

NOVEL ECO-FRIENDLY APPROACHES FOR THE PRODUCTION OF UPHOLSTERY LEATHER*

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ABSTRACT

In recent years, considerable research has been done to replace chrome tanning with alternative tanning systems. But there are very few methods that are environmentally friendly and cost effective that give leather with performance as good as chrome tanned leather. DasGupta and Debchoudhury reported systems based on oxazolidine and mimosa that gave satisfactory leather with high shrinkage temperature. Vitolo et al reported a tara-aluminum sulphate tanning system as an alternative to traditional chrome tanning. But these are not yet commercially accepted. In this report, a novel eco-friendly approach for the production of upholstery leather is given that avoids pickling. The leather is pretanned after bating at pH 7.5-8.5 with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane) to obtain shrinkage temperature around 75-80°C for hides and 80-85°C for skins. These pelts are simultaneously or after treated with 2-3% replacement syntan. These pretanned hides and skins may be split and/or shaved at this stage, without any difficulty, to the required thickness. This provides opportunities for a tanner to either chrome tan with 4-5% chrome powder 25/33 (25% Cr₂O₃ content / 33% basicity) following the LASRA ThruBlu system or organically tan the shaved hides as reported earlier by DasGupta and Debchoudhury.

The splitting and shaving at this stage has the added advantage of lowering the amount of chrome use, very low chrome in effluent, flatter grain, higher area yield of the final leather, and biodegradable chrome-free shavings. This would considerably minimize the disposal problem for a tannery. The details of these methods are given with performance data to show that the leather satisfies all requirements of modern upholstery leather. The

mechanism of the tanning is explained with atomic force microscopy and mass spectroscopy data and the improvement of effluent discharged from a tannery is discussed.

RESUMEN

En los últimos años, considerable investigación se ha efectuado para reemplazar con sistemas alternos la curtición al cromo. Hay muy pocos métodos medioambientales amistosos y a la vez económicos que resulten en desempeños tan buenos como el del cuero al cromo. Das Gupta y Debchoudhury describieron sistemas basados en oxazolidina y mimosa que produjeron cuero satisfactorio con alta temperatura de contracción. Vitolo et al reportaron un sistema de curtición basado en tara-sulfato de aluminio como alternativa al curtido tradicional al cromo. Pero estos no son todavía comercialmente aceptables. En este informe, un novedoso y eco amistoso enrutamiento hacia la producción de cuero de tapicería, evitando piquelado, se presenta. El cuero (sic) se precurte luego de un rendido a pH 7,5-8,5 con 2% de oxazolidina E (1-aza-3,7-dioxabicyclo-5-etilo (3,3,0,) octano) para obtener temperaturas de contracción alrededor de 75-80°C en pieles mayores y 80-85°C en pieles pequeñas. Estas pieles se tratan simultáneamente o luego con 2-3% con un curtiente sintético de sustitución. Estas pieles así precurtidas pueden ser divididas y/o rebajadas sin dificultad en este estado, al grueso requerido. Esto provee al curtidor de opciones de curtir con 4-5% de sal de cromo 25/33 (25% contenido de Cr₂O₃/ 33% de basicidad) siguiendo el sistema LASRA ThruBlu o orgánicamente curtir las pieles rebajadas tal como anteriormente reportado por DasGupta y Debchoudhury.

El dividido y rebajado en esta etapa tiene la ventaja adicional de reducir la cantidad de cromo utilizado,

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bajos niveles de cromo en los efluentes, flor más plana, aumentado rendimiento superficial en cuero producido, y rebajaduras exentas de cromo biodegradables. Esto considerablemente minimizaría el problema de disposición de residuos en la curtiembre. Los detalles concernientes a estos métodos se presentan con datos de rendimientos para demostrar que el cuero satisface todos los requerimientos de tapicería moderna. El mecanismo de la curtiembre se explica con datos de microscopía por fuerza atómica y espectroscopía de masa y las mejoras en las descargas de efluentes de la curtiembre se discuten.

INTRODUCTION

A new school of chrome tanning¹ that minimized or almost eliminated chrome discharge to the environment was established at LASRA in 1992. Thereafter, a number of papers²⁻⁶ on LASRA ThruBlu process were published, culminating with a paper⁷ in 1997 at the XXIV International Union of Leather Technologists and Chemists Societies Congress, London. These contributions established beyond doubt that chrome tanning may be conducted successfully after delimiting without the conventional salt/acid pickling. But this process was then limited to skins and lime split hides as penetration of chrome with such a low chrome offer was incomplete on heavy hides.

But Larosa⁸ in 1996 and Hanna⁹ in 2003 published papers where they claimed to remove this limitation by employing a masked chrome complex to obtain complete penetration of chrome on full thickness hides.

Researchers at the Central Leather Research Institute, India (CLRI) published their papers in 2002/3 suggesting that they had solved the problem by adjusting the pH with addition of sodium formate and organic acids to pH 5.0-5.5 before addition of chrome powder.¹⁰ At LASRA, progress was made through wet white route and splitting and shaving after pretanning with oxazolidines was recommended. Two papers were published on modified ThruBlu processes, one each for lambskins and lime split hides.¹¹⁻¹² It was known that oxazolidine E may also be employed at higher pH without adversely affecting the grain quality.^{13,14} Combining these two concepts, DasGupta and Debchoudhury¹⁵ reported chrome free systems that gave satisfactory leather with high shrinkage temperature. Vitolo *et al*¹⁶ reported tara-aluminum sulphate tanning system as an alternative to traditional chrome tanning. Simon and Pizzi¹⁷ reported production of high shrinkage temperature leather using vegetable tannins and melamine-urea-formaldehyde tanning formulations. But these are yet to be commercially accepted.

In this paper, a novel approach for the production of upholstery leather is given that avoids acid/salt pickling. Hides and skins are pretanned after delimiting and bating at pH 7.5-8.5 with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-

5-ethyl (3,3,0) octane) to obtain shrinkage temperature around 75-80°C for hides and 80-85°C for skins. These pelts are simultaneously or after treated with 2-3% replacement syntan. These pretanned hides and skins may be split and/or shaved at this stage to the required thickness without any difficulty. This provides opportunities to a tanner either to chrome tan with about 5% chrome powder (25/33) following the LASRA ThruBlu system⁷ or novel chrome tanning process as given in this paper or organically tan as reported earlier by DasGupta and Debchoudhury.¹⁵ Each of these processes challenges the tanner to select and adjust his retanning and fatliquoring agents to obtain optimum performance of the leather.

METHODOLOGY

Materials

Delimited hides at pH 8.5-9.0 were collected from a commercial tannery. These were cut through the backbone to obtain matched sides for various experiments to develop and standardize the process for upholstery leather. The options studied were as stated in Scheme A.

Tanning processes

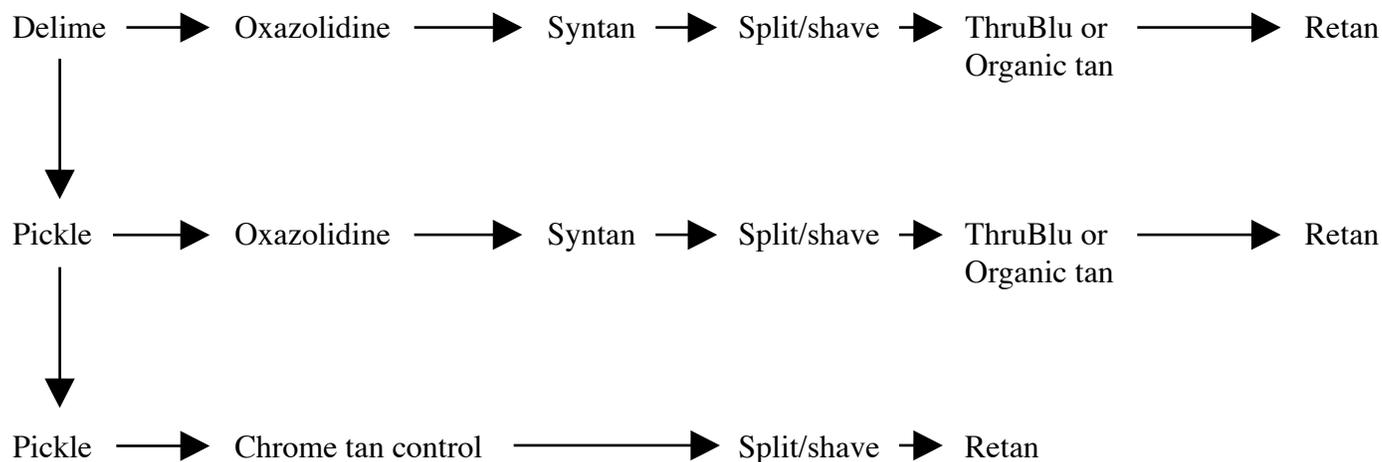
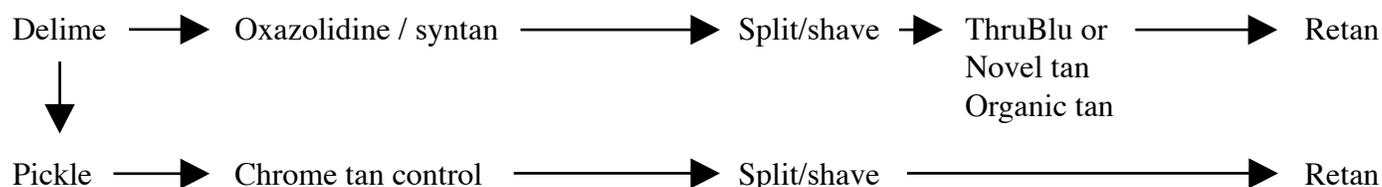
Delimited pelts were pretanned with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane) and 50% water at 40°C overnight. The shrinkage temperature of the treated pelts was 80-85°C. After adjusting the pH to 5-5.5 with 0.5% formic acid, these pelts were treated with 2-3% replacement syntan (Tanicor PW- Clariant). All these pretanned hides was split and shaved to the required thickness (1.0mm). These were either chrome tanned following the LASRA ThruBlu system or organically tanned following the process as described earlier.¹⁵ Matched sides were pickled and either chrome tanned overnight to act as control or treated with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane) at 25°C and pH gradually raised with sodium formate and sodium bicarbonate to pH 8.0 and run overnight at 40°C. The shrinkage temperature of the treated pelts was 80-85°C. The details of the processes employed are given in Appendix A.

Novel Tanning process

Delimited pelts were pretanned with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane) and 50% water at 40°C overnight with 6% Paralene WX-A (a replacement syntan from YCL, England). The shrinkage temperature of the treated pelts was 80-85°C. These pretanned hides were split and shaved to the required thickness (1.0mm). The shaved skin weight was 24.4% of the delimited weight. These were tanned following the process given in Appendix B.

Physical and chemical tests

All tests were conducted following the relevant methods prescribed by the *International Union of Leather Technologists and Chemists Societies* (IULTCS).

Scheme A**Scheme B****RESULTS AND DISCUSSION****Pickle vs Delime**

Visual assessment showed that the no pickle stock was softer and flatter than the pickled stock. Dry leather from both sets looked very good. Leather was also assessed as similar after finishing. Samples from both sets were taken for physical tests. Both these sets gave similar leather as may be seen from Table 1:

Similarly, the comparative performance of vegetable/oxazolidine E tanned hides with or without pickle is shown in Table 2.

These results showed that there were no significant differences between the properties of leather processed with or without pickling but there were some significant differences between chrome and vegetable tanned leather. Repeat matched pair trials had in collaboration with a local tannery gave the physical properties shown in Table 3.

Once again these results showed that even though no-chrome organically tanned leather had satisfactory properties to pass all physical requirements of upholstery leather, there were some significant differences in the properties between the chrome tanned and no-chrome leather. The reduction of strength might be partly due to the fact that the similar fatliquor mixture was used for chrome and no-chrome processes. This might be improved by changing to fatliquors that are more suitable for mainly vegetable tanned organic leather. Further studies in this direction are continuing and

will be reported in the future. The exhaust liquors from standard chrome tanning and the novel process were analyzed to indicate the improvement in discharge. The figures given in Table 4 are the averages of two repeat trials.

This clearly indicates the benefits of tanning using a combination of oxazolidine and mimosa. The significant improvement in TKN might be partly attributed to the dissolved protein from the pickling process.

Novel process vs Chrome and no-chrome leather

The pH profiles of the two processes are shown in Figures 1 and 2.

This clearly reflects the advantage of the process where no acid had been used and the acidity of chrome powder was used to fix dye and fatliquor. The amount of water used is shown in Fig 3.

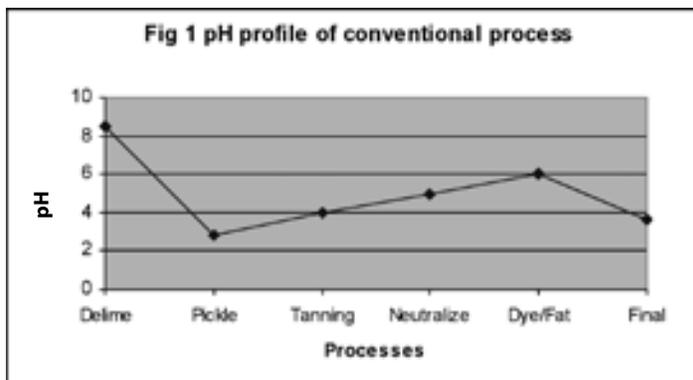
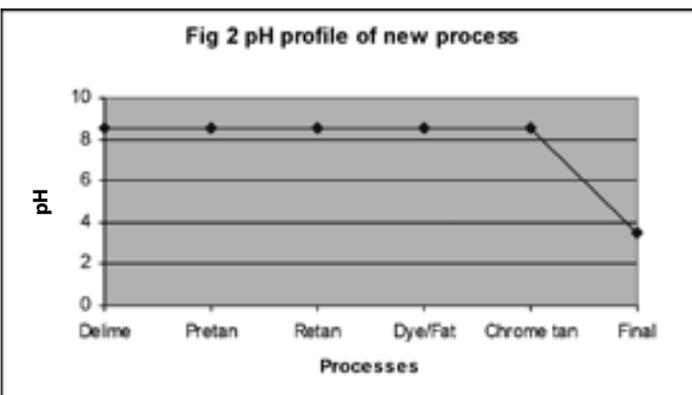


TABLE I

Comparative physical properties of chrome tanned upholstery leather

Characteristics	Delimed stock		Pickled stock	
	Mean	SD	Mean	SD
Chrome content in leather, % (moisture free basis)	6.0	-	5.4	-
Thickness, mm	0.90	0.06	1.07	0.08
Tear strength, N	46.9	9.9	47.9	5.4
Tear strength, N/mm	51.4	10.9	47.8	5.4
Load at grain crack, Kg	13.0	5.19	15.3	0.94
Distension at grain crack, mm	7.4	0.49	7.27	0.60
Tensile strength, N/mm ²	15.1	2.7	14.7	3.1
Elongation at break, %	54.5	10.2	63.7	7.8
Softness, BLC values	5.25	0.24	5.21	0.10

* Differences in values are not significant (p > 0.05)



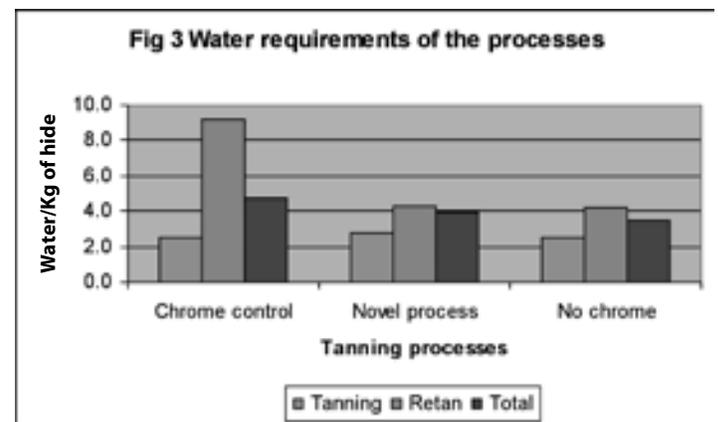
The total water used for tanning and retanning was reduced from 4.8 l/kg for the control chrome tanning process to 3.9l/kg and 3.5l/kg respectively for the novel process and no-chrome process, minimizing the waste water quantity. The physical properties of leather are given in Table 5 and illustrated in Figures 4 to 6.

TABLE II

Comparative physical properties of vegetable tanned upholstery leather

Characteristics	Delimed stock		Pickle stock	
	AVG	SD	AVG	SD
Thickness, mm	1.30	0.03	1.30	0.08
Tear strength, N	41.7a	4.89	41.01a	5.4
Tear strength, N/mm	37.6a	3.9	40.9b	5.4
Load at grain crack, Kg	17.3a	3.7	18.3a	5.1
Distension at grain crack, mm	7.58a	0.04	7.99a	0.06
Breaking Load, N	187.7a	20.4	162.1a	19.3
Tensile strength, N/mm ²	16.6a	1.8	14.4b	1.1
Elongation at break, %	54.8a	3.1	48.9b	7.2
Softness, BLC values	4.00a	0.03	4.42b	0.23

* Values in rows with different letters are significant (p < 0.05)



These results showed that even though no-chrome leather had satisfactory properties to pass all requirements of upholstery leather there were significant differences in the properties between the chrome tanned and no-chrome (vegetable tanned) leather. However, there were no significant differences between the leather from the novel chrome tanning process and the control chrome tanning process except elongation and softness. These are indications that fatliquors need to be modified.

TABLE III
Properties of upholstery leather

Characteristics	Chrome tanned control		No-chrome leather	
	Mean	SD	Mean	SD
Thickness, mm	1.28a	0.02	1.38b	0.03
Grain strength				
Load at grain crack, Kg	14.7a	1.2	18.7b	1.2
Distension at grain crack, mm	16.49a	0.93	14.88b	0.98
Tear strength, N	57.2a	3.4	40.1b	3.1
Tear strength, N/mm	46.2a	2.9	30.8b	2.7
Breaking Load, N	179.2a	17.4	142.7b	8.4
Tensile strength, N/mm ²	14.0a	1.5	10.3b	0.7
Elongation at break, %	101.0a	9.8	60.5ba	4.3
Softness, BLC values	2.80a	0.07	2.40b	0.17

* Values in row with different letters are significant (p < 0.05)

Fig 4a Effect of tannage on grain strength

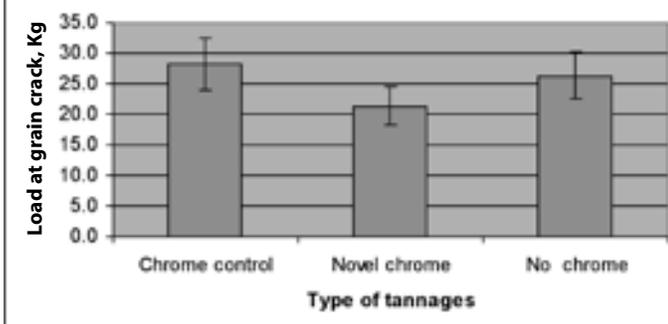


TABLE IV

Comparative discharges from tanning processes

	Chrome tanned control, ppm	No-chrome process, ppm	Reduction from chrome tanning, %
TKN	1093	362	66.9
SS	1175	570	51.5
COD	21559	8054	62.6
BOD5	12615	4052	67.9
Chloride(as Cl)	7316	1625	77.8
Chrome in exhaust tanning bath (as Cr)	8523	0	100.0

Fig 4b Effect of tannages on the grain strength

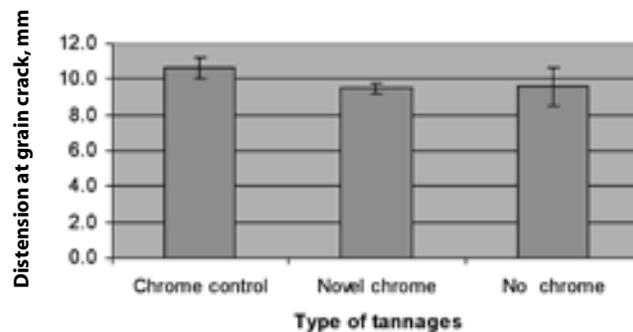


Fig 5a Effect of tanning on the tear strength

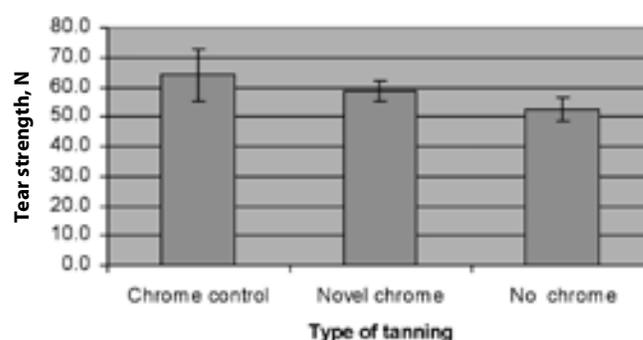
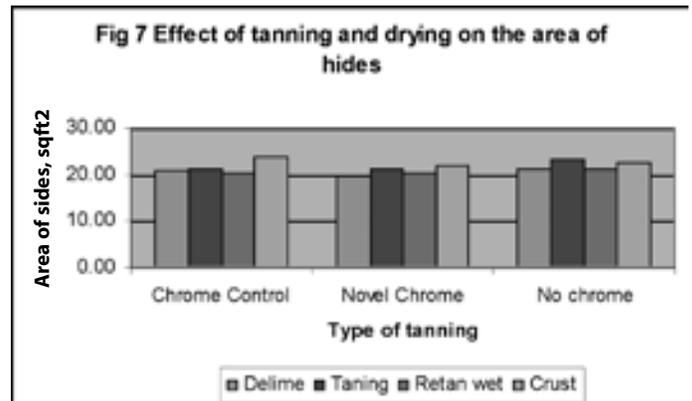
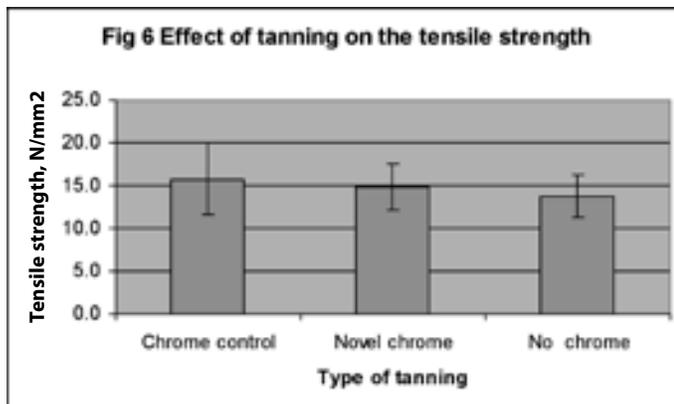
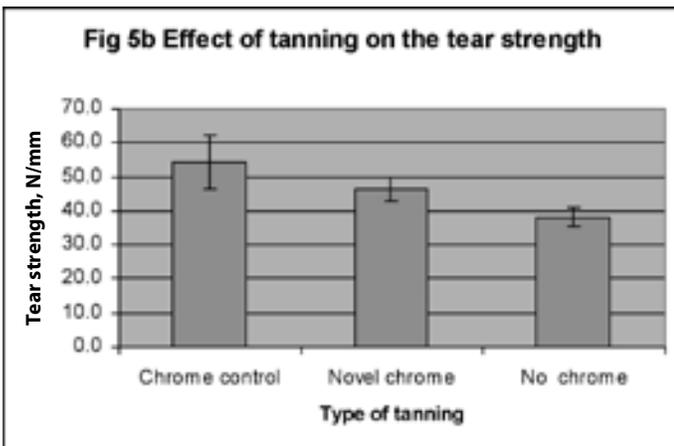


TABLE V
Properties of upholstery leather

Characteristics	Chrome tanned control		Novel chrome tanned leather		No-chrome leather	
	Mean	SD	Mean	SD	Mean	SD
Thickness, mm	1.21a	0.15	1.30a	0.06	1.38b	0.21
Grain strength						
Load at grain crack, Kg	28.3a	4.1	21.3b	3.0	26.3a	3.7
Distension at grain crack, mm	10.64a	0.58	9.47b	0.29	9.59ab	1.01
Tear strength, N	64.0a	10.57	58.5a	3.90	58.5a	3.90
Tear strength, N/mm	54.3a	9.44	46.5a	4.06	38.2b	3.49
Tensile strength, N	190.3a	56.4	191.0a	42.3	178.8a	30.4
Tensile strength, N/mm ²	15.8a	5.0	14.9a	3.2	13.7a	3.0
Elongation at break, %	87.2a	9.2	65.6b	14.0	50.9c	4.4
Softness, BLC values	3.6a	0.3	3.2a	0.3	2.8b	0.3

* Values with different letters in rows are significant (p <0.05)



The effect of various tannages and drying on the area of hides are given in Table 6 and shown in Fig 7.

It was interesting to note that the chrome free leather gained area after tanning and retanning but lost area during drying. This is also reflected in firming up of the leather and lower elongation at break and indicated that the fatliquors needed further adjustments. The control chrome remained softer and was easier to stretch toggle giving increased area. A trial in collaboration with a local tannery gave the physical properties shown in Table 7.

TABLE VI

Effect of tanning and drying on the area of leather

Type of tannage	Area in sq ft2 after						
	Delime	Tanning	% of delime	Retan wet	% of delime	Crust	% of delime
Chrome control	20.8	21.2	101.8	20.1	96.5	23.9	114.9
Novel chrome	19.6	21.3	109.1	20.1	102.6	22.0	112.1
No-chrome	21.3	23.2	109.0	21.2	99.9	22.5	105.8

TABLE VII

Properties of upholstery leather

Characteristics	Chrome tanned control		Novel chrome tanned leather	
	Mean	SD	Mean	SD
Thickness, mm	1.07a	0.08	0.90a	0.06
Grain strength				
Load at grain crack, Kg	15.3a	0.9	13.0a	5.2
Distension at grain crack, mm	7.27a	0.60	7.41a	0.49
Tear strength, N	47.8a	5.4	47.0a	9.9
Tear strength, N/mm	47.8a	5.4	51.4b	10.8
Tensile strength, N/mm ²	14.7a	3.1	15.1b	2.7
Elongation at break, %	63.7a	7.8	54.5a	10.2
Softness, BLC values	5.21a	0.10	5.25a	0.24

* Values with different letters in rows are significant ($p < 0.05$)

Once again these results showed that there were no significant differences in the properties between the control chrome tanned and the novel chrome tanned leather.

TABLE VIII

Comparative discharges from tanning processes

	Chrome tanned control, ppm	Novel process, ppm	Reduction of novel chrome process from chrome tanning, %
TKN	1000	342	65.8
SS	755	417	44.8
COD	28441	18885	33.6
BOD ₅	14293	11452	19.9
Sodium salt (as Na)	19742	13952	29.3
Chrome in exhaust tanning bath (as Cr)	5650	36	99.4

Environmental benefits

The exhaust liquors from standard chrome tanning and the novel process indicated improvement in discharge from the processes. The figures given in Table 8 are the average of two repeat trials.

This clearly indicated the benefits of the novel tanning process over conventional chrome tanning.

MECHANISM OF TANNING

Reaction of oxazolidine with collagen and vegetable tanning agent

The effect of oxazolidine on cross-linking of collagen molecules was investigated in collaboration with Massey University, Palmerston North through the regeneration of collagen fibrils from monomers with or without oxazolidine with an atomic force microscope.¹⁸ These micrographs show the effect of oxazolidine in opening up the structure at a molecular level. It could be seen also that collagen in solution with oxazolidine reacted strongly to form a gel that could not be reformed into fibers

Circular Dichroism Spectropolarimeter studies also showed¹⁸ clearly for the first time that unlike any other known tanning agent, oxazolidine affected the secondary structure of collagen. Electrospray ionization mass spectrometry (ESI-MS) analysis showed that the peptide after reaction with both oxazolidine A and E gave a product with a mass increase of 12 Da. On removal of excess oxazolidine after reaction, the 12 Da increase in mass was reduced significantly, indicating a reversible reaction with lysine. This mass increase might be due to reaction with the amino group of lysine to form methylol derivatives and subsequent partial condensation to form an imine also known as "Schiff-base". Further studies suggested formation of an imine and subsequent cross-linking of this imine with the tyrosine residue. To prove that this increase of mass was due to Schiff base, oxazolidine and sodium cyanoborohydride, NaCNBH³ were added simultaneously to the peptide solution. A mass increase of 14Da and 28Da were then observed because of reduction of N-terminal amino groups of the collagen with the formation of methylated and dimethylated amine respectively. Therefore, a mechanism of reaction¹⁸ with tyrosine, given in Fig 8 was suggested and the mechanism of tanning with oxazolidine alone and in combination with mimosa was postulated as given in Figures 9 and 10 respectively.

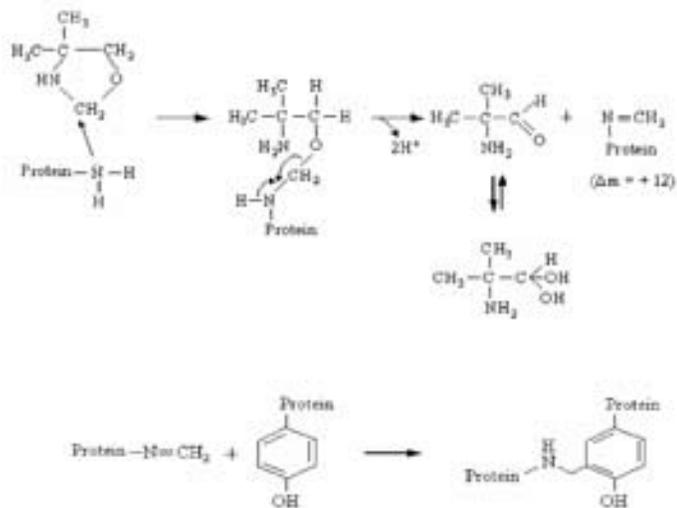


Figure 8: Reaction of tyrosine with oxazolidines

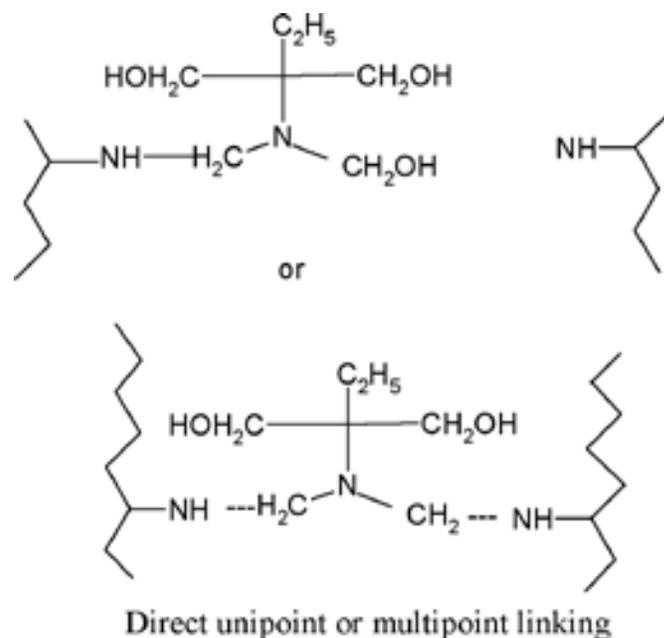


Figure 9: Reaction of oxazolidine with collagen

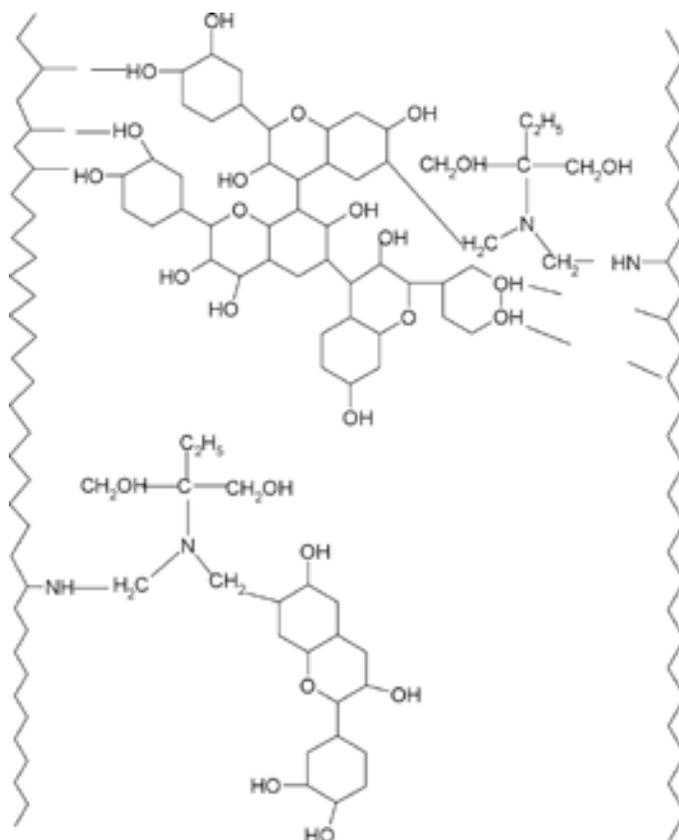


Figure 10: Mechanism of mimosa-oxazolidine collagen reaction

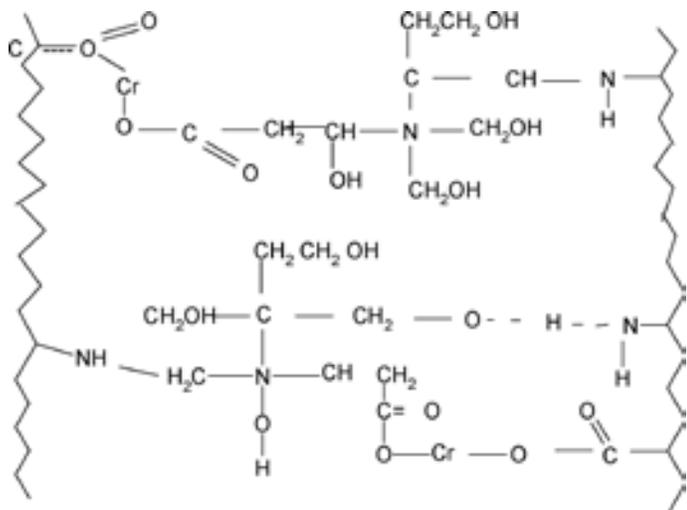


Figure 11: Mechanism of chrome - oxazolidine - collagen crosslinking

These reactions might also take place alone or in steps or simultaneously. These results of molecular level changes in collagen structure have improved our understanding of tanning of the leather. This might confirm the mechanism of oxazolidine tanning as postulated by DasGupta and supported by Lu, Liao and Shi¹⁹, and D'Aquino, *et al.*²⁰

Reaction mechanism with chrome combination tannage

Oxazolidine reacts with the basic group of collagen irreversibly to improve shrinkage temperature of leather. It was thought that this might release carboxylic groups producing more combining sites for the chrome fixation. This might explain why oxazolidine tanned leather gives higher chrome content. The reactions as given in Figure 11 might take place either alone or in steps as shown for natural polyphenol (see 4.1) or simultaneously during tanning of leather:

CONCLUSION

1. A novel approach of chrome tanning for upholstery leather has been presented where chrome in the exhaust liquor (as Cr) was only 35ppm against 1500ppm for conventional chrome tanning.
2. A process in combination of oxazolidine and mimosa without acid/salt pickling and without chrome for upholstery leather was suggested.
3. Results of molecular level changes in collagen structure have been discussed to improve our understanding of the tanning mechanisms involved.

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APPENDIX A

Processes for tanning with or without chrome tanning agents

A-1. Process used as control Chrome Tanning of hides

All percentages are on delime pelt weight

Set A
Pickle: 8% Salt
 80% Water at 25°C
 Run 10min.
Add: 0.6% Formic acid (1:5)
 Run 30min.
Add: 1.3% Sulphuric acid (1:10) prediluted and cooled
 Run 2h. Check pH- 2.8
Add: 6% Chrome powder (25/33)
 Run 1h
Add: 0.5% Magnesium oxide (Tanbase Ex. Clariant, Germany)
 and then raise temperature to 40°C.
 Run overnight maintaining temperature at 40°C.
 Drain and Rinse with cold water for 5min.
 Take out and Horse up for 48h.
 Shave to 1-1.2 mm
Wash: 200% Water at 40°C
 Run 20min.Drain.
Retan: 100% Water at 40°C
 1% Cynthopol PAE
 20 min.
Neutralise:
Add: 2% Tanigan SR
 0.5% Sodium bicarbonate
 Run 40min. Check pH - 5.0-5.5.
Wash: 150% Water at 40°C for 10min.
Dye/Fat: 100% Water at 35°C
 2% Chromopal SG (90% active)
 Run 10min.
Add: 3% Paralene PWG
 2% Mimosa
 Run 30min.
Add: 2% Airedale Black NGW250
 0.5% Ammonia
 150% Water at 35°C
 Run 30min. Check penetration- should be complete
Add: 5% Coripol ZXX (70% active)
 2% Chromopal SG (90% active)
 5% Derminol CFS (78% active)
 50% Water at 50°C (in 2 instalments)
 10 + 50min.
Add: 2% Paramel PA
 Run 30 min.
Add: 1.5% Formic acid (1:10) in two instalments
 Run 30min. Check pH – 3.5
Add: 1% Lipamin Liquor SO (60% active, cationic)
 Run 20min.
 Drain
Wash: 200% Water at 20°C
 Run 10min.
 Take out.
 Sam, set and dry as usual.

A-2. ThruBlu process- Syntan used after Oxazolidine E tannage

Pretan : 2% Oxazolidine E
 60% Water at 30°C
 Run overnight @12rpm.
 Check pH -9.31 and Ts-82°C

Add: 0.75% Formic acid (1:10)
 Run 30min. Check pH -5.5
 3% Paralene PWG
 0.1% Preventol WB
 Run 1h. Check Ts - 80°C
 Rinse and Take out.
Chrome Tan: 100% Water at 35°C
 1% Cynthopol PAE
 Run 10min
Add: 5% Chrome powder 25/33
 Run 1h and then overnight at 40°C. Check pH -3.8; Ts- 104°C
 Rinse and take out. Horse up.
Wash: 200% Water at 40°C
 Run 20min.Drain.
 Retan as control

A-3. ThruBlu process from pickled pelt - Syntan used after Oxazolidine E tannage

Stock: Pickle pelt
Pretan : 2% Oxazolidine E
 60% pickle float at 25°C
 Run 3h
Add: 1% Sodium formate
 Run 1h
Add: 1% Sodium bicarbonate
 Run 30min
Add: 1% Sodium bicarbonate
 Run 30min
Add: 1% Sodium bicarbonate
 Run 30min. Check pH -8.0
 Adjust with more bicarbonate, if required
 Run overnight @12rpm.
 Check pH -8.3 and Ts-82°C
Add: 0.75% Formic acid (1:10)
 Run 30min. Check pH -5.5
 3% Paralene PWG
 0.1% Preventol WB
 Run 1h. Check Ts - 82°C
 Rinse and Take out.
Chrome Tan: 100% Water at 35°C
 1% Cynthopol PAE
 Run 10min
Add: 5% Chrome powder 25/33
 Run 1h and then overnight at 40°C. Check pH -3.8; Ts- 104°C
 Rinse and take out. Horse up.
Wash: 200% Water at 40°C
 Run 20min.Drain.
 Retan as control

A-4. No-chrome tanning –From delime

Pretan : 2% Zolidine E
 60% Water at 30°C
 Run overnight @12rpm.
 Check pH-8.8 and Ts-82°C
Add: 1% Formic acid (1:10)
 Run 30min. Check pH -5.0
Add: 3% Paralene PWG
 0.1% Preventol WB
 Run 1h.
 Rinse and Take out.
Veg Tan: Sam, Split and shave to 1mm
 50% Water at 30°C
 2% Tanigan CK
 Run 20min.
Add: 5% Mimosa ME
 3% Paralene PWG
 1% Chromopal SG
 Run 10min
Add: 6% Mimosa ME
 1% Atlas SulCod HCR
 Run 1h
Add: 2% Oxazolidine E
 Run 2h raising temperature to 50°C
Add: 5% Relugan DLF liquid (Melamine resin)
 Run 1h. Check pH- 5.5
Add: 0.5% Oxalic acid
 Drain
 Wash out at 40°C for 10min
Neutralise: 2% Tanigan SR
 100% Water at 40°C
 Run 30 min.
 Check pH- 5.0
 Drain.
Refloat: 150% Water at 35°C
 2% Airedale Black NGW250
 0.5% Ammonia
 Run 30min. Check penetration- should be complete
Add: 4% Atlas SulCod HCR
 4% Derminol CFS
 4% Coripol ZMB
 0.5% Coripol ICA
 50% Water at 50°C (in 2 instalments)
 60min.
Add: 0.5% Formic acid (1:10)
 Run 30min. Check pH – 3.5
Add: 1% Lipamin Liquor SO
 0.03% Antimold
 Run 30min. Drain
Wash: 200% Water at 20°C
 Run 10min.
 Take out and Horse overnight.
 Next day, sam, set and dry as usual

A-5. No-chrome tanning –From pickle

Pretan : 2% Oxazolidine E
60% pickle float at 25°C
Run 3h

Add: 1% Sodium formate
Run 1h

Add: 1% Sodium bicarbonate
Run 30min

Add: 1% Sodium bicarbonate
Run 30min

Add: 1% Sodium bicarbonate
Run 30min. Check pH -8.0
Adjust with more bicarbonate, if required
Run overnight @12rpm.
Check pH -8.3 and Ts-82°C

Add: 0.75% Formic acid (1:10)
Run 30min. Check pH -5.5

Add: 3% Paralene PWG
0.1% Preventol WB
Run 1h. Check Ts - 82°C
Rinse and Take out.
Sam, Split and shave to 1-1.2 mm.
Rest of Veg tan as A-4

APPENDIX B**Novel Tanning process with chrome and No-chrome organic tanning processes****B-1. Standard Pickle /chrome tanning**

All percentages are on delime pelt weight

Pickle/Tan: 8% Salt
80% Water at 25°C
Run 10min.

Add: 0.6% Formic acid (1:5)
Run 30min.

Add: 1.3% Sulphuric acid (1:10) prediluted and cooled
Run 2h. Check pH 2.5

Add: 6.5% Chrome powder (25/33)
0.1% Preventol WB (1:5)
Run 1h

Add: 0.4% Tanbase
Run 1h
Raise temperature to 40°C and Run overnight
Next day. Check pH -3.9; Ts- stood boil

Drain.

Rinse: 150% Water at 20°C
Run 10 min.
Take out and horse up overnight.
Sam, Split and shave to 1mm.

Retannage: All percentages are on shaved weight

Wash: 100% Water at 35°C
0.2% Tetrapol LTN
0.1% Formic acid
Run 30min.
Drain

Neutralise: 2% Tanigan PAK-N
0.5% Sodium bicarbonate
150% Water at 35°C
Run 45min.

Add: 3% Paralene PWG
2% Mimosa
1% Chromopal SG (1:5)
Run 60min.
Drain.

Wash: 150% Water at 35°C

Drain.

Dye/ Fat: 150% Water at 35°C

Add: 1.5 % Derma Brown 3R

Run 1h

Add: 5% Coripol ZXK (70% active)
3% Chromopal SG (90% active)
5% Derminol CFS (78% active)
50% Water at 50°C (in 2 instalments)
Run 60min.

Add: 2% Paramel PA (1:5)
Run 40min.

Add: 1% Formic acid (1:10)
Run 30min. Check pH -3.5-3.8
Drain

Wash: 150% Water at 20°C

Run 10 min.

Drain. Collect sample

Wash: 150% Water at 20°C

Run 10 min.

Drain.

Horse up. Dry as usual. Condition and stake

B-2. ThruBlu chrome tanning process

Pretan : 2% Oxazolidine E
80% Water at 30°C
Run 5min

Add: 6% Paralene WX-A (40% active)
Run overnight @12rpm.
Check pH -8.8 and Ts-83°C

Add: 0.75% Formic acid (1:10)
Run 30min. Check pH -5.0
0.1% Preventol WB
Run 1h. Check Ts 82°C : pH-5.8
Rinse and Take out.
Sam, Split and shave to 1-1.2 mm.

Wash: 100% Water at 35°C

Run 20min.

Drain.

Chrome tan: 5% Chrome powder 25/33

60% Water at 30°C

Run 1h and then overnight at 40°C. Check pH -4.0; Ts- 100°C

Rinse: 100% Water at 20°C

Run 10min. Drain

Retan: As chrome control

B-3. Novel chrome tanning process

Pretan : 2% Oxazolidine E
80% Water at 30°C
Run 5min

Add: 6% Paralene WX-A (40% active)
Run overnight @12rpm.
Check pH -8.8 and Ts-83°C

Add: 0.75% Formic acid (1:10)
Run 30min. Check pH -5.0
0.1% Preventol WB
Run 1h. Check Ts 82°C : pH-5.8
Rinse and Take out.
Sam, Split and shave to 1-1.2 mm.

Retannage: All percentages are on shaved weight

Wash: 100% Water at 35°C

Run 20min.

Drain.

Neutralise: 100% Water at 40°C

2% Tannigan SR

0.25% DSP

Run 30min.

Drain.

Refloat: 50% Water at 40°C

2% Derminol CFS (1:5)

Run 10min.

Add: 3% Mimosa ME

2% Paralene PWG

Run 10min,

Add: 2% Relugan RV(1:5)

2% TIS(1:5)

Run 10min. Check pH -5.66

Add: 1.5 % Derma Brown 3R

Run 2h

Add: 5% Coripol ZXK (70% active)

3% Chromopal SG (90% active)

5% Derminol CFS (78% active)

50% Water at 50°C (in 2 instalments)

Run 60min.

Add: 2% Paralene PWG

30min.

Add: 5% Chrome powder 25/33

Run 1h and then overnight at 40°C. Check pH -4.14; Ts- 100°C

Rinse: 100% Water at 20°C

Run 10min. Drain

Take out. Horse up.

Take out. Horse up.