

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

# **MINIMISING THE ENVIRONMENTAL IMPACT OF CHROME TANNING**

A thesis presented in partial fulfilment of the  
requirement for the degree of

**DOCTOR OF PHILOSOPHY**

in Process and Environmental Technology Department  
in Massey University, Palmerston North, New Zealand

**Samir DasGupta**  
**1996**

MASSEY UNIVERSITY LIBRARY



1061923675

## Dedication

To my mentor and uncle  
Mr Debangshu Dasgupta,  
a pioneer Leather Technologist of India.

## **ABSTRACT**

Internationally about 400000 tons of Chrome tanning agents are used annually. The efficiency of the present state of the art tanning technology would suggest that about 60000 tons of chrome tanning agents remain unutilised during the chrome tanning and might be discharged into the environment. Apart from environmental problems, this costs the industry ninety million dollars worth of valuable chrome tanning agents annually.

The research was aimed at minimising the environmental impact of chrome tanning by the improvement of the efficiency of the classical system through the addition of auxiliary chemicals during chrome tanning, changing the present technology and by modifying the chrome tanning agent itself.

Two different chemicals were synthesised. These were included in a detail study with six other commercial auxiliary chemicals to improve the classical system. Here the possibilities of improving the availability of carboxylic groups for better efficiency of chrome tanning were explored. A considerable improvement, about 90-93% for hides and 95-96% for lamb skins was obtained with these two synthesised chemicals.

A novel chrome tanning technique for tanning of lamb skins was developed where conventional acid-salt pickling was completely eliminated and tanning conducted after delimiting at pH 7 to 8.5. This novel technique also did not require basification and masking agents for the completion of chrome tanning and saved considerable amount of money for the tanner. This new approach of tanning gave higher exhaustion of chrome to the extent of 96-97% with improved physical properties and yield of leather. The mechanism of the new tanning system was also postulated.

Seventy percent of sodium sulphate, one of the pollutants of chrome tanning, was removed from the commercial sulphur dioxide reduced 33% basic chrome sulphate by crystallisation technique. Attempts were made to separate various species of chrome complexes with HPLC, Gel filtration (Saphadex G25) and Ion exchange chromatography (SP Saphadex C25) and finally six species of chrome complexes were separated from the commercial sulphur dioxide reduced 33% basic chrome sulphate liquor with ion exchange columns (Dowex 50W x 8 and Dowex 1X8-50). It was interesting to find that about 20% of the commercial basic chrome sulphate were anionic and nonionic complexes.

In an attempt to understand their reactivity, separated species of complexes were studied for their ageing and tanning characteristics. This showed that as long as the pH of the liquor was kept constant, there was no significant change in these complexes due to ageing. Tanning affinity of each of these complexes was studied on pickled lamb skins at three different temperatures, namely 20, 30 and 40°C.

In general, anionic complex had no reactivity and the nonionic species was less reactive at normal tanning pH between 3.0 and 4.2. Similar tanning trials with cationic complexes showed that the affinity of these complexes with skin collagen increased progressively with the cationic charge of the complexes up to  $(Cr)^{4+}$ , and then remained constant for complexes with higher charges than  $(Cr)^{4+}$ .

The reactivity of the combined cationic complexes was studied against standard commercial chrome control on similar pickled and degreased lamb skins. It was found that this combined cationic fraction tanned leather rapidly and more efficiently. The exhaustion of chrome, established through the analysis of chrome in the exhaust chrome liquor with the atomic absorption spectrophotometer, was 95.11% against 72.25% for the control. The quality of leather obtained was shown to meet the requirements of leather prescribed in the European Commission's guide lines.

A polyamide resin was synthesised. Initially 0.75g to 1.25g resin/mole of  $\text{Cr}_2\text{O}_3$  was used to modify the 33% basic chrome sulphate liquor. The ageing characteristics of these complexes were also studied over a six month period. It was clear that the polyamide formed a stable complex with basic chrome sulphate and the ageing did not alter their characteristics significantly. Ion exchange separation (Dowex 50W x 8) of the chrome-polyamide complex showed that this complex had an ionic distribution closer to phthalate masked basic chrome sulphate.

Tanning trials with chrome-polyamide complex on pickled lamb skins and cow hides at low pH like the conventional chrome tanning showed slightly better chrome exhaustion for lamb skin but no significant improvement for side leather. But when lamb skins were tanned according to the newly developed chrome tanning process, a significant improvement in chrome tanning was obtained. The exhaustion of chrome was more than 99% and leather stood boil within two hours, shortening the chrome tanning process considerably. The quality of leather obtained was shown to meet the requirements of leather prescribed in the European Commission's guide lines

The novel process without pickling was tried successfully in the industry. The principle of this no-pickle novel chrome tanning system was extended to the pretanned lamb skins where chrome tanning was successfully carried out at high pH after degreasing without readjusting the pH of the tanning bath with acid to 3.0-3.5 and tanning completed without basification.

## PUBLICATIONS ARISING OUT OF THIS RESEARCH

1. DasGupta, S - High exhaust chrome systems, *Report of the Annual Conference of Tanners and Leather Technologists*, New Zealand Leather and Shoe Research Association, New Zealand, **42,57** (1992).
2. O'Donnell, P and DasGupta, S - Chrome leaching from Bovine wet blue, *Report of the Annual Conference of Tanners and Leather Technologists*, New Zealand Leather and Shoe Research Association, New Zealand, **42,83** (1992).
3. DasGupta, S - Wet blue lamb pelt production, *Report of the Annual Conference of the Fellmonger and Hide Processors*, New Zealand Leather and Shoe Research Association, New Zealand, **44,99** (1993).
4. DasGupta, S - High exhaust systems for the chrome tanning of lamb skins, *Report of the Annual Conference of Tanners and Leather Technologists*, New Zealand Leather and Shoe Research Association, New Zealand, **43,23** (1993).
5. DasGupta, S - Solid waste utilisation, *Report of the Annual Conference of Tanners and leather Technologists*, New Zealand Leather and Shoe Research Association, New Zealand, **44,69** (1994).
6. DasGupta, S - A novel chrome tanning system, **New Zealand Patent** (Application pending).
7. DasGupta, S - Aqueous degreasing and ThruBlu Tannage of New Zealand lamb skins, *Report of the Annual Conference of Tanners and Leather Technologists* New Zealand Leather and Shoe Research Association, New Zealand, **45, 25** (1995)

## ACKNOWLEDGMENT

I wish to express my sincere gratitude to Prof. Rao Bhamidimarri, Department of Process and Environmental Technology, Massey University for his advice, guidance and continuous encouragement towards the successful completion of the project.

I gratefully acknowledge the help and guidance I have received from Mr. T Passman, Director, New Zealand Leather and Shoe Research Association, Palmerston North, New Zealand in conducting this research. I am also grateful to him for his permission to submit the results of this research, conducted at the Leather and Shoe Research Association as a part of the thesis.

I also gratefully acknowledge the financial support of the Foundation of Research, Science and Technology, New Zealand without which this project could not be completed.

I also acknowledges the assistance of Mr. Peter O'Donnell for the leaching study, Dr. Tim Allsop and Dr. A.K Hewavitharana for the HPLC work and Mr. Murray Shaw for the tanning trials, chemical analysis and physical testing of leather. I would like to express my thanks to Ms. Lisa Bowyer for her help in the preparation of this manuscript.

I take this opportunity to express my sincere gratitude to my late father and mother, and to my sisters and brothers, particularly my two elder brothers, Mr. Dipok Dasgupta and Mr. Dilip Dasgupta without their moral and financial support it would not have been possible for me to continue my tertiary education.

Finally, my sincere thanks to my wife *Banani* and my three children, *Anouska*, *Arijit* and *Surupa* who have been patient and tolerant when I stayed long in the laboratory and sacrificed many of their Saturday and Sunday outings for my research.



## LIST OF TABLES

Tables	Title	Page
Chapter 3		
3.1	Reactive groups of collagen	37
3.2	Number and locations of chrome bridges in 1D	72
Chapter 4		
4.1	Some comparative results of high exhaust systems vs conventional tannages	91
4.2	Chrome exhaustion of various systems	106
4.3	Mass balance for chromium and the efficiency of various chrome tanning systems	110
4.4	Chrome in wet blue and in discharge liquors	111
4.5	Mass balance for chromium in retanning sides from commercial wet blue	117
4.6	Mass balance of chromium in retanned sides from high exhaust chrome tanning systems	118
4.7	Comparative tensile strength of chrome tanned crust leather from various chrome tanning systems	122
4.8	Comparative tear strength of chrome tanned crust leather from various chrome tanning systems	122
4.9	Comparative grain strength of chrome tanned crust leather from various chrome tanning systems	123
4.10	Mass balance for chromium and efficiency of chrome tanning systems : commercial processes	124

4.11	Mass balance for chromium and efficiency of chrome tanning systems : high exhaust systems on New Zealand lamb skins	125
4.12	Chromium concentrations of post tannage discharges	126
4.13	Chromium levels of wetblue lamb skins from high exhaust tanning trials	129
4.14	Chromium concentrations of discharges from the high exhaust tanning trials	130
4.15	Tear strength of chrome tanned New Zealand lamb skins	133
4.16	Grain strength of chrome tanned New Zealand lamb skins	133
4.17	Tensile strength of chrome tanned New Zealand lamb skins	134
4.18	Elongation at break of chrome tanned New Zealand lamb skins	134
4.19	Chrome exhaustion of various chrome tanning systems on New Zealand lamb skins	136
4.20	Tear strength of chrome tanned New Zealand lamb skins	137
4.21	Tensile strength of chrome tanned New Zealand lamb skins	137
4.22	Elongation at break of chrome tanned New Zealand lamb skins	137
4.23	Grain strength of chrome tanned New Zealand lamb skins	138

## Chapter 5

5.1	Comparative properties of chrome tanned crust New Zealand lamb skins with or without pickling	148
5.2	Chrome and fat content of chrome tanned lamb skins	153

5.3	Chrome and fat content in lamb skins	154
5.4	Comparative grain strength of New Zealand lamb skins with or without pickling	155
5.5	Comparative tear strength of New Zealand lamb skins with or without pickling	155
5.6	Comparative tensile strength of New Zealand lamb skins with or without pickling	156
5.7	Comparative elongation at break of New Zealand lamb skins with or without pickling	157
5.8	Shrinkage temperature	159
5.9	Area and yield of wet blue lamb skins	160
5.10	Percentage distribution of flatness of wet blue lamb skins	160
5.11	Percentage distribution of various grades of wet blue lamb skins	161
5.12	Chemical analysis of wet blue lamb skins	161
5.13	Percentage distribution of various grades of crust leather	162
5.14	Area yield of finished nappa leather(sq ft)	162
5.15	Effect of different fleshing systems on double hole stitch tear strength	163
5.16	Effect of different fleshing systems on grain strength	163
5.17	Effect of different fleshing systems on tear strength	164
5.18	Effect of different fleshing systems on tensile strength	164
5.19	Comparative fat and chrome content of New Zealand lamb skins	166

5.20	Chrome content of Oxazolidine A pretannage and high pH chrome tanning	166
5.21	Leaching behaviour of wet blue lamb skins pretanned with Oxazolidine A	167
Chapter 6		
6.1	Reduction of sodium sulphate from commercial chrome tanning solutions	175
6.2	Comparative tanning power of anionic complex and chrome control	176
6.3	Comparative tanning power of nonionic complex and chrome control	177
6.4	Effect of cationic complex on the tanning	177
6.5	Effect of tanning temperature on area yield	180
6.6	Effect of tanning temperature on chrome exhaustion	180
6.7	Comparative tanning characteristics of chrome/polyamide complex and standard chrome tanning agent	189
6.8	Comparative properties of lamb skins tanned with standard chrome tanning agent and chrome/polyamide complex	190
6.9	Comparative properties of side leather tanned with standard chrome tanning agent and chrome/polyamide complex	191
6.10	Distribution of complexes in polyamide modified basic chrome sulphate solution	192
6.10	Distribution of complexes in polyamide modified basic chrome sulphate solution	192
6.11	Mass balance of chromium and efficiency of chrome tanning systems	195
6.12	Comparative physical properties of lamb skin from different tanning systems	196

6.13	Mass balance of chromium and efficiency of chrome tanning systems	199
6.14	Comparative physical properties of lamb skins from different tanning systems	200

## LIST OF FIGURES

Figure	Title	Page
Chapter 3		
3.1	Coiled structure of the Collagen Molecule	33
3.2	Electron micrograph of collagen fibrils	35
3.3	Aldol condensation of two lysine derived aldehydes	36
3.4	Formation of a Schiff base by condensation of an aldehyde with an amino group of lysine	36
3.5	Separation of chrome tanning solution (12.45% Cr <sub>2</sub> O <sub>3</sub> ) on SP Sephadex G 25	53
3.6	Separation of chrome tanning solution (12.45% Cr <sub>2</sub> O <sub>3</sub> ) on SP Sephadex C 25	54
3.7	Gel filtration chromatography of chromosal B	55
3.8	Separation of commercial 33% basic, sulphur dioxide reduced chromium sulphate solution	56
3.9	Spatial extensions of glutamic acid side chain	71
3.10	Side view of two triple helics	72
3.11	Position of reactive sites in the polypeptide	76
Chapter 4		
4.1	Glyoxylic acid with chrome linking in a starlike structure	105
4.2a	Layerwise distribution of chrome in wet blue hide: Set one	107
4.2b	Layerwise distribution of chrome in wet blue hide: Set two	108

4.3	Chromium losses(post tanning processes) : Code 1 to code 3	112
4.4	Chromium losses(post tanning processes) : Code 4 to code 6	112
4.5	Chromium losses(post tanning processes) : Code 7 to code 9	113
4.6	Chromium losses(post tanning processes) : Code A to code C	113
4.7	Chromium losses(post tanning processes) : Code D to code F	114
4.8	Chromium losses(post tanning processes) : Code G to code I	114
4.9	Chromium losses (post tanning processes) : Code J	115
4.10	Combined effluent (tannery survey)	119
4.11	Combined effluent (high exhaustion trials)	119
4.12	Percentage of chromium loss (post tanning processes): commercial systems	121
4.13	Percentage of chromium loss (post tanning process): high exhaust systems	121
4.14	Chromium release from commercial wet blue	127
4.15	Chromium release from high exhaust trials A to E	127
4.16	Chromium release from high exhaust trials F to I	128
4.17	Total chromium released( tannery survey)	128
4.18	Total chromium released (high exhaust trials)	129

## Chapter 5

5.1	Chrome and grease content of lamb skins	153
5.2	Effect of pretannage on chrome content of wet blue	168

5.3	pH profile during chrome tannage of pretanned pelts	169
5.4	Shrinkage temperature of chrome tanned skins	169
5.5	Rate of exhaustion of chrome of pretanned skins	170
Chapter 6		
6.1	Effect of temperature on the shrinkage temperature of lamb skin	179
6.2	Effect of polyamide addition on the chromium sulphate complex	181
6.3	Effect of polyamide on the chromium complex (Fraction 1- Anionic)	182
6.4	Effect of polyamide on the chromium complex( Fraction 2- Nonionic)	182
6.5	Effect of polyamide on the chromium complex{( Fraction 3- Cationic(1+)}	183
6.6	Effect of polyamide on the chromium complex{( Fraction 4- Cationic(2+)}	183
6.7	Effect of polyamide on the chromium complex{( Fraction 5- Cationic(3+)}	184
6.8	Effect of polyamide on the chromium complex{( Fraction 6- Cationic(4+)}	184
6.9	Effect of ageing on the chrome complex: Fraction 1 and its polyamide modified fraction	185
6.10	Effect of ageing on the chrome complex: Fraction 2 and its polyamide modified fraction	186
6.11	Effect of ageing on the chrome complex: Fraction 3 and its polyamide modified fraction	186
6.12	Effect of ageing on the chrome complex: Fraction 4 and its polyamide modified fraction	187



6.13	Effect of ageing on the chrome complex: Fraction 5 and its polyamide modified fraction	187
6.14	Effect of ageing on the chrome complex: Fraction 6 and its polyamide modified fraction	188
6.15	Effect of ageing on the chrome complex: Fraction 7 and its polyamide modified fraction	188
6.16	pH profile of chrome tanning bath tanned with poly/chrome complex and Tannachrome S	193
6.17	Shrinkage temperature of lamb skin tanned with Poly/chrome complex and Tannachrome S	193
6.18	Rate of exhaustion of chrome (as $\text{Cr}_2\text{O}_3$ ) during tanning with Poly/chrome complex and Tannachrome S	194
6.19	pH profile of chrome tanning bath tanned with poly/chrome complex and Tannachrome S	197
6.20	Shrinkage temperature of lamb skin tanned with Poly/chrome complex and Tannachrome S	197
6.21	Rate of exhaustion of chrome (as $\text{Cr}_2\text{O}_3$ ) during tanning with Poly/chrome complex and Tannachrome S	198
6.22	Exhaust liquors from conventional and novel tanning systems	200

## GLOSSARY OF TERMS

Butt	That part of the hide left after the bellies and shoulder have been removed.
Chrome tanned	Leather tanned either solely with chromium salts or with chromium salts together with quite small amounts of some other tanning agents used merely to assist the chrome-tanning process, and not in sufficient amount to alter the essential chrome tanned character of the leather.
Chrome retan	Leather which has been first chrome tanned throughout its thickness and subsequently further treated or tanned with vegetable and/or synthetic tanning agents and/or resin filling materials, these retanning agents penetrating notably, but not necessarily completely, into the interior.
CIELAB colour values	The colour values measured from CIE L* a* b* colour order system( or CIELAB ). This system was published in 1976 by the Commission International de l'Eclairage(C.I.E) and widely adopted by all industries. The CIELAB colour space is a three dimensional space where L* represents the dark to light scale or grey scale, a* represent the red-green component, and b* represents the yellow-blue component of colour.

Cow hide	The outer covering of a mature bovine animal.
Crust leather	Leather which, after tanning, has not been further processed but has been merely dried out.
Lamb skin	The outer covering of a young ovine animal before removal of the wool.  Leather made therefrom, used principally for clothing and gloving purposes.
LASRA	New Zealand Leather and Shoe Research Association, Palmerston North, New Zealand.
MFB	Moisture free basis. The term is used in expressing the results of leather analysis.
Pelt	In the leather trade, as opposed to the fur trade, commonly used to designate the hide and skin prepared for tanning by removal of the hair or wool, epidermis and flesh.
Pickle	An acid liquor, e.g, a solution of sulphuric acid and sodium chloride, used to preserve pelts or to prepare them for tanning, especially chrome tanning.
Pickling	The treatment of pelts with an acid liquor, e.g, a solution of sulphuric acid and sodium chloride, used to preserve pelts or to prepare them for tanning, especially chrome tanning.
Split	If a hide or skin is split over the whole area into

several layers, this process is termed "splitting".  
The layers thus obtained are termed (1) grain split;  
(2) flesh split(inner split); (3) in heavy hides there  
can also be a middle split.

Shrinkage

Temperature

The temperature at which a skin or leather decreases  
in dimensions when heated under a specified condition,  
e.g when heated in water.

Side

The half of the whole cattle hide with the attached  
offal, obtained by dividing it along the line of the  
backbone.

Tannage

A term used in describing a special type of tanning  
method, e.g, chrome tannage, quick tannage.

# MINIMISING THE ENVIRONMENTAL IMPACT OF CHROME TANNING

## CONTENTS

<b>Dedication</b>	<b>i</b>
<b>Abstract</b>	<b>ii</b>
<b>Publication arising out of this Research</b>	<b>v</b>
<b>Acknowledgement</b>	<b>vi</b>
<b>List of Tables</b>	<b>vii</b>
<b>List of Figures</b>	<b>xii</b>
<b>Glossary of Terms</b>	<b>xvi</b>
<b>0 Introduction</b>	<b>1</b>
<b>1. Chapter 1 - History of the development of chrome tanning</b>	<b>7</b>
1.1 Discovery of chrome tanning	7
1.2 Early developments	7
1.3 Commercial marketing of chrome tanning agents	10
1.4 Ready made chrome powder	10
1.5 Self basifying tanning agents	11
1.6 High exhaust chrome tanning systems	12
1.7 Modern developments	12
<b>2. Chapter 2 - General Methodology</b>	<b>17</b>
<b>2. Methodology</b>	<b>17</b>
2.1 Raw materials	17
2.2 Chemicals for tanning	18
2.3 Chemicals for analysis	19
2.4 Methods of chrome tanning	19
2.5 Methods of retanning	22

2.6	Physical testing of leather	24
2.7	Chemical analysis	24
2.8	Separation of chrome species	25
2.9	Removal of sulphate from chrome tanning agents	25
<b>3.</b>	<b>Chapter 3 - The scientific basis of chrome tanning</b>	<b>27</b>
3.1	Nature of raw hides and skins	28
3.2	Nature of chrome tanning agents	38
3.2.1	Hydrolysis, ololation and polymerisation	40
3.2.2	Complex formation	44
3.3	Masking and masking solutions	57
3.4	Theory of chrome tanning	64
<b>4.</b>	<b>Chapter 4 - High exhaust chrome tanning systems</b>	<b>89</b>
4.0	Introduction	89
4.1	High exhaust systems for hides	89
4.2	High exhaust systems for lamb skins	93
4.3	Experimental	94
4.3.1	Hides	94
4.3.2	Lamb skins - series A	98
4.4	Results and discussions	101
4.4.1	General	101
4.4.2	Hides	105
4.4.3	Lamb skins	123
4.5	Experimental - series B : reduced chrome offer	135
4.6	Conclusion	138
4.6.1	Hides	138
4.6.2	Lamb skins	139

<b>5. Chapter 5 - Novel technique of chrome tanning of lamb skins</b>	<b>144</b>
5.0 Introduction	144
5.1 The novel chrome tanning process	145
5.2 Results of small scale trials	148
5.3 Large scale trials	150
5.3.1 Experimental trial 1	150
5.3.2 Results and discussion on trial 1	152
5.4 Experimental trial 2	158
5.4.1 Details of the industrial trial 2	158
5.4.2 Results and discussion on trial 2	160
5.5 Extension of the novel principle to pickle lamb skin tanning	165
5.6 Suggested mechanism	167
5.7 Conclusion	171
<b>6. Chapter 6 - Novel polymeric chrome tanning systems</b>	<b>174</b>
6.0 Introduction	174
6.1 Reduction of sodium sulphate	174
6.2 Reactivity of various chrome complexes	176
6.3 Polymer modification of chromium complexes	180
6.4 Tanning trials with chrome/polyamide complex	189
6.5 Conclusion	201
<b>7. Chapter 7 - Summary and Recommendations</b>	<b>203</b>
7.0 Summary	203
7.3 Recommendations	207
<b>8. Appendix A                      Bibliography</b>	<b>210</b>