (China) in water medium (Ts<95°C) or glycerol-water (75:25) solution (Ts>95°C). Each reported value is an average of three measurements.

Analysis of Titanium Content of Leather and Concentration of Tanning Solution

Titanium content was assayed by spectrophotometry.[8] Spent titanium tanning liquors, titanium-tanned hide power and leathers were digested by a mixture of nitric and sulfuric acids. Then, the clear digested solution was diluted and reacted (colored) with the addition of dilute hydrogen peroxide. The absorbance was determined at 407nm using UV-2501PC spectrophotometer (Shimadzu). The titanium content was obtained by comparing the absorbance to a standard (calibration) curve.

Physical Testing of Leather Samples

The samples for physical testing were obtained and conditioned as per ASTM method.[9] Physical properties such as tensile strength,

TABLE IV
Results of Titanium Tanning at Different Initial Ti Concentrations

Initial concentration TiO_2 (g/L)	40	30	25	20
Ti-absorbed rate (%)	88.69	93.99	96.18	96.96
TiO_2 content in leather (%)	19.87	20.45	20.85	20.68
Ti distribution uniformity (%)	86.44	92.10	94.52	93.79
Leather T_S (°C)	99.0	101.0	101.5	102.0

TiO_2 dosage is 10%

TABLE V
Effects of Pretreatment on Titanium Tanning

Materials	Phthalate	Benzene-tetracarboxylate	Salicylate	Quinol	Pyrogallol	glyoxylic acid	None control
TiO_2 content in leather (%)	17.28	19.84	19.55	15.99	18.58	17.76	19.07
Leather Ts (°C)	101	99	102	102	101	102	102

Dosage of pretreatment material: 5%; treating time: 12 hours; Titanium tanning: 50% basicity Lact-Ti solution; 7.5% TiO_2 offer; ending pH 3.5.

elongation and tear strength were determined as per ASTM standard procedures.

Evaluation of Organoleptic Properties

Crust leathers were assessed for softness, grain smoothness, fullness and general appearance by tactile evaluation. Five experienced tanners rated the leathers on a scale of 0-5 points for each functional property.

Results and Discussion

Influence of tanning medium on titanium tanning

Generally, metal tanning is carried out in a pickling solution with a high salt concentration (more than 6% NaCl) to depress acidic swelling of the skins.[10] So, conventional titanium tanning is also implemented in a pickling solution. But, the type of tanning medium and the salt concentration have a large influence on the tanning power, as shown in Table I. Depickled goatskins (salt-free) were tanned by Lact-Ti tanning solution under otherwise identical conditions but different media, but the tanning results were largely different. Sodium chloride highly impaired the tanning effect of the titanium salt, especially at high concentrations. With increasing NaCl concentration in tanning medium, the T_s and Ti content of leather dramatically declined; Ts decreased 20°C and Ti content reduced 50 percent when increasing NaCl concentration from 0 to 10% (w/w). Sodium sulfate has a slightly negative influence on titanium tanning compared with sodium chloride. As we know, the NaCl concentration in a conventional pickling solution is more than 6% (w/w), hence the titanium tanning effect is poorer in a conventional pickling solution than in a salt-free pickling solution. Consequently, the traditional pickling process with high NaCl concentration is not suitable for titanium tanning.

Titanium tanning in a water medium without salt has the best result in terms of the T_s and Ti content, and we did not find any acidic swelling during the tanning process. It is well known that the maximum skin swelling occurs at pH of 2.5, and at lower pH the concentration of added counter ions becomes so high that this leads to deswelling.[11] The pH of titanium tanning solution is low, about 1.6 (B 50%, 80g/L TiO_2), and when titanium tanning solution mixes well with water and skins, the balance pH of tanning bath goes down to 1.8, where the skin swelling is minimal. On the other hand, the mole ratio of Ti to sodium sulfate in 50% basicity titanium solution is 1:1, which means the concentration of sodium sulfate in the tanning bath

Titanium Tanning Process

Five and a half bated goat pelts, pH 7.5

Water	200%	25°C	
Cationic fatliquor (Atlasol KTW)	2.0%	30min	
Lact-Ti tanning solution (amount to TiO_2)	7.5%	120min	check pH 1.8
$NaHCO_3$ (dissolved in 10 times water)	8.0%	6x20min, 60min	
Water (60°C)	100%	60min	

check pH 3.5, temperature 35°C

Run 5min/60min overnight; run 60min next morning; total tanning time 20h.

All percentages based on skin weight with 65% moisture content.

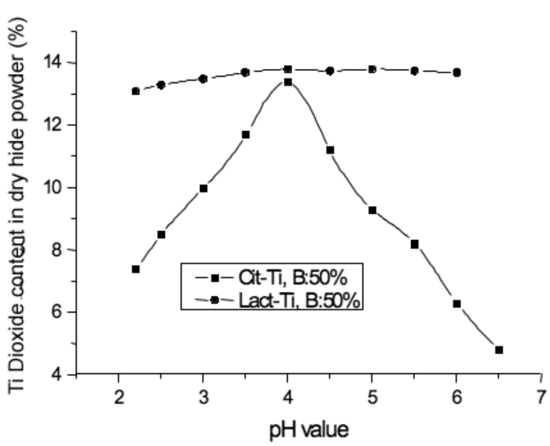

Figure 1. **TiO_2 content in hide power tanned at different end pH**
(20% TiO_2 offer based on dry hide powder weight)

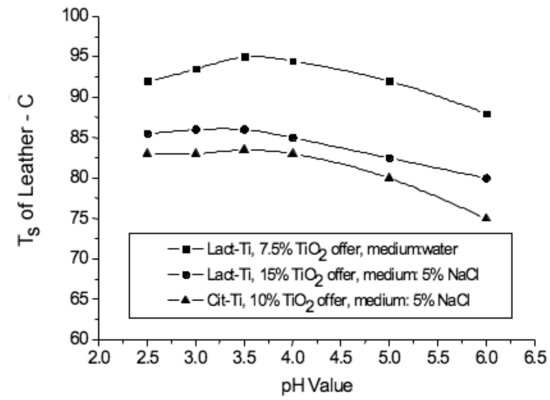

Figure 3. **T_s of leathers tanned at different end pH**
(titanium tanning solution's basicity: 50%)

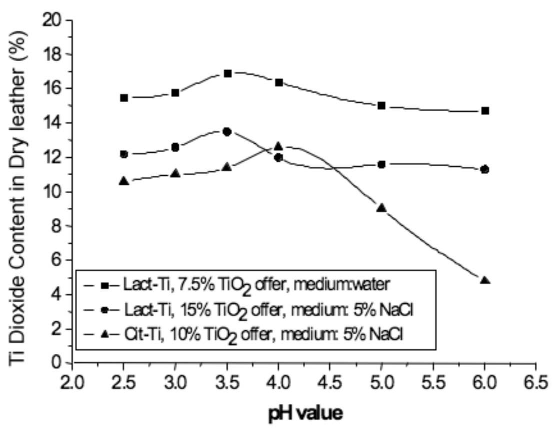

Figure 2. **Ti content in leather tanned at different end pH**
(titanium tanning solution's basicity: 50%)

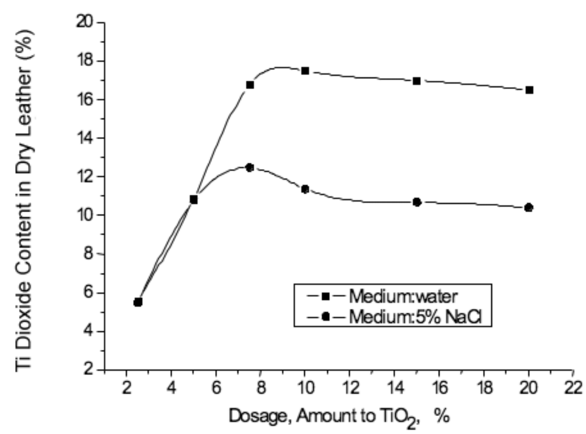

Figure 4. **Ti content in leather tanned with different tanning agent dosages**
(titanium tanning solution's basicity: 50%; tanning end pH: 3.5)

(mixture of titanium tanning solution, water and skin) is about 0.35 M (5%, w/w) at 7.5% TiO_2 offer. Obviously, acidic swelling is repressed in this solution. And the goat skin is so thin compared with cattle hide that titanium tanning agent can easily penetrate. No acidic swelling was observed, even in the middle layer of the skin, in our titanium tanning experiments, described here. Actually, the analogous process for chrome tanning, named pickle-less chrome tanning, has also been researched and reported, where bated pelts were directly chrome tanned in an aqueous medium without pickling.[12]

In fact, NaCl has a similar effect on aluminum and chromium tanning. The H^+ concentration in basic chromium sulfate solution increases and the precipitation point pH of aluminum sulfate solution slightly decreases when adding NaCl.[13] Likewise for titanium sulfate solution. Table II shows that pH and precipitation point pH of titanium sulfate solution decline by 0.4 and 1.0, respectively, with increasing NaCl concentration from 0 to 2M. It has been accepted that the Cl^- can enter the inner-sphere of chrome complex to substitute for $SO4^{2-}$, hence, the charge and reactivity of chrome complex are changed.[14,15] So, we can presume the same change can happen in titanium solution at high NaCl concentration. When NaCl concentration increases to 2.0M, Cl^- may partially substitute lactate ligand in Ti-complex and this leads to the precipitation point decreasing 1.0 pH. The negative influence of NaCl on titanium and aluminum tanning is more significant than on chromium tanning. Leather tanned with aluminum masked with phthalate in water has a 90°C Ts and 15% Al content. But T_s and Al content decline to 82°C and 10%, respectively, when aluminum tanning is carried out in 40g/L NaCl solution.[13] The reason may be that the complexes of Ti and Al are electrovalent complexes (outer-orbital complexes), mainly based on ion pair interactions. The influence of electrolyte, especially NaCl, largely affects their stability and coordination ability with collagen.

Titanium tanning at different ending pH

Hide powder and depickled goat pelts were tanned by Cit-Ti and Lact-Ti solutions under otherwise identical conditions but different tanning ending pH. The tanning results are given in Figures1, 2 and 3. Obviously, the tanning ability of Lact-Ti is higher than that of Cit-Ti; hide powder or leather tanned with Lact-Ti has higher Ts and Ti content. Notices that pH 4.0 is the optimum tanning ending pH for Cit-Ti tanning solution, where the T_s and Ti content of leather reaches the highest point. When pH >4.0, the tanning power of Cit-Ti drastically decreases and detanning effects are observed. The reason is that

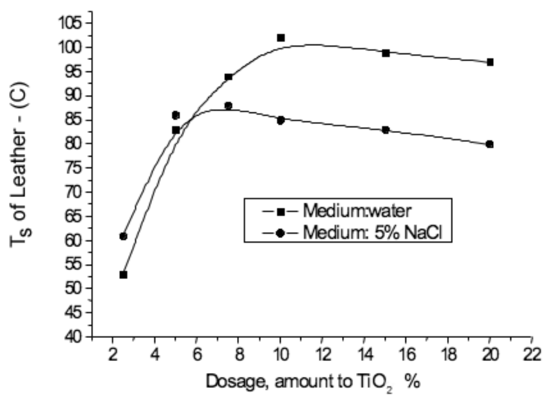

Figure 5. **T_s of leathers tanned with different tanning agent dosages**
(titanium tanning solution's basicity:50%; tanning end pH :3.5)

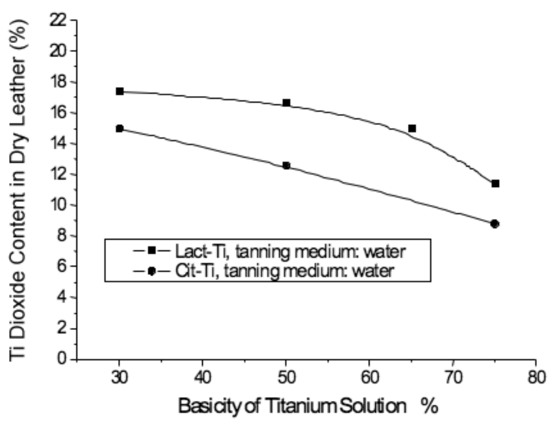

Figure 6. **Ti content in leather tanned with tanning solutions of different basicity**
(7.5% TiO_2 offer, tanning end pH 3.5)

the extent of the ionization of citric acid increases with pH rising, which enhances the coordination extent of citrate with Ti^{4+}; hence, the reactivity of collagen with Ti^{4+} is weakened because ionized citrate has very strong coordinating ability to Ti^{4+}, which can substitute collagen ligands from the inner-sphere of the Ti-complex.

The lact-Ti reagent has significant affinity toward collagen; hide power and leather tanned with it have rather large Ti content, especially tanned in water. There are no such remarkable changes for Lact-Ti tanning compared to Cit-Ti as regards Ti content and T_s of leather with varying tanning ending pH, ranging from 2.0 to 6.0. But T_s and Ti content are somewhat higher in pH 3.5-4.0. Figures 2 and 3 also show that titanium tanning in water has better tanning performance than in 5% NaCl solution.

Titanium tanning at different dosages and initial concentrations of tanning agent

Depickled goat skins were tanned with Lact-Ti tanning solution of 50% basicity under otherwise identical conditions but different tanning agent dosages, and the ending tanning pH was adjusted to 3.5. The tanning results are shown in Figures 4 and 5.

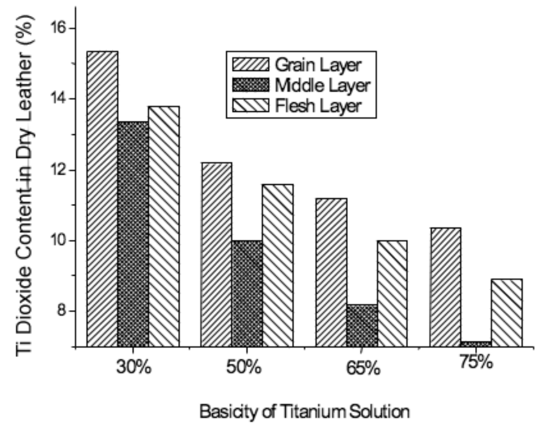

Figure 7. **Ti-distribution in leather tanned with Lact-Ti solutions of different basicity**
(7.5% TiO_2 offer, tanning end pH 3.5, in water medium)

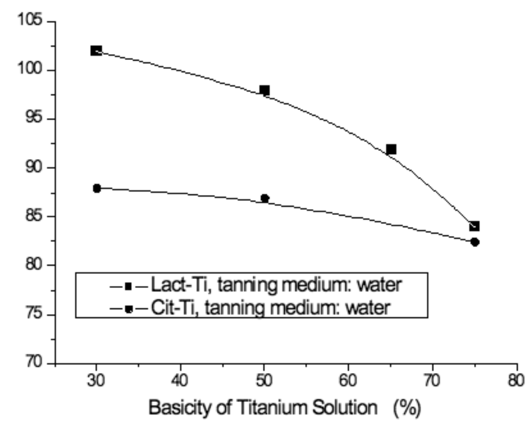

Figure 8. **T_s of leather tanned with tanning solutions of different basicity**
(7.5% TiO_2 offer, tanning end pH 3.5)

When the dosage of Lact-Ti (based on TiO2) is lower than 5%, the titanium agent is completely absorbed by the skin in both water and 5% NaCl medium. The T_s of the leather tanned in water is lower than in 5% NaCl solution, as shown in Figure 5, because titanium complexes penetrate into skin better in 5% NaCl solution than in water. We found that about 1/4-1/5 middle layer of the leather tanned with 5% TiO_2 offer in water became transparent and T_s decreased from 83°C to 56°C after it was washed with water. This indicates that little to no titanium arrived at the middle layer; hence, acidic swelling occurred in the middle layer when it was washed. But, the leather tanned in 5% NaCl solution with the same tanning agent dosage (5%) had no remarkable change after it was washed. T_s did not decrease and no acidic swelling was detected in the middle layer. This indicates that titanium had penetrated and combined well with collagen in middle layer of the skin. Table III also shows that the Ti-distribution uniformity in the leather tanned with 5% TiO_2 offer in 5% NaCl solution is 95.22%, whereas, it is only 75.61% when tanned in water. Hence, titanium tanning agent has larger affinity and combination ability with collagen in water than in NaCl solution. In other words, NaCl reduces the affinity and reactivity of Ti-complexes with collagen, thus, titanium agent more easily penetrates

TABLE VI
Effects of Treatment on Titanium Tanning during Basification

Materials Dosage*	Phthalate 5%	Implenal DC* 5%	Relugan RF* 5%	Oxalate 1:1	Gluconate 1:1	Control
Ti-absorbed rate (%)	95.67	92.22	98.34	60.46	43.40	98.55
TiO2 content in leather (%)	15.08	15.14	16.12	8.96	8.06	16.88
Leather Ts (°Ê)	98	99	100	86	82	101

Implenal DC is a product of BASF, which is a kind of multi-carboxylate; Relugan RF is a kind of small-molecule acrylic resin, which is also from BASF.
Dosage: 5% means 5 percent of skin weight; 1:1 means the mole ratio of material to Ti is 1:1.

TABLE VII
Influence of Basifying Agents on Ti content in Leather

Basifying Agent	$NaHCO_3$	Urotropine + Na_2SO_3(1:1)	TEA	EDA	MgO	Na_2CO_3
TiO2 content In leather (%)	16.88	14.14	14.81	15.18	16.56	14.53

TEA: triethanolamine; EDA: ethanediamine

TABLE VIII
Influence of Pre-fatliqouring on Titanium Tanning

Fatliqours	KTW	400-R	177-C	no control
TiO_2 content in leather (%)	18.22	16.15	16.85	18.08
Ti-distribution uniformity (%)	95.87	93.16	93.81	91.10

KTW: a cationic fatliqour; 400-R: a sulfited fish oil; 177-C: an electrolyte-stable fatliqour; all of them are from Atlas Company. Their dosages are 2%.

the skin in NaCl solution. But, when dosage is beyond 6%, the Ti content and T_s of the leather tanned in water medium extend to higher values than for the leather tanned in NaCl solution. We believe that there is enough titanium tanning agent to ensure sufficient titanium complex arrival at the middle layer of the skin. With increasing dosage of titanium tanning agent, both the Ti content and T_s of leather increase. When the dosage reaches 10%, Ti content and T_s of the leather tanned in water achieve their maximum values, about 18% and 102°C, respectively, as shown in Figures 4 and 5. With further increases in dosage, T_s, Ti content and Ti-distribution uniformity only slightly decrease. The optimum dosage is 7.5% for tanning in 5% NaCl solution. Here, T_s, Ti content and Ti-distribution uniformity also trend to lower values with further increases in dosage (beyond 7.5%).

These decreasing trends of Ti content, Ti distribution uniformity and T_s with increasing Ti dosage (especially beyond 7.5%) may be related to the Ti concentration in tanning bath because the initial titanium concentration in tanning bath also increases with the dosage increasing. Probably, the reactivity of titanium tanning agent with collagen increases with the increasing Ti concentration in solution. A strong and quick reaction of Ti^{4+} with collagen makes titanium combination more likely on the surface of the skin in a high concentration titanium solution. This impedes the further penetration of titanium complexes into skin; hence, the titanium distribution uniformity in leather reduces. Consequently, the Ti content and T_s also decrease. This concentration effect on titanium tanning is also shown in Table IV. Titanium tanning trials were performed with the same titanium agent dosage (10%) but different Ti concentrations (different liquor ratios). Results show that Ti-absorbed rate, Ti content, Ti-distribution and T_s of the leather have a little bit decrease with increasing initial titanium concentration of tanning bath at the same dosage. The concentration effect on titanium tanning is reverse to chrome tanning.

Influence of titanium solution's basicity on tanning effects

The effects of basicity on titanium tanning are shown in Figures 6, 7 and 8. With increasing basicity of titanium solution, including Lact-Ti and Cit-Ti solutions, the Ti content, Ti-distribution uniformity and T_s decrease, especially when the basicity is larger than 65%. In fact, stability of the titanium solution masked with lactate or citrate will be very poor, easily forming colloids and eventually precipitating at the basicity higher than 65%. Basicity is a very important property for a mineral tanning agent, which impacts on molecular size

TABLE IX
Performance Comparison of Titanium-tanned and Chrome-tanned Leathers

	Ti-tanned leather	Cr-tanned leather
Tanning agent dosage (%)*	7.5 (amount to TiO_2)	2.8 (amount to Cr_2O_3)
Tanning end pH	3.50	4.00
Leather color	white	blue
Tanning agent exhausted rate (%)	99.27	83.10
Ts of leather (°C)	102	119
Leather Thickness increase rate (%)	98.97	57.69
Tensile strength (N/mm^2)	30.72	23.52
Tear strength (N/mm)	79.72	60.89
Elongation at 10N/ mm^2 load (%)	31.76	35.30
Organoleptic properties:		
Dye property	5	4
Softness	3.5	5
Fullness	5	3.5
Grain smoothness	5.0	4.5
Stiffness	5.0	3.5

*Percentages of tanning agent dosage based on weight of bated pelts with 65% moisture content.

and the reactivity of the tanning agent. It is well known that the higher the basicity, the larger and more difficult for the tanning agent molecules to penetrate into skins. So, optimum basicity of the titanium solution is 30%, because a lower basicity will impart difficulty for the basifying process.

It is important to notice that the Ts of leather has extended above 100°C for tanning with Lact-Ti solution (30% basicity, 7.5%TiO_2 offer) in water medium. This is 15°C higher than that of the leather tanned with traditional citrate-making titanium tanning agent. This is also the highest T_s for titanium tanned leather among the titanium tanning methods that have been reported to date.

Influence of pretreatment and post-treatment on titanium tanning

Pretreating the skin before tanning or post-treating leather after tanning with carboxylates will raise the leather's T_s for both aluminum and chrome tanning. For example, a skin is pretreated with phthalate before tanning, then tanned with aluminum salt, the T_s of the leather will be 10°C higher compared to no pretreatment.[13] It has also been reported that pretreating the skin with phthalate improved titanium tanning performances.[5] But, Table V shows that pretreating depickled skins before tanning with phthalate, benzenetetracarboxylate, salicylate, quinol or pyrogallol, respectively, does not remarkably influence titanium content and T_s. It is well known that adding multicarboxylates during basification in chrome or aluminum tanning will increase tanning agent combination with collagen. But adding phthalate, amulti-carboxylate (Implenal DC, from BASF) or a small molecule acrylic resin (Relugan RF, from BASF) during basification in titanium tanning does not increase titanium absorption and T_s, and the Ti content slightly decreases, as shown in Table VI. Moreover, Ti absorption, Ti content and T_s of the leather dramatically decrease when adding oxalate and gluconate in the end period of titanium tanning, perhaps because they compete with collagen for coordination with titanium ions.

We also see that the Ts of titanium-tanned leather has not substantially changed after treatment with phthalate, salicylate, quinol and pyrogallol, but decreases 6°C after treatment with benzenetetracarboxylate (data not shown). The Ts of chrome-tanned leather post-treated with benzenetetracarboxylate rose 15°C.[17] Pretreating the skin with glyoxylic acid increases the amount of carboxyl groups in collagen molecules, thus, absorption and complexation of chrome can be increased.[18] But, this pretreatment is not effective for titanium tanning. Thus, we surmise that the carboxyl in collagen may not be the main coordination sites of titanium tanning agent complexes.

It has been reported that a mixture of urotropine and sodium sulfite was the best basifying agent for titanium tanning, using ammonium titanyl sulfate as the tanning agent, as shown by the increase in the T_s of leather.[1] But it has not remarkable and special effects in our titanium tanning experiments, as shown in Table VII. Sodium bicarbonate and MgO are suitable basifying agents for titanium tanning. Stronger basic materials, such as sodium carbonate and amines, limit penetration and coordination of titanium salts.

Table VIII shows that pre-fatliquoring improves Ti-distribution uniformity, with cationic fatliquors having better results in terms of Ti complexation and penetration than anionic fatliquors. The choice of fatliquors is very important; they should be acid-resistant and electrolyte-resistant.

Performance of Titanium-tanned leather

A pilot plant trial of titanium tanning showed that pickle-less titanium tanning process was feasible, because no acid-swelling occurred and Lact-Ti easily penetrated into the middle layer of skin (within 60min). Almost all of Lact-Ti tanning agent (7.5% TiO_2 offer) was absorbed and complexed by collagen. And, the titanium exhaustion level reached 99.27%, while the chrome exhaustion level was only 83.10% (2.8% Cr_2O_3 offer), as shown in Table IX. So, this titanium tanning method is a very clean and eco-friendly process, by which there is no NaCl discharge (pickle-less) or ammonium evolution (compared with ammonium titanyl sulfate) and there is a high Ti exhaustion. Moreover, T_s of the leather reaches 102°C.

Important properties of titanium-tanned and chrome-tanned leathers are given in Table IX. We see that Ti-tanned leather is white while Cr-tanned leather is blue. The thickness of titanium-tanned leather increases nearly 100% compared with untanned skin while chrome tanned leather only has a 58% thickness increase. Titanium-tanned leather has higher strength, including tensile and tear strengths, but lower elongation than chrome-tanned leather.

Evaluation of organoleptic properties of titanium-tanned leather and chrome-tanned leather indicates that titanium tanned leather has smoother grain and higher fullness, especially in belly area, than chrome-tanned leather. But chrome tanned leather has better softness and a better spongy feel. Titanium tanned leather has greater affinity to anionic dyestuffs and has a darker, more vivid color, than chrome-tanned leather when dyed with the same recipe. Titanium-tanned leather also has a finer nap for suede leather.

Generally speaking, titanium-tanned leather has good fullness and is well filled, because the titanium tanning agent dosage is lager than that of chrome and titanium forms larger molecule complexes in aqueous solution. Although the softness, especially spongy feel, of titanium-tanned leather is not as good as that of chrome tanned leather, it is better than that of aluminum and zirconium tanned leathers. Our next research report shows that the softness and sponginess of titanium-tanned leather can be largely improved by chrome retanning (0.5%-1% Cr_2O_3). Suitable retanning procedures give titanium tanned leather greater performance attributes and make titanium-tanned leather satisfy requirements for leathers suitable for different types of end-use applications.

Conclusions

Key factors affecting the accomplishment of titanium tanning and the performance attributes of the resulting leathers have been studied. A high concentration sodium chloride tanning bath has a largely negative influence on titanium tanning; hence, the traditional pickling process is unsuitable for titanium tanning. Either pickle-less or salt-free pickling is the best choice for titanium tanning. The optimum titanium tanning agent dosage is 7.5%-10% TiO_2 offer (based on the weight of the skin with 65% moisture content) and the titanium concentration of tanning bath is 20-30g/L TiO_2. The best basicity of titanium solution is 30% and the tanning ending pH should be controlled to around 3.5. Sodium bicarbonate and MgO are good basifying agents for titanium tanning. Also pretreating the skin with cationic or electrolyte-resistant fatliquors is beneficial for titanium tanning agent penetration and uniform distribution in the leather. Bated goat pelts were tanned by lactate-titanium solution in a water medium as per the above parameters. The resulting leather had a 102°C shrinkage temperature. Overall, the tanning process is eco-friendly. The white titanium-tanned leather has better strength, fullness and firmness than chrome tanned leather. However, the softness and spongy feel of titanium tanned leather are inferior to chrome tanned leather, but superior to aluminum and zirconium leather. These can likely be improved by suitable retanning and fatliquoring.

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Development of Formaldehyde-free Leathers in Perspective of Retanning: Part 1. Benchmarking for the Evolution of a Single Syntan System

by
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Abstract

The awareness of health risks due to the use of leather products is escalating day by day. The demand for eco-labeled leather and leather products is increasing in the developed countries. Eco-labeling concepts force the tanners to look into various options for developing eco-benign products. Formaldehyde is classified as a probable human carcinogen. In this study, an attempt has been made to produce leather without formaldehyde by employing formaldehyde-free syntans. A relative measure of performance of formaldehyde-free and formaldehyde based syntans has been done to test their ability to produce leathers with desired properties by employing these syntans individually. Three formaldehyde-free syntans (resin, acrylic and protein) and two formaldehyde based syntans have been chosen for optimization trials. Trials have been carried out to find out the optimal amount of individual syntans required for providing sufficient properties to the leather. Based on organoleptic and strength properties as well as other property evaluation, it has been found that 12 and 8% formaldehyde based syntans A and B and 8, 10 and 12% formaldehyde-free resin, acrylic and protein syntans are capable of providing sufficient properties to the leather. There seems to be a considerable relation between the nature of the syntans and properties imparted to the leather. Aromatic syntans tend to decrease the strength and softness properties of leathers with increasing offer. Relation between the fullness of leathers and offer of syntans has been substantiated through scanning electron microscopy. The leathers treated with formaldehyde-free syntans do not contain free formaldehyde when analyzed using standard procedure and hence do not possess any health risks.

Resumen

El reconocimiento de riesgos de salud debido al uso de productos de cuero está extendiéndose día a día. La demanda de cueros y productos de cuero eco-etiquetados está aumentando en los países desarrollados. El concepto de eco-etiquetado fuerza a los curtidores a mirar entre varias opciones para desarrollar productos eco-benignos. El formaldehído se clasifica como probable agente carcinógeno humano. En este estudio, se ha intentado producir un cuero sin formaldehído empleando sintanes libres de formaldehído. Una medida relativa del funcionamiento de sintanes libres de formaldehído y sintanes con base en formaldehído ha sido realizada para probar su capacidad de producir los cueros con las características deseadas empleando estos sintanes individualmente. Tres sintanes libres de formaldehído (resina, acrílico y proteína) y dos sintanes en base formaldehído se han elegido para los ensayos de optimización. Los ensayos se han realizado para encontrar la cantidad óptima de sintanes individuales requeridos para proporcionar suficientes características al cuero. De acuerdo con propiedades organolépticas y de resistencias así como otras evaluaciones de las características del cuero, se ha encontrado que 12 y 8% sintanes con base formaldehído A y B y 8, 10 y 12% de sintanes libres de formaldehído resínicos, acrílicos y proteínicos son capaces de proporcionar suficientes propiedades al cuero. Parece haber una relación considerable entre la naturaleza de los sintanes y las propiedades impartidas al cuero. Los sintanes aromáticos tienden a disminuir las características de resistencia y suavidad de los cueros con el aumento de la oferta. La relación entre la plenitud de cueros y la oferta de sintanes se ha verificado con microscopía de barrido electrónico. Los cueros tratados con sintanes libres de formaldehído no contienen formaldehído libre analizado por medio de procedimientos estándares y por lo tanto no posee ningún riesgo para la salud.

Introduction

Formaldehyde is a volatile colorless gas that is present in small amounts in natural sources like apples, tomatoes and blood.[1] It

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is a very versatile chemical, which is used in many industrial applications in many branches of industry. Formaldehyde and its products are employed in tanning, retanning and finishing. Blends of formaldehyde with metal tanning agents such as aluminum or chromium are also employed for tanning and retanning application. Formaldehyde in combination with oil is used to produce chamois leather. Formaldehyde is used as topcoat in protein finishing. Formaldehyde is a strong polymerizing agent and is used to polymerize phenolic compounds in the production of Novolac (epoxy) types of resins. The properties imparted on leather by these types of syntans are fine and firm grain pattern, heat resistance, fine break, level dyeing and softness.

The use of formaldehyde in finishing is decreasing due to the ban in many countries.[2] It plays an integral role in the production of leather, but the demands for more stringent limits are increasing and this poses a challenge to the leather industry and its suppliers.[3] Presently, formaldehyde has not yet been completely eliminated from the manufacture of synthetic tanning agent and auxiliaries for technical reason and for reasons of cost. It is an extremely efficient crosslinking agent and its performance cannot be matched by any other aldehyde.

Formaldehyde can exist in free form in syntans, which has been detected; the amount depends upon the manufacturing process employed.[1] Formaldehyde has been classified as a probable

Process Details for Experimental Trials

Process/Chemicals	%	Duration (min)	Remarks
Retanning, dyeing and fatliquoring			
Water	75		
Acrylic syntan	3	30	
Natural oil based fatliquor	1	15	
Syntan X	**Y**	45	
Acid brown dye	3	30	Check for the penetration of dye
Synthetic oil based fatliquor	4		
Natural oil based fatliquor	4	2x15+30	
Fixing			
Formic acid	3	3x10+30	The exhaustion of the bath was checked. Bath was drained. The leathers were sammed, set, hooked for drying then conditioned, staked and buffed.

X was two commercial phenol formaldehyde based syntans A and B (E1 and E2) and three commercial formaldehyde-free syntans based on resin, acrylic and protein (E3, E4 and E5)
Y was varied as 8, 10 and 12%

Process Details for Control (C) Process

Process/Chemicals	%	Duration (min)	Remarks
Retanning, dyeing and fatliquoring			
Water	75		
Acrylic syntan	3	30	
Natural oil based fatliquor	1	15	
Urea-melamine syntan	4	30	
Wattle powder	4		
Phenol formaldehyde syntan	4	60	
Acid brown dye	3	30	Check for the penetration of dye
Synthetic oil based fatliquor	4		
Natural oil based fatliquor	4	2x15+30	
Fixing			
Formic acid	3	3x10+30	The exhaustion of the bath was checked. Bath was drained. The leathers were sammyed, set, hooked for drying then conditioned, staked and buffed.

human carcinogen by the U.S. Environmental Protection Agency.[4] Formaldehyde as classified has certainly stimulated efforts to establish limits on formaldehyde in leather or to make formaldehyde-free leather. According to European eco-label, formaldehyde content in the leathers should not exceed 150 ppm for adult wear and 75 ppm for children wear.[1] Various strategies such as the use of formaldehyde scavengers, use of resin tanning agents and formaldehyde-free fixing agents have been adopted to eliminate formaldehyde or to reduce formaldehyde content in leather.[3]

Although the use of formaldehyde in finishing and tanning can be avoided, the use of formaldehyde based syntans pose serious challenges in the development of formaldehyde-free leathers. Syntans based on protein or acrylics do not contain formaldehyde. Very few formaldehyde-free resin syntans are commercially available. An attempt has been made to produce leather without the presence of formaldehyde by employing formaldehyde-free syntans. Before developing a post tanning process using formaldehyde-free syntans, it is necessary to compare the formaldehyde-free syntans with the formaldehyde based syntans for their ability to produce desired properties in the leather. Conventionally, combinations of synthetic tanning agents are employed to achieve the desired properties. In this study, an attempt has been made to evolve a single syntan system, which would provide desired properties to the leather. Two formaldehyde based syntans and three formaldehyde-free syntans have been chosen to optimize their offer for evolving a single syntan system. The strength characteristics and bulk properties have been evaluated. Leathers have been analyzed for free formaldehyde. Spent post tanning solution liquors have been analyzed for chemical oxygen demand (COD) and total solids (TS). Scanning electron microscopy and color difference studies have also been carried out.

Experimental Methods

Materials

Compact and fine wet blue cow sides (1.2±0.1 mm thickness) were selected as raw material for this study. The wet blue leathers were neutralized to a pH 5.2±0.2 and washed using a conventional process. All the chemicals used for leather processing were of commercial grade. The chemicals used for the analysis of spent liquors were of analytical grade.

Optimization of Formaldehyde-free and Formaldehyde Based Syntans

Thirty two wet blue cow sides were taken. Two cow sides were used for each trial. Two phenol formaldehyde syntans and three different kinds of formaldehyde-free syntans were chosen and their percentage offers were varied as 8, 10 and 12%. In all these systems, 3% acrylic syntan along with 9% fatliquor and 3% dye was constant. For comparison, control leathers were made using standard combination retanning system. The process details are given below.

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.[5]

TABLE I
Comparison of Bulk Properties of Experimental and Control Leathers

Sample/syntan offered	Fullness	Softness	Grain tightness	Roundness	Dye affinity	General appearance
C	9	9	9	8	7	9
E1 - 8%	6	8	7	7	5	7
E1 - 10%	7	8	7	8	6	7
E1 - 12%	8	7	8	8	7	8
E2 - 8%	7	8	7	8	6	8
E2 - 10%	8	7	7	8	6	7
E2 - 12%	9	6	8	8	7	8
E3 - 8%	7	7	7	8	7	7
E3 - 10%	7	7	6	7	6	7
E3 - 12%	7	7	7	8	7	7
E4 - 8%	7	8	7	7	8	8
E4 - 10%	8	8	7	8	8	8
E4 - 12%	7	9	8	8	8	8
E5 - 8%	8	7	7	8	8	7
E5 - 10%	8	8	7	8	8	7
E5 - 12%	8	8	8	8	8	8

C- Control; E1 - Phenol formaldehyde syntan A; E2 - Phenol formaldehyde syntan B; E3 - Formaldehyde-free resin syntan; E4 - Acrylic syntan; E5 - Protein syntan.

TABLE II
Comparison of Strength Properties of Control and Experimental Leathers

Sample/ syntan offered	Tensile strength (kg/cm^2) Average value[a]	% Elongation at break Average valuea	Tear strength (kg/cm) Average value[a]	Grain crack strength (Average value)[b] Load (kg)	Distension (mm)
C	216±6	59±1	68±2	>50±1	12.1±0.4
E1 - 8%	212±4	67±2	69±4	38±1	10.8±0.2
E1 - 10%	208±6	60±2	53±2	40±2	11.2±0.6
E1 - 12%	196±5	45±1	49±4	38±2	11.2±0.4
E2 - 8%	242±6	71±4	106±8	42±1	10.5±0.2
E2 - 10%	234±4	65±2	78±4	>50±1	11.0±0.4
E2 - 12%	192±4	60±4	62±2	42±4	12.2±0.4
E3 - 8%	218±8	63±2	77±4	40±2	12.0±0.2
E3 - 10%	224±6	65±4	82±4	>50±1	11.7±0.6
E3 - 12%	203±2	60±2	76±2	38±2	10.1±0.4
E4 - 8%	218±4	67±6	76±4	34±2	10.3±0.2
E4 - 10%	202±6	59±2	84±4	>50±1	13.4±0.2
E4 - 12%	198±4	69±8	72±2	>50±1	12.5±0.4
E5 - 8%	224±6	60±4	59±4	38±4	12.1±0.2
E5 - 10%	214±4	53±2	68±2	40±2	13.3±0.6
E5 - 12%	206±6	63±4	72±4	34±2	10.2±0.2

C- Control; E1 - Phenol formaldehyde syntan A; E2 - Phenol formaldehyde syntan B; E3 - Formaldehyde-free resin syntan; E4 -Acrylic syntan; E5 - Protein syntan

[a]Values are average of mean of along and across backbone values for two leathers along with standard error.

[b]Values are average of two leathers along with standard error.

TABLE III
Color Measurement Values for Control and Experimental Leathers

Sample	L	a	b	C	H	ΔL	Δa	Δb	ΔC	ΔH	ΔE
C	38.25	15.02	15.04	21.26	45.02	-	-	-	-	-	-
E1 - 8%	37.50	16.04	15.36	22.19	43.78	-1	1.02	0.32	0.93	-0.468	1.289
E1 - 10%	41.28	14.32	15.28	20.93	45.02	2.78	-0.7	0.24	-0.325	0.684	3.118
E1 - 12%	44.96	15.97	18.02	24.08	48.43	6.46	0.95	2.98	2.82	1.349	7.40
E2 - 8%	42.33	15.45	16.46	22.57	46.82	3.83	0.43	1.42	1.31	0.684	4.336
E2 - 10%	39.55	16.12	17.36	23.80	47.11	1.05	1.1	2.32	2.54	0.820	2.875
E2 - 12%	42.12	15.97	17.24	23.51	47.19	3.62	0.95	2.2	2.25	0.846	4.557
E3 - 8%	32.67	14.21	12.79	19.12	41.98	-5.83	-0.81	-2.25	-2.14	-1.069	6.094
E3 - 10%	32.59	13.83	12.61	18.72	42.36	-5.91	-1.19	-2.43	-2.54	-0.926	6.274
E3 - 12%	32.58	14.95	12.69	19.61	40.32	-5.92	-0.07	-2.35	-1.65	-1.675	6.137
E4 - 8%	29.46	13.42	10.12	16.81	37.02	-9.04	-1.6	-4.92	-4.45	-2.637	10.201
E4 - 10%	30.89	13.77	11.42	17.89	39.68	-7.61	-1.25	-3.62	-3.37	-1.815	8.295
E4 - 12%	27.55	11.56	9.61	15.03	39.73	-10.95	-3.46	-5.43	-6.23	-1.651	12.486
E5 - 8%	34.15	13.54	12.39	18.36	42.46	-4.35	-1.48	-2.65	-2.9	-0.82	5.101
E5 - 10%	36.97	15.28	14.39	20.99	43.29	-1.53	0.26	-0.65	-0.27	-0.637	1.45
E5 - 12%	33.83	15.50	13.62	20.64	41.30	-4.67	0.48	-1.42	-0.62	-1.362	4.662

C- Control; E1 - Phenol formaldehyde syntan A; E2 - Phenol formaldehyde syntan B; E3 - Formaldehyde-free resin syntan; E4 - Acrylic syntan; E5 - Protein syntan

TABLE IV
Softness Values of Control and Experimental Leathers

Sample/ syntan offered	Line equation	Slope angle (negative)
C	Y =3.35364-0.068054 X	4.356
E1 - 8%	Y =3.306563-0.074631 X	4.742
E1 - 10%	Y =3.225725-0.04356 X	2.771
E1 - 12%	Y =3.188208-0.057036 X	3.627
E2 - 8%	Y =3.306558-0.084968 X	5.395
E2 - 10%	Y =3.261652-0.060256 X	3.831
E2 - 12%	Y =3.283948-0.043226 X	2.750
E3 - 8%	Y =3.339188-0.062452 X	3.970
E3 - 10%	Y =3.221791-0.058045 X	3.691
E3 - 12%	Y =3.297049-0.060915 X	3.873
E4 - 8%	Y =3.278522-0.059181 X	3.763
E4 - 10%	Y =3.367118-0.065507 X	4.164
E4 - 12%	Y =3.286221-0.06246 X	3.971
E5 - 8%	Y =3.21754-0.049109 X	3.123
E5 - 10%	Y =3.293355-0.055419 X	3.524
E5- 12%	Y =3.24211-0.043863 X	2.790

C- Control; E1 - Phenol formaldehyde syntan A;
E2 - Phenol formaldehyde syntan B;
E3 - Formaldehyde-free resin syntan;
E4 - Acrylic syntan;
E5 - Protein syntan

Specimens were conditioned at 80±4ºF and 65±2% R.H. over a period of 48 hrs. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures.[6-8] Crust leathers from control and experiments were assessed for fullness, softness, grain tightness, roundness, dye affinity and general appearance by hand and visual examination. The leathers were rated on a scale of 0-10 points for each functional property by an experienced tanner, where higher points indicate better property.

Objective Assessment of Softness through Compressibility Measurements

Softness of leathers can be numerically measured based on their compressibility.[9] Circular leather pieces (2cm^2 area) from experimental and control crust leathers were obtained as per IUP method[5] and conditioned at 80±4ºF and 65±2% R.H. over a period of 48 hrs. The samples were spread uniformly over the solid base of the C & R (compressibility and resilience) tester. The initial load acting on the grain surface was 100 g. The thickness at this load was measured 60 sec after the load was applied. Subsequent loads were added and the change in thickness was recorded one minute after the addition of each load. Logarithm of leather thickness (Y axis) was plotted against logarithm of load (X axis).

Analysis of Spent Post Tan Liquor

Spent post tan liquors from both control and selected experimental trials were collected and analyzed for COD and TS (dried at 103-105ºC for 1 hr) as per the standard procedures.[10] From this, emission loads were calculated by multiplying concentration (mg/L) with volume of effluent (L) per metric ton of shaved wet blue cow sides processed.

Analysis of Formaldehyde in Leather

Leather samples from selected experimental trials and control were cut from an official butt portion[5] and taken for formaldehyde estimation. The formaldehyde in samples was extracted using 50 mL of detergent solution in a bottle shaker for 60 min at 40ºC. The formaldehyde in the extract solution was analyzed using PerkinElmer UV-visible spectrophotometer.[11] Leather samples were initially analyzed for moisture content[12] and the formaldehyde content was expressed on dry weight basis of leather.

Reflectance Measurements

The principle involves measuring the amount of light reflected from the surface of opaque specimen at wavelengths throughout the visible spectrum as a fraction of that reflected by a white standard identically illuminated. It is known as the reflectance factor. The white standard used should be an absolute one i.e., it should be a perfect reflecting diffuser whose reflectance at every wavelength is 100%. The control and experimental leathers were subjected to reflectance measurements using a Mitton Roy Color Mate HDS instrument.

Color Measurements

Color measurement parameters such as L, a, b, h and C were recorded using a Milton Roy Color Mate HDS instrument for control and experimental crust leathers. The total color difference (ΔE) and hue difference (ΔH) were calculated using the following equations:

(1) $$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

(2) $$\Delta H = \sqrt{\Delta E^2 - \Delta L^2 - \Delta C^2}$$

where ΔL, lightness difference; Δa and Δb, difference in 'a' and 'b' values, where 'a' represents red and green axis and 'b' represents yellow and blue axis; ΔH, hue difference; ΔC, chromaticity difference. ΔL, Δa, Δb and ΔC were calculated by subtracting the corresponding values for experimental leathers (E1, E2, E3, E4 and E5) from control leathers.

Scanning Electron Microscopic Analysis

Samples from selected experimental and control crust leathers were cut from the official sampling position.[5] Samples were cut into specimens with uniform thickness. All specimens were then coated with gold using Edwards E306 sputter coater. A Jeol JSM-840A scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at high vacuum with an accelerating voltage of 15 KV in different lower and higher magnification levels.

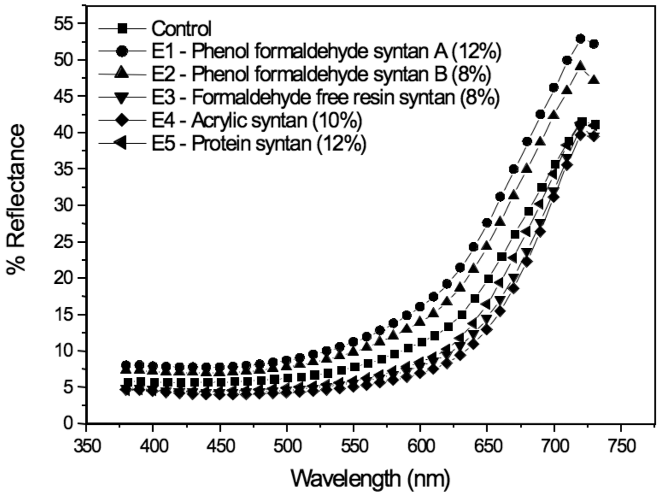

Figure 1. Plot of percentage reflectance versus wavelength for control and experimental leathers

Results and Discussion

Evolution of a Single Syntan System

Global leather industry is being transformed towards the manufacture of eco-benign products and simple processing techniques. The manufacture of formaldehyde-free leathers is gaining importance in the global market. Tanners are currently looking for compact or simple leather processing system. In this study, optimization trials have been made to benchmark the offer of formaldehyde based retanning agents as well as formaldehyde-free syntans. The offer of formaldehyde based and formaldehyde-free syntans was varied from 8 to 12% to find the actual amount of syntan required for optimal properties of upper leathers. Two commercial products were selected based on phenol formaldehyde syntans and the experiments are termed as E1 and E2. Three commercial syntans free from formaldehyde were selected and the experiments are termed as E3, E4 and E5. Hence, this study provides an optimal amount of syntan required for manufacturing formaldehyde-free leather and also an amount of single syntan (formaldehyde or formaldehyde-free) that can provide leathers with optimal properties.

Organoleptic Properties

Control and experimental crust leathers were evaluated for various organoleptic properties such as fullness, softness, grain tightness, roundness, dye affinity and general appearance by hand and visual evaluation. The rating for all the experimental and control leathers for each functional property is given in Table I. Higher numbers indicate better properties. The increase in the offer of phenol formaldehyde syntans (E1 and E2) results in the increase in fullness, grain tightness and roundness and a decrease in softness. On the other hand, an increase in the offer of protein and acrylic based formaldehyde-free syntans results in an increase in softness. It is seen that the dye affinity for the leathers retanned with phenol formaldehyde based syntans is slightly lower compared to control leather, while it is slightly improved for the leathers retanned with formaldehyde-free syntans, especially acrylic and protein based syntans. It is apparent that an offer of 12% phenol formaldehyde syntan A (E1), 8% phenol formaldehyde syntan B (E2), 8% resin based syntan (E3), 10% acrylic syntan (E4) and 12% protein syntan (E5) provides leathers with comparable properties to that of control leather (C).

Strength Characteristics

Tensile and tear strength tests were carried out for all the crust leathers both along and across the backbone line. The average of the mean of the values corresponding to along and across the

TABLE VI
Free Formaldehyde in Control and Experimental Leathers

Sample	Free formaldehyde* (ppm)
C	124±4
E1 - 12%	183±2
E2 - 8%	134±6
E3 - 8%	N.D
E4 - 10%	N.D
E5 - 12%	N.D

C- Control; E1 - Phenol formaldehyde syntan A; E2 - Phenol formaldehyde syntan B; E3 - Formaldehyde-free resin syntan; E4 - Acrylic syntan; E5 - Protein syntan
* Dry weight basis
N.D - Not Detectable

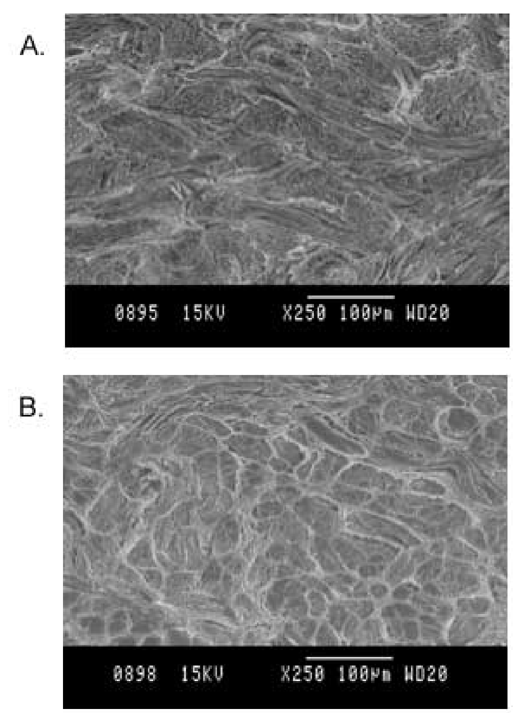

Figure 2. Scanning electron micrographs of cross sectional view of crust leather samples at magnification of x250
a) Phenol formaldehyde syntan A (8%)
b) Phenol formaldehyde syntan A (10%)

TABLE V
Characteristics and Emission Loads of Spent Post Tan Liquor from Control and Experimental Processes

Process/ syntan offered	COD (ppm)	TS (ppm)	Volume of effluent (L/kg of shaved weight)	Emission load (g/kg of shaved weight)	
				COD	TS
C	10049±12	18652±24	1.500	15.07	27.97
E1 - 12%	14236±8	21636±22	1.270	18.07	27.47
E2 - 8%	7536±12	16268±20	1.280	9.64	20.82
E3 - 8%	18004±10	20522±18	1.250	22.50	25.65
E4 - 10%	8374±6	13690±32	1.320	11.05	18.07
E5 - 12%	16330±12	14520±24	1.250	20.41	18.15

C- Control; E1 - Phenol formaldehyde syntan A; E2 - Phenol formaldehyde syntan B; E3 - Formaldehyde-free resin syntan; E4 - Acrylic syntan; E5 - Protein syntan

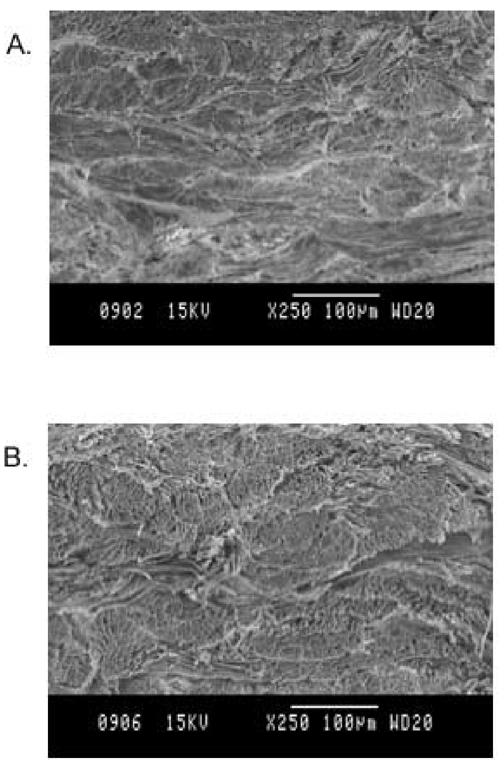

Figure 3. Scanning electron micrographs of cross sectional view of crust leather samples at magnification of x250
a) Phenol formaldehyde syntan B (10%)
b) Phenol formaldehyde syntan B (12%)

backbone was calculated for two leathers for each strength character and given in Table II along with standard error values. The grain crack strength for all the crust leathers was carried out. The mean values corresponding to each experiment were averaged and values are given in Table II along with standard error values. It is intriguing to note that the tensile and tear strength of leathers treated with phenol formaldehyde syntans (E1 and E2) decreases with increasing offer of syntan. This may be due to the filling nature of these syntans. The strength of leathers is inversely proportional to the filling ability of the syntan. It is possible that most of the aromatic syntans lead to reduction in strength of leather when offered excessively, which may be due to toughening of fiber bundles. This is evident from the results obtained in this study. It is important to note that formaldehyde-free acrylic and protein syntans do not reduce the tensile strength appreciably. The grain crack strength increases upon increase in the offer of acrylic syntan. This may be due to the grain tightening nature of the acrylic syntans.

Reflectance Measurements

Figure 1 shows the reflectance measurements vs visible wavelengths for the control and selected experimental crust leathers. The absorption maxima are around 425 nm for all the leathers. An absorption maximum is the wavelength at which the reflectance is minimum. It is seen that the phenol formaldehyde based syntans provide leathers with slightly higher reflectance values at reflectance minima compared to control leather. On the other hand, formaldehyde-free syntans provide leathers with slightly lower reflectance values at the reflectance minima compared to the control leather. Lower reflectance values at reflectance minima or absorbance maxima mean higher absorbance values. In other words, the intensity of color is high. Hence, it is seen that the formaldehyde-free syntans provide leathers with darker shade compared to control or phenol formaldehyde based syntan systems. Phenol formaldehyde based syntans provide leathers with lighter shade compared to control or formaldehyde-free syntan systems. This could be due to the bleaching nature of phenol formaldehyde based syntans.

Color Difference Studies

The L, a, b, C, H values of control and experimental leathers and the color difference values are given in Table III. As stated earlier in the experimental section, 'L' represents whiteness on a scale of 0-100. Higher value means lighter shade. 'a' represents red and green axis, where 'a'>0 means red and 'a'<0 means green and 'b' represents yellow and blue axis, where 'b'>0 means yellow, 'b'<0 means blue and 'C' represents the

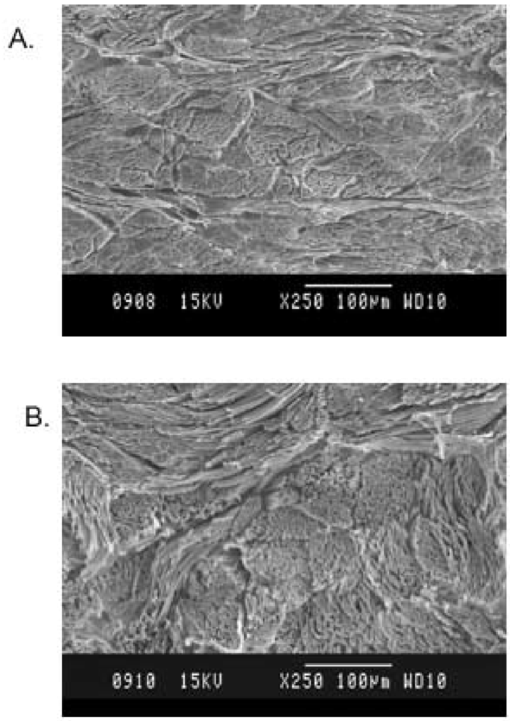

Figure 4. Scanning electron micrographs of cross sectional view of crust leather samples at magnification of x250
a) Resin syntan (10%)
b) Resin syntan (12%)

chromaticity of the color, which means the intensity of the color. Change in lightness is represented as 'ΔL', which provides the depth of the shade. The positive value of 'ΔL' represents lighter shade. It is seen that the leathers from E1 and E2 show positive 'ΔL' values while the leathers from E3, E4 and E5 show negative 'ΔL' values. This reveals that the leathers retannned using phenol formaldehyde syntans are lighter in shade and formaldehyde-free syntans provide leathers with darker shade. The lighter shade of experimental leathers (E1 and E2) could be due to the bleaching nature of the phenol formaldehyde condensed syntans. The darker shade of experimental leathers (E3, E4 and E5) could be due to the more reactive nature of the syntans. Formaldehyde-free syntans based on resin, acrylic and protein provide additional reactive sites, which increase the uptake of dye resulting in darker shade.

Softness Measurements

This study aims at benchmarking of individual syntans for their application as a single syntan system. It employs various kinds of syntans. Hence, it is essential to evaluate the effect of syntans on the softness. Quantitative assessment of softness for both control and experimental leathers has been made through compressibility measurements. The logarithm of thickness was plotted against logarithm of load for the control and experimental leathers, which exhibited a linear fit. The corresponding equation of the line was obtained. The negative slope angles were calculated and the values are given in Table IV. It could be seen that the softness value of leathers decreases with increasing offer of filling type of syntans such as phenol

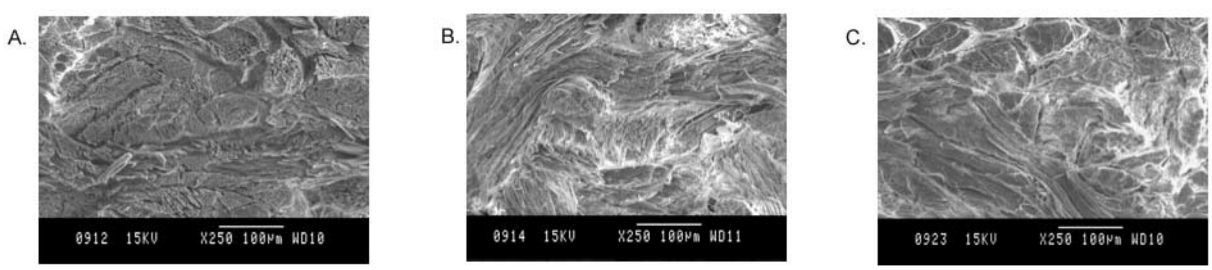

Figure 5. Scanning electron micrographs of cross sectional view of crust leather samples at magnification of x250
a) Acrylic syntan (8%)
b) Acrylic syntan (10%)
c) Acrylic syntan (12%)

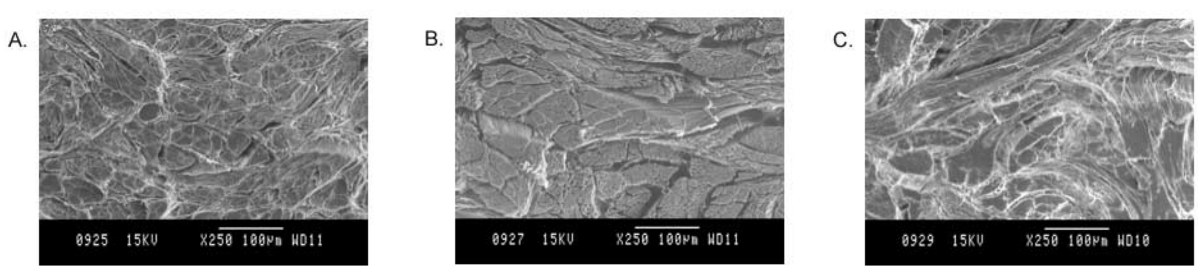

Figure 6. Scanning electron micrographs of cross sectional view of crust leather samples at magnification of x250
a) Protein syntan (8%)
b) Protein syntan (10%)
c) Protein syntan (12%)

formaldehyde syntan B (E2). Softness of leather mainly depends on the loading or toughening nature of the syntan. The phenol formaldehyde based syntans are known for filling and toughening of leather matrix. Softness can be reciprocally related to fullness. These results are in agreement with the postulation arrived with the strength properties. For all the other kinds of syntans, an increase in the offer of syntan does not alter the softness of leathers significantly.

Scanning Electron Microscopic Analysis

Fullness of leathers can be assessed through viewing the cross section of leather samples using scanning electron microscopy. Selected experimental samples were subjected to scanning electron microscopy analysis. The scanning electron micrographs of those leather samples showing the cross section at x250 are Figures 2 to 6. It is seen from Figures 2a and 2b that the increase in the offer of phenol formaldehyde syntan results in a slight increase in compactness of the leather matrix. This may be due to the higher filling nature of syntan A. There is no significant difference between the two samples treated with 10 and 12% offer of phenol formaldehyde syntan B as seen in Figures 3a and 3b. A similar trend to that of syntan B is observed for the samples treated with 10 and 12% offer of formaldehyde-free resin syntan as shown in Figures 4a and 4b. This may be due to the lower filling nature of those syntans. Increase in the offer of formaldehyde-free acrylic and protein syntans seems to lead to fiber cohesion owing to the coating nature of those syntans, as is evident in Figures 5a-c and 6a-c. These results are in agreement with the postulation arrived for softness and strength property analysis.

Spent Post Tanning Liquor Analysis

The spent post tan liquors have been collected from control and selected experiments based on best organoleptic properties in the leathers comparable to that of control leathers. COD and TS are the two parameters that have been chosen for analyzing the environmental impact. A direct correlation of the observed COD and TS values with the environment may not give proper consequences. Hence, the COD and TS values have been converted into emission loads. The COD and TS values and the calculated emission loads are given in Table V. It is observed that there is no significant reduction in COD load for the experimental processes when compared to control process. This is primarily due to the difference in the offer as well as nature of the single syntans. On the other hand, all the selected offer of single syntans results in slight reduction in TS load.

Formaldehyde in Leather

Free formaldehyde present in leathers from control and optimized trials are given in Table VI. It is seen that the use of phenol formaldehyde syntans results in significant amount of free formaldehyde in leathers from control and E1 and E2. In these leathers, the amount of formaldehyde is higher than the limits set for children wear under European eco-label. There is no detectable amount of formaldehyde in the other samples (E3, E4 and E5) since they were retanned using formaldehyde-free syntans.

Conclusions

In this work, an attempt has been made to produce formaldehyde-free upper leathers. Benchmarking of formaldehyde based and formaldehyde-free syntans has been carried out in order to find out the efficacy of these syntans to provide desired properties in the leather. This strategy would also yield a single syntan based retanning system, if appropriate. It is found that the increase in the offer of phenol formaldehyde syntans results in a small increase in fullness, grain tightness and roundness and a small decrease in softness and strength. Increase in the offer of acrylic syntan results in increase in grain crack strength of the leathers. This is possibly due to the grain tightening nature of acrylic syntan. Estimation of free formaldehyde in the leathers shows that leathers retanned with phenol formaldehyde syntans contain significant amount of free formaldehyde compared to the formaldehyde-free leathers.

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