MINIMISING THE ENVIRONMENTAL IMPACT OF CHROME TANNING

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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 deliming 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 Cr_2O_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)

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LIST OF TABLES

LIST OF FIGURES

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 smal 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 prepard 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 dimentions 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.

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CONTENTS