



Optimum chrome tanning of hides and modified ThruBlu process for lime-split hides

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Chrome tanning for a long time enjoyed a unique position amongst tanners all over the world and almost 90% of leather produced is chrome tanned. Of all these benefits, high shrinkage temperature has been the paramount feature in favour of chrome tanning as this cannot be achieved by any other tanning systems. A number of studies have been published recently suggesting that Chromium(III) itself may be toxic at higher levels under certain ligand environment^{1,2} and Chromium(VI) is a known carcinogen^{3,4}. So, tanners have to consider how best to modify their chrome tanning process for better exhaustion of chrome and look for alternative means to minimise the impact of tanning on the environment. LASRA research has shown that none of the alternatives to chrome free tanning systems are as cost effective and cheap than chrome tanning. The best commercial option is, therefore, to develop an effective chrome management system for the tannery.

Several chrome management technologies have emerged recently. Among the options available is the no pickle ThruBlu process, first introduced for lambskins in 1993 at LASRA Conference by DasGupta⁵ and further developed and subsequently extended to split hides tannages⁶⁻⁷. It is the most cost effective and easily adoptable. But this novel system challenges the basic established theory of chrome tanning and therefore demands conviction from tanners. The partial substitution of chromium with alternative tanning agents⁸ like Oxazolidine E (*Zolidine E*, Angus Chemicals), THPS (*Albrite AD*, Rhodia) is also promising because this combines benefits of both the tanning materials.

To develop an effective optimum system, a tanner must first find out what is the minimum amount of chrome that is required to satisfy his customer requirements, both in respect of dye ability and other performance requirements. This is a must before subsequent options can be considered, such as:

- Simply recycling the chrome exhaust in pickle
- Precipitate the chrome in the exhaust liquor, then deposit the cake in land fill
- Precipitate the chrome in the exhaust liquor, regenerate as chrome tanning agent for reuse.

This report outlines systems which give an optimum chrome tanning of hides. Further, LASRA ThruBlu process that was

originally devised for delimed hides, has been modified for chrome tanning of pickled hides to minimise chrome in exhaust liquors.

The optimum chrome tannage of hides

Six pickled hides were collected from a side leather tannery. Each was sided and cut into six pieces (*backbone to belly*) and allotted at random in six groups and chrome tanned overnight at 40°C with 4.0 - 6.5% chrome powder (25/33) and basified with MgO (*Tanbase*). The shrinkage temperature, chrome content of leather, and exhaust liquor was determined following standard IULTCS methods, and are shown in *Panel 1*.

This shows that about 5% chrome powder was enough to obtain satisfactory wet blue sides, and a higher amount of chrome offer gives disproportionately higher amount of residual chrome in exhaust liquor. Also, there were no significant adverse effects on the properties of leather that could be attributed to lower chrome offer in terms of tear, tensile, and grain strength. This is shown in *Panel 2*.

This shows that side leather may be chrome tanned successfully with a much lower chrome offer than presently followed by tanners.

Modification of the ThruBlu process

To investigate this possibility, six pickled lime split hides were taken, cut through the backbone and coded. These were allotted at random to four groups, each containing three sides.

One set was chrome tanned with 5% chrome powder (25/33) following a standard commercial process.

The other three sets were pretanned with 2% Oxazolidine E, raising pH gradually to pH 7.0 - 7.5. They were then drained, and chrome tanned with 3, 4 and 5% chrome powder (25/33) overnight without any basification.

Outline details of both the original ThruBlu Process, and the modified process are given in *Panel 3*. With 3% chrome offer, there were some areas, particularly thicker neck parts, where the chrome did not penetrate completely. With 4% and 5% offers there were no such problems. The effects of these types of tannages on shrinkage temperature, chrome content in the leather and exhaust liquor, and the layerwise distribution of chrome throughout the leather are illustrated in *Panel 4*. ➤



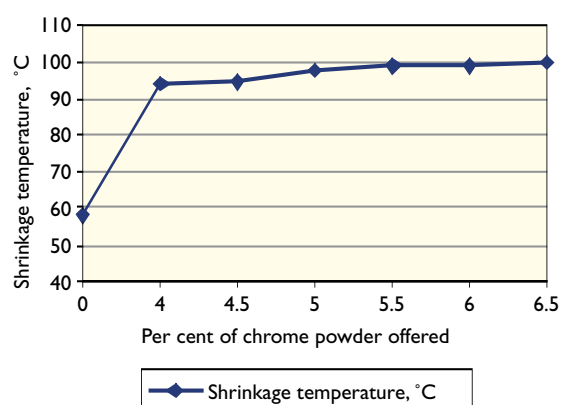
OPTIMUM CHROME TANNING OF HIDES AND MODIFIED THRUBLU PROCESS FOR LIME-SPLIT HIDES

The physical properties of these leathers and controls are given in *Panel 5*.

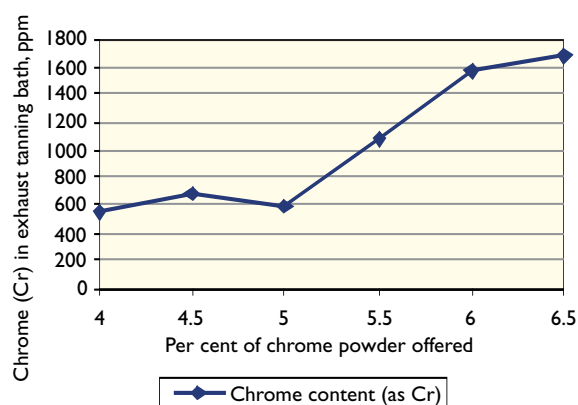
There are some differences in softness between these treatments. The modified ThruBlu with 5% chrome offer gave the softest leather, and modified ThruBlu with 3% chrome offer giving the firmest leather as shown in *Panel 6*.

Panel 1

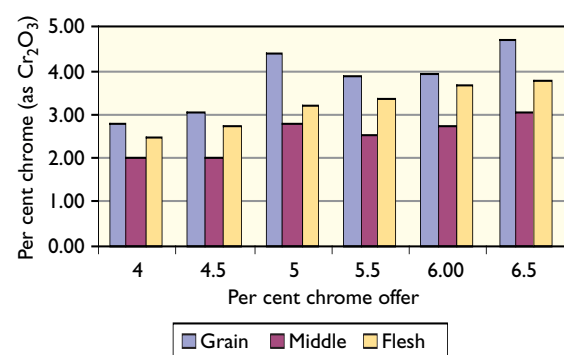
I/1: Effect of chrome offer on shrinkage temperature of wet blue sides, °C



I/2: Effect of chrome offer on the residual chrome in exhaust liquor



I/3: Layerwise distribution of chrome in side leather



RESIDUAL FORMALDEHYDE IN THE MODIFIED THRUBLU LEATHER

The formaldehyde content of wet blue sides was determined by the HPLC method (*JIS L1041: 1980*) and is shown as *Panel 7*.

These formaldehyde values may further be reduced by washing the chrome tanned hides with hot water, with a scavenging agent like hydrogen peroxide or other commercial agents such as Tanigan SR (*Lanxess*) and Formolstop (*Trumpler*).

This demonstrates that:

- Based on full substance hides, chrome tanning may be optimised with a chrome offer of about 5%.
- Based on a modified non-pickle tanning system (*Modified ThruBlu process*), lime-split hides may be chrome tanned successfully with about 4% chrome powder. This provides a significant reduction of the chrome content of the exhaust bath, and does not have any adverse effect on the quality of leather.

Panel 2

2/1: Tear and tensile strength of chrome tanned side leather

Properties leather tanned with chrome powder offer of:	Tear strength N/mm	Tensile strength, N/mm ²	
	Average	SD	Average SD
4.0	70.6a	19.9	11.8a 2.7
4.5	86.9bc	19.2	12.6ac 1.4
5.0	87.8bc	8.1	15.3bd 2.3
5.5	66.5a	13.8	11.5a 2.6
6.0	83.5bc	16.2	12.7bcd 1.4
6.5	81.1ac	17.4	13.8ad 3.7

- SD = Standard Deviation.
- Values with different letters are significant ($p < 0.05$).
- The difference in tear and tensile strength between 4% and 6.5% chrome offer is not significant.

2/2: Grain strength of chrome tanned side leather

Properties leather tanned with chrome powder offer of:	Distention at grain crack, mm	Load at grain crack, Kg	
	Average	SD	Average SD
4.0	8.75a	0.46	25.1a 6.3
4.5	9.00a	0.54	30.9a 8.6
5.0	8.07b	0.76	18.6b 5.9
5.5	7.66bc	0.55	18.8b 5.1
6.0	8.21bd	0.48	24.2a 5.2
6.5	7.85b	0.62	19.8b 3.9

- SD = Standard Deviation.
- Values with different letters are significant ($p < 0.05$).
- The difference in grain strength between 4% and 6.5% chrome offer is significant; 4 - 4.5% giving higher values.

**Panel 3****The original LASRA ThruBlu process***(Originally developed for lime-split hides.)*

Stock:	Lime split hides
Delime and bate:	Complete (colourless to phenolphthaleine indicator);
	Wash and drain
Chrome tan:	60% Water at 30°C
	5% Chrome powder (25% Cr ₂ O ₃ ; 33% basicity)
	Run overnight as normal at 40°C
Next day: check shrinkage temperature – stand boil and pH 3.6-3.7 and then proceed as normal. <i>NOTE: Ordinary, commercial normal chrome powder was used. No basification required.</i>	

The modified ThruBlu process*To enable tanners who do not have access to limed hides and start from pickle material, the modified ThruBlu process was developed.*

Stock:	Lime split hides in pickle condition
Pretan:	Pickle float 60% at 25°C; pH - 3.0
	2% Oxazolidine E
	Run 2-3 hours
	1% Sodium formate
	Run 1 hour
	1% Sodium bicarbonate
	Run 1 hour
	Raise temperature to 30-35°C
Add:	1% Sodium bicarbonate
	Run 1 hour
	Check pH = 7.0 -7.5
	Drain
Refloat:	50-60% Water at 30°C
	5% Chrome powder (25/33)
	Run 1 hour, and then overnight at 40°C (as normal for chrome tanning but without any basification.)
Next day:	Check shrinkage temperature and pH and proceed as normal.

Panel 5**5/1: Tear and tensile strength of chrome tanned side leather**

Properties leather tanned with chrome powder offer of:	Tear strength, N/mm	Tensile strength, N/mm ²		
	Average	SD	Average	SD
5% Control (normal process)	49.8a	8.5	12.37a	2.64
Mod ThruBlu with 5% chrome powder	44.1a	6.3	10.67ac	1.09
Mod ThruBlu with 4% chrome powder	42.1a	15.3	13.47ab	4.13
Mod ThruBlu with 3% chrome powder	44.4a	18.5	10.72a	2.26

• SD = Standard Deviation.

• Values with different letters are significant ($p < 0.05$).

• The differences in tear and tensile strength between these treatments are not significant.

5/2: Grain strength of chrome tanned side leather

Properties leather tanned with chrome powder offer of:	Load at grain crack, Kg	Distention at grain crack, mm		
	Average	SD	Average	SD
5% Control (normal process)	26.7a	5.92	9.38a	0.42
Mod ThruBlu with 5% chrome powder	22.4ac	6.98	8.68ac	0.91
Mod ThruBlu with 4% chrome powder	26.4a	6.98	9.30ab	1.01
Mod ThruBlu with 3% chrome powder	18.0bc	3.61	8.56bc	0.43

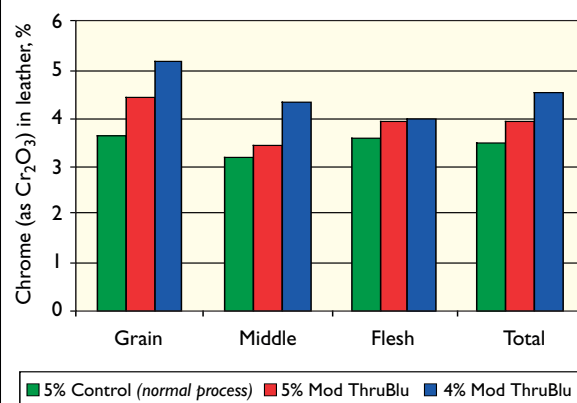
• SD = Standard Deviation.

• Values with different letters are significant ($p < 0.05$).

• The differences in grain strength between control and modified ThruBlu with 3% chrome offer are significant, all others are similar.

Panel 4**4/1: Effect of tannage on the shrinkage temperature and chrome in exhaust bath**

Process	Shrinkage temperature, °C	Chrome (as Cr) in exhaust liquor, ppm	Reduction of chrome in exhaust from control, %
5% Control (normal process)	102	762	-
Mod ThruBlu with 5% chrome powder	107	233	69.4
Mod ThruBlu with 4% chrome powder	104	174	87.2
Mod ThruBlu with 3% chrome powder	94	trace	99.9

4/2: Layerwise distribution of chrome in leather

OPTIMUM CHROME TANNING OF HIDES



Panel 6

Softness of chrome tanned side leather

Properties leather tanned with chrome powder offer of:	Softness, BLC values	
	Average	SD
5% Control (normal process)	2.41a	0.20
Mod ThruBlu with 5% chrome powder	2.56b	0.22
Mod ThruBlu with 4% chrome powder	2.31a	0.14
Mod ThruBlu with 3% chrome powder	2.03c	0.13

• SD = Standard Deviation.

• Values with different letters are significant ($p < 0.05$).

Panel 7

Formaldehyde content of chrome tanned side leather

Properties leather tanned with chrome powder offer of:	ppm
5% Control (normal process)	10.5
Mod ThruBlu with 5% chrome powder	70
Mod ThruBlu with 4% chrome powder	84
Mod ThruBlu with 3% chrome powder	74

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