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

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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.

MINIMISING THE ENVIRONMENTAL IMPACT OF CHROME TANNING

CONTENTS

Minimising the Environmental Impact of Chrome Tanning

INTRODUCTION

Commercial chrome tanning of hides and skins are carried out at pH 2.5 to 4.0 with trivalent basic chrome sulphate as a tanning agent. The efficiency of chrome utilisation of the process is between 75-85%. The discharge of the waste liquor containing the residual chrome cause environmental concerns for the leather industry as chromium compounds are regarded as hazardous chemicals. Trivalent chromium compounds have very low order of acute toxicity in comparision to the hexavalent compounds[1-3]. Certain hexavalent chromium compounds may be considered carcinogenic to human[4-7] and toxic to plants and animals, and also mobile in soils. Rutland[8] have reviewed extensively on the environmental compatibility of chromium containing tannery and other leather product wastes and stated that trivalent chromium should not be treated as environmentally hazardous chemical. Griffins, *et al* [9]concluded from their extensive studies that landfill disposal of trivalent chromium would not present a pollution problem but that disposal of hexavalent chromium could cause serious problems because of its mobility even at low pH where its adsorption by clay minerals was high. It followed that trivalent chromium could be a pollution hazard if it should be converted into hexavalent chromium. Bartlett and James[10] showed that trivalent chromium could be converted into hexavalent chromium in moist soil containing manganese. The uptake of chromium from the soil by plants depends strongly on the type of plant and the concentration of the chromium within the same plant varies between the different parts of that plant[11]. Ross, *et al* [12] showed from their extensive studies that both Cr(III) and Cr(VI) inhibited microbial activity in soil and suggested that more caution should be employed in handling chromium containg wastes, regardless of the form of the chromium. McCahon and Pascoe[13] showed that the aquatic toxicity of trivalent chrome even though was considerably low at pH 7.8, the toxicity at pH 4.5 was very near to hexavalent chromium. The values given by him were as given below:

Fish toxicity(Lc_{50}) of Chromium,mg/l

pH	Cr^{3+}	Cr^{6+}
7.8	>10000	94
4.5	65	60

Therefore, discharge limits are imposed on total chromium without due regard to valance differences. New Zealand model general bylaws for trade waste[14]recommended a maximum concentration limit for chromium of $5g/m^3$ but suggested allowable higher concentration limit where trivalent chromium makes up a large proportion of the discharge.

Following "state of the art" technology, with the reduction of chrome offer, lower float, higher temperature and pH of tanning, and using improved masking and basifying agents, this absorption of chrome could be further increased to 85-90%. Basically, these have focused on providing additional carboxylic sites for fixing loose chrome or activating the existing sites through enlargement of the chrome complexes to bring these complexes in proximity to the carboxylic groups in the hide protein. Even with this improvement, a tanner cannot comply with the more stringent pollution control specifications for chrome discharge without involving costly chrome pollution treatment plants. This is a constraint on tanneries wanting to sustain growth.

Germann[15] estimated that internationally about 400,000 tons of chrome tanning agents are used annually. As per the present state of the art technology, this would mean that about 60,000 tons of chrome tanning agent remain unutilised during the main chrome tanning and might be discharged into the environment. This research was aimed to overcome this mounting problem of waste chrome disposal from the tanning process by modifying the reagent and technique of tanning to avoid generating waste chrome and sodium salt in the effluent.

Commercial chrome tanning agents are produced from sodium dichromate and therefore equivalent amounts of sodium sulphate are present as an impurity. Gustavson[16] has shown that the presence of sodium sulphate reduced the amount of cationic complexes and increased the corresponding amount of nonionic complexes. This excess salt slowed down the chrome tanning process at the normal pH (2.5-4.0) of conventional chrome tanning. Further, the chrome tanning solution, even though primarily a 33% basic chromium sulphate, always contains various species of chromium complexes. The reactivity of these individual complexes are not clearly understood.

The aim of this study was to look afresh into the basic tanning system. The following alternative approaches were explored to improve the exhaustion of chrome during tanning and minimise its environmental impact:-

1. Improvement of the classical system through the addition of auxiliary chemicals during tanning, or complexes with chromium. Here, the possibilities of improving the availability of carboxylic groups for better fixation of chrome in the skin were explored.

2. Changing the present technology of tanning, ie. no pickle, high pH tanning after deliming. This enabled us to explore the possibilities of releasing more of the carboxylic group of skins at high pH and also the fixation of chrome by non-carboxylic group of the skin, at least initially.

3. Changing the chrome complex itself, ie. removing or modifying the non reactive species of chrome complexes contained in chrome tanning agents. The aim was to remove a major amount of the sodium sulphate impurity present in the commercial chrome tanning agents and to separate and study the reactivity of these individual chrome complexes towards hides and skins and to develop a modified chrome tanning agent to improve chrome fixation.

The following chapters provides the detail of these studies in a systematic manner. Chapter I gives a historical background of the development of chrome tanning. Chapter II gives the general methodology of the research. Chapter III deals with the scientific basis of chrome tanning. High exhaust systems for hides and skins were considered in Chapter IV. These systems included two of the chemicals synthesised and first applied to leather industry by the author. The leaching behaviour of wet blue obtained through these systems for hides and skins were also considered. The chapter provides the scientific explanation of the results of addition of high exhaust auxiliaries and suggest probable mechanism of reaction. In Chapter V a new technique of tanning New Zealand lamb skins, developed by the author has been suggested where in it was established that non carboxylic groups of collagen has a significant role in chrome tanning at high pH. Chapter VI gives the details of the development of a novel polymeric chrome tanning complex and its application in tanning leather. Chapter VII concludes with the summary and recommendation for the minimising the environmental impact of chrome tanning.

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CHAPTER I

HISTORY OF THE DEVELOPMENT OF CHROME TANNING

1.1 Discovery of Chrome Tanning

The tanning effect of chromium salt was discovered by Friedrich Knapp[1] in 1858. But his idea that chrome alum has a leathering effect was then largely ignored. It was not until the end of 1870s and the beginning of 1880s that a leather manufacturing process was industrialised where the need was felt for a faster tanning method than the prevalent vegetable tannages. In 1850, Carl Cavallin[2] patented a tanning process which involved impregnating the delimed hide with a mixture of potassium dichromate and alum and then immersing the hide in a solution of ferrous sulphate. The hexavalent salt was reduced by the ferrous ion to give a combined Iron-chromium tannage. In 1851, Rene de Kercado Molac[3] patented a similar process but indicated the importance of basification of chromium and iron salts to function as a proper tanning agent. He was also the first to indicate that the chrome tanned leather had a tendency to give a hard cracky grain. He suggested that this problem could be solved by drying the leather from a solvent or by impregnating the leather with soap.

1.2 Early Development

A considerable amount of research was carried out in Europe by Heinzerling (1878) and Eitner (1881). Heinzerling first patented[4] a process for tanning by the use of alum and Zinc salt, Chromic acid, potassium ferrocynide, barrium chloride and other ingredients.

During 1879, Heinzerling sat up a company in Frankfurt to exploit this patent. Within a short time, many tanneries took licence to produce chrome tanned leather as Heinzerling claimed a 25% saving in overall costs and a considerable shorter throughput time. But some tanners, shoemakers and researchers including

Eitnerthe Director of the Viennese Leather High School, complained about the poor edge stability, inability to attach soles by pegging and, in particular, the yellow colour which was difficult to cover with the blacking systems formulated for the vegetable tanned leathers[5]. Despite such criticisms, the new tanning process started to gain favour. Heinzerling took out a series of patents in Germany, England and the United States of America[6-11]. Thomson[5] and Rosenbusch[12] have given an excellent account of the early development of chrome tanning.

Rosenbusch described how, from the middle of the 1880s, Heinzerling lost his interest in trying to develop the process further and started to concentrate his efforts in other fields. Gradually, during the last 20 years of the nineteenth century, tanneries relinquished their licences for Heinzerling process. Other chrome tanning systems were developed and what might have been the start of a new era petered out. It was Augustus Schulz (1884) who finally introduced in the USA the first two-bath chrome tanning for hides & skins. In his process[13], the hides & skins after deliming and bating were tumbled in a solution of potassium dichromate and hydrochloric acid until complete penetration of dichromate, after which they were horsed or piled and allowed to drain. They were then tumbled in a solution of sodium thiosulphate, acidified with hydrochloric acid which reduced the dichromate to chromic salt, in which condition, it combined vigorously with the skin protein, yielding a very stable leather. This process is called the two-bath process, so named because the stock was first tanned with a bath of dichromate and then with a bath of thiosulphate and acid. His leather solved his customers immediate needs but Schulz was unable to develop the process further. After seven years unsuccessful experimentation, he sold them to Ludwig Roth, who sold them to Tannage Patent company. Robert Foerderer of this company finally made it a commercial success[14]. Like Knapp and Heinzerling, Foerderer realised that simple chrome tanned leather dried out to give a hard, tinny, cracky-grained product. Instead of applying lubricants in a currying process of vegetable tanning system, he used an emulsion prepared by treating neatsfoot and olive oils with soap. After fatliquoring the leather in the drum, the skins were horsed up to drain and then treated with glycerin on the grain surface to give extra flexibility[15]. During the years that Schultz was trying to develop his process, a series of other patents were published using a wide range of chromium salts. In 1893 alone, 11 patents were granted in America, the most important were those of Martin Dennis[16]. He described a process of tanning the skin directly in a solution of basic chromic chloride along the lines suggested by Knapp in 1958. Because this was done in a single bath, it came to be known as the one-bath tannage. Dennis recognised the possibility of offering leather manufacturer a ready-made chrome tanning material for his one-bath process and founded the first American Company to produce chrome tanning agent[17]. In general, his process was to precipitate chromic hydroxide from a chrome alum solution, redissolving the precipitate in hydrochloric acid and finally adjusting the basicity with sodium carbonate. He marketed a 10% basic chrome chloride solution with the following analytical data[18]:-

10.9%	Chromium Chloride, approximately 33% basicity
2.75%	Sodium Sulphite
1.13%	Sodium Chloride

Discovered in Europe, developed to technical maturity in America, chrome tanning came back to Europe via England in 1896 after Proctor's visit to the USA where he saw the new chrome tanning in practice. Procter[19-20] advocated the new process for light leather production. However, he thought that the method Dennis employed to produce basic chrome tanning agent was complicated and suggested a simple method by the reduction of dichromate with glucose in presence of sulphuric or hydrochloric acid. He also gave a series of lectures to promote chrome tanning and gradually chrome tannage became established towards the end of nineteenth century as a number of tanneries restarted chrome tanning[15].

1.3 Commercial Marketing of Chrome Tanning Agents

The two-bath process developed by Schultz was first used for making shoe upper leather like imitation glace kid from sheep skins, later for the tannage of box calf. The one-bath process extended the application of chrome tanning for the production of all types of leather. The rapid development of chrome tannage was due mainly to the flourishing chemical industry and the availability of large quantity of chromium(III) salts as a by-product of the dyestuffs production which were processed into ready made chrome preparations, mostly basic chromic sulphates. While Borgmann[21] in 1902 mentioned only two ready made chrome tanning agents, one of them being Dennis's product, Wagner and Passler in their manual published in 1925[22] listed 20 different chrome tanning materials encountered in German speaking countries alone. These are chrome tanning materials with 25-38% chrome oxide and a basicity of 33-50% based on chromic sulphate with an alkali salt content between 1-26%. Only one formate masked product was listed. Both solid and liquid tanning agents were available.

1.4 Ready Made Chrome Powder

This was normally believed that the sulphate complexed with chrome during the manufacture of concentrated chrome liquors or powders, must be released again before tannage and therefore, upto the fifties, chrome tanning materials were diluted or dissolved before use. It was a common practice to dissolve powdered chrome tanning materials at 40°C in a ratio of 1:3 to 1:4, left for several hours, preferably overnight, before use. Leather were tanned always with aged chrome solutions, although it was well known[23] that the method of dissolving, hot, cold duration of heating and the age of the solution had an effect on the composition of the tanning liquor and consequently on the tanning action. A fundamental change came with the publication of the research work of Spahrkas and Schmid[24-25] in 1959. They showed that the temporary sulphate masking of spray dried powdered tanning agent could be used with advantage, provided their solubility is good.

The temporary sulphate masking of such spray dried powder depends on temperature of tanning. The higher the temperature, the more quickly the sulphate masking of a freshly prepared solution of a powdered, 33% basic chrome tanning material breaks down and higher the basicity, less pronounced the sulphate masking effect. In addition to dispensing with the need of dissolving the tanning materials separately, the undissolved process has also contributed to the rationalisation of process, basification could be done much earlier and so helping to speed up the tanning process. With all these products, the exhaustion of chrome during tannage remained very low and hardly was better than 60%. By controlling the temperature, pH, float and duration of tannage, the efficiency of tannage could be improved to a certain extent. Spray dried and consequently ready made soluble basic chrome tanning agents paved the path of further development towards the control and improvement of the tanning process.

1.5 Self Basifying Chrome Tanning Agents

At the beginning of sixties, self-basifying chrome tanning agents which had with the tanning powder, built in slow dissolving alkalies, were introduced. Due to the differential particle sizes of this alkalies, like dolomite and limestone (Calcium magnesium carbonate), basification took place slowly over time as particles of different sizes gradually went into solution and basified the chrome. These products had normally 21% Cr_2O_3 and a theoretical basicity 66%[26]. The theoretical basicity was computed from the total utilisation of the alkali included in the powder. In 1966, Spahrkas and Schmid[27] described in detail the products and processes of tanning. These tanning agents enabled the tanner to start the tanning in the evening and leave it running overnight without supervision. These took the industry one step nearer to a 24h work cycle from deliming to wet blue production.

1.6 High Exhaust Chrome Tanning Systems

At the end of the sixties, another type of ready made chrome tanning materials, which did not require for the tanner to basify during tannage, were developed by Erdmann[28]. He discovered that, with formate and alkali, it was possible to obtain from 33% basic chrome sulphate, uniform masked products which do not require additional basification during the course of tanning. Such products have, for example, a basicity of 50% and contain 30% Cr_2O3 [29]. These have extremely high temporary masking effect which is apparently due to the entrance of organic agents into the chrome complex during spray drying. On dissolving in water, this masking breaks down in a similar manner to the sulphate masking. The exhaustion of chrome also improved from 60% to 70-75%.

1.7 Modern Developments

In recent years, due to stricter environmental regulation, tanners and chemical companies made considerable investment in research to improve further the exhaustion of chrome during tanning. This, towards the end of the seventies, lead to the development of new types of chrome tanning materials. These products contain complexing agents like dicarbixylic acids and are based on the same principle as the self basifying chrome tanning agents[30]. These agents may be use in combination of the conventional chrome tanning agents to obtain considerably better exhaustion (80-85%) of tanning floats[31]. DasGupta[32,33] in 1977 introduced a novel concept to improve the hydrothermal stability of chrome tanned leather through the application of a suitable polyfunctional carboxylic acid such as pyromellitic acid (1:2:4:5-benzentetracarboxylic acid), the method in principle being similar to that of the "Bavon" process, developed by Briggs[33,35]. DasGupta[36,37] also patented the application of Oxazolidines in combination with chrome to obtain improved exhaustion and better quality chrome tanned leather. The technique of chrome tanning ,however, remained basically same for a long period. Many claims have been made by the chemical companies, but yet hardly any tannery in the world can comply with the pollution regulations for the discharge of chromium into the water system without, at least, a secondary treatment of tannery effluent, say by co-precipitation, aeration etc. Many tanneries, all over the world have closed down due to this problem.

The aim of this research was to look afresh into the basic tanning systems to improve the exhaustion of chrome and minimise the environmental impact of chrome tanning.

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CHAPTER 2

GENERAL METHODOLOGY

2. METHODOLOGY

The details of the methodology used in various experiments are given in the individual chapter. In general these are as given below:-

2.1 Raw Materials

2.1.1 Hides

New Zealand ox hides (~28 kg) were collected from a local slaughter house and fleshed. These hides were cut into four quarters each and coded. Seven quarters were selected per set at random following incomplete block design. Each set was then allotted to treatments (chemicals), keeping a set as untreated controls. Small scale tanning trials were done with cut pieces from adjacent locations of pickled hides.

2.1.2 Lamb Skins

New Zealand pickled pelts were collected from a local fellmongery and one dozen each was randomly allotted to each treatments, unless other wise stated specifically for any particular experiment. Small scale trials were conducted on matched pieces cut from the opposite sides of the backbone of a pickled lamb pelt.

2.2 Chemicals for Tanning

2.2.1 The following chemicals were used for various tanning trials:-

Trade Name	Chemical	Supplier
Baychrome CP	Masked chrome syntan	Bayer, Germany
Baychrome 2420	Highly masked chromed syntan	Bayer, Germany
Chrome tanning agent	Basic chrome sulphate (12 - 15% Cr_2O_3, 33% Basic)	Chrome and Chemicals (NZ) Ltd, Auckland
Chromosol BS	Chrome tanning agent (25% Cr_2O_3, 33% Basic)	Bayer, Germany
Cromeno A	Acrylic polymer	Rohm Tech, Germany
Cromeno FN	MgO	Rohm Tech, Germany
Feliderm CSN	Glyoxal, modified	Hoechst, Germany
Imlenal DC	Dicarboxylic acid	BASF, Germany
Isophthalic acid	- This was converted into a mixed salts, partly with caustic soda and partly with ammonia	Amoco Chemicals Corporation, USA
Polyamide	Synthesised from adepic acid and amine	
Neosyn EE	Neutral syntan	Hodgson Chemicals, UK
Nutrol DP	Disodium phthalate	Hodgson Chemicals, UK
Tannachrome S	Chrome tanning agent	Chrome and Chemicals (NZ) Ltd, Auckland
Uberol 8027	Mixture of polycarboxylic acid	Carpetex, Germany
Zolodine ZE	Oxazolidine E	Angus Chemicals, USA - synthesised and patented by the author
Zolodine ZA-78	Oxazolidine A	Angus Chemicals, USA - synthesised and patented by the author

2.3 Chemicals for Analysis

2.3.1 All chemicals used for analysis were laboratory reagent grade chemicals.

2.4 Methods of Chrome Tanning

2.4.1 Hide

A standard method[1] as given below was followed in all cases. Where advised by the chemical supplier modifications required were carried out to suit the product.

Method for Chrome Tanning of Hides

OPERATION	%	CHEMICAL	TEMP °C	RUNNING DETAILS
Raw Material = Green or wet salted cattle hides. Cut as required.				
Weigh Sides				
Add	300%	Water	20	
	+ 0.1%	Sodium Hydroxide		
	+ 0.03%	Imprapell CO		
	+ 0.2%	Teric GN9		7rpm, 10/50 overnight
Drain				
Add	300%	Water	28	1 hour
Drain				
Flesh				
Trim				
Reweigh				
Add	25%	Water	20	
	+ 1.5%	Sodium Hydrosulphide		
	+ 0.7%	Sodium Carbonate		
	+ 0.2%	Teric GN9		7 rpm, 1 hour
Add	3.0%	Lime		30/30, 2.5 hours
Add	25%	Water	26	5/12, 20 minutes
Add	25%	Water	26	5/15, 20 minutes
Add	25%	Water	26	5/15, 20 minutes
Add	50%	Water	26	2/28, O/N.
Drain				
Add	200%	Water	28	10 minutes
Drain				
Add	200%	Water	28	10 minutes

... cont

OPERATION	%	CHEMICAL	TEMP °C	RUNNING DETAILS
Drain				
Add	100%	Water	28	
	+ 0.1%	Hydrochloric Acid		10 minutes
Drain				
Add	50%	Water	30	
	+ 3.5%	Ammonium Chloride		
	+ 0.2%	Teric GN9		7 rpm, 15 minutes
Add	0.5%	Formic Acid		14 rpm, 30 minutes
Check pH = 8.0 to 9.0 : pH = _____				
Add	50%	Water	30	
	+ 0.05%	Tryptec		14 rpm, 30 minutes
check pH = 8.0 to 9.0 : pH = _____				
check cut through neck with Phenolphthalein - COLOURLESS : _____				
Drain				
Add	200%	Water	20	15 minutes
Drain				
Add	200%	Water	20	15 minutes
Drain				
Add	60%	Water	20	
	+ 8.0%	Salt		10 minutes
Add	10%	Water	20	
	+ 1.0%	Sulphuric Acid		
	+ 1.0%	Formic Acid		2 hours
check pH = 2.9 to 3.1 : pH = _____				
Check cut through neck with BCG = YELLOW : _____				
Add	7.0%	33% Basic Chrome Powder		1 hour
	+ 0.6%	Tanbase		30 minutes
Run		Heating to 40°C		Overnight
Check pH = 3.6 to 3.8 : pH = _____				
Check degree of tannage:		- Chrome Penetration - 2 minute Boil Test (Shrinkage < 5%) : _____		
Drain				
Add	100%	Water	40	
	+ 0.05%	Busan 1034		45 minutes
Drain				
Horse Overnight				
Samme/Set, Split and Shave				

2.4.2 *Lamb skins*

A standard method[2] as given below was followed in all cases. Where advised by the chemical supplier modifications required were carried out to suit the product.

Method for Chrome Tanning of Lamb Skins

OPERATION	%	CHEMICAL	TEMP °C	RUNNING DETAILS
Weigh Pickle Pelt				
Add	200%	Water	20	
	+ 20%	Salt		2 hours FAST
	+ 0.25%	Teric GN9		
Drain				
Flesh				
Trim				
Reweigh Skins				
Add	50%	Water	35	
	+ 5%	Salt		10 minutes
Add	4%	Iragol DA		20 minutes
Add	100%	Water	35	
	+ 6%	Salt		60 minutes
Drain				
Wash	100%	Water	35	
	+ 6%	Salt		10 minutes
Repeat Wash 5 more times				
Drain				
Chrome Tan :	100%	Water	20	
Add	+ 8%	Salt		
	+ 1.0%	Nutrol DP		
	+ 1.0%	Formic Acid		10 minutes
Check pH = 3.0 to 3.2 : pH = ______				
Add	5.0%	33% Basic Cr PDR		
	+ 0.1%	Unislip		Run 1 hour
	+ 0.5%	Tanbase		Run 30 minutes
Run		Heating to 40°C Slow Overnight		
Check pH = 3.5 to 3.7 : pH = ______				
Check degree of tannage : - Chrome Penetration : ______ - 2 minute Boil Test (shrinkage < 5%) : ______				
Drain				
Refloat	100%	Water	20	
	+ 0.06%	Busan 1034		30 minutes

Drain
Horse Overnight
Samme and Shave where required

2.5 Methods of Retanning

2.5.1 Side

A standard method[3] as given below was followed for retanning of all side leather.

Method for Retanning of Side Leather

OPERATION	%	CHEMICAL	TEMP (°C)	RUNNING DETAILS
Weigh Sides				
Add	150%	water		
	0.25%	GN9	40	10 minutes
Check pH				
Drain				
Add	100%	water	50	
	+ 0.25%	sodium bicarbonate		
	+ 1.5%	sodium formate		40 minutes
Check pH = 4.5 - 5.0 pH = ______				
Check cut through neck with BCG = Green: ______				
Add	+ 2.0%	Mimosa extract powder		
	+ 3.0%	Neosyn PFW		
	+ 3.0%	Retingan R7		
	+ 50%	water		45 minutes
Drain				
Add	100%	water	50	
	+ 0.5%	Sandolix WWL		5 minutes
Add	1%	Dermalight Black PL-RS		30 minutes
Add	20%	water	60	
	+ 5.0%	Remsynol SWM		
	+ 2.0%	Trisul ML		
	+ 0.5%	Derminol Oil NS		30 minutes
Add	+ 0.5%	Formic Acid		15 minutes
Check pH = 3.8 - 4.0 : pH = ______				
Add	1.0%	Lipamin Liquor SO		15 minutes
Drain				
Rinse	300%	water	25	10 minutes
Take out, Samme, Set and Dry - Condition and Stake				

2.5.2 *Lamb skins*

A standard method[4] as given below was followed for retanning of all lamb skins.

Method of Retanning of Lambskins

OPERATION	%	CHEMICAL	TEMP (°C)	RUNNING DETAILS/TIME
RAW MATERIAL = WET BLUE LAMB PELTS				
Weigh Skins				
WET BACK	200%	Water	30	
	+ 0.2%	Teric GN9		10 minutes
Drain				
Neutralise	150%	Water	30	
	+ 1.0%	Sodium Formate		
	+ 0.5%	Sodium Bicarbonate		60 minutes
Check pH = 4.9 to 5.1 : pH =				
Check cut through neck with BCG = GREEN:				
Retan				
Add	6.0%	Neosyn PFW		30 minutes
Drain				
Add	300%	Water	50	10 minutes
Drain				
Dye	100%	Water	60	
	+ 0.2%	Ammonia		10 minutes
Add	0.6%	Dermacarbon Black		
Run		Heating to 60°C		45 minutes
Add	20%	Water	60	
	+ 8.0%	Remsynol SWM		30 minutes
Add	5.0%	Water	60	
	+ 0.5%	Formic Acid		20 minutes
Check pH = 3.5 to 3.7 : pH =				
Drain				
Add	300%	Water	20	15 minutes
Take out, Samme, Set and Dry - Condition and Stake				

2.6 Physical Testing of Leather

2.6.1 All physical tests were conducted on the crust leather conditioned and tested as per the following methods prescribed by the International Union of Leather Technologists and Chemists, UK:-

Shrinkage Temperature, 0°C	IUP/16[5]
Distention at Grain Crack, mm	IUP/9[6]
Load at Grain Crack, kg	IUP/9[6]
Tear Strength, N/mm	IUP/8[7]
Tensile Strength, N/mm^2	IUP/6[8]
Elongation at Break, %	IUP/6[8]

2.6.2 Softness

This was measured with BLC ST300 Softness Tester, British Leather Confederation, UK.

2.6.3 Colour Values

CIELAB Colour values of wet blue and crust leather were measured with Microflash 200d, Colour Meter of Data Colour International Ltd, USA.

2.7 Chemical Analysis

2.7.1 Chrome content in wet blue and crust leather were determined by the method prescribed in IUC 8 of the International Union of Leather Technologists and Chemists[9].

2.7.2 Chrome content in liquor samples were determined by Atomic Absorption spectrophotometer, Shimadzu model AA670.

2.7.3 The absorption of Various fractions of chrome liquors were analysed with UV/VIS spectrophotometer, Shimadzu model UV-160A.

2.8 Separation of Chromium Species

2.8.1 Separation of various species of chrome from commercial chrome tanning agents were carried out initially with ion exchange chromatography, SP Saphadex C 25 and gel filtration with SP Saphadex G 25(Pharmacia Diagnostics, Switzerland) with 0 - 5.0 M Sodium chloride or with 0 - 5.0 M Sodium nitrate as eluent and checked with HPLC, Shimadzu model LC-4A. This was not very successful. Finally, separation of species were carried out with cationic exchange resin, Dowex 50 W x 8 (Sodium form) and anionic exchange resin, Dowex 1X8 - 50 with 0 - 4 N HCl or 0 - 5N NaCl as eluent. Tanning tests were conducted with fractions eluted with 0 - 5 N NaCl to determine their respective tanning activity on pickled lamb pelts and pickled cow hides.

2.9 Removal of Sulphate from Chrome Tanning Agents

2.9.1 Removal of sodium sulphate from the commercial chrome tanning agent was carried out by simply crystallising out at low temperature. The chrome solution was cooled in stages, first at -5 to -7°C, filtered and then further cooled to - 10°C and refiltered to remove the crystallised sodium sulphate.

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CHAPTER 3

THE SCIENTIFIC BASIS OF CHROME TANNING

3. THE SCIENTIFIC BASIS OF CHROME TANNING

The process by which the putrescible raw hides and skins are converted into a substance which does not putrify, dries out soft and does not swell when wetted back is called tanning[1]. The raw hides and skins after such treatment is called leather and the agent through which this transformation takes place is called tanning agent. When chromium salt is used as a tanning agent, the process is called chrome tanning. Chemically, the conversion takes place through a series of cross-linking inside the fibre matrix which renders them stable to moist heat and putrifaction. Different tanning agents impart different characteristics to leather. Chrome tanning gives leather with the following characteristics:-

- high shrinkage temperature (100 - 120°C)
- high hydrothermal stability
- good flexibility
- less full leather
- poor perspiration resistance
- poor buffing properties
- excellent fastness properties
- good comfort characteristics
- good moulding and shape retention properties

Different theories of chrome tanning were suggested by different researchers at different times to explain these facts and most of them were ruled out one after another as our knowledge increased. Chrome tanning, basically is the reaction between two macro molecules, namely collagen, which is a natural polymer consisting of various amino acids, and chrome tanning agents, which contain various species of chrome complexes. To understand the chemical mechanism of chrome tanning we should therefore look into these two substrates briefly.

3.1 Nature of Raw Hides and Skins

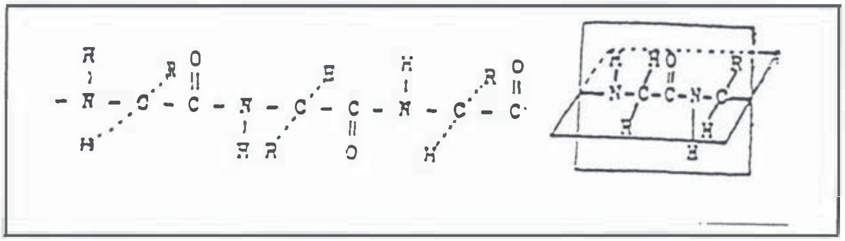
Hides and skins are made of proteins, fats, carbohydrates, mineral matters and water. In tanning, the protein which is of foremost importance is collagen. At present at least 19 different types of collagen are known[2]. Structures and functions of collagen type I through type X are collected in a monograph edited by Maine and Burgeson[3]. Nimni[4] has published a more comprehensive collection of data. Heidemann[2] has recently published an excellent review of our present knowledge of collagen. All proteins including collagen are made up of eighteen to twenty different amino acids. Collagen contains a number of basic and acidic groups. Macro molecules of a protein is made up of polypeptide chains which are formed by the elimination of water between the carboxyl (COOH) and amino (NH_2) groups of a large number of alpha amino acids.

$$\begin{array}{l} NH_2 \\ | \\ CH\text{-}R \\ | \\ COOH \end{array}$$

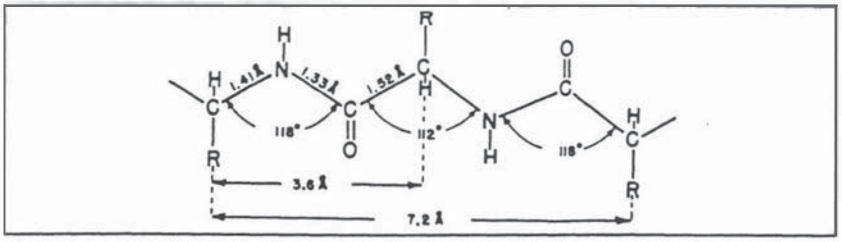
In forming the protein molecules the -COOH group of one amino acid combine with the NH_2 group of the second amino acid. The two molecules are thus linked up together by -CO.NH- or amide linkage with the elimination of one molecule of water. A large number of amino acids are linked up in this way forming a long chain, known as polypeptide chain which constitutes the structure of protein that may be represented as follows:-

$$\begin{array}{l} NH_2 - CH.R^1.\ CO[OH + H]\ NH.CH.R^2.CO.\ [OH + H]\ NH.CHR^3.COOH \\ \quad \rightarrow NH_2.CH.R^1.CO.NH.CH.R^2.CO.NH.CH.R^3CO- \end{array}$$

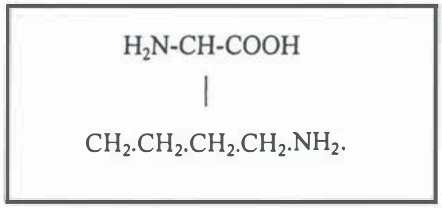
The groupings -CO.NH- and -NHCHR.CO- within the chain are respectively called “amide link” and “amino acid residue”. A large number of these are present in the protein molecule. The polypeptide chain are three dimensional structures, the hydrogen and oxygen atoms of the amide groups form a two dimensional plane with the -N-C-C- chain. The side chains and hydrogen atoms attached to alpha-carbon atoms form another two dimensional plane which isnearly at right angles to the former. This is represented in the diagram below



The spatial configuration of the amino acid residues in the protein chain is a zig-zag structure with R groups alternately above and below the -N-C-C- plane. The bond distances and the bond angles are also fixed. This zig-zag structure is represented by the following formula:-

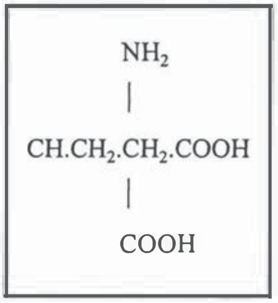


The repeated -N-C-C- unit forms the backbone of the polypeptide and is the characteristic for the structure of all kinds of protein. In the generalised polypeptide formula of protein stated above, R is representative of individual and distinctive portion of the amino acid molecule. The R groups of the side chain may be widely different in chemical character, from R = H to strongly polar groups of acidic or basic function. Thus, when a polypeptide is composed of a single amino acid like glycine $NH_2.CH_2.COOH$, the R group consists of a H atom only. But when a polypeptide chain is composed of a complex amino acid, R may contain many radicals of either aliphatic or aromatic compounds having free amino (NH_2) or carboxylic (COOH) groups. Thus, when a polypeptide is composed of the amino acid Lysine, [$HN_2.CH_2.CH_2.CH_2.$ $CH_2.CH(NH_2).COOH$], R will consist of the long side chain $NH_2.CH_2.CH_2.CH_2.CH_2$ and there will be a free NH_2 group in this which is positively charged:-



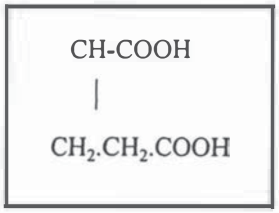
$$\begin{array}{c} H_2N\text{-}CH\text{-}COOH \\ | \\ CH_2.CH_2.CH_2.CH_2.NH_2. \end{array}$$

Similarly, when a polypeptide chain is composed of the amino acid glutamic acid,



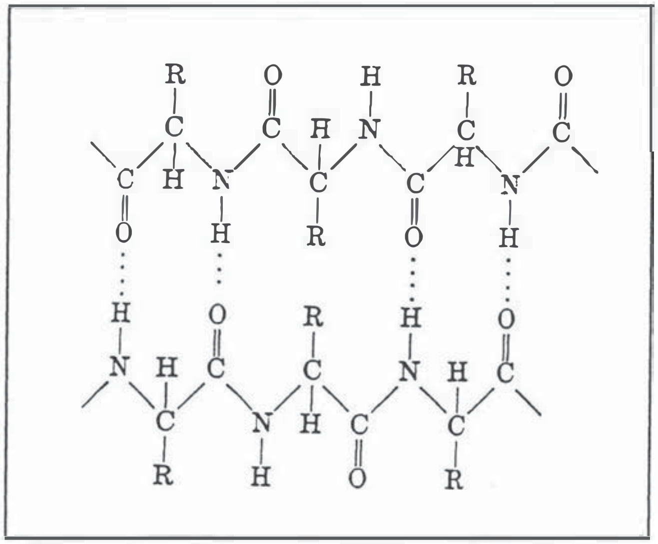
$$\begin{array}{l} \quad NH_2 \\ \quad | \\ CH.CH_2.CH_2.COOH \\ \quad | \\ \quad COOH \end{array}$$

R will consist of $CH_2.CH_2.COOH$ containing a free carboxyl group which is negatively charged



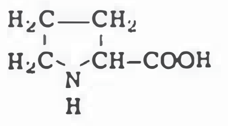
$$\begin{array}{l} \quad CH\text{-}COOH \\ \quad | \\ CH_2.CH_2.COOH \end{array}$$

The polypeptide chains of protein molecules or micelles are orientated parallel to the fibre axis and are also parallel to one another. They are held tightly together by means of co-ordinate bonds or hydrogen bridges between -CO- and -NH- groups of the peptide chains. This arrangement is represented by the following graphic formula:-

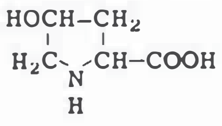


Arranged in this way the peptide chain forms a two dimensional plane. Such individual planes are again held tight by cross-linkages formed between the projected side chains of the different planes.

The amino acid composition, first reported in full in 1948, is now well established. It has been shown that, regardless of species and the tissue from which they come, all mammalian collagen fibres have a similar and characteristic composition in which glycine, the simplest amino acid constitutes one third of the total residues and the amino acids proline and hydroxyproline a further 25% [5,6].



Proline



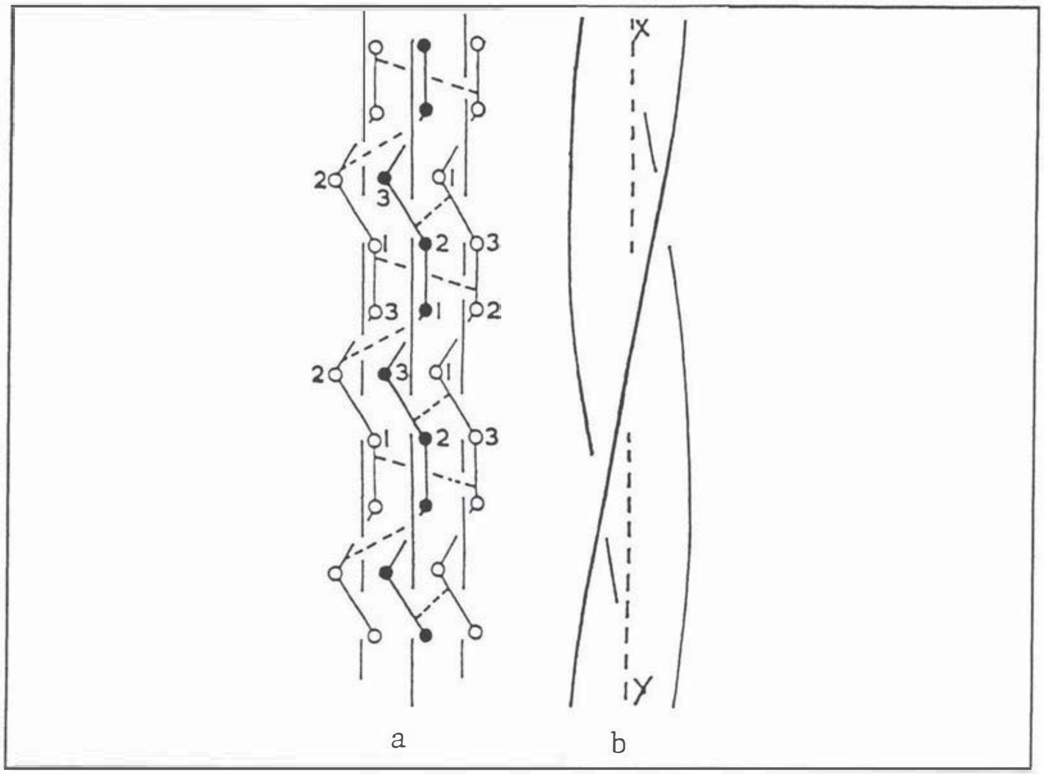
Hydroxyproline

With these, the ring structure is built into the chain when the peptide bond is formed. This leads to certain restrictions on the folding of the chain and is responsible for the specific configuration of collagen molecule. The high hydroxyproline (14%) is characteristic of collagen which contain no cystine (the amino acid characteristic of wool and hair), no tryptophan and only small amounts of other essential aromatic amino acids, tyrosine and phenylalanine. Considerable information is now available on the sequence of the amino acids in the three polypeptide chains which make up the collagen macro molecule.

Studies of the partial degradation of collagen with acids and enzymes has demonstrated the wide spread distribution of glycine, which has been found to be linked to all the amino acids including itself, and the frequent occurrence of a peptide, Gly-Pro-X, where X is often hydroxyproline. The general picture is of a chain built up of alternating sequence of peptides containing predominantly neutral amino acids with polar regions containing acidic and basic residues.

Collagen gives a characteristic X-ray diffraction pattern and shows a specific banded appearance in the electron microscope. Both of these have been instrumental in arriving at the present accepted structure of this protein. It is now accepted that the collagen macro molecule, referred to as tropocollagen, is a stiff rod-like structure about 2800 A long and 14 - 15 A in diameter with a molecular weight of 280,000 to 300,000. It is composed of three polypeptide chains of approximately equal length with their terminal amino acid residues[7,8,9,10], two of these chains designated α_1, are the same in composition and the third, α_2, is slightly different. The restrictions imposed by their high proline and hydroxyporline content causes each of these individual chains to coil into a helix characteristic of the polymer, poly-1-proline. Each chain has a left handed helical twist, taking approximately 3.3 amino acid residues to make one complete (360 degrees) rotation about the polypeptide helical long axis[11]. The three chains are then twisted about a central axis to give a slight right handed super helix as shown in Figure 3.1.

Figure 3.1:Coiled Structure of the Collagen Molecule



(a) Three polypeptide chains each twisted into a helix. The two outer chains are in the plane of the paper and the central one is placed in front of these. The circles represent amino acid residues and the lines peptide bonds. The numbers 1, 2 and 3 indicate different types of side chain positions; for steric reasons position 1, which is located near the main axis X-Y, must be occupied by a glycine residue in which the side chain is hydrogen. Dotted lines represent hydrogen bonds.

(b) Shows the deformation when the three chains are twisted about the common axis XY to give the super helix. The lines represent the axes of the three individual chains.

The small amino acid, glycine, which occurs at every third residue and which for steric reasons must occupy position 1, allows the three chains to come close enough together for hydrogen bonding to occur between the -C = group of one chain and -NH- group of the other as in the polymer polyglycine. In this way a very stable and compact structure is obtained. The main feature of the collagen triple helix were defined mainly from the wide angle X-ray by Ramachandran[7] and by Rich and Crick[12]. It takes 27-29 amino acid residues depending upon the model used, for a single polypeptide chain to make one complete rotation about the triple helical axis. At the amino terminal end of each of the three chains of the molecule there is a length of uncharacteristic amino acid composition containing some fifteen residues.

These telopeptides contain no proline or hydroxyproline and this area is therefore, not in the specific helical configuration of the main bulk of the molecule. Both intra and intermolecular cross-links have been shown to be located in this area. There have been suggestions that similar non-helical peptides also protrude from the body of the molecule but so far no direct evidence for this has been obtained. Soluble collagen obtained from extraction of skins of young animals with neutral salts or dilute acetic acid, when heated at 37-40°C shows a sharp change of properties due to collapse of helical structure.

Tropocollagen aggregate in a highly specific way to give native fibrils, each molecule overlaps its neighbour by one quarter of its length. The banded structure seen in the electron microscope results from this regular packing which gives rise to dense and less dense areas.

The dark bands as shown in Figure 3.2 represent the less dense areas into which the stains used in the preparation of the material for electron microscope can penetrate and light bands the more dense areas where it cannot.

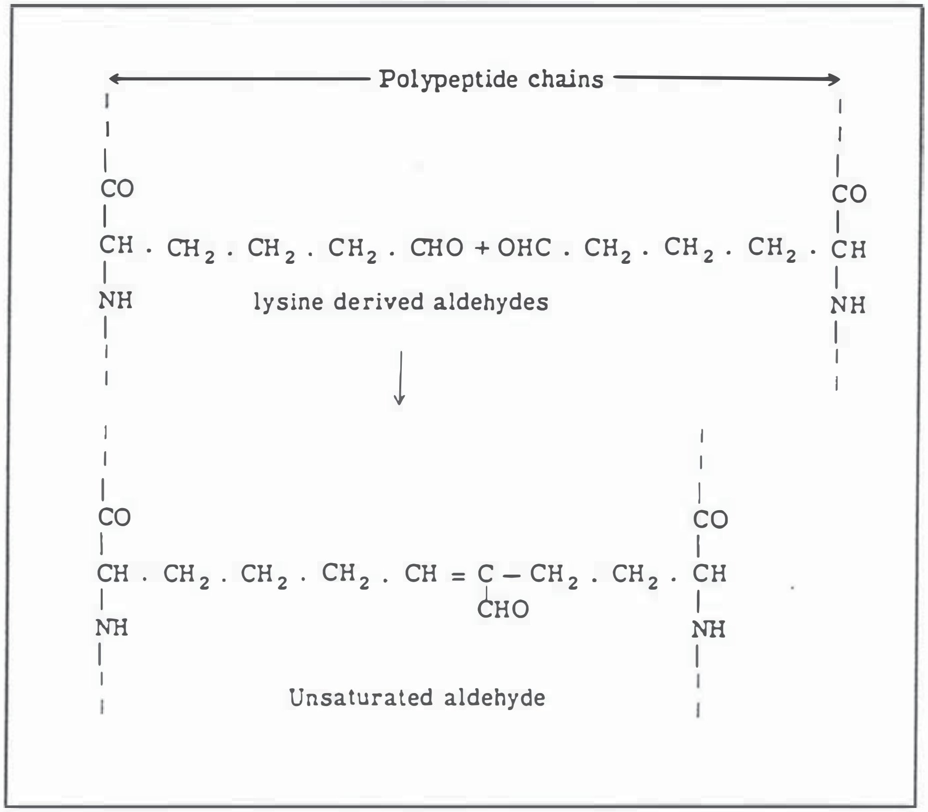
Figure 3.2: Electron micrograph of collagen fibrils from skin showing banded structure due to regular packing of the molecules*.

* reproduced from *J. BLMRA*[11]

About 5,000 molecules are required to make up fibrils of this diameter. Magnification approximately 20,000 times.

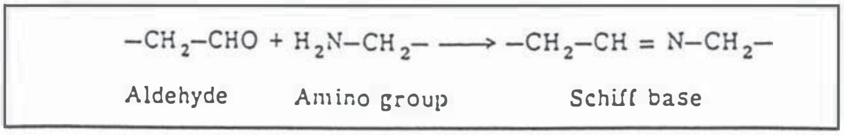
The fibrils are further stabilised as shown in Figure 3.3 through cross linking of two lysine residues in the telopeptides to the corresponding aldehydes and the aldol condensation of these to give an unsaturated aldehyde.

Figure 3.3: Aldol condensation of two lysine derived aldehydes



The intermolecular bonds are considered to arise from the interaction of this unsaturated aldehydes or another aldehyde derived from lysine in the third chain with an amino group in another molecule to give shift bases as given in Figure 3.4. Recently, Chen, Feairheller and Brown[13,14] have applied molecular modelling methods to the development of three dimensional structures of Type I collagen triple helices to better our understanding of the specific nature of the reaction of chromium and other agents with collagen.

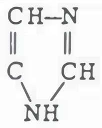
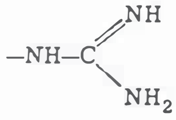
Figure 3.4: Formation of a Schiff base by condensation of an aldehyde with an amino group of lysine



$$-CH_2-CHO + H_2N-CH_2- \longrightarrow -CH_2-CH = N-CH_2-$$

Thus to summarise, we have a picture of a very long molecule composed of three chains twisted together rather like a three-stranded rope. At one end there is an area in which the three chains are frayed. These rope-like structures are then arranged in parallel array overlapping each other by a quarter of their length and are joined together by cross-links, one end of which originates in the disorganised telopeptide or frayed area. For the presence of reactive amino acid side chains given in Table 3.1, collagen behaves like a complex chemical and is capable of reacting with a variety of compounds.

Table 3.1: Reactive groups of collagen

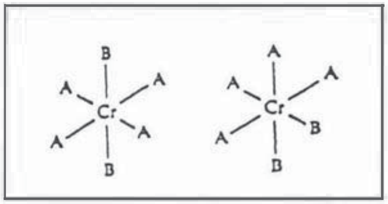
Amino acid	Reactive group	Amount present moles per 10^5g
Histidine	 Imidiazole	4.5
Lysine and hydroxylysine	$-NH_2$ Amino	27.1 7.0
Arginine	 Guanidyl	47.2
Aspartic and glutamic acid	$-COOH$ Carboxyl	52.2 75.6
Tyrosine	 Phenolic Hydroxyl	5.4

The reactive side chains all protrude from the surface of the three stranded helical molecule and are therefore fairly readily accessible to most chemical reagents. Because collagen contains acidic and basic groups it combines with a specific amount of acid or alkali. In the pH range 5 to 8 both acidic and basic groups are charged; as the pH is decreased, carboxylic groups combine with hydrogen ions and the protein carries an excess positive charge, and as the pH is raised above 8, hydrogen ions are lost from the basic groups and protein becomes negatively charged. From the knowledge of the total number of acidic and basic groups and the range in which they titrate it is possible to make an estimate of the amount of acid or alkali required to bring a given amount of pelt to any pH value. The acidic and basic groups are also concerned with the uptake of tanning agents and other compounds. Chromium combines with charged carboxyl groups and the amount taken up is governed by the number of these groups available during particular pH of chrome tanning. Raising the pH from 2 or 3 to 4 therefore facilitates uptake of chromium. The action depends on the introduction of a relatively small number of stable crosslinks. Since the reactive groups stick outwards from the molecule it is probable that in the main these cross links are inter rather than intramolecular and the final structure is lattice-like.

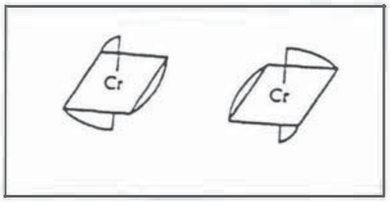
3.2 Nature of Chrome Tanning Agents

Tanning materials except in the case of aldehydes are very complex chemicals. None of them are a single chemical like ordinary salt or bases in the normal chemical sense. They are mostly polynuclear complexes having different tanning potency. Further, this becomes complicated when we consider the commercial tanning agents. Most of them are agglomeration of various species of a generic complex chemical.

Chromium has an atomic number of 24 and atomic weight 52, with an electronic structure of $1s^2$, $2s^2$, sp^6, $3s^2$, $3p^6$, $3d^5$, $4s^1$ electrons[15]. Chromium is unique in having six unpaired electrons in its outer valence shells. The closeness of the energy levels of these six valence electrons gives rise to variable valency, the most common states being Cr_3^+ and Cr_6^+, with the latter usually encountered as an oxygenated anion CrO_4^{--}. Chromium may lose 2 electrons to form chromous compounds, 3 electrons to form chromic compounds, or 6 electrons to form the chromates. Chromous compounds are easily oxidised and, for this reason, are of little practical value in the leather field. The chromic compounds include the basic chromium slats which are of major interest to leather chemists. In chromium, there are six positions available for co-ordination and twelve co-ordination electrons can be accommodated. The six positions are identical and they lie at the six corners of a regular octahedron. When the legends are dissimilar, stereo-isomers may be obtained:-



Bidentated ligends, ie. those capable of donating two pairs of electrons from different parts of the ligand molecule, may form chelated complexes with isomeric forms:-



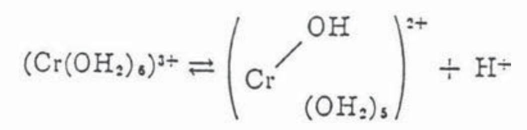
X-ray diffraction studies indicate that in the solid crystalline state, the six co-ordination positions are occupied by ligands. In aqueous solution, experiments with water enriched with heavy oxygen, H_2O^{18} also established that there are six water molecules directly attached to chromium[16]. The simplest complex cation, hexaquochromium, $[Cr(OH_2)6]^{3+}$, carries as a result of electron transfer, three positive electrovalent charges. The linking of the water molecule to the chromium atom takes place by means of the oxygen atom of the OH_2 molecule, each of which contributes two electrons, forming a co-ordinate bond with the chromium atom. Irving[17] in an attempt to find how firmly the water molecules are attached in the hydrated ion $Cr(H_2O)_6^{3+}$ studied the exchange reaction between these ions and water enriched with heavy oxygen:-

$$Cr(H_2O)_6^{3+} + H_2O^{18} \rightleftharpoons Cr(H_2O)_5(H_2O^{18})^{3+} + H_2O$$

and showed that the half-life for isotopic exchange was very long, 54h at 27°C compared to about 10^{-2} sec for $Al(H_2O)_6^{3+}$

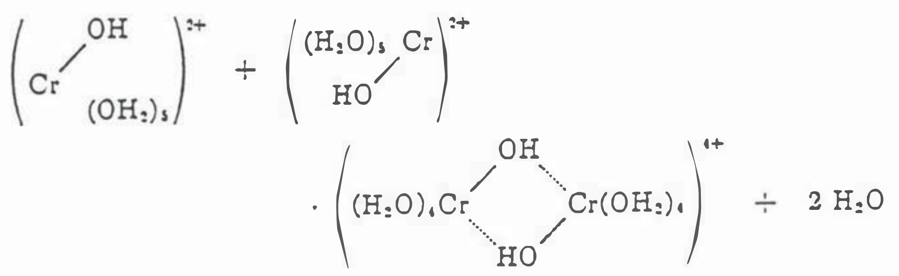
3.2.1 Hydrolysis, Olation, Oxolation and Polymerisation

The penetration of anions in the chrome complexes in aqueous solutions is accompanied by a series of other reactions involving hydrolysis and molecular association. By introduction of a hydroxyl group in the complex, due to the release of a proton to the solution, hydroxy compounds are formed[18]. The net positive charge on the complex is thus reduced by one unit, as shown by the formula:-



$$(Cr(OH_2)_6)^{3+} \rightleftharpoons \left(Cr(OH)(OH_2)_5\right)^{2+} + H^+$$

The hydroxy compound originally formed stabilises itself by forming a double co-ordinate bond between two chromium atoms[19,20] as shown below:-



This is termed olation and the link, the Ol linkage. An “olated” chromium complex is therefore one in which one or more of the hydroxyl group is held between two chromium atoms by a primary valence of one and a secondary valance of the other. The olation of a chromium complex is accompanied by an increase in molecular weight and by an increase in the resistance of the OH group to acid titration. The addition of alkali to the solution facilitates the protolysis of the salt owing to the removal of protons. The equilibrium will hence be displaced in favour of the hydroxy compound. The reaction of chromium with the OH takes place in stages. The tendency of the first step of the reaction is very strong, and even at pH 2 (a concentration of OH in the solution of 10^{-12}), the chromium will hold the first OH group. As the pH is raised to pH 3-4 by the addition of more alkali, the second OH group enters into the reaction. Near pH 4 the third OH group enters into the reaction but to complete the reaction it is necessary to raise the pH to about 8 or 9 and to bring the temperature of the solution to boil.

$$[Cr]^{+3} + OH^{-} \rightleftharpoons [Cr-OH]^{++}$$

pH 2.0 and below—approximately

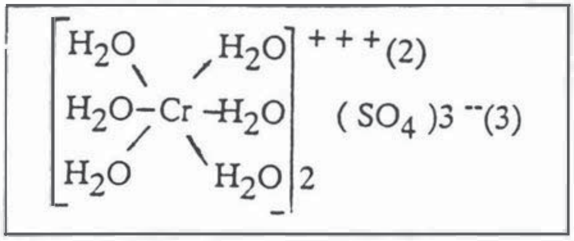
$$[Cr-OH]^{++} + OH^{-} \rightleftharpoons [Cr(OH)_2]^{+}$$

pH 2.0–pH 4.0—approximately

$$[Cr(OH)_2]^{++} + OH^{-} \longrightarrow [Cr(OH)_3]^{0} \downarrow \text{ppt}$$

pH 4.0–pH 8 or 10 may require heat

The di or polynuclear complexes thus formed are called basic salts. The percent of the primary valence bonds of chromium in solution occupied by OH group is called the basicity of the solution. Thus, chromium sulphate or chloride as known to general chemists has no tanning power.



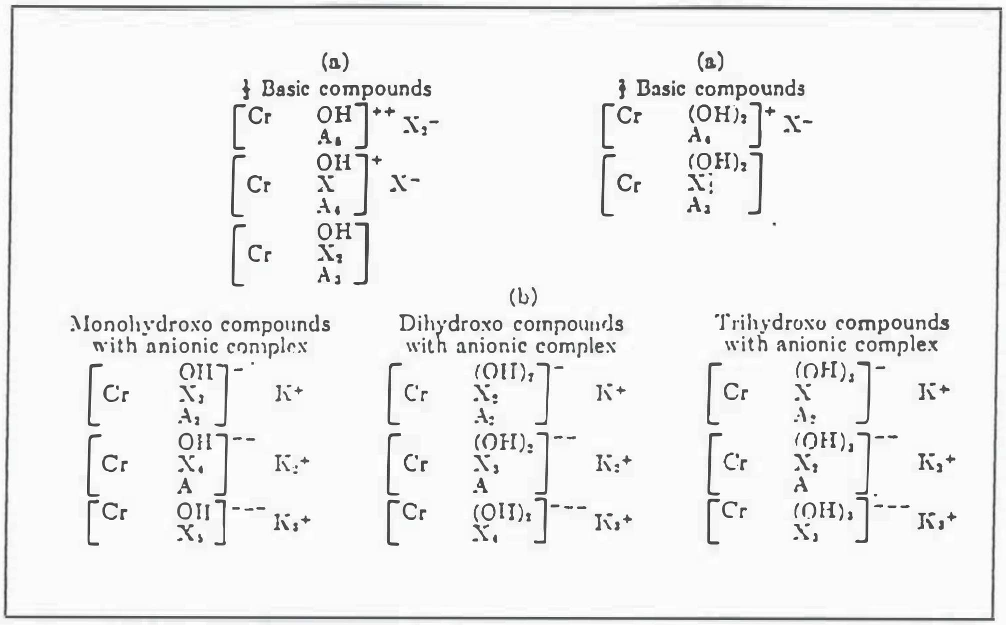
These hexaquo compounds can not act as an ion and exhibit its basic properties owing to its close linkage with the central atom. But these compounds can exhibit basic properties that is tanning power, if hydrolysis is promoted by neutralisation of the free acid formed during hydrolysis. Thus, if an alkali is added to these normal salts, the acid formed is neutralised leading to the increased hydrolysis, formation of basic salts and penetration of hydroxyl into the complex. The hydroxo salt so formed can act as a "tan".

$$\boxed{[(H_2O)_6.Cr]_2\,(SO_4)_3 \rightleftharpoons 2[(H_2O)_5Cr.OH]\,SO_4 + H_2SO_4}$$

With increasing hydroxyl content or basicity, there is an increasing tendency towards insolubility, since greater hydroxyl content favour olation. Staisny[19] differentiated the two types of basic compounds, namely:-

(a) a chrome complex which is either positively charged or is neutral

(b) a chrome complex which is negatively charged, as shown below, where A stands for aquo group and X any acid anion:-



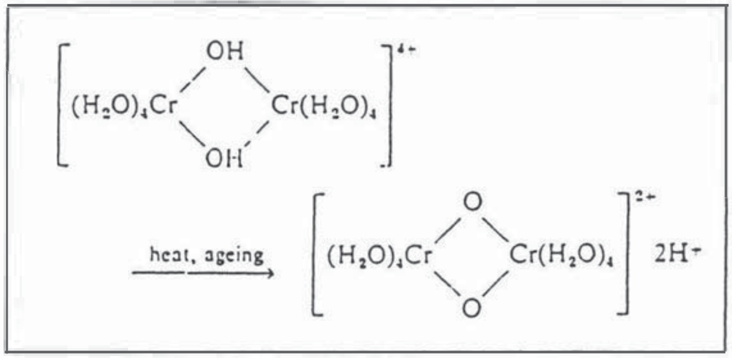
A further distinction between (a) and (b) could be found in their reaction to alkali. Addition of alkali to the cationic compound reduces its positive charge, thus:-

$$\boxed{[CrA_5OH]^{++} \rightarrow [CrA_4(OH)_2]^{+} \rightarrow [CrA_3(OH)_3]}$$

As these compounds approach the hydroxide state, their solubility decreases and their tanning astringency increases. When alkali is added to anionic complexes, their negative charge is increased, solubility increased and tanning power lowered:-

$$\boxed{[CrA_2X_3(OH)]^{-} \rightarrow [CrAX_3(OH)_2]^{--} \rightarrow [CrX_3(OH)_3]^{---}}$$

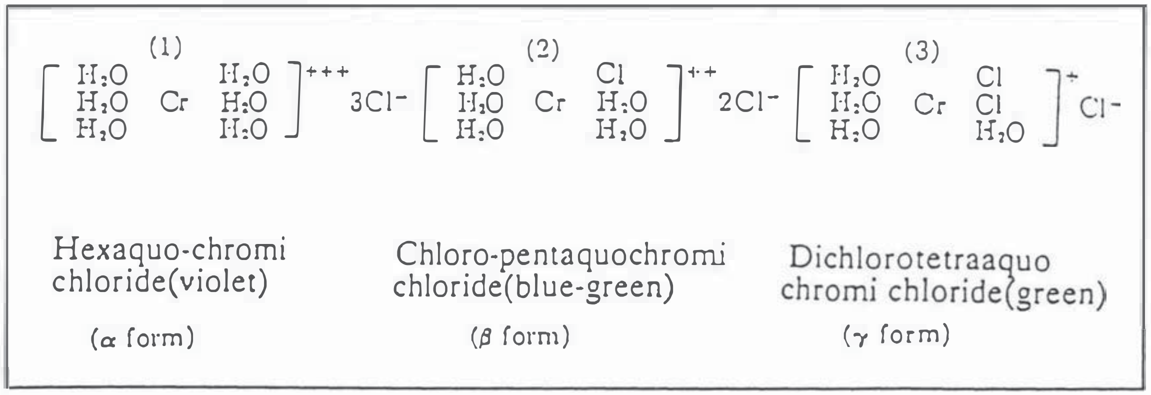
Stiasny[19] first observed that the solutions of chromium salts on ageing becomes more acidic, while heating made the salts less soluble. To account for this, he suggested the reaction of oxolation, ie. the conversion of Ol group to Oxo groups by the loss of protons:-



Such Oxo forms are thought to be present in the solutions of basic chromium salts which show extreme resistance to the action of acids, since Oxo compounds are even more resistant to acid than the Ol compounds. Molecular size of chromium compounds may also be increased through polymerisation but this differs from olation in the fact that when the latter occurs water is eliminated. The hydrolysis, olation, polymerisation and oxolation are favoured by various conditions of temperature, concentration of chromium, concentration of anions, acidity and ageing. Each of the aforementioned changes which may occur in solutions containing chromium complexes have been extensively reported by Stiasny[20], Balany[21], Riess and Kuntzel[22], Shuttleworth[23], Serfass and Theis[24], Theis & Thorstensen[25] and Gustavson[26].

3.2.2 Complex Formation

According to Werner[27], there are three different forms of chromic chloride as indicated below:-

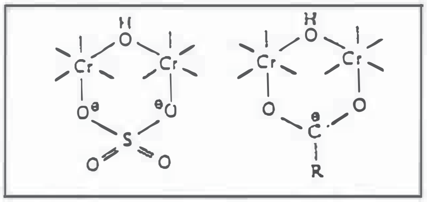


When the salt is dissolved in water, it yields three chloride ions where as the chlorine atoms which entered the co-ordinative sphere in the α and β forms are not present as ions. This penetration of chloride ions into the complex has been demonstrated by precipitation with silver nitrate and by conductance measurements. Equilibrium among the several forms in solution has been shown by Olie[28]. When an ion, such as chloride ion, enters the co-ordinate sphere it carries its charge with it, and reduces the net charge of the complex. Thus, the penetration of six chloride ions may cause the complex to exhibit a triple negative charge. The presence of three oxalate groups, each of which occupies two co-ordinate positions around the central atom, likewise will produce a complex with three negative charges.

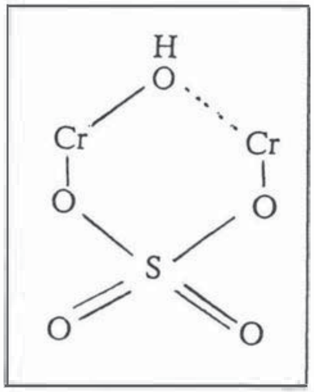
The ease with which various anions and groups penetrate the complex is of importance in determining the tanning behaviour of a chrome compound. As per Stiasny and Balanyi[19] the ions may be arranged, at comparable molar concentration, in a series of decreasing penetrative power as follows:-

> hydroxyl, oxalate, citrate, malonate, lactate, glycolate, tartrate, succinate, acetate, formate, sulphate, chloride, nitrate and finally perchlorate

According to Otto[29], the most effective complexing agents are the aromatic acids. Thus, sulphophthalates, sulphosalicylates, resorcylates even top the hydroxyl group. The order may vary with concentrations, and other experimental conditions and may also be reversed if a weaker complexing anion, for instance the chloride ion, is present in a great excess compared to a more strongly co-ordinated anion, as for example the sulphate. Therefore, it would be possible to displace part of the sulphate groups in a basic chromium complex by concentrated solutions of sodium chloride. Shuttleworth proved that the mass action effect also plays a dominant role in shaping the final form the complex[30]. Mixed bridge formation may also occur when other anions are present in solutions of chromium salts as given below:-



Stiasny and Balanyi[19] found that sulphate favour olation of chrome complexes. He agreed with Atkin[31] and Mitchell[32] and suggested that the sulphate forms a six member stable ring between the two chromium atoms already joined by a hydroxyl group by occupying two co-ordination positions as shown below. This was later confirmed by Shuttleworth[33].

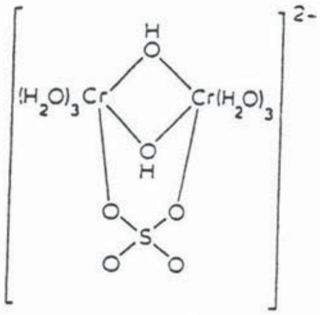


Kawamura and Wada[34] using electrophoresis separated the three main components of 33.3% basic chromic sulphate with more highly aggregated species.

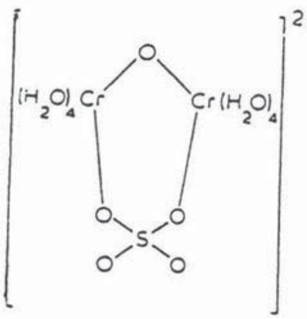
These cationic complexes were:-

1. $Cr(H_2O)_6^{3+}$
2. $[Cr_2(OH)_2SO_4]^{2+}$ and
3. $[Cr_2(OH)(SO_4)_2]^{+}$

They suggested the structure of the binuclear complex with two ol- and one bridging sulphato-group as follows:-



µ-hydroxy-µ-sulphato-hexaaquodichromium(III) ion



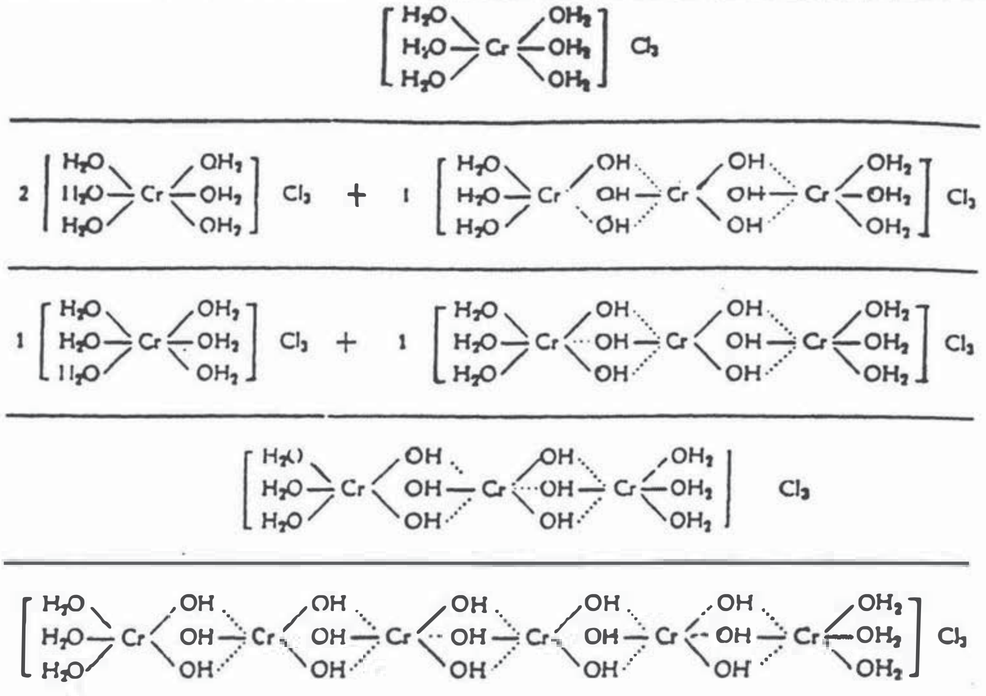
µ-oxo-µ-sulphato-octaaquodichromium(III) ion

Finholt et al[35] using IR spectra have established that the sulphate is unidentate in penta aquo compound, $[Cr(H_2O)_5SO_4]^{+}$. Indubala and Ramaswamy[36] concluded from similar studies that sulphates are bidentate and presumably bridging in both $[Cr_2(OH)_2SO_4]^{2+}$ and $[Cr_2(OH)(SO_4)_2]^{2+}$.

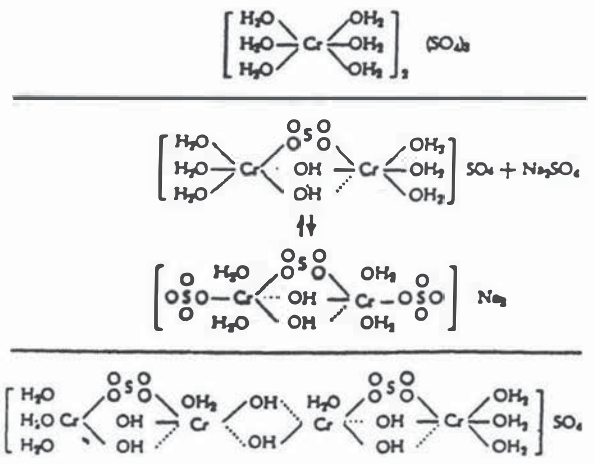
The presence of these two cationic complexes were also confirmed by Irving[17]. He also reported the results of radio actively labelled SO_4^{2-} on the exchange of ligand sulphate with ionic sulphate and found the value of this order t½ = 20h at 20°C for the monsulphato pentaaquo complex, $[Cr(H_2O)_5(SO_4)]^{2+}$ and of the order of 30 h at 25°C for the bidentate $[Cr_2(OH)_2SO_4]^{2+}$ and $[Cr_2(OH)(SO_4)_2]^{+}$, suggested by Kawamura and Wada[34].

These results confirmed the much slower rate of exchange of a chelated sulphate group, indicating doubts on the claim of Kawamura and Wada[34] that co-ordinated sulphate groups can shift easily from chromium fixed by hide to chromium complex in liquid which contain fewer co-ordinated sulphate groups.

Erdmann[37] using particle size determination by diffusion studies showed that there was a great difference between chloride and sulphate in complex formation. As a ligand the sulphate group has a strong bridging action, but the chloride group does not. Sulphate complexes form binuclear species, chloride complexes form trinuclear species as the first stable aggregation. In the case of sulphate complexes, duplication leads stepwise to species containing 2 - 4 - 8 - 16 chromiums where as for chloride, complexes contain 3 - 6 - 12 chromiums:-



Chromium Chloride



Chromium Sulphate

Gustavson[38] prepared a sodium sulphate free basic chrome sulphate solution from a solution of chrome acid and sulphuric acid with a 30% solution of hydrogen peroxide and using an ion exchange resin, showed that it contained 92% cationic salt of the type:-

$$\boxed{[Cr_2(SO_4)(OH)_2]^{2+}\ SO_4^{2-}}$$

and 8% nonionic complex of the type:-

$$\boxed{[Cr_2(OH)_2(SO_4)_2]^0}$$

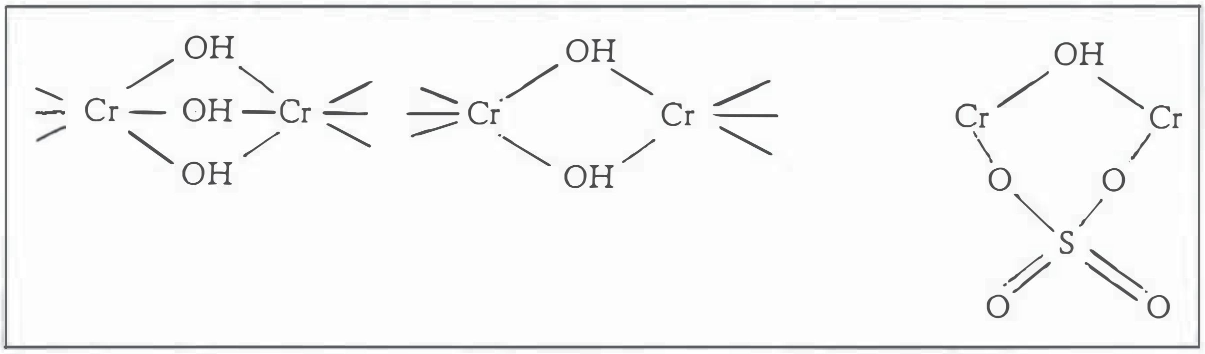
Takenouchi[39] separated seven species of chrome complexes by ion exchange chromatography (SP Saphadex C25) with a gradient of water to 3M NaCl and established their structure as given below from his IR and Visible Spectrophotomatric studies:-

I $[Cr\ (SO_4)_2]^-$
II $[Cr\ OH\ SO_4)$
III $[Cr\ SO_4]^+$
IV $[Cr\ (OH)_2\ SO_4\ Cr]^{2+}$
V $[Cr]^{3+}$ and $[Cr\ OH\ SO_4\ Cr]^{3+}$
VI $[Cr\ (OH)\ Cr]^{4+}$
VII $[Cr\ (OH)_2\ Cr\ (OH)_2\ Cr]^{5+}$

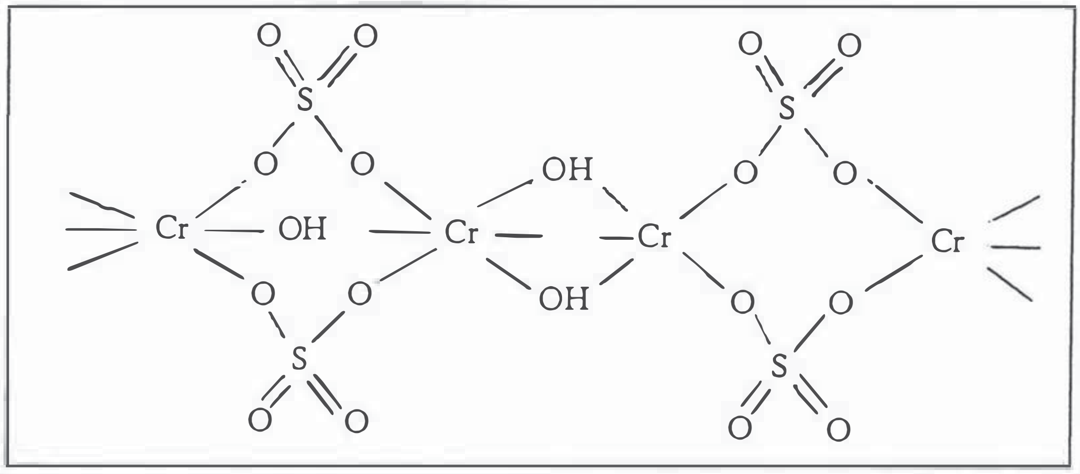
These structures are essentially similar to those suggested by Kuntzel and Mahdi[40] and Slabbert[41]. From the elution patterns of each component of aged solution, Takenouchi concluded that the following changes took place in these complexes, due to the isolation of the sulpho group and olation.

Components	**Changes**
II	$2\,[Cr\,OH\,SO_4] \xrightarrow{-\,SO_4} [\,Cr\,(OH)_2\,SO_4\,Cr]^{2+}$
III	$[Cr\,SO_4]^{+} \xrightarrow{-\,SO_4} [Cr]^{3+}$
	$[Cr\,SO_4]^{+} + [Cr]^{3+} \xrightarrow{+\,2\,OH} [Cr\,(OH)_2\,SO_4\,Cr]^{2+}$
IV	$[Cr\,(OH)_2\,SO_4\,Cr]^{2+} \xrightarrow{-\,SO_4} [Cr\,(OH)_2\,Cr]^{4+}$
V	$2\,[Cr]^{3+} \xrightarrow{+\,2\,OH} [Cr\,(OH)_2\,Cr]^{4+}$
VI	$3\,[Cr(OH)_2Cr]^{4+} \xrightarrow{+\,2\,OH} 2\,[Cr\,(OH)_2\,Cr\,(OH)_2\,Cr]^{5+}$
VII	$[Cr\,(OH)_2\,Cr\,(OH)_2\,Cr]^{5+}$ very stable

The stability of the complexes are mainly due to the ring formation of the type:-



Mono-ol complexes are unstable unless reinforced by ring formation. When 33% basic chrome sulphate complex is boiled, the following complex is thought to be formed:-



When the size of the complex is increased, it can not remain suspended in solution and ultimately precipitated out. Harrap[42] used Gel filtration technique to characterise the complexes in chrome tan liquor. He found that those fast running complexes are bigger and contain lower amount of sulphate.

However, this has to be pointed out that neither Gustavson nor Takenouchi used commercial chrome powder or chrome liquors which contain equimolecular amount of sodium sulphate in their solution. As neutral salts like sulphate has a significant effect on the composition of the complex, the distribution pattern of the species of chrome complex in commercial chrome tanning agents might not be similar to their findings. Gustavson[43] showed that neutral sulphate favoured formation of nonionic complexes in basic chrome sulphate solutions, in particular the nonionic complexes increased and small amounts of anionics were also formed. He reported that by addition of 0.25 to 0.5 M Na_2SO_4 in 33% basic chrome sulphate solution, the following changes in the character of the complex was found:-

Added Na_2SO_4 (Mol/l)	**Cationic**	**Nonionic**	**Anionic**
0	96%	4%	0%
0.1 M	91%	9%	0%
0.25 M	86%	12%	2%
0.50 M	82%	14%	4%

In fact, our repeated attempt with this column either with 0 - 5.0 M Sodium chloride or 0 - 5.0 M Sodium nitrate, as suggested by Takenouchi[39] and Takata, Shirai and Okada[44] respectively failed to obtain such clear separation as Takenouchi had claimed. We have always obtained a long tail which made it very difficult to obtain clear separation as will be seen from the Figures 3.5 and 3.6. Similar attempt by Davis and Scroggie also gave diffused patterns with no clear resolution into discrete separation as would be clear from Figure 3.7 reproduced from their report[45].

Figure 3.5: **Separation of chrome tanning solution (12.45% Cr_2O_3) on SP Sephadex G 25 using 0-5 M Sodium chloride gradient**

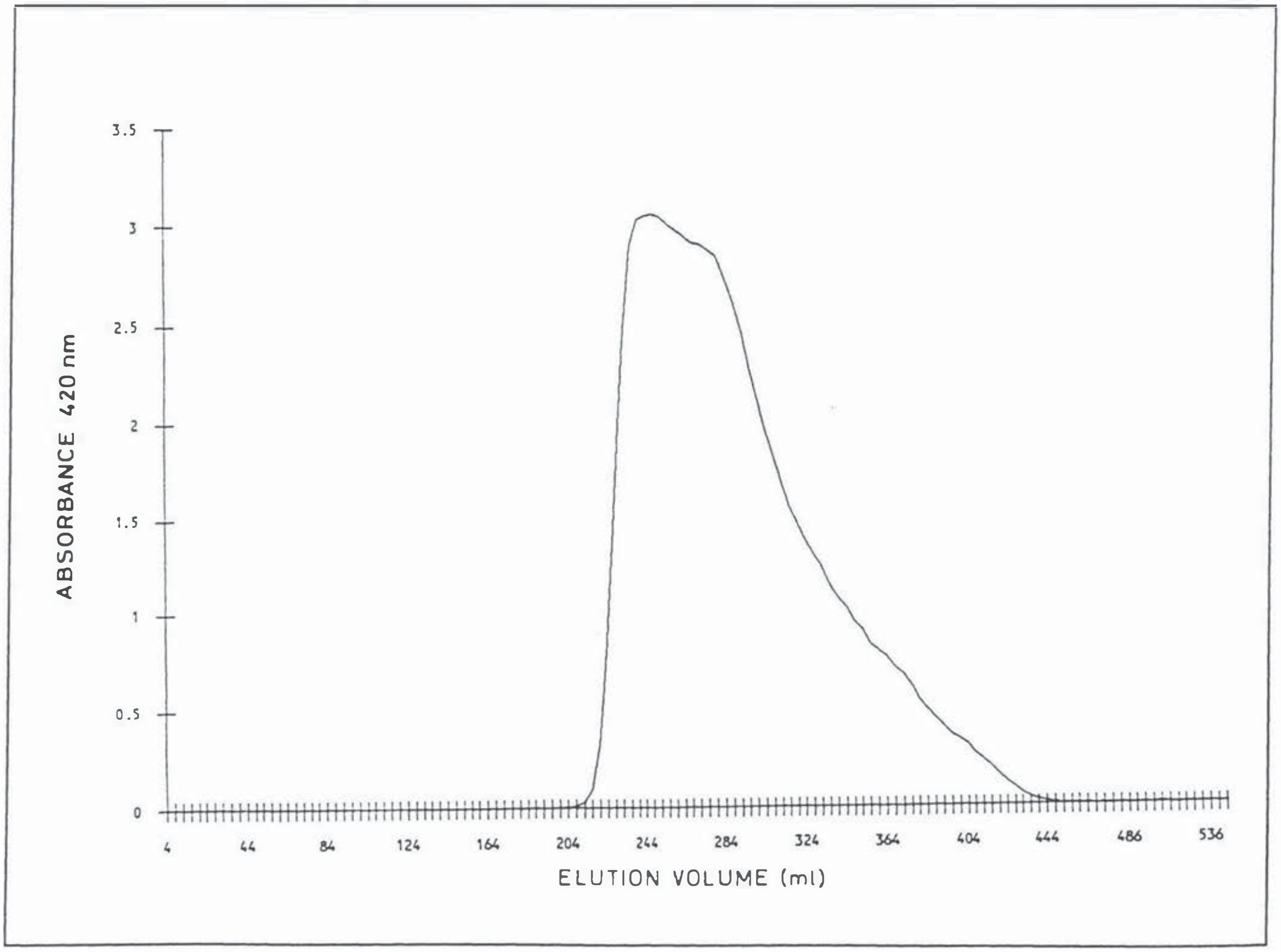


Figure 3.6: Separation of chrometanning solution (12.45% Cr_2O_3) on SP Sephadex C 25 using 0-5 M Sodium nitrate gradient

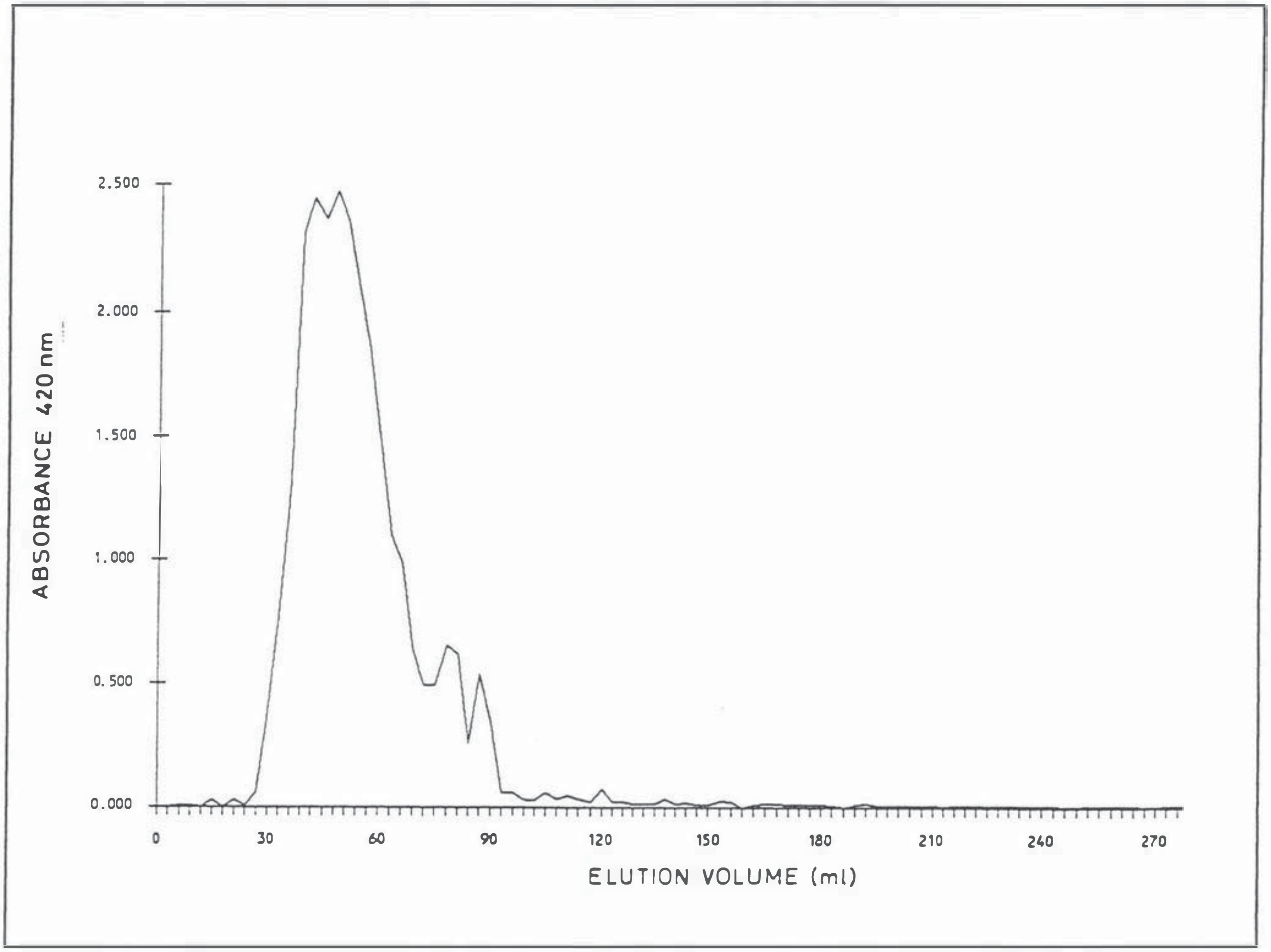
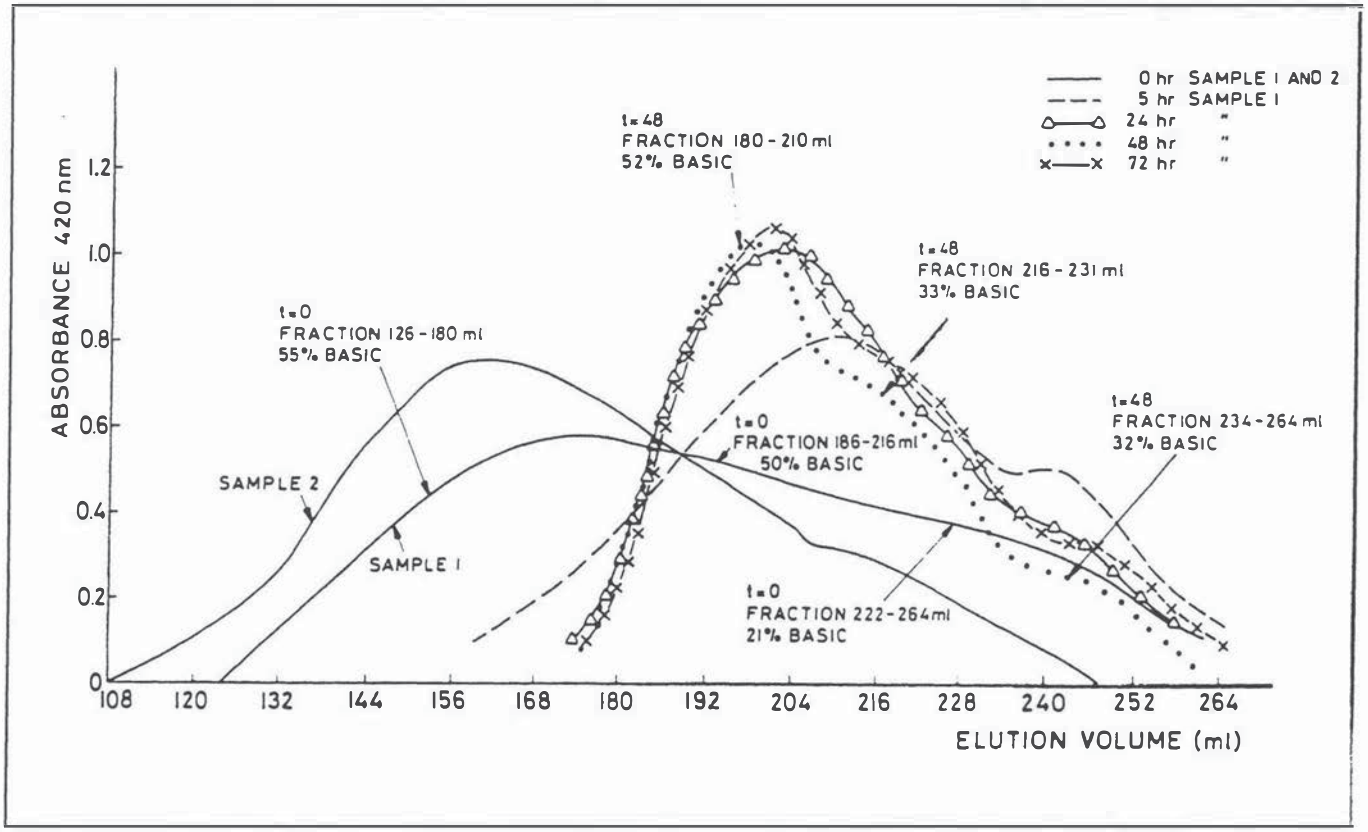


Figure3.7: Gel filtration chromatography of Chromosal B at time, *t* = 0, 5, 24, 48 and 72 h on Sephadex G-25 (90 x 2.5 cm) eluted with H_2O; 3 ml fractions; absorbance read at 420 nm



This study with commercial 33% basic sulphur dioxide reduced chromium sulphate liquor, containing about 15% Cr_2O_3, following Gustavson's approach with cationic exchange resin, Dowex 50W x 8 (Sodium form) and anionic exchange resin, Dowex 1X8-50 gave good separation when eluted with 0-4N HCl or 0-5N NaCl. The separation was monitored with a UV/VIS spectrophotometer and HPLC and actual amount of chromium was determined by Atomic Absorption spectroscopy. The composition of sulphur dioxide reduced commercial chrome tanning solution (33% basic) was as follows:-

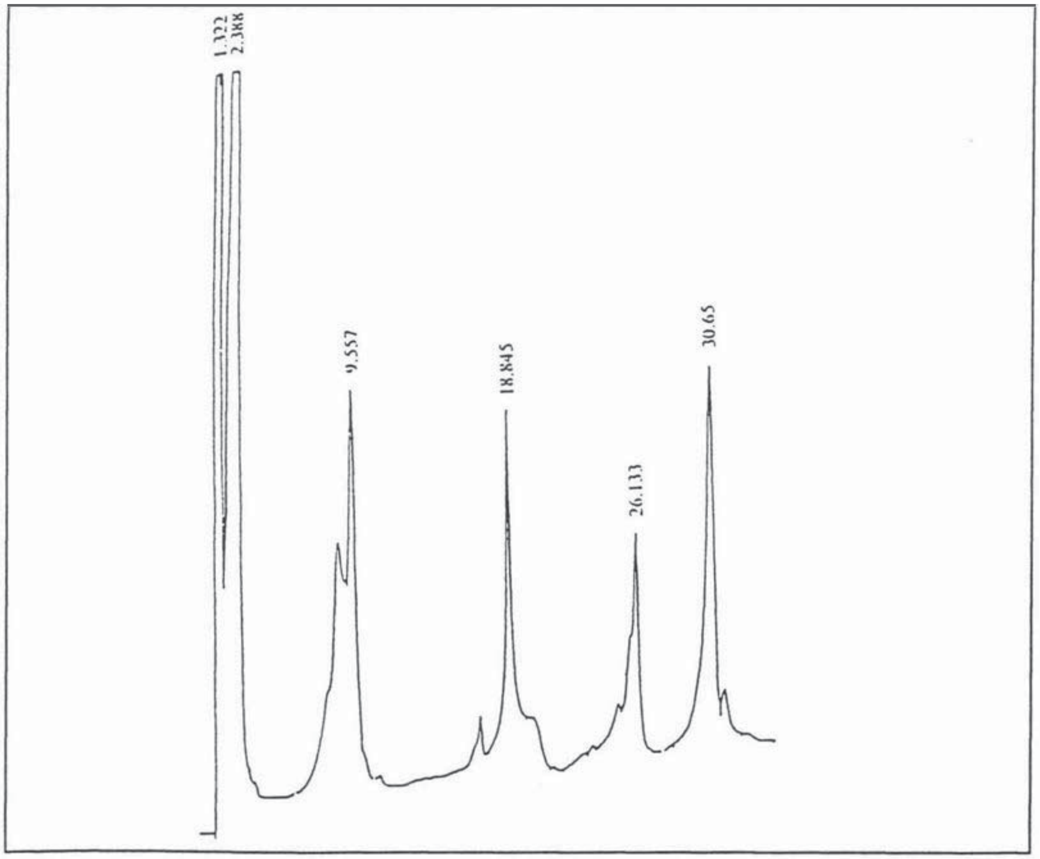
Anionic complex:-	
$[Cr(SO_4)_2]^-$ -	5.0%
Nonionic complex:-	
$[Cr(OH)SO_4]^0$	27.0%

Cationic Complexes:-

$[CrSO_4]^+$	12.8%
$[Cr(OH)_2SO_4Cr]^{2+}$	18.1%
$[Cr]^{3+}$ and $[Cr(OH)SO_4Cr]^{3+}$	13.4%
$[Cr(OH)_2Cr]^{4+}$ and $[Cr(OH)_2Cr(OH)_2Cr]^{5+}$	23.7%
	100%

Reverse phase HPLC method of separation developed by Hewavitharana at New Zealand Leather and Shoe Research Association[46] also indicated the separation of various fractions of commercial sulphur dioxide reduced 33% basic chrome liquor containing 15% Cr_2O_3 as shown in Figure 3.8.

Figure 3.8: **Separation of 33% basic commercial, sulphur dioxide reduced chromium sulphate solution.**



Peaks are shown for complexes with charges -1 and 0, and +1 upto +5 respectively. Conditions: 10mM hexanesulphonate, 5mM triethylammonium and 3mM formate buffer at pH 3 in water/methanol gradient system:-

time = 0	**10% methanol eluent (90% aqueous eluent)**
time = 5	**10% methanol eluent (90% aqueous eluent)**
time = 12	**65% methanol eluent (35% aqueous eluent)**
time = 30	**35% methanol eluent (65% aqueous eluent)**
time = 40	**10% methanol eluent (90% aqueous eluent)**

The absorbance units full scale (AUFS) was 0.5

3.3 Masking and Masked Solutions

Organic acids and their salts are able to alter the properties of chrome tanning liquors, reducing their astringency and retarding or preventing the formation of large olated and insoluble complexes. The action is called masking and the reagent responsible for this action as masking agent. Generally, industrial chrome tanning liquors which contain ligands of greater penetrating power than sulphate are referred to as masked liquors. This is most useful for eluciding the mechanism of chrome tanning and for the assessment of the use of any particular complexes as potential tanning agent for the improved chrome tanning. Shuttleworth[47] has extensively studied the complex formation of chromium employing conductivity techniques and has drawn up five rules governing the formation of complex ions. Irving[17] after critically examining these rules in the light of our present day knowledge found that these rules except rule 4 which states "formation of chelate rings greatly enhances the coordinate stability" were acceptable in its simple form. Reed[48] has summarised these factors responsible for the entry of masking agents into chrome complexes in solution of basic chromium sulphate as follows:-

- Concentration of chromium in solution

- pH value of the system

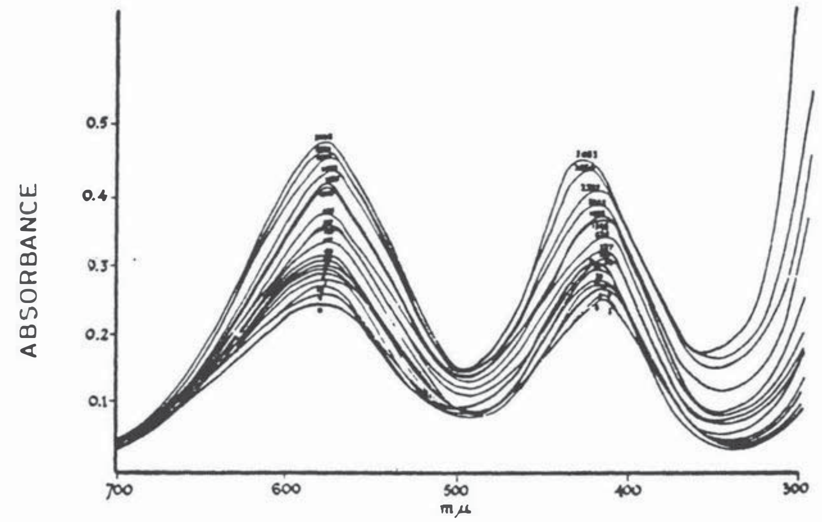
- Temperature and duration of the reaction

- Relative amount of the masking agent and chromium concentration

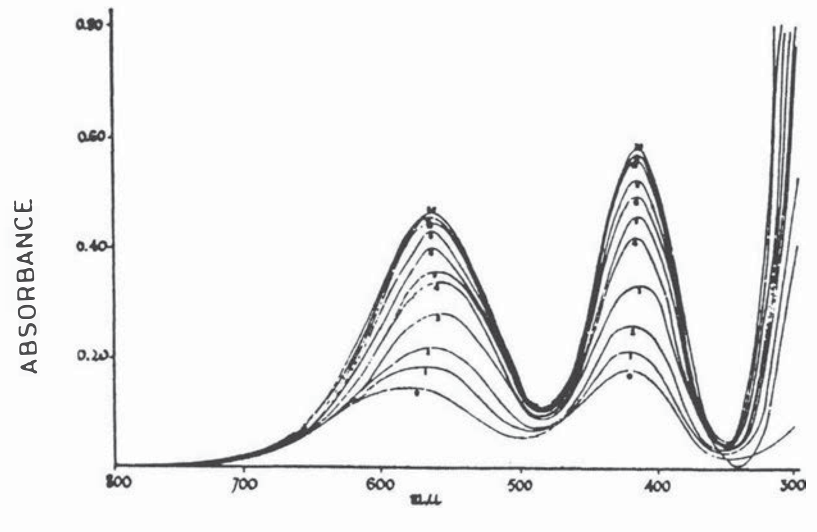
- Presence of other ligends eg. sulphate, chloride, hydroxide
- Whether the complexing ligends are added separately or together
- Whether the ligends are added as free acids or as a salt

Masked chromium complexes have been studied extensively. They were generally characterised by their higher stability to alkali. Masking also lowers the charge, increase the molecular size and strengthens the absorption of chromium complexes. Shuttleworth[49-56] from conductometric studies, postulated certain formulas for the complexes of chromium with a number of anions and suggested that masking is simply a mass action effect and with very few exceptions, mixtures, rather than any specific complexes are formed. Ramaswamy and Nayudamma[58] studied the complexes of 33% basic chrome sulphate, free from neutral salts, with various organic acids and mixtures of these acids and their salts with spectrophotometer in the ultraviolet region (230 to 350 millimicrons) and compared their results with earlier studies in the visible region. Their results indicated that the sulphuric and hydrochloric acids deolated the basic chromium sulphate complex, complete deolation took place at 5-10 mole ratios of acid to chromium. The chloroacetic acid, formic acid, and acetic acid either caused partial deolation, slowly forming complexes with deolated complex, or the acids formed unstable complexes. They suggested various structures on the basis of the definite evidence obtained for the formation of complexes containing 2 glycolate, 1 tartarate, 1 citrate and both 2 and 3 oxalate molecules per atom of chromium.

Gustavson[59] has shown that the addition of oxalate and acetate to chromium solution resulted in a greater decrease of cationic complexes than addition of formate. Serfass and colleagues[60] have shown that large sized complexes can be formed with the addition of acetate and tartarate, while the formato complexes were small. Theis and Thorstensen^{25} measured the extinction (E) and transmission (T) of salt free, aged 33% basic chromium sulphate solution, containing 0.005 to 0.10% Cr_2O_3 and similar masked solutions with formate, formic acid, oxalate and oxalic acid with spectrophotometer and noted that these ligands gave an increase in the amplitude of the maxima at 575 and 420 nm in the UV/VIS spectrum and also a slight shift in the wavelength of the maximum absorption values as shown in the graphs reproduced from their above mentioned paper:-



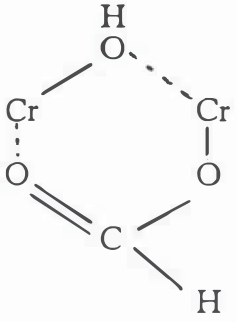
Spectrophotometric Extinction against Wavelength for a $CrOHSO_4$ Solution (0.10% Cr_2O_3) with Added Formic Acid. (Numbers at the peaks indicate moles formic acid per mole Cr_2O_3).



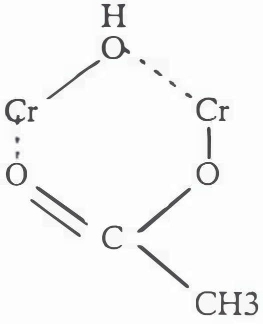
Spectrophotometric Extinction against Wavelength for a $CrOHSO_4$ Solution (0.05% Cr_2O_3) with Added Oxalic Acid. (Numbers at the peaks indicate moles oxalic acid per mole Cr_2O_3).

They also noted that the extinction values for each absorption peak increase rapidly with oxalate addition up to 10 moles adder per mole of Cr_2O_3 and thereafter changed little or nothing and became constant at 15 mole per mole of Cr_2O_3. Further, the spectral absorption was greater at 420nm than at 560. With sodium formate of similar chromium concentration as that used for oxalic acid, it was found that the peaks were very close together and did not follow any apparent order. But with formic acid (85%) addition to basic chrome solution to give a 0.10% Cr_2O_3 solution, the increased absorption was smaller at 420nm but a marked increase at 580-585nm was noticed. This was exactly opposite to that found for oxalic acid. It was also noted that the extinction values of the complex decreased with small addition of formic acid until a minimum value was reached. With further addition of formic acid the extinction values increased to the value of the basic chrome solution and eventually passed it with continually increased absorption. They concluded from these results that the oxalate ion penetrates the complex by displacing a weak coordinately bound water molecule or sulphate radical forming a trioxalato chromiate complex. They also showed through their further studies with cationic exchange resin that 3 moles sodium oxalate per mole Cr_2O_3 cause a decrease from 90% cationic complex to 38% and the oxalate anion quickly displaces sulphate anion from the chrome complex forming readily both nonionic and anionic complexes. But with formic acid or sodium formate they could not demonstrate the formation of anionic chromium complexes, even though the sulphato groups were readily displaced and completely removed when 6 moles sodium formate were present per mole of Cr_2O_3. Erdmann[61,62] also conducted similar spectrophotometric investigation with formate, acetate and oxalate and concluded that the stronger increase in the maxima at 420nm is caused by bridging in the complex. He explained the relationship between the spectrum amplitude and structure of acetate-trichromium complex in terms of bridging acetate to bridging hydroxyl ration 1:1. Acetate has stronger complexing affinity than formate. Acetate fixation in the complex is so strong that 3 moles of NaOH can be reacted to bridges without leading to precipitation. He also found that adding dicarboxylic acids to chromium sulphate solutions produced nearly double the acido complex than the equivalent addition of monocarboxylic acid. This greater affinity is the basis of the increase in chrome complex size obtained by the addition of dicarboxylic acid or polyacrylates. Displacing the bridging sulphate from basic chrome sulphate, which has already hydroxyl and sulphate bridge is less readily achieved with monocarboxylic acid than dicarboxylic acid. This could be appreciated from the greater increase in amplitude at 420nm for the dicarboxylic acids.

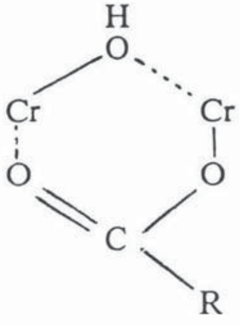
Based on these studies, it was suggested that monocarboxylic acids lead to the formation of trichromium complexes but they are bridged by organic acido ligands. The weaker the acid, the stronger the complexing ability. Trichrome salts formation is only possible if there are two acids or hydroxyl ligand available per chromium. Acetates, formates and other organic salts form stable six member rings as follows:-



Formate



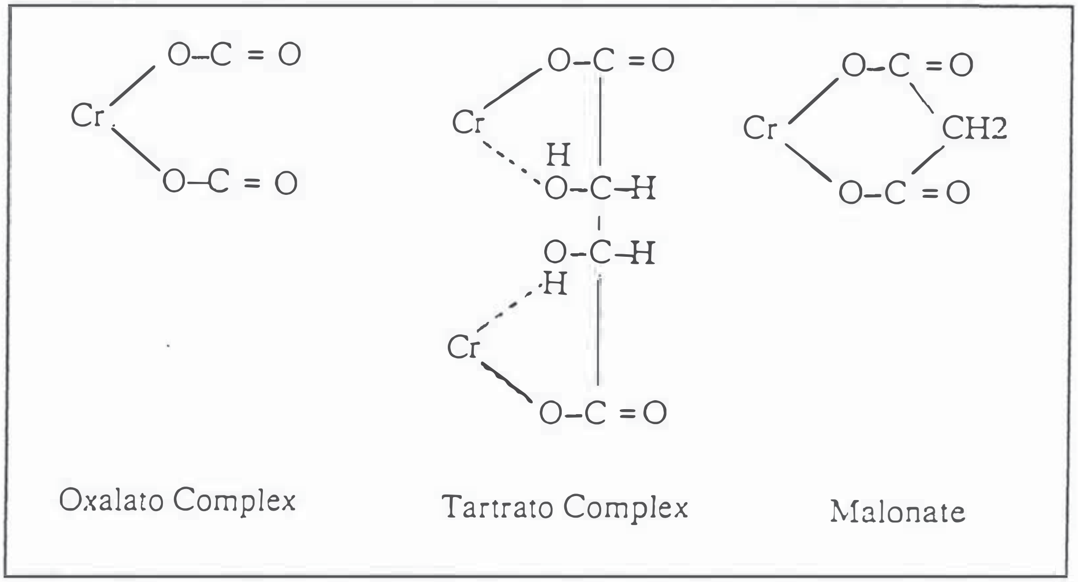
Acetate



General Formula

Takenouchi[63-65] used ion-exchange (SP-Sephadex C 25) and Gel filtration (Sephadex G 25) chromatography to establish the structure of chromium chloride and sulphate solution masked with salts of formic, acetic and oxalic acids. He showed that the masked solution contained different sized complexes with varying charges and the composition of complexes varied with the amount of the added salts. He also characterised the complexes with infra-red absorption spectra and found that almost all or most of the sulphato and hydroxo complexes transformed to organo ones as the amount of salts were increased to 1.0 M/M Cr. He emphasised that he did not notice formation of any sulphato organo complexes. Takenouchi, Kondo and Nakamura[66] found no anionic complex with formate. All complexes were very small sized, mono or binuclear formato chromium complexes. But few large sized high polymeric anionic acetochromium complexes were found. Nonionics were medium size trinuclear chromium complex. All other cationic complexes were small size like the formate. With oxalate, anionic complex was dioxalato chromiate and nonionics were olated oxalatochromium complexes. Masked chromium sulphate solutions as compared to masked chromium chloride solutions, contained low charged organo complexes in large quantities, suggesting that formation of masked complexes were not retarded by sulpho groups. With oxalate, several complexes different from formate and acetate were formed. Takenouchi[63] reported the changes due to masking of chromium sulphate with organic salts. Dicarboxylic acid ligands are strong bridge formers as evident from the increase in the amplitude of spectra at

420nm, shown by Theis and Thorstensen[25] and Erdmann[61,62]. They occupy all the bridging sites and can only be displaced by a particular concentration of alkali in solution[36]. Because of this, molecular size increase is strongly hindered and the complex remain small and anionic. Oxalate, tartarate and malonate which have stronger power of penetration, form five member rings including only one chromium atom as shown :-

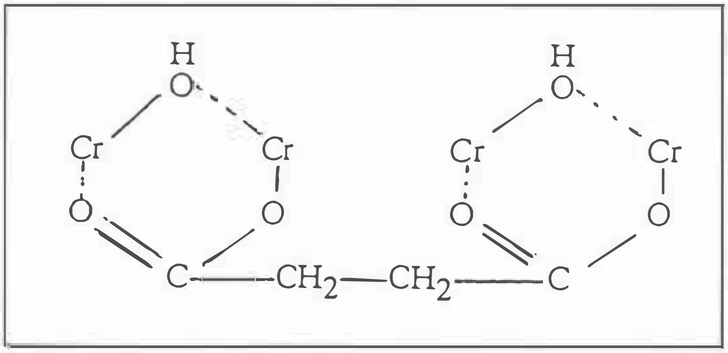


Oxalato Complex

Tartrato Complex

Malonate

Salts like succinate, fumarate, adipate and phthalate where two carboxyl groups are separated by several CH_2 groups also increase the molecular size of the complex which ultimately might help in fixation of chromium through the intra molecular bonding of collagen during chrome tanning:-



Gustavson[67] through the use of three different cationic and anionic exchange resins established that the phthalate masked basic chromium sulphate contained considerable amount of nonionic complexes and gave their approximate concentration as follows:-

Cationic complexes:	45%
Nonionic complexes:	50%
Anionic complexes:	5%

3.4 Theory of Chrome Tanning

Knapp[68] who discovered the chrome tanning regarded chrome tanning as a covering of the outer surface of the hide fibre by the insoluble chromium compound produced by the hydrolysis of chromium salt and thus protecting the leather from swelling and putrefaction. As a support of his theory, he showed that the collagen treated with stearic acid, dissolved in alcohol, had a comparatively higher shrinkage temperature than untreated collagen, and had also some resistance against putrefaction. This surface covering theory was discarded when Kuntzel[69] and Elod & Siegmund[70] proved by microscopic means that the chrome in the leather was not merely present on the fibre surface but was distributed throughout its cross section.

In 1893, Fahrion[71] and Korner[72] in 1905 suggested that chrome was essentially a solid solution of tanning material in hide and the insoluble nature of the chrome compound explained the behaviour of chrome leather towards hot water. Stiasny[73] in 1908 suggested that the mechanism of one bath chrome tanning consisted of the fixation of hydrolysed acid by the hide substance and due to hydrolysis the basicity of chrome salt present in the liquor gradually increased with the gradual decrease in solubility, the highly basic chrome being precipitated on the surface. This original concept was the basis of all other deposition theory of chrome tanning. Essentially, similar views were expressed by Procter[74] and

Burton[75]. Merry[76] suggested that the cationic chrome tanning consisted of the deposition of $66^{2}/_{3}\%$ basic chrome sulphate in and on skin fibres. He also thought that part of this basic salt combined with collagen chemically, possibly by an interaction involving its NH_2 groups with the OH groups of the chrome salt. In support of this, he showed that only 2/3 of the total chromium fixed on freshly tanned leather could be removed by the treatment with oxalic acid, rest could not be stripped out at low temperature. He therefore suggested that 1/3 of chrome was fixed chemically. However, Cameron, McLaughlin and Adam[77] repeated this experiment and found similar result which apparently confirmed Merry's view. But on replacing oxalic acid with sodium oxalate to repress the swelling due to the acid, they found that the remaining chrome in the skin could also be removed. They also found a quantitative relationship between the fixation of acid and subsequent chrome deposition and also noticed that the basicity of the fixed chromium compound was always $66^{2}/_{3}\%$, regardless of the original basicity of the chrome sulphate liquor used in the tanning.

In 1940, McLaughlin, Adam and Cameron[78] proved that when the acid binding capacity of collagen was satisfied, the collagen had no affinity to fix cationic chrome. These observations apparently supported the deposition theory which on the other hand cannot explain the thermal stability of chrome tanned leather. But Gustavson[79] showed that the acid fixation of collagen was independent of the temperature of tanning where chrome fixation was dependent and the acidity of fixed chromium compound varied widely. Further, Kuntzel, Riess, Papayannis and Vogl[80] that collagen saturated with acid took up chromium and therefore the deposition of chromium could not be due to the absorption of acid from chrome liquor by protein. Moreover, Shuttleworth[81] had demonstrated that at any stage of chrome tanning, the protein could be washed rapidly with normal hydrochloric acid without removing the fixed chromium. Thus it was clear that the deposition theory could not fully explain the mechanism of chrome tanning, even though some of the chromium may physically be deposited on the fibre.

Cobb and Hunt[82] explained the fixation of chromium at the isoelectric point of collagen by suggesting that the fixation is caused by the residual valency forces. Cockbain[83] thought that the fixation is due to the attachment of the hydroxyl group of the hydroxyproline with the chromium. Elod, Schachowskyoy and Sinn[84] reported that almost all the mineral tanning compounds react with the alcoholic - OH group of polyvinyl alcohol and form water insoluble compound. They therefore believed that a large percentage of chromium was fixed by the hydroxyamino acids like hydroxyproline present in the collagen. They also emphasised the importance of molecular size of the chrome complex for better fixation of chromium through hydrogen bonding. However, Kuntzel, Riess, Papayannis and Vogl[85] have criticised the theory of multiple molecular attraction by residual valency forces as these do not contribute to hydrothermal stability of collagen. Stiasny and Pakkala[86] observed that a definite percentage of chromium was fixed by the activated charcoal, alumina or kieselguhr when chrome liquor was passed through them. They therefore believed that this type of fixation was due to the residual valency force and thought that chrome was fixed to collagen by the similar residual valency forces.

Shuttleworth[87] on the other hand, showed that chrome complexes containing oxalato sulphito chromiate gave very high fixation of chrome on hide powder but these high fixations were not related to the high thermal stability of leather. Pressley[88] and Bowes, Davis, Pressley and Robinson[89] have found that a steady increase of chrome fixation were obtained by varying salt content, liquor concentration, and basicity of normal chrome liquors and this lead them to suggest that fixation by residual valency and hydrogen bond played a minor role in the normal commercial process. The fixation of chromium by residual valency was a filling action rather than the chief mechanism of chrome tannage.

Wilson[90] proposed that collagen acting as an acid and chromium acting as a base would combine to form a very stable salt, chromium collagenate. He postulated that even though the charge on collagen was predominantly positive, there still remains a small number of negative charged group scattered throughout its structure. The chromic ions would diffuse into the fibre and combine with such groups. Further, ionisation of both collagen and chromium then could occur and tanning completed. This was the first chemical theory of chrome tanning Assuming the equivalent weight of collagen as 750, Wilson[91] calculated that the smallest amount of chromic hydroxide required for 100g of collagen would be 3.3g and thought of the possibility of monochrome, dichrome and polychrome leather.

Baldwin[92] and Thomas and Kelly[93] supported Wilson when they thought that they have formed tetrachrome and octachrome collagen under certain condition of chrome concentration. These compounds corresponded to the maximum and minimums on the concentration - fixation curve. However, this combination ratios have no stoichiometric basis as the actual equivalent weight lies between 850 to 1300, not 750 as assumed by Wilson. Further, not 750 as assumed by Wilson. Further, Kuntzel, Kinzer and Stiasny[94] and Mclaughlin and Adam[95] have shown that the maximum and minimum obtained are due to the presence of neutral salts. The function of the salt linkage, being an electrovalent link between the positive charge amino group and the negative charge chrome complexes already attached by a coordinate link to an adjacent protein chain, as reported by Shuttleworth[96], was to reinforce the chrome tannage. This explanation was used by Hudson[97] and by Kuntzel et al[80] to explain greater hydrothermal stability of chrome sulphate as compared to chrome chloride tannage. Although salt link between negative charge chrome complexes and positive charged amino groups might take place, it seemed very unlikely that such link contribute much to the thermal stability of chrome tanned leather.

Freudenberg[98] in 1921 suggested that groups like - NH2 , - NH - and - CO -of collagen could penetrate into the chrome complex displacing coordinately held groups and still remain a part of the collagen molecule. This would form a chemical link between chromium atom and the collagen of the hide and skin. Thompson and Atkin[99] suggested that since cationic chrome tanning agents might contain anionic complexes, such negatively charged complexes could react with the positively charged collagen. Seymour-Jones[100] demonstrated that this hypothesis could not be of general application to chrome tanning as at the low pH of chrome tanning, there could not be any anionic chrome complexes in the tanning bath. However, Thomson and Atkins' suggestion was of considerable importance as this drew attention to non cationic complexes and the necessity of explaining their contribution to chrome tannage. Erdmann[101] reported that anionic oxalato chrome complexes firstly form salt-like linkages with the basic group of collagen (untrue chrome tannage) and then after a rather long period of transformation react coordinately with the carboxyl group of the hide protein. This process, he thought, was a kind of exchange of ligands (true chrome tannage) and was identical to a cationic chrome tannage. Because of the reduced chrome fixation on deaminized protein, Thomas and Kelly[93] and Gustavson[102] concluded that nitrogen group of protein plays a significant role in chrome tanning. Gustavson[103,104] thought that the coordination of amino group of collagen was directly responsible for the anionic chrome tannage.

Bowes[105] had stated that the bridge formation between amino and carboxyl groups of collagen through entry of the carboxylic group of collagen into the chrome complex, followed by the formation of a coordinate link with amino group might be a satisfactory theory of chrome tanning. This view was also shared by Gustavson[78] and Otto[106]. Green[107] considered the reduction of chrome fixation by acetylated hide powder as the evidence of the coordination of amino or hydroxyl radicals during chrome tanning. Sykes[108] repeating Green's experiment on the fixation of chromium on acetylated collagen used dehydrated Marino sheep skin and confirmed that even though major reaction during chrome tannage was the reaction between carboxyl group of collagen and the basic chrome sulphate, combination between the hydroxyl residues were sufficient to provide stable leather which could withstand exhaustive washing. He also agreed with Shuttleworth[80,109] that the reaction involved either residual valency force or hydrogen bonding. Gustavson[110] also later changed his mind and stated that under normal pH condition of chrome tannage, the positively charged amino acid group must be excluded as a probable centre of reaction with chromium.

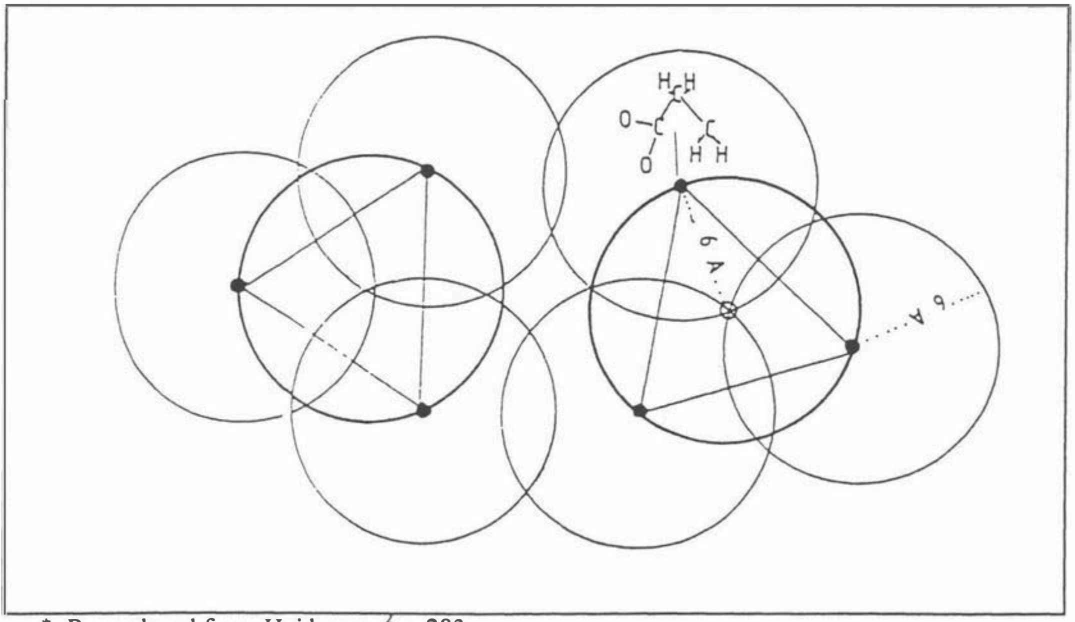
His and Shuttleworth[109] studies indicated that masking with sodium sulphite may cause fixation of chromium without the expected enhancement of shrinkage temperature. A possible explanation of this effect, Sykes[108] suggested would be that the carboxyl ion of collagen were unable to displace the sulphite ion from the chrome complex thus preventing the formation of stable coordinate linkage. However, this would not prevent the sulphite complex from entering into other form of association with the hydroxyl groups of collagen, thus accounting for high fixation of chrome without a corresponding increase in the shrinkage temperature. In general it may be concluded that nitrogen group do not take place during normal acid pH of chrome tanning. But it should be pointed out that even though Sykes[108] work has been extensible quoted in leather literature and accepted by Shuttleworth[95] to criticise Gustavson's argument of the fixation of noncationic chrome complexes by collagen through groups other than carboxyl groups, it was strange to notice that Sykes[108] used impractical condition of tannage in his experiment. He used 40ml of 3 month old basic chrome sulphate liquor, containing 25.3g/l Cr_2O_3 for 2g of dehydrated sheep skin pelt and tanned for 48h with constant agitation on a shake machine running at 60rpm. This would actually account for an offer of about 10-12.5% Cr_2O_3 offer on wet pelt basis, ie. 40%-50% commercial chrome powder, containing 25% Cr_2O_3. This when viewed against normal Cr_2O_3 offer of 1.25-1.50%, used during commercial tannage looked unrealistic. His conclusion about the effect of hydrothermal stability and chrome fixation both for control and modified collagen raises serious doubt.

Further, Shuttleworth[47] criticised Gustavson's view as he proved that neither the dioxolatochromium complex nor basic chrome alum coordinated with methylamine or urea at pH 5.0. Similarly Cooper[111] objected on the ground that below pH 7.0, even five member ring forming diamines were incapable of displacing oxalate from chrome complex in aqueous solution. Strangely, none of them studied the possibility of such reaction suggested by Gustavson at pH above 7.0 and both accepted that the fixation might be possible through hydrogen bonding. It should be pointed out that in many tannage like glutaraldehyde, higher percentages of reacting substance even though do not contribute to shrinkage temperature, are required for the production of satisfactory stable leather. Similarly, higher fixed chrome could also contribute towards minimising the use rate of chrome in production of leather thus minimising the environmental impact of chrome tanning. Further, shrinkage temperature should not be regarded as the only criteria of tanning.

It is now generally accepted that chrome tanning is mainly due to the coordination of carboxyl group of collagen with chromium. Freudenberg[98] was one of the first to suggest this to be the main theory of chrome tannage. Extensive reactivity studies of collagen with various chrome complexes by Gustavson[110,112], conductometric titration studies of Shuttleworth[113-116] and spectrophotometric studies by Serfass, Wilson and Theis[24,25] have established that wide range of organic carboxyl groups are capable of forming stable coordinate complexes with chromium under similar condition of chrome tannage. Importance of protein carboxylic groups in chrome tanning have been established by Gustavson[112], Bowes and Kenton[117] and Sykes[108] who have also shown that the elimination of carboxyl group through esterification drastically reduced chrome fixation. Sykes also established that this occurs with both cationic and anionic chromium. Plant[118] has also concluded from a study of the combination of cetyl trimethyl ammonium bromide that the free or nonzwitterion carboxyl of protein are blocked by chrome tannage, but it seemed most unlikely that unionised carboxyl groups will coordinate, so that a hydrogen bond mechanism might also operate. Shuttleworth[81] has carried out kinetic studies comparing the reaction velocities of chromium fixation by hide powder with the rate of the reaction of sodium acetate with chromium sulphate at concentration level similar to chrome tannage. He has shown that at various pH between 2.3 to 5.2 and at temperatures from 10 to 40°C, the rates of reaction agree remarkably.

The close agreement in rates of fixation over these temperature and concentration established the coordination of chromium with the carboxyl group as the major reaction in chrome tanning, and the fact that hydrogen bonds and residual valency forces account for relatively little of fixed chromium using normal basic chrome sulphate. As the degree of coordination increased with temperature, it explained why this reaction was responsible for high thermal stability of chrome tanned leather. Jordan Lloyd and Garrod[119] have discussed the structural implication of the thermal stability of the protein and have shown that collagen contain salt links and hydrogen bonds, the breaking of either of which lowered the thermal stability. It would therefore appear that the comparatively high thermal stability of chrome tanned leather required the concept of bridge formation between the neighbouring protein chain. The insensitivity of chrome tanned leather to reagents which swell or even disperse collagen fitted well with the bridge concept. Hiedmann[120] has given an excellent review of our present day knowledge of the theory of chrome tanning and the sites where chrome might actually be fixed in leather. Figure 3.9 according to him, gives an idea of two collagen molecules arranged in distance corresponding to the hydrated state:-

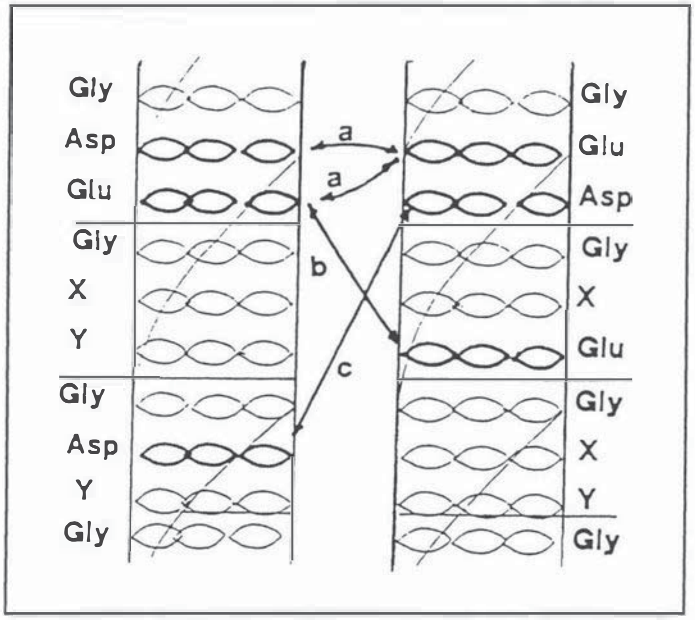
Figure 3.9:Spatial extensions of glutamic acid side chain*.
Side chain distance 15 A, Backbone distance 6 A
Glutamic side chain 6 A, C-C 1.5 A, C-O 1.3 A



* Reproduced from Heidemann[2], p 283

The three outer circles provide the space which can be covered by the flexible side chain of glutamic acids and Figure 3.10 show the side views of the two triple helics:-

Figure 3.10: **Side view of two triple helics showing the position of carboxylic acid groups Asp = Aspartic acid; Glu = Glutamic acid**



The reaction between two carboxyl groups in a side by side position is shown by category (a). This also include the reaction between position X and Y. Category (b) describes interactions between tripeptide units which are longitudinally separated by one unit. Category (c) represents reaction between tripeptides which are further apart. The interaction for categories (a), (b) and (c) are indicated having a distance of 9, 15 and 20 Angstroms. The possibilities of reaction are given in Table 3.2 which account for a 1D section.

Table 3.2: Number and locations of chrome bridges in 1D*

	Positions	Distance (Angstrom)	Number (Intra/Inter)	Equivalence (Intra/Inter)
a	same level	5 - 9	25/63	75/189
b	next level	9 - 15	14/61	42/123
c	over next level	10 - 20	10/25	39/75

* Reproduced from Heidemann[2], p 285

33% basic chrome sulphate solutions consists mainly of complexes containing mainly 2, 3 chromium and a small amount of 4 chromium containing complexes which correspond to extensions of 7, 12 and 17 Angstrom. These lengths fit well in the above mention spaces. It may be said that the charge of the complex is the primary factor for initiating the binding of chromium. The protons as well as the complex chromium cations will be attracted to the anionic groups of collagen, COO^- .P. NH_3 $^+$ -. Competition would be set up among the protons and cationic chrome complex for the discharge of these groups. Simultaneously, the compensating SO_4 ions would associate with the cationic protein groups, forming a reversible system of compensated link: - NH_3 $^+$. SO_4-/2. By the binding of the protons by collagen, the following structures might form:-

$$\boxed{HOCO.P.NH_3^+.SO_4^-/2}$$

The initial reaction of reaction between cationic chromium and carboxyl group of collagen may be shown as below:-

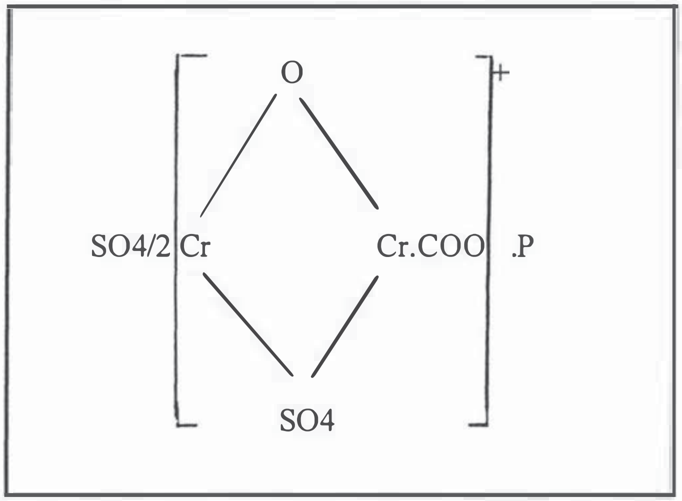
$$\{Cr_2(OH)_2SO_4\}^{2+} + COO^-.P.NH^{3+}.SO_4^-/2 \rightarrow$$

$$\{Cr_2(OH)_2SO_4\}^+.COO.P.NH_3^+ \text{ and}$$

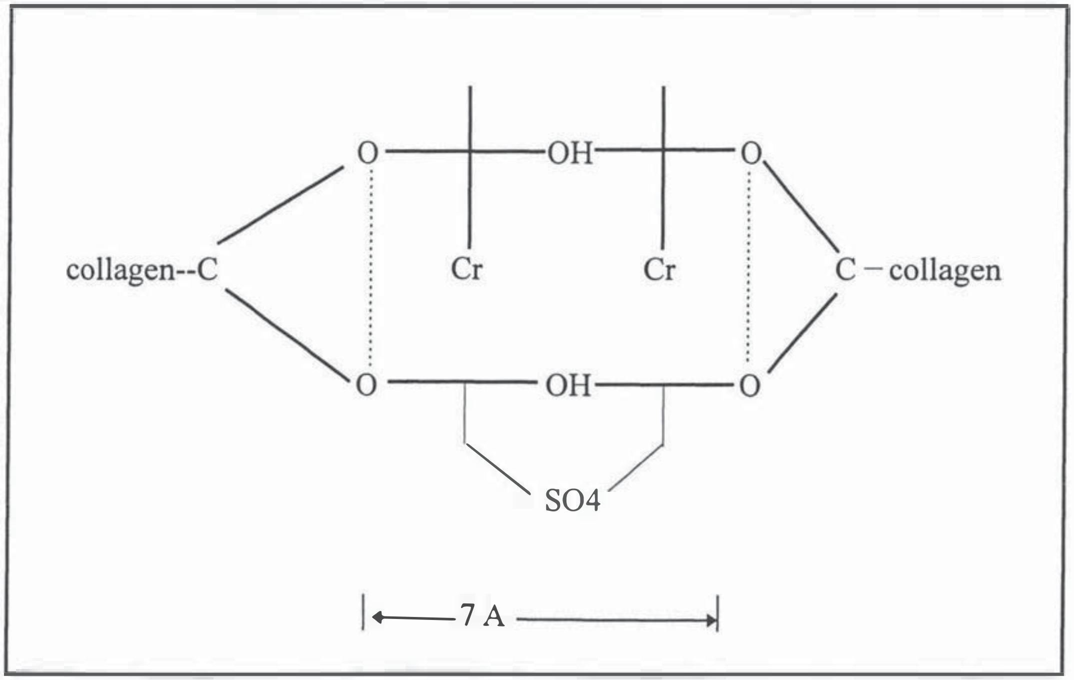
$$\{Cr_2(OH)_2SO_4\}^{2+} + (COO^-)_2..P.(NH_3^+)_2 \rightarrow$$

$$\{Cr_2(OH)_2SO_4\}(COO)_2.P.(NH_3^+)_2$$

Since the carboxyl ion has a pronounced tendency to become directly attached to the chromium atom by coordination, an immediate penetration into the chrome complex should take place. The initially formed electrovalent bond would then be converted into a very stable coordinate bond, tending toward the covalent type of binding. The resulting chrome - collagen compound[121] may be as follows:-

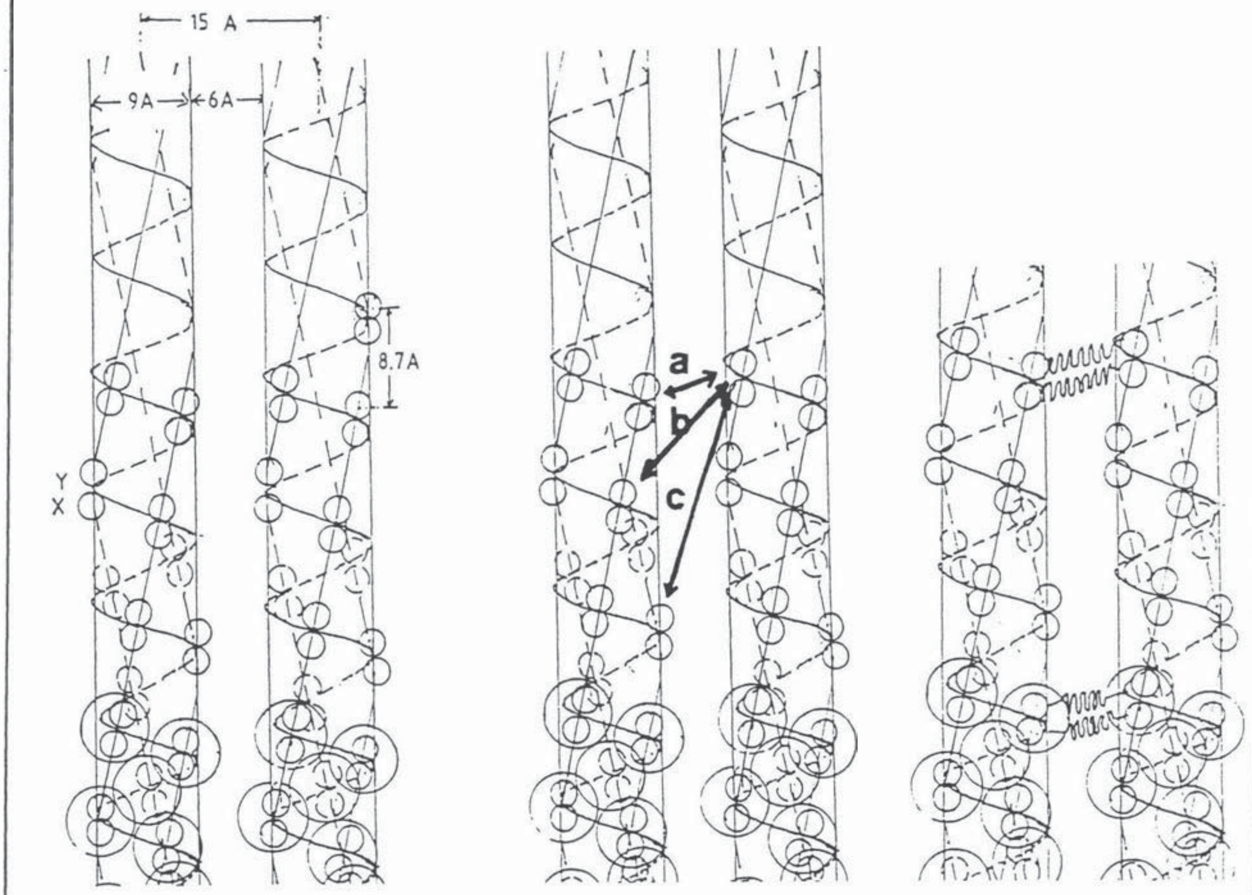


If due to steric hindrens, the binding of the bivalent complex is restricted to one carboxylic group of collagen, the unipoint binding would take place. The stability of the structure would require the interaction of one cationic chromium complex with at least two carboxylic groups on adjacent protein chain. The two nuclear chromium complexes react in extended form over 7 Angstrom to provide multipoint linkage as shown below:-



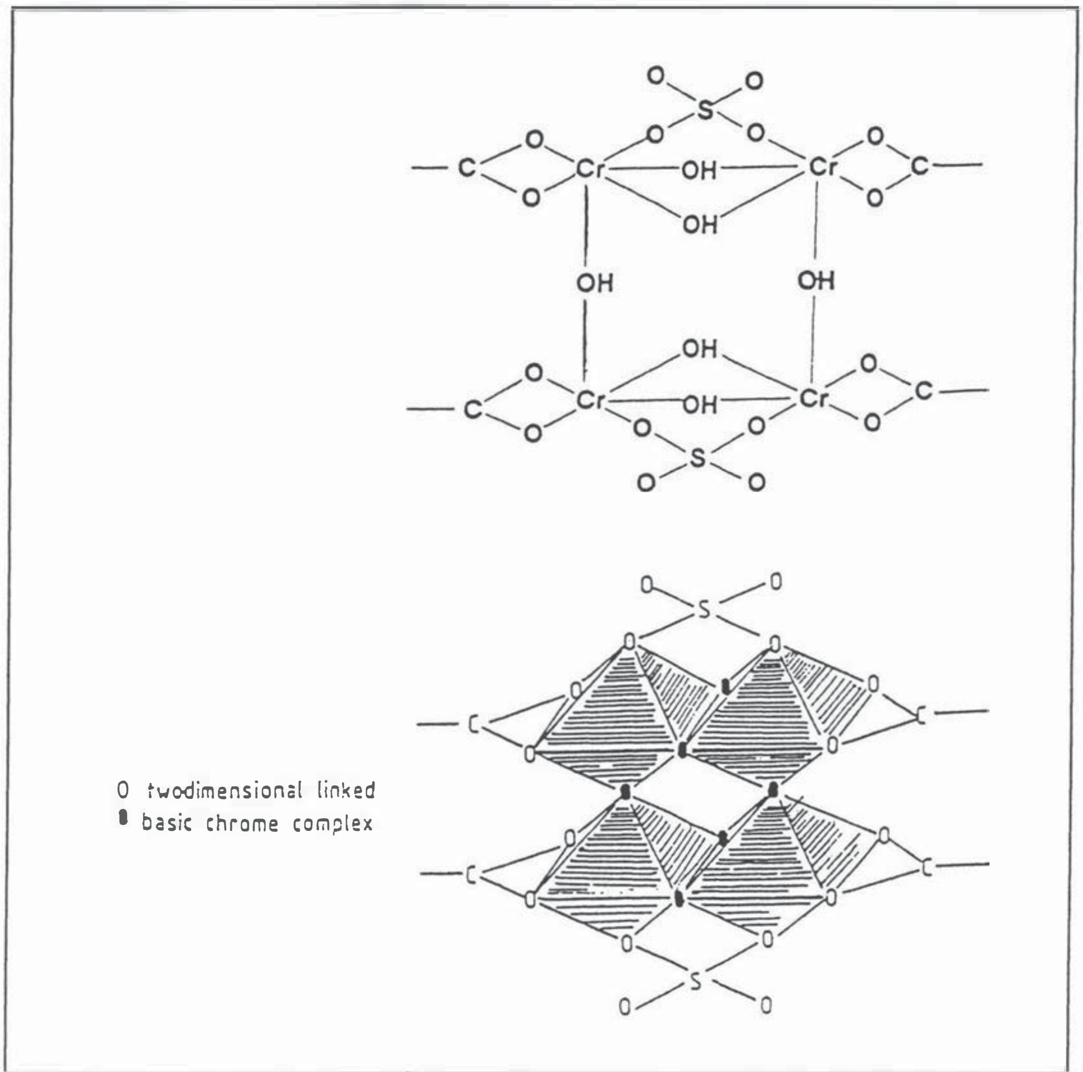
The carboxyl groups in this section find corresponding carboxyl groups in lateral direction, that is, they are in intermolecular mode and there are only occasional intra molecular bond. It may be seen from Figure 11 that the number of possible bonds in the category (a) is much more than category (b). Category (c) bonds are rare. This implies that the collagen lattice is so arranged with respect to its charged groups that the most carboxyl groups are located preferable strictly side by side in closest distance and two or more bonds are arranged parallel due to the parallel arrangement of the molecules and due to the parallel arranged carboxyl group stretched strictly lateral to the molecule axis.

Figure 3.11: Position of reactive sites in the polypeptide*



* Reproduced from Heidemann[2], p 287

If there exist multinuclear bonds of chrome complexes they should touch each other side wise and a lateral fusion is easily to imagine. Therefore, Heidemann suggested a lateral crosslinking of chrome complexes as shown overpage:-



* Reproduced from Heidemann[2], p 289

This attachment may occur at neutralisation or after ageing of leather and would also explain the increase of shrinkage temperature and insolubility which occur on ageing of leather. Shirai, Takahashi and Wada[122] found that organic anions imparted more or less an additional stabilising effect to the main framework of chrome tanned leather and that might be caused by increase in molecular weight of chrome complex by the replacement of sulphate with organic anions. These would also help better attachment as suggested by Heidmann. In summary therefore, it may be said that major amount of chrome is fixed by the carboxylic group of collagen, the rest are fixed by either hydrogen bond or other groups of collagen. However, it must be pointed out that most of the researchers have restricted themselves in their work at conventional tanning pH between 2.5 to 4.5, and therefore what happens at higher pH above 6 might not be explained with only the so called cationic chrome tanning. In that type of high pH chrome tannage, the role of nonionic and anionic chrome complexes would be different. Further, most of the researchers assumed chrome tanning agents as a single cationic complex or cationic complexes with similar affinity to collagen.

But we have found that the commercial chrome tanning agents contain small amount of anionic and mostly cationic and nonionic complex species with different reactivity to skin. In that case, during tanning, there will be progressive and rate-controlled changes in the composition of the chrome tanning liquor itself. Cationic complexes, particularly higher charge complexes react faster than nonionic and therefore would be depleted faster. This would lead to concomitant changes in concentration and composition which will upset existing equilibria and alter both relative and absolute concentrations with consequential effects on all the rate processes on which they depend, particularly pH and temperature of tanning. Such considerations are highly relevant to problems of chrome fixation and exhaustion but have been ignored by most researchers in leather field. We would discuss those in Chapter 5 in connection of our new technique of chrome tannages.

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CHAPTER 4
HIGH EXHAUST CHROME TANNING SYSTEMS

4.0 INTRODUCTION

4.1 High Exhaust Systems for Hides

There has been considerable research in the past decade to improve chrome exhaustion of the classical chrome tanning system. Significant improvement in the efficiency of the classical chrome tanning process can be achieved by controlling the pH, concentration, temperature and time,. By reducing the chrome offer from 8 - 10% chrome powder to 6%, increasing the end pH from 3.5 - 3.8 to 4.0 - 4.2 and temperature from 35 to 38°C, the efficiency of tanning could be increased from 75% to 85%. However, this improvement, though significant could not be enough to discharge the chrome exhaust liquor from tanneries without prior treatment. Prentiss and Prosad[1] showed that by reducing the Cr_2O_3 offer from 1.5 to 1.25% , the efficiency did not increase by more than 2% . This indicated the need for other means to improve chrome tannage.

Research efforts with self-basifying, masked chrome liquors or powders with dicarboxylic acid and straight forward use of various dicarboxylic acids and their salts were more successful in further reduction of residual chrome at the end of tannage. Goniprow and Fields[2] showed that addition of dicarboxylic acid after the penetration of chrome into the hide at the basification stage gave higher exhaustion of chrome than addition at the pickle stage. However, these types of dicarboxylic acids might give penetration and distribution problems for chrome within the whole thickness of the leather and normally gave very good results on lime split hide rather than full thickness heavy hides.

Mizutani et al[3] used 0.8% organic acids with sulphuric acid in the pickle at pH 3.0 and showed that pickle liquor treated with formic acid, acetic acid or lactic acid did not improve chrome exhaustion but adipic or phthalic acids gave significant improvement (about 70%) in reducing the residual chrome in spent liquors. The linking of dicarboxylic acids like adipic and fumaric acids improved chrome exhaustion but caused penetration problem. On the other hand chelate forming dicarboxylic acids like oxalic acid and maleic acids reduced chrome exhaustion but improve penetration. DasGupta[4] showed that the position of the carboxylic group in the polycarboxylic acid was very important for deciding which one would improve chrome exhaustion and the hydrothermal stability of the leather.

Recently, Francke[5] showed that the application of the two isomers maleic acid and fumaric acid offered most interesting possibilities for the overall improvement of chrome uptake and penetration. Maleic acid with the arrangement of carboxylic groups could not act as a linking agent but helped in better penetration. When heated in acid medium this would be converted into fumaric acid where carboxylic groups are in the trans position which would then act as a bridging ligand. As the conversion was a slow process, Francke suggested the addition of 1% maleic acid, with 0.2% thiourea to work as a catalyst, after two hours of tannage with 5% normal chrome powder. This looked to be a very good idea and only bulk trials in the future would help in establishing this type of approach.

In the mid-seventies considerable development of chrome tanning processes were advocated by Bayer which gave particularly good exhaustion of chrome during chrome tannage[7-9]. Luck in 1980[9] stated that it was not uncommon for chrome tanning floats to have 9 - 10 g/l Cr_2O_3 at the end of tanning. Assuming that the concentration of unbound chrome was the same both inside and outside the tanned hides, sammying and washing would release great portions of unbound chrome from the leather to the effluent. They also developed various processes for high exhaust chrome tanning with masked chrome with or without dicarboxylic acids. In these processes, addition of chrome to the leather was kept low initially and tanning started with standard commercial 33% basic chrome liquor or powder and completed with self basifying chrome tanning agent or dicarboxylic acids or their salts.

The advantages of these processes were claimed as follows:-

(a) low chrome content in the exhaust tanning bath, and

(b) low chrome release from subsequent washing, sammying and retanning.

Luck[7,8] claimed that these types of tannage gave about 1 g/l Cr_2O_3 (0.68 g/l Cr) and release of chrome during washing, sammying and retanning was significantly lower than conventional tannage. Emanuelson et al[10] thought that recycling of the residual floats of chrome tannage itself did not remove enough of the unutilised chrome tanning materials to satisfy the regulations which apply in some countries as generally residual floats and sammying liquids are only covered in recycling. Precipitation of all chrome from the residual tanning floats and from the various liquors from subsequent operations up to and including retannage is very complicated and expensive.

Luck et al[11,12] thought that for these, high exhaust chrome tannage recycling would not be necessary as the amount of unutilised chrome tanning material remaining is roughly the same as in recycling. Table 1 below gives the summary of various recent comparative work on the high exhaustion systems.

Table 4.1: Some comparative results of high exhaust systems vs conventional tannages

Treatments	Percentage of Cr_2O_3 (offered on lime pelt weight basis)		Percentage Cr_2O_3 in			
			Leather (MFB)		Residual Float (g/l)	
	Control	Experiment	Control	Experiment	Control	Experiment
Goniprow et al						
[*JALCA*, **74**, 6, (1979)]						
(a)	1.46	1.5% DC + 1.46	3.21	4.75	0.503	0.419
• final pH	3.9	3.9				
• final temperature	100°F	100°F				
• finished crust leather			3.44	4.92		
(b)	1.46	1.46 DC + 1.5%	3.21 DC	4.41	0.503	0.395
• final pH	3.8	3.9				
• final temperature	100°F	100°F				
• finished crust leather			3.44	5.06		

....continued.

Treatments	Percentage of Cr_2O_3 (offered on lime pelt weight basis)		Percentage Cr_2O_3 in			
	Control	Experiment	Leather (MFB)		Residual Float (g/l)	
			Control	Experiment	Control	Experiment
Luck						
[*JALCA*, **75**, 378, (1980)]	1.924	1.426	4.76	4.83	5.5 - 6.4	0.7
• final pH	3.5	4.0				
• temperature	38°C	49 - 50°C				
• finished leather (after retanning)			4.14	4.32	5.5 - 6.4	1.5 - 3.2
Luck						
[*JALCA*, **77**, 90, (1983)]	1.93 - 1.95	1.514 - 1.597	5.33	5.42	5.5 - 6.4	1.5 - 3.2
• final pH	3.6	4.2				
• final temperature	40°C	50°C				
• finished leather (after retanning)			4.49	4.68		
Luck, Rosentreter & Wehling						
[*JALCA*,**82**,125,(1987)]						
(a) unsplit hide	1.80	1.35	3.49	3.31	5.07	2.0
. final pH	3.3	4.0				
. final temperature	45°C	53°C				
(b) unsplit uphostery leather	1.80	1.0	3.3	3.5	7.29	0.35
. final pH	3.4	4.0				
. final temperature	33°C	45°C				
Francke,						
[*Das Leder*, **43**,21,(1992)]						
(a) unsplit	2.0	1.5	3.8	3.7	4.76	1.43
• final pH	4.0	4.0				
• final temperature	40°C	40°C				
(b) split upholstery	2.0	1.5	3.8	3.7	3.44	0.95
• final pH	4.0	4.0				
• final temperature	40°C	40°C				
Schlosser						
(*IULTC* Congress, Barcelona 91)						

(a) unsplit	2.00	1.25	-	3.541	-	1.5 - 3.0
- final pH		4.0				
- final temperature		40°C				
(b) split upholstery		1.1	-	3.9 - 4.4	-	0.3 - 0.6
- final pH		4.2 - 4.4				
- final temperature		40 - 45°C				
Mayer						
[*JALCA*, **76**, 35, (1981)]	1.7 - 2.0	1.2 - 1.4	-	3.6 - 3.8	-	3
- final pH	3.8	4.0 - 4.1				
- temperature	38°C	40 - 42°C				

It was noticed that almost all experiments were conducted with 1.8 - 2.0% Cr_2O_3 as control which was not the practice in New Zealand at present. The advantages when compared to the present system of chrome tanning of 1.5% Cr_2O_3 offer and end pH 4.0 and temperature of 40 - 45°C might not be so significant. To study the benefits of various high exhaust systems to New Zealand conditions, we planned experiments with New Zealand wet salted hide.

4.2 High Exhaust Systems for Lamb Skins

It was surprising to note how little published work exists on high exhaust chrome tanning systems for lamb skins, even though considerable work has been reported on hides[13,14]. We therefore attempted a comprehensive study on lamb skin tannage. The following alternative approaches were pursued to improve the exhaustion of chrome and minimise its environmental impact:-

(a) improving the classical system, ie. reduced chrome offer, lower float, higher temperature and pH of tannage.

(b) addition of auxiliary chemicals, ie. so called high exhaustion aids, during tanning, or complexed with chrome.

(c) changing the present technology of tanning, ie. no pickle, high pH tanning after deliming without any pretannage.

(d) changing the chrome complex itself, ie. removing or modifying the non-reactive species of chrome complexes contained in chrome tanning agents.

The first two options were considered here. The other options would be discussed in Chapter 5 and 6.

4.3 Experimental

4.3.1 Hides

Eighteen New Zealand ox hides (~28 kg) were collected from a local slaughter house, fleshed and salted out following standard procedures. These salted hides were cut into four quarters each and numbered. Seven quarters were selected per set at random following an incomplete block design. Each set was then allotted to the following eight chemicals, keeping two sets as controls. Isophthalic was obtained from Amoco Chemicals Corporation, USA. This was converted into a mixed salts, partly with caustic and partly with ammonia. Oxazolidine E used in the trial was also developed and patented by the author[15].

Trade Name		**Chemical**	**Supplier**
1.	Neosyn EE	Natural syntan	Hodgson Chemicals, UK
2.	Baychrome P	Masked chrome syntan	Bayer, Germany
3.	Cromeno A	Acrylic polymer)	
	Cromeno FN	MgO)	Rohm Tech, Germany
4.	Feliderm CSN	Glyoxyl	Hoechst, Germany
5.	Uberol 8027	Mixture of Polycarboxylic Acids	Carpetex, Germany
6.	Zolodine	Oxazolidine E	Angus Chemical, USA*
7.	Implenal DC	Dicarboxylic Acid	BASF, Germany
8.	-	Part sodium, part ammonium salt of Isophthalic acid	Author's preparation

* this product was developed and patented by the author

4.3.1.1 Chrome Tanning Process

The salient features of the overnight processes for hides tanning were as given below:-

Systems	Pretreatment	Chrome Offer Percent*	Exhaust Aid	Final pH	Temp °C
LASRA Standard					
(a) with oil	1% Atlasol 177°C	6	0.5% Tanbase	3.85	43
(b) without oil		6	0.5% Tanbase	3.85	42
(c) Neosyn EE		5	1% Neosyn EE	4.0	47
(d) Baychrome CP		4.6% 2.5%	4.6% Chromosol BS 2.5% Baychrome CP	4.25	46
(e) Cromeno A/FN		5	1% Cromeno A 0.9% Cromeno FN	4.05	45
(f) Feliderm CSN	1% Feliderm CSN	5	0.5% Tanbase	3.8	44
(g) Uberol 8027		5	0.6% Tanbase 0.3% Uberol 8027	4.14	46
(h) Oxazolidine E		5	1.75% Oxazolidine E	3.85	46
(i) Sod/Amm phthalate		5	1.18% Sod/Amm phthalate	3.80	40
(j) Implenal DC			1.2% Implenal DC 0.2% Tanbase	3.60	45

* Tannachrome S (25% Cr_2O_3, 33% basic) unless otherwise stated

4.3.1.2 Chemical Analysis

The chrome in the initial chrome tanning bath was determined after ten minutes runing and at the end of the tanning process. The wet blue was then analysed for chrome (Cr_2O_3) and moisture content. The efficiency of the tanning systems were calculated. However, this did not take account of the chrome lost during washing, sammying and retanning. This may be calculate from formula x = 0.438 y given by Backer *et al*[7] where:-

x = chrome oxide released after tanning, expressed in Kg/ton
y = chrome oxide of the residual tanning float, expressed in g Cr_2O_3/l

Stratographical analysis of wet blue was also carried out in four layers for Cr_2O_3 to study the distribution of chrome within the cross section of the wet blue.

Two wet blue hides (export grade) were also collected from each of the nine commerical tanneries in New Zealand for compairson purpose.

4.3.1.3 Retannage

All wet blue sides were then split and shaved to 2.0 to 2.2 mm and crusted out following the process of retannage given overpage. At each stage of this retanning process exhaust liquors were collected, weighed and sampled for chromium analysis to study chrome leaching characteristics of these systems. The dry leather was analysed for chrome and tested for all physical properties to find out any differences.

Retanning process

Operation	%	Chemical	Temp (°C)	Running Details
Weigh Sides				
Add	150%	water		
	0.25%	GN9	40	10 min
Check pH				
Collect Sample of Liquor				Sample 1
Drain				
Add	100%	water	50	
	+ 0.25%	sodium bicarbonate		
	+ 1.5%	sodium formate		40 min
Check pH = 4.5 - 5.0 pH = ______				
Check cut through neck with BCG = Green: ______				
Add	+ 2.0%	Mimosa extract powder		
	+ 3.0%	Neosyn PFW		
	+ 3.0%	Retingan R7		
	+ 50%	water		45 min
Collect Sample of Liquor				Sample 2
Drain				
Add	100%	water	50	
	+ 0.5%	Sandolix WWL		5 min
Add	1%	Dermalight Black PL-RS		30 min
Add	20%	water	60	
	+ 5.0%	Remsynol SWM		
	+ 2.0%	Trisul ML		
	+ 0.5%	Derminol Oil NS		30 min
Add	+ 0.5%	Formic Acid		15 min
Check pH = 3.8 - 4.0 : pH = ______				
Add	1.0%	Lipamin Liquor SO		15 min
Collect Sample of Liquor				Sample 3
Drain				
Rinse	300%	water	25	10 min
Collect Sample of Liquor				Sample 4
Sammying Liquor				Sample 5

4.3.2 Lamb Skins : Series A

4.3.2.1 Allocation of Experimental Pickled Lamb Pelt Material

Twenty four dozen New Zealand pickled pelts were collected from a local fellmongery and randomly allotted to the following:-

(i) Five sets each of 30 skins - one set each was given to five New Zealand commercial lamb pelt tanners, each coded 1 to 5.

(ii) Ten sets each of 12 skins - two sets were allotted to a standard LASRA process, one with 6% Tannachrome S and the other with 5% Tannachrome S (coded A and B). The other sets were allotted to high chrome exhaust systems and coded C to J.

4.3.2.2 Tannages

Commercial lamb pelt tanners were asked to tan their experimental lot of skins with their regular production lots. After tannage the experimental skins were brought back to LASRA with their exhaust chrome liquors. All other sets were tanned at LASRA in Dose drums, following the chemical suppliers' recommendations. The salient features of these processes are given overpage:-

Systems	Pretreatment	Chrome Offer Percent*	Exhaust Aid	Final pH	Temp °C
Code A	1% Nutrol DP	5	0.45% Tanbase	3.8	38
Code B	1% Nutrol DP	6	0.5% Tanbase	3.9	38
Code C	Oxazolidine E	4.6	2.5% Oxazolidine E	3.85	40
Code D	Cromeno A/FN	4.6	1% Cromeno A 0.9% Cromeno FN	3.9	40
Code E	Neosyn EE	4.6	1% Neosyn EE	3.9	3.9
Code F	Baychrome 2420		6% Chromosol 2420 2.5% Baychrome CP	4.65	38
Code G	Uberol 8027	4.6	0.6% Tanbase 0.3% Uberol 8027	4.04	40
Code H	Sod/Amm phthalate	4.6	1.4% Sod/Amm phthalate	3.84	38
Code I	Implenal DC	5	1.5% Implenal DC 0.2% Tanbase	4.0	40

* Tannachrome S (25% Cr_2O_3, 33% basic) unless otherwise stated

4.3.2.3 Chemical Analysis

Samples from the pickled pelts and wet blue skins were taken for moisture and chrome analysis. Exhaust liquors were analysed for chrome content and the efficiency of the tanning systems calculated.

4.3.2.4 Retannages

All wet blue skins were shaved and retanned following the method given below. At each stage of this retanning process exhaust liquors were collected, weighed and chrome contents were analysed to study chrome leaching characteristics. The crust leather was evaluated for quality and physical properties.

OPERATION	%	CHEMICAL	TEMP° C	QTY	RUNNING DETAILS/TIME
RAW MATERIAL = WET BLUE LAMB PELTS					
Sam, collect sammying liquor for chrome analysis (L_1)					
WEIGH SKINS				kg	
Collect three cut pieces for chrome analysis (S_1)					
WET BACK	200%	Water	30		
	+ 0.2%	Teric GN9			10 minutes
* Collect exhaust liquor for chrome analysis (L_2)					
DRAIN					
NEUTRALISE	150%	Water	30		
	+ 1.0%	Sodium Formate			
	+ 0.5%	Sodium Bicarbonate			60 minutes
CHECK pH = 4.9 to 5.1 : pH =					
CHECK cut through neck with BCG = GREEN:					
RETAN					
ADD	6.0%	Neosyn PFW			30 minutes
* Collect exhaust liquor for chrome analysis (L_3)					
DRAIN					
ADD	300%	Water	50		10 minutes
* Collect exhaust liquor for chrome analysis (L_4)					
DRAIN					
DYE	100%	Water	60		
	+ 0.2%	Ammonia			10 minutes
ADD	0.6%	Dermacarbon Black			
RUN		Heating to 60°C			45 minutes
ADD	20%	Water	60		
	+ 8.0%	Remsynol SWM			30 minutes
ADD	5.0%	Water	60		
	+ 0.5%	Formic Acid			20 minutes
CHECK pH = 3.5 to 3.7 : pH =					
* Collect exhaust liquor for chrome analysis (L_5)					
DRAIN					
ADD	300%	Water	20		15 minutes
* Collect exhaust liquor for chrome analysis (L_6)					

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* After normal drying staking and toggling, examine leather for quality. Cut three pieces at random from three skins for chrome analysis (S_2)

4.3.2.5 Physical Tests

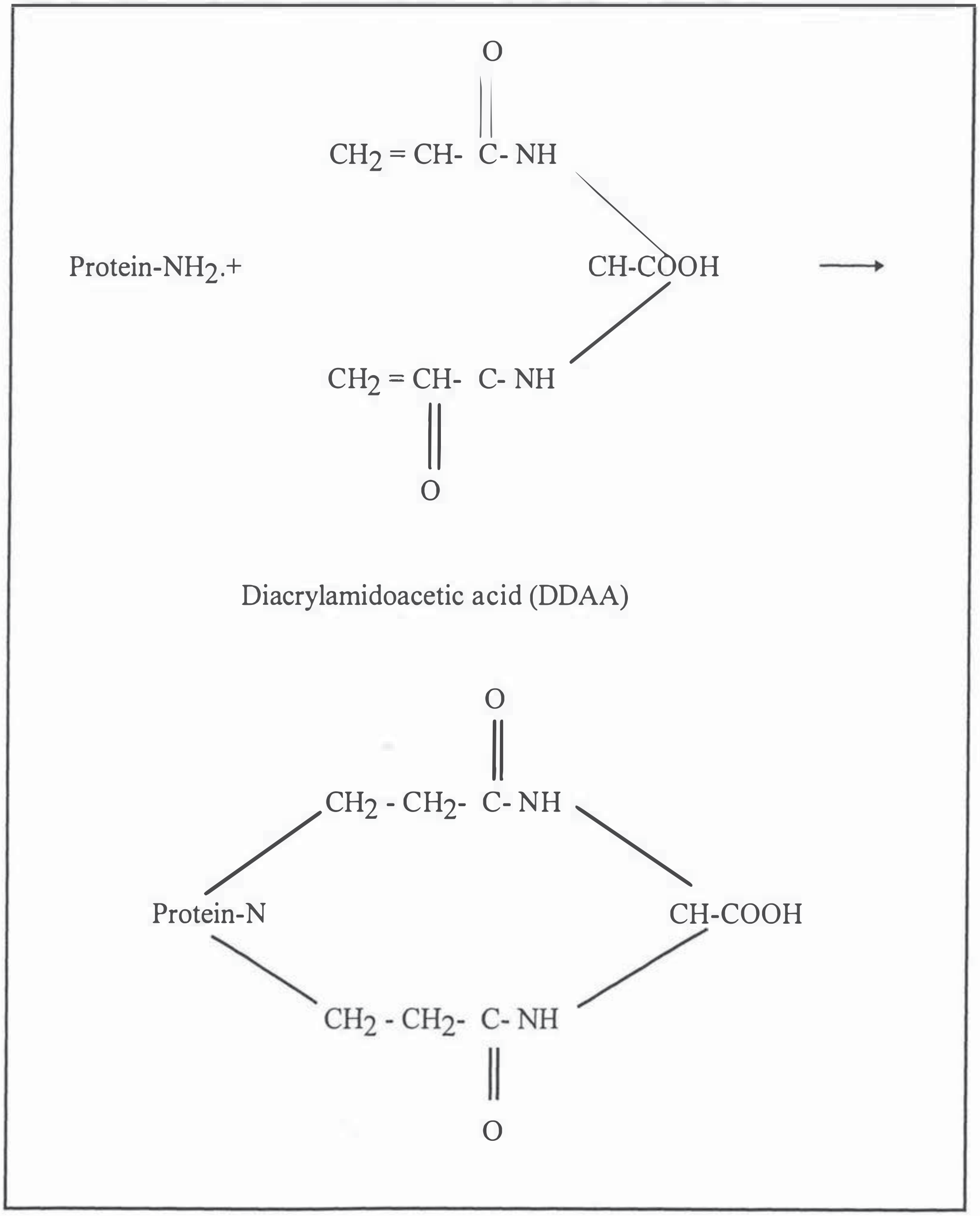
Tensile strength, elongation at break, tear strength, lastometer distension at grain crack and load at grain crack were determined following the test methods of the International Union of Leather Technologists and Chemists.

4.4 Results and Discussion

4.4.1 General

Each of the high exhaust auxiliaries worked in a different way depending upon their chemical nature. The neutral syntans have very low tanning power and they might initially link up with the chrome forming a loose complex. These complexes, like Neosyn EE initially retarded the direct reaction with the carboxylic group of the hide protein, allowing better penetration of chromium into the cross-section of hide. Gradually, they were replaced by the stronger carboxylic group of the hide protein and thus helped in the better exhaustion of chrome during tanning. The chrome-syntan complexes worked in the same manner as the neutral syntan. Recently sulphophthales have received attention for masking but their complex formation was slower than phthaltes. Otto[16] recommended that owing to their stronger acidity, they might be employed at the beginning of the tanning. Products like Baychrome CP were pre masked and modified so that these products might be added directly into the tanning drum as a single product.

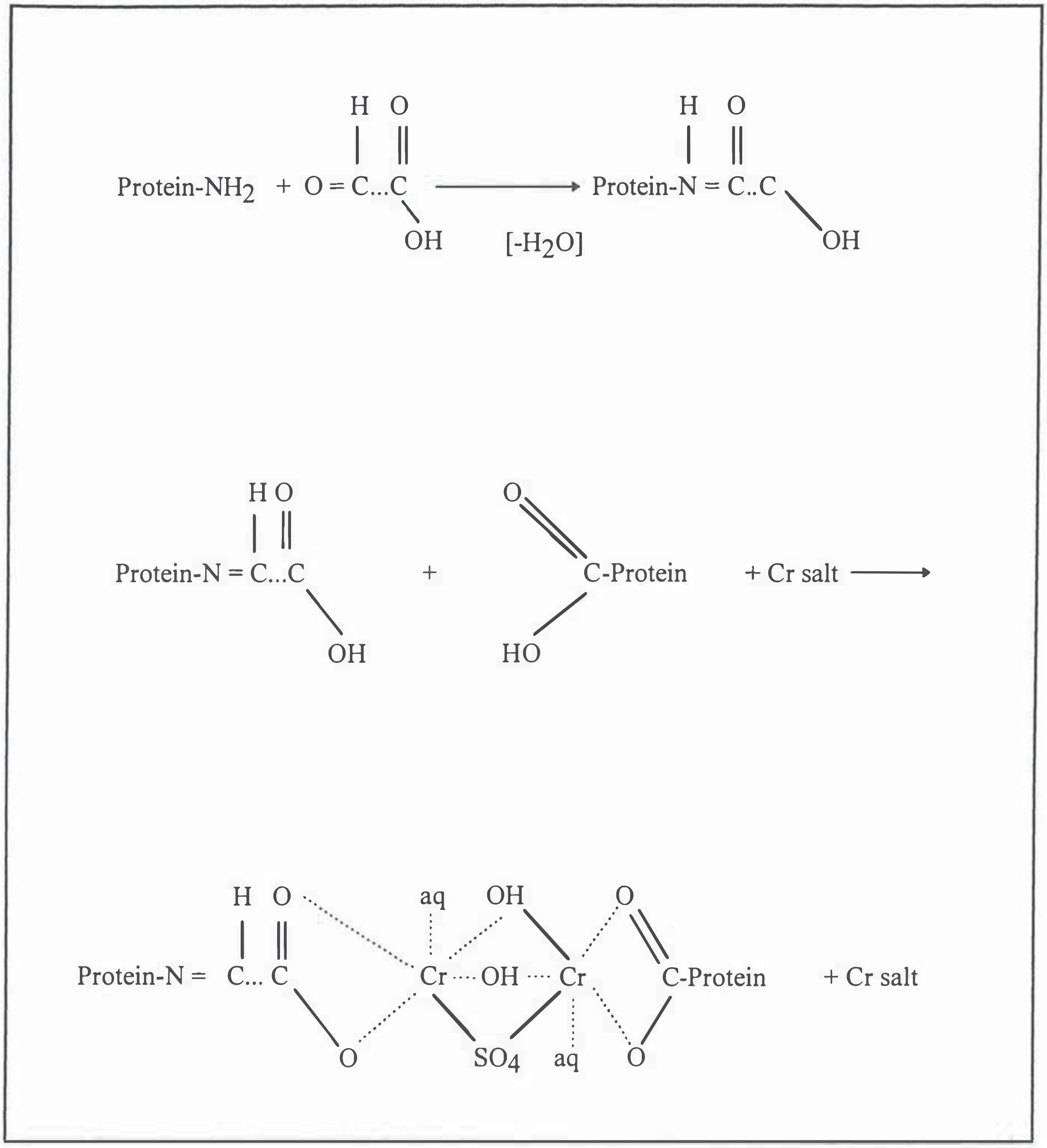
Scholnick, Diffendorf, Feairheller and Kronick[17] obtained 30.5 to 33.5% higher chrome uptake than control by blocking the basic groups with 3-10% Diacrylamidoacetic acid (DAAA). Similarly, Scholnick, Liao, Brown and Feairheller[18] reacted the basic groups of collagen with N-hydroxysulphosuccinimide esters of dicarboxylic acid (C4--C16) and noticed on subsequent chrome tanning a significant increase in the shrinkage temperature of the treated leather. They thought that these higher shrinkage temperature and high chrome exhaustion was due to the following reactions which provide additional site for chrome fixation during tanning.



Other acrylic polymers, like Cromeno A even though much simpler in nature also worked in the same manner. Mizutani, Mohri, Arima and

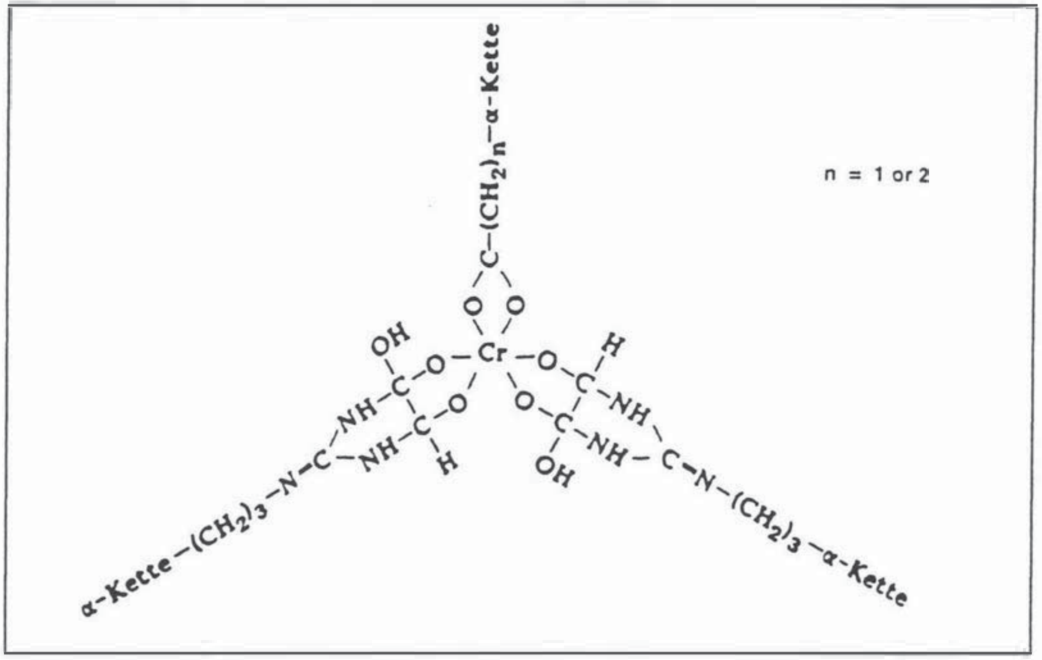
Okada[3] when employed adipic acid or phthalic acid, found hardly any change in the shrinkage temperature of the resultant leather but the quantity of chrome remaining in the exhaust chrome bath was reduced by about 70%. Implenal DC and Uberol 8027 both containing dicrboxylic acids were intended to work on the same principle.

DasGupta[4] originally applied and patented aromatic polycarboxylic acids like pyromallitic acid and showed that chrome tanned leather could be given increased shrinkage temperature and decreased contraction on prolonged heating if treated with such polyfunctional acid followed by another offer of chromium. He postulated that these benefit in reduction of chrome in the exhaust tanning bath were due to the fact that additional cross-links were introduced between the chromium complexes bound initially to the collagen and the second chromium offer via the polyfunctional carboxylic acid. This principle has been successfully extended by DasGupta[19] for the improvement of aluminium tannage and later on by Davis, Montgomery and Scroggie[20] to develop a white leather of exceptionally high stability using Zirconium and Aluminium with pyromellitic acid salts. Feliderm CSN was based on aldehyde carboxylic acid, glyoxyl. Their reaction as shown by Chang and Heidemann[21] and Fuchs[22] might be depicted as given overpage:-



Chang and Heidemann[23] also determined experimentally with model compounds that stable 3- point binding complexes with structure shown in Figure 4.1 might be formed by glyoxylic acid with chrome linking in a starlike structure, one glutamic acid side chain carboxyl group with two arginine side chains of the hide protein. This would reduce the amount of chromium needed to provide boil resistance leather and improve the exhaustion of chrome during tanning.

Figure 4.1: Glyoxylic acid with chrome linking in a starlike structure



Oxazolidine E patented by DasGupta[15,24], on the other hand reacted with the basic groups of the collagen directly through the aldehyde group and thereby depressed the isoelectric point of the collagen. These then would cause further dissociation of the carboxylic groups of collagen which would become available to the basic chrome sulphate for fixation. This mechanism, therefore, would be pH dependent and apart from giving better exhaustion of chrome would also provide additional characteristics like softness and perspiration resistance to such chrome tanned leather.

4.4.2 Hides

Table 4.2 gives the exhaustion of chrome liquors from these systems. From this, we can see that in general, all high exhaust systems give about 10 - 12% more chrome exhaustion from the tanning offer, but it should be noted that this figure does not include chrome lost to effluent during subsequent sammying, washing and retannage. Neither does it take into consideration the final dilution that will normally take place in a tannery before the effluent is discharged.

For wet blue tanning however a 96% exhaustion should be aimed at to allow for discharge without prior treatment or recycling. None of the systems reached that efficiency, but Baychrome CP, oxazolidine E and Neosyn EE, Uberol 8027 and Cromeno A/FN systems all reached very near to that figure and deserve further large scale trials.

Table 4.2:Chrome exhaustion of various tanning systems

Treatments	Initial Chrome as Cr* (mg/l) (2)	Final Chrome as Cr (mg/l) (3)	Exhaustion (%) (4)
A : LASRA standard (with oil)	12,699.96	1,809.67	85.75
B: LASRA standard (without oil)	12,473.75	2,359.02	81.10
C: Neosyn EE (Hodgson)	10,113.80	818.70	91.90
D: Baychrome CP (Bayer)	9,143.30	511.70	94.29
E: Cromeno A/FN (Rohm)	11,301.10	1,003.10	91.12
F: Feliderm CSN (Hoechst)	11,250.96	1,387.60	87.67
G: Uberol 8027 (Carpetex)	10,214.50	769.00	92.47
H: Oxazolidine E (Allied)	9,311.70	635.30	93.18
I: Sodium/Ammonium Salt of lsophthalic acid	12,925.00	1,317.00	89.81
J: Implenal DC (BASF)	12,930.50	2,026.70	84.32

* chrome sample taken after ten minutes from the start of tannage

Significant differences in leather appearances and softness at the wet blue stage was noticed. LASRA control with oil and oxazolidine E gave the softest "wet blue". Neosyn EE, Cromeno A/FN and Uberol 8027 had almost similar colour as the standards, while Baychrome CP, Implenal DC and LASRA modified with dicarboxylic acid gave masked coloured leather. The grain layers with Baychrome CP looked dry and rough compared to the standard. Figure 4.2 gives the stratographical distribution of chrome (as Cr_2O_3), on moisture free basis within four layers.

Figure 4.2a: Layerwise distribution of chrome in wet blue hide : set one

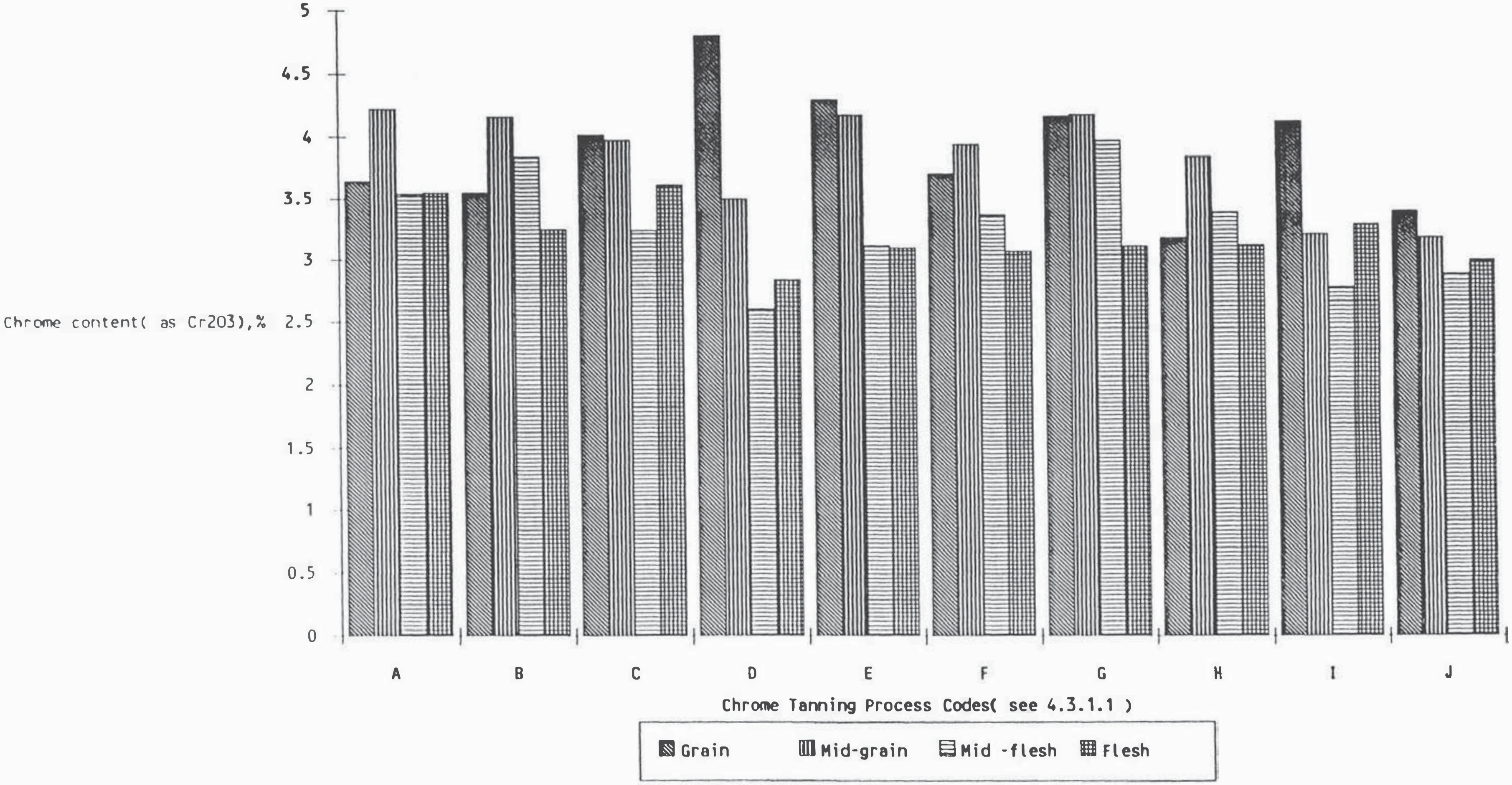
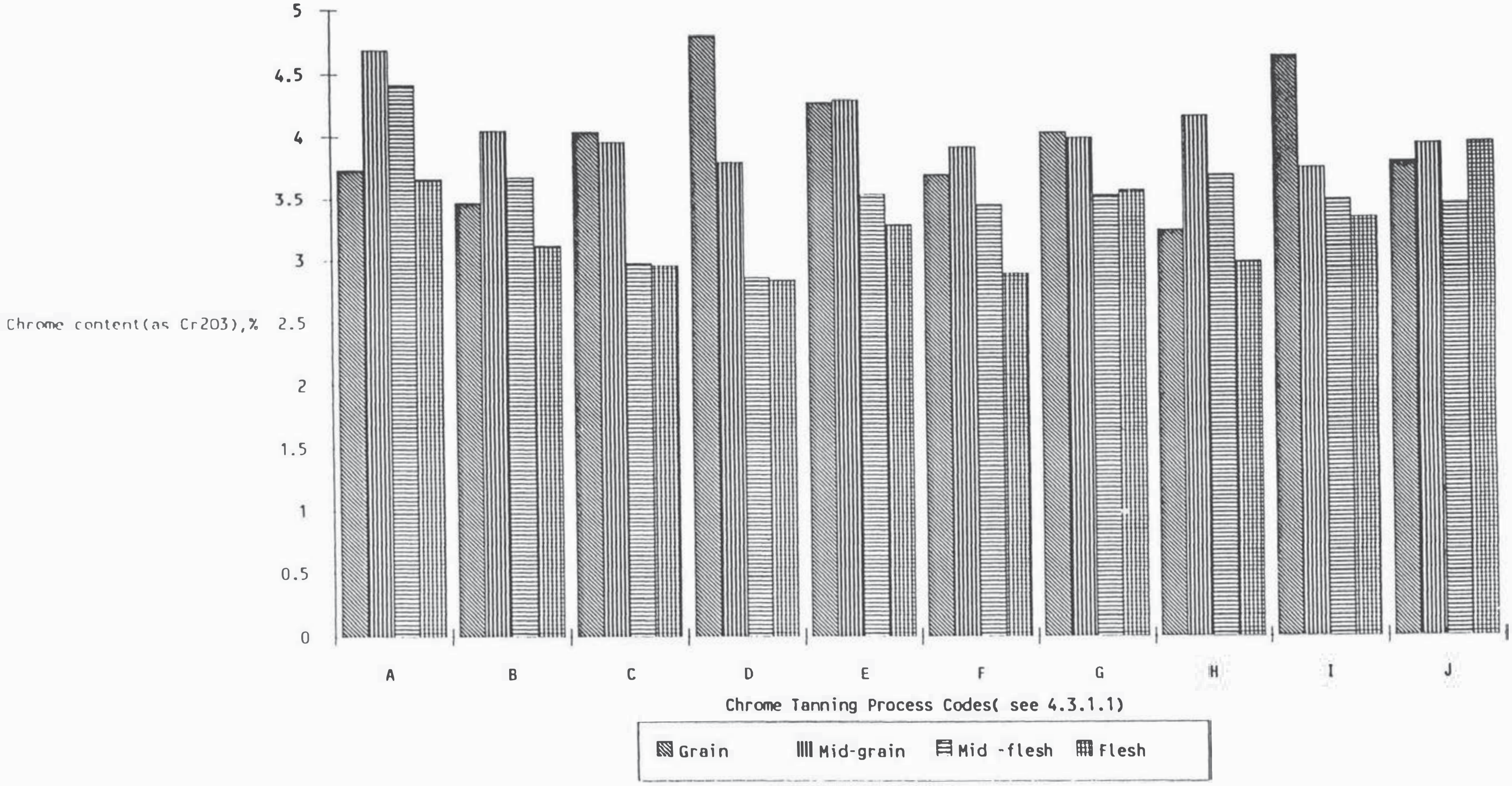


Figure 4.2b: Layerwise distribution of chrome in wet blue : set two



The results show that there were few problems in any process but Baychrome CP gave considerably more chrome in the first two layers. A slight problem was also noted for Cromeno A/FN and LASRA dicarboxylic modified process. Comparative efficiency and mass balance for chromium of various chrome tanning systems when calculated from the chrome content in unsplit hide versus actual chrome offered are given in Table 4.3.

Slightly different values of exhaustion than those obtained from liquor analysis were obtained but in general the order remained similar. Of interest was the difference of efficiency between the two LASRA standards, with or without oil. The small amount of oil seemed to benefit the efficiency of chrome absorption into leather and also improve the physical strength properties. Another very important fact was confirmed that isophthalic acid salt gave 5 - 6% better efficiency over Implenal DC type mixed dicarboxylic acids.

Table 4.3 Mass balance for chromium and efficiency of high exhaust chrome tanning systems of hides

	Tanning process codes for High exhaust chrome tanning systems									
	A	B	C	D	E	F	G	H	I	J
Weight of limed pelt,Kg*	50.9	58.3	53.8	57.4	57.95	60.65	55.65	46.31	67.4	71.6
Moisture in pelt, %	69	70	68	68	68	67	68	67	68	67
Chrome offered%,(as Cr**),%	1.02	1.02	0.85	0.904	0.85	0.85	0.85	0.85	0.85	0.85
Total Chromium,(as Cr),g	519.18	594.66	457.3	519.8	492.66	515.61	473.11	393.55	572.9	608.6
Chromium in exhaust, (as Cr**),g/l	1.810	2.359	0.819	0.512	1.003	1.388	0.769	0.635	1.32	2.03
Total Chromium in exhaust#,(as Cr),g	69.78	115.52	32.9	21.7	41.91	59.01	31.35	21.14	61.38	98.76
Actual Chrome in wet blue after tanning,(as Cr**),%	2.57	2.502	2.44	2.28	2.448	2.3324	2.38	2.3	2.35	2.2
Calculated Chrome in wet blue after tanning,(as Cr),g	0.877	0.825	0.781	0.83	0.783	0.77	0.785	0.793	0.752	0.726
Efficiency: calculated,%	85.95	80.58	92.8	94.29	91.49	88.56	93.37	94.6	89.28	84.32
: :actual ,%	86.55	80.88	91.88	91.82	92.15	90.55	92.4	93.29	88.5	85.42

* Accuracy of the tannery balance : + or - 0.1 Kg.
**Accuracy of chrome determination : + or - 0.3%

Chromium Leaching Characteristics

The chrome discharge from various retanning operations were as given in Table 4.4

Table 4.4: Chromium in wet blue and in discharge liquors

Tannery Code	Chromium in Wet Blue (% Cr_2O_3)	Washing S1	Neutralisation S2	Dye/Fatliquoring S3	Wash S4	Sammying S5
C1	5.14	226	230	198	56	50
C2	3.37	162	130	111	24	71
C3	4.93	275	243	217	41	41
C4	3.93	81	120	94	33	33
C5	4.18	227	107	110	62	62
C6	3.34	110	83	47	16	47
C7	3.39	81	87	47	23	34
C8	3.20	54	61	27	8	26
C9	3.51	216	169	101	27	74
A+	4.2	122	137	165	44	40
B+	4.4	206	154	171	34	94
C	4.8	60	60	51	17	60
D	4.8	17	26	26	17	26
E	4.9	88	106	79	53	70
F	4.1	141	97	106	106	106
G	5.1	96	70	175	106	70
H	3.8	87	103	70	114	70
I	4.2	88	70	44	53	61
J	3.9	158	78	52	35	80

Code C1 to C9 were for leather obtained from commercial wet blue production where as Code A to Code J were for wet blue processed at LASRA.

All values are in mg-Cr/l

\+ These are not a high exhaust process but included for control purposes

The data obtained from analysing the post-tanning process liquors were shown in Figures 4.3 to 4.9.

Figure 4.3: Chromium losses (post tanning processes) : code 1 to code 3

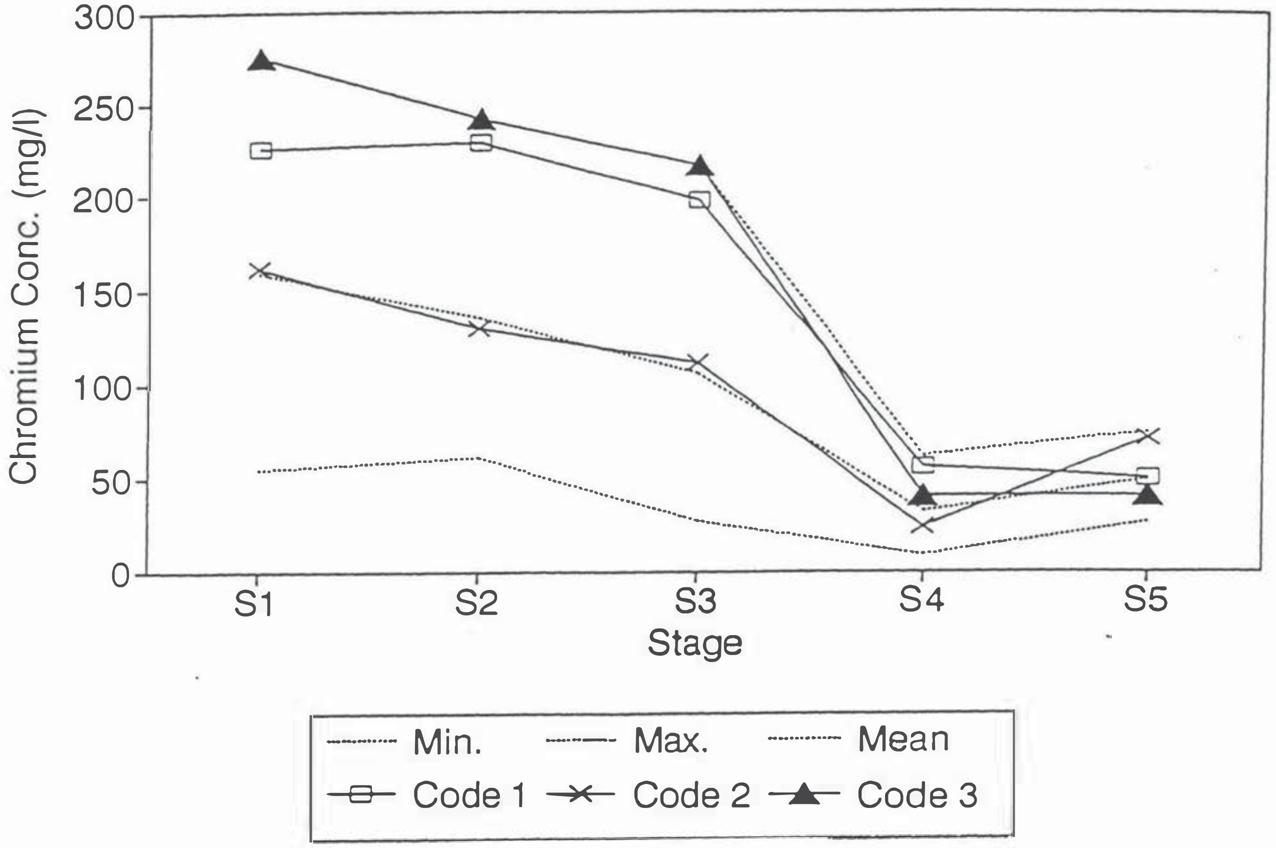


Figure 4.4: Chromium losses (post tanning processes) : code 4 to code 6

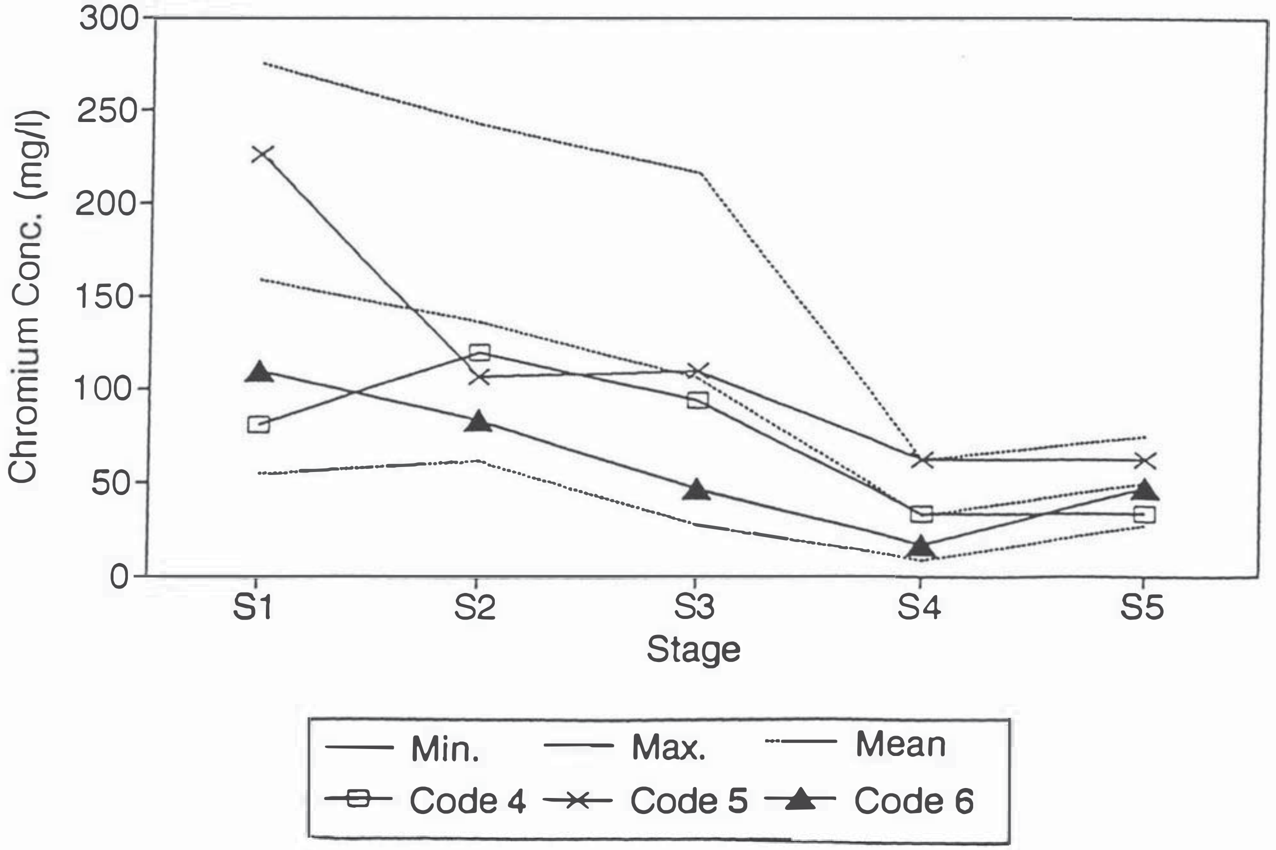


Figure 4.5: Chromium losses (post tanning processes) : code 7 to code 9

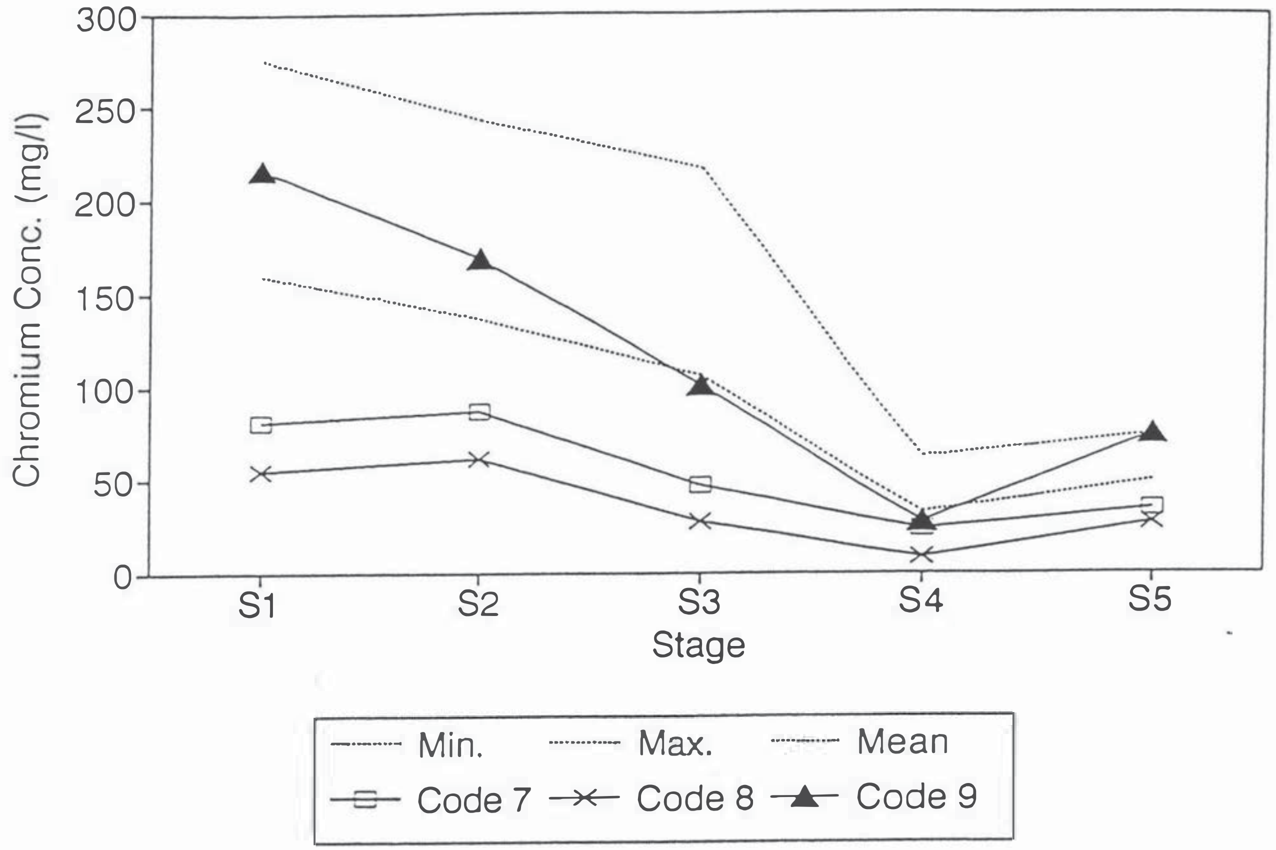


Figure 4.6: Chromium losses (post tanning processes) : code A to code C

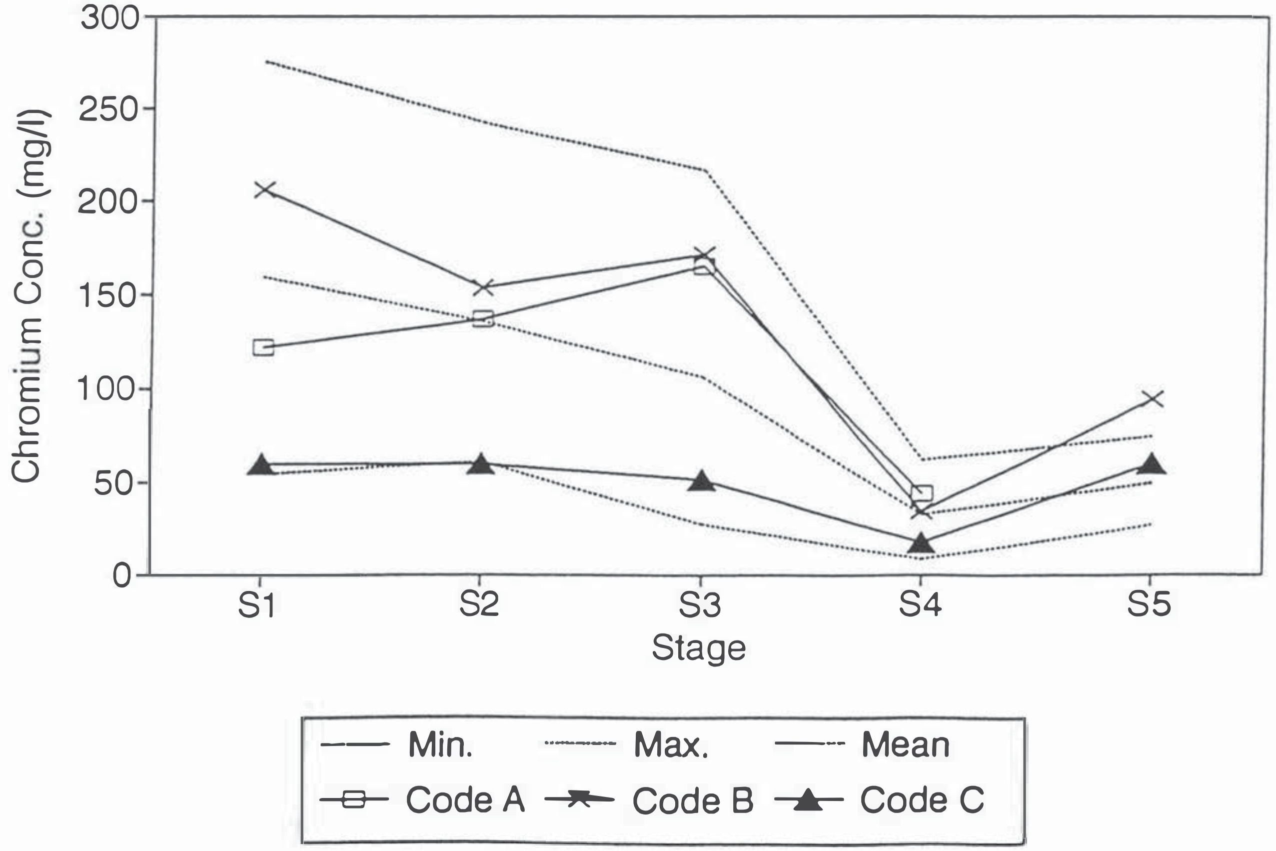


Figure 4.7: Chromium losses (post tanning processes) : code D to code F

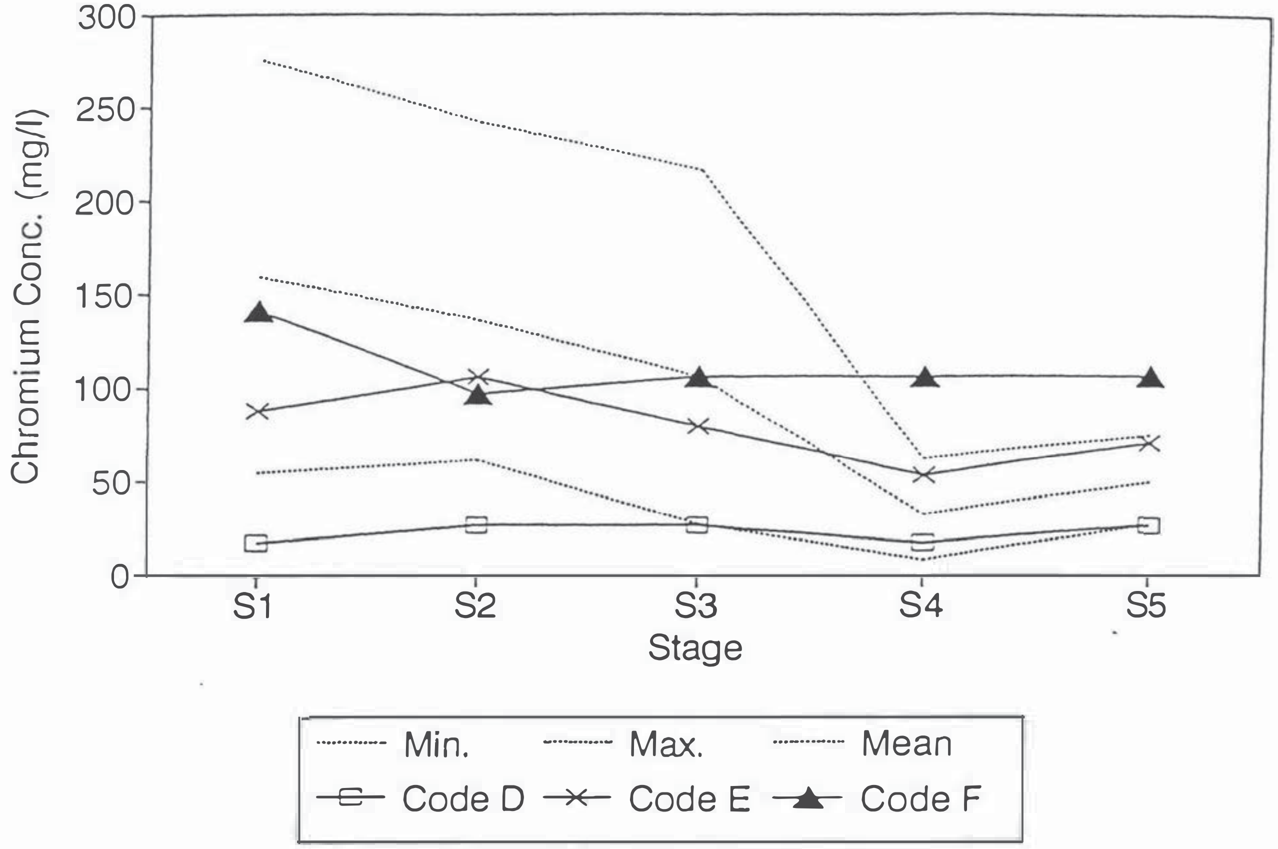


Figure 4.8: Chromium losses (post tanning processes) : code G to code I

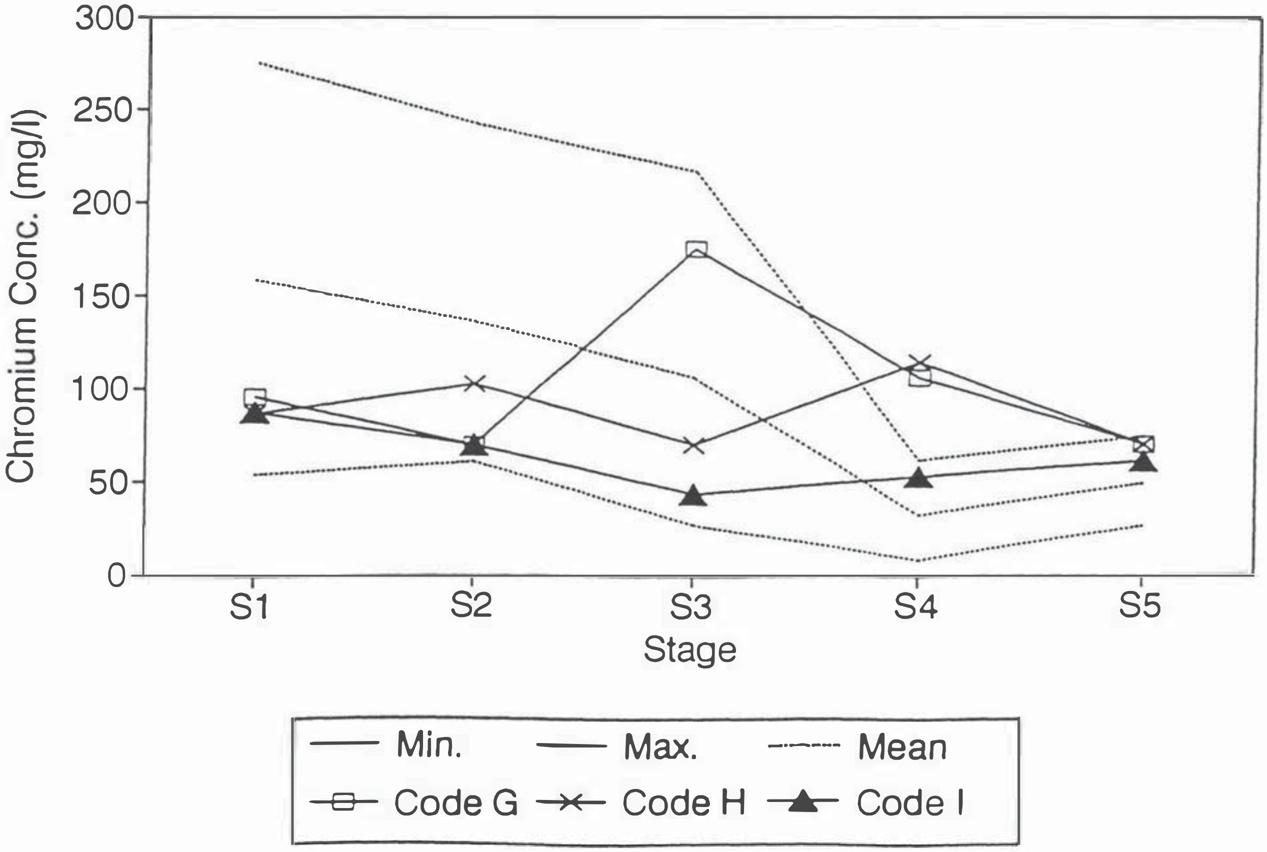
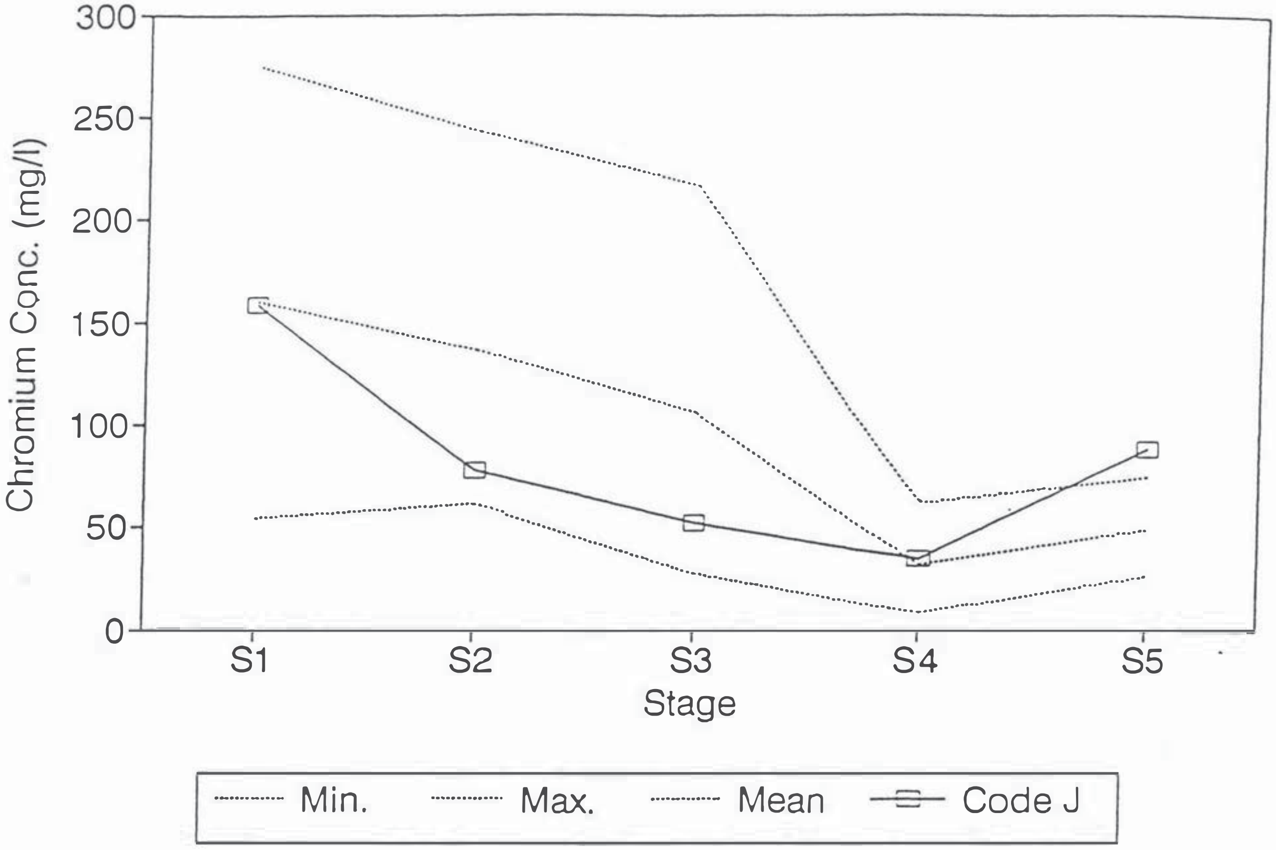


Figure 4.9: **Chromium losses (post tanning processes) : code J**



For the tannery survey, the minimum, maximum and average values were calculated for the nine runs over each process stage. These statistical parameters were included in each of the seven figures for comparison purposes. A large variation was observed in the chromium leaching characteristics between all nine processes. Tannery Code 8 gave the best results (least chrome leaching) followed closely by Codes 7 and 6.

For the high exhaust process, a large variation also existed between the processes. Processes A and B are not high exhaust processes and were used as controls. Process D gave the best results which were significantly lower than the best results obtained in the tannery survey.

Combined Effluent and Mass Balance of Chromium

The final chromium concentration of the combined effluent and the mass balance of chromium from the post-tanning process given in Table 4.5 and 4.6. These were calculated from the chromium concentration in each liquor and the quantity of the liquor discharged.

When comparing trade waste limits with combined effluent concentrations an important factor to consider was that of dilution. In this trial the water usage per kg of wt blue was 7.4 litre. In general commercial processes[26] use 30 - 35 l/kg, depending on the availability of the water and the costs associated with waste treatment. The information from Table 4.5 and Table 4.6 were graphically presented in Figure 4.10 and Figure 4.11.

Table 4.5 Mass balance for chromium in retanned sides from commercial wetblue

	Treatment code of Tannery wet blue								
	C1	C2	C3	C4	C5	C6	C7	C8	C9
Weight of Wetblue,Kg*	17.1	17.25	18.7	15	14.65	21.4	15.5	17.95	18.65
Moisture in wet blue, %	60.6	63.2	58.1	63.6	64.8	63.6	63.1	62.5	55.8
Chrome in wet blue%,(as Cr**),%	1.38	0.84	1.40	0.97	1	0.83	0.85	0.82	1.08
Total Chromium,(as Cr),g	235.12	145.42	262.74	145.95	146.5	176.98	131.90	146.47	201.23
Chromium in exhaust, (as Cr**),g/l	0.1405	0.101	0.148	0.056	0.100	0.063	0.053	0.036	0.11
TotalChromium in exhaust,(as Cr),g	17.84	12.89	20.48	0.64	10.84	9.82	6.08	4.78	15.60
Actual Chrome in wet blue after retanning,(as Cr**),%	1.27	0.76	1.3	0.93	0.93	0.78	0.81	0.79	1.0
Calculated Chrome in wet blue after retanning,(as Cr),g	1.27	0.77	1.29	0.96	0.93	0.79	0.82	0.79	1.0
Chrome lost from wet blue,%	7.3	8.9	7.8	4.4	7.4	4.3	4	3.3	7.9

* Accuracy of the tannery balance : + or - 0.1 Kg.

**Accuracy of chrome determination : + or - 0.03%

Table 4.6 Mass balance for chromium in retanned sides from high exhaust chrome tanning systems

	Tanning processing codes for High exhaust chrome tanning systems									
	A	B	C	D	E	F	G	H	I	J
Weight of Wetblue,Kg*	16.5	18.5	16.5	17.4	15.6	16.6	14.4	14.2	18	18.5
Moisture in wet blue, %	58	57.5	60	60.5	60	59	58.5	59	60	60
Chrome in wet blue%,(as Cr**),%	1.2	1.27	1.92	1.289	1.332	1.143	1.16	1.059	1.142	1.06
Total Chromium,(as Cr),g	197.47	235.2	316.8	224.29	207.8	189.74	167.1	150.378	205.56	196.1
Chromium in exhaust, (as Cr**),g/l	0.094	0.137	0.058	0.025	0.082	0.109	0.097	0.078	0.062	0.088
TotalChromium in exhaust,(as Cr),g	11.47	18.76	7.08	3.22	9.47	13.39	10.34	8.2	8.26	12.05
Actual Chrome in wet blue after retanning,(as Cr**),%	1.13	1.18	1.86	1.27	1.26	1.02	1.06	0.95	1.06	0.96
Calculated Chrome in wet blue after retanning,(as Cr),g	1.12	1.16	1.88	1.27	1.27	1.06	1.08	1	1.09	0.99
Chrome lost from wet blue,%	5.6	7.4	3.2	1.4	4.4	6.9	4.9	5.3	3.9	6

* Accuracy of the tannery balance : + or - 0.1 Kg.

**Accuracy of chrome determination : + or - 0.03%

Figure 4.10 : Combined effluent (tannery survey)

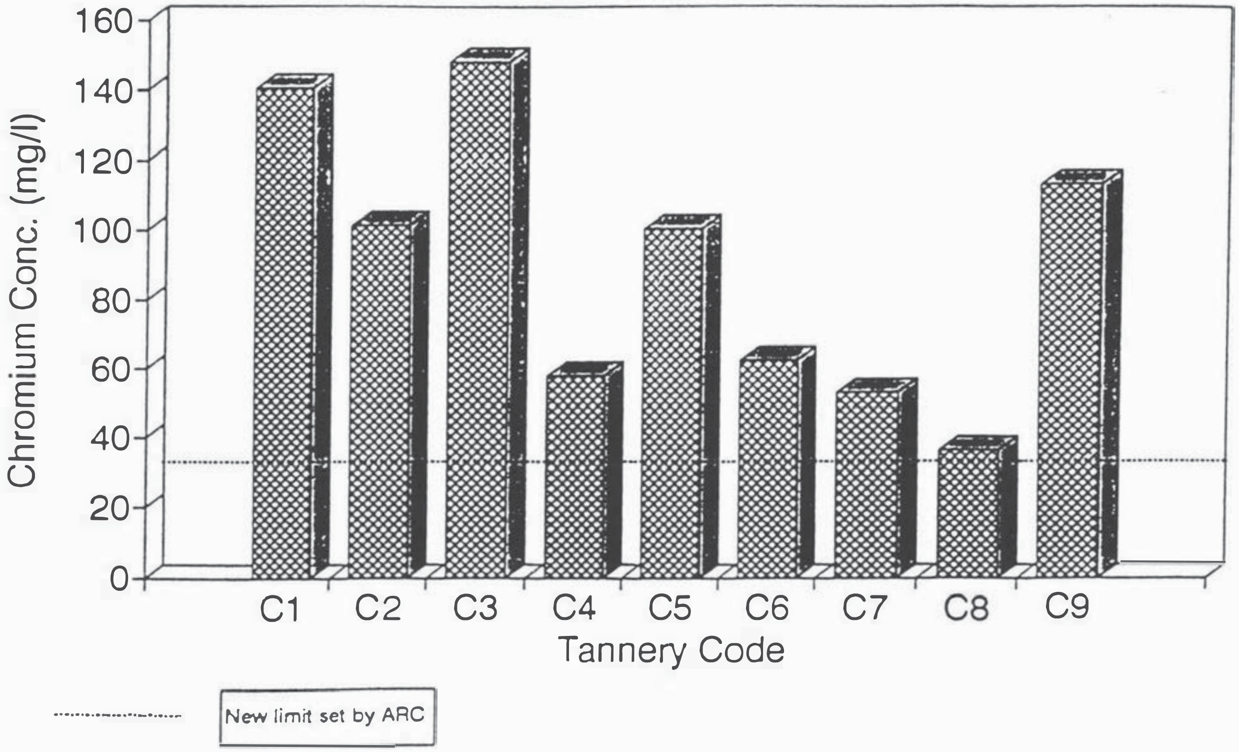
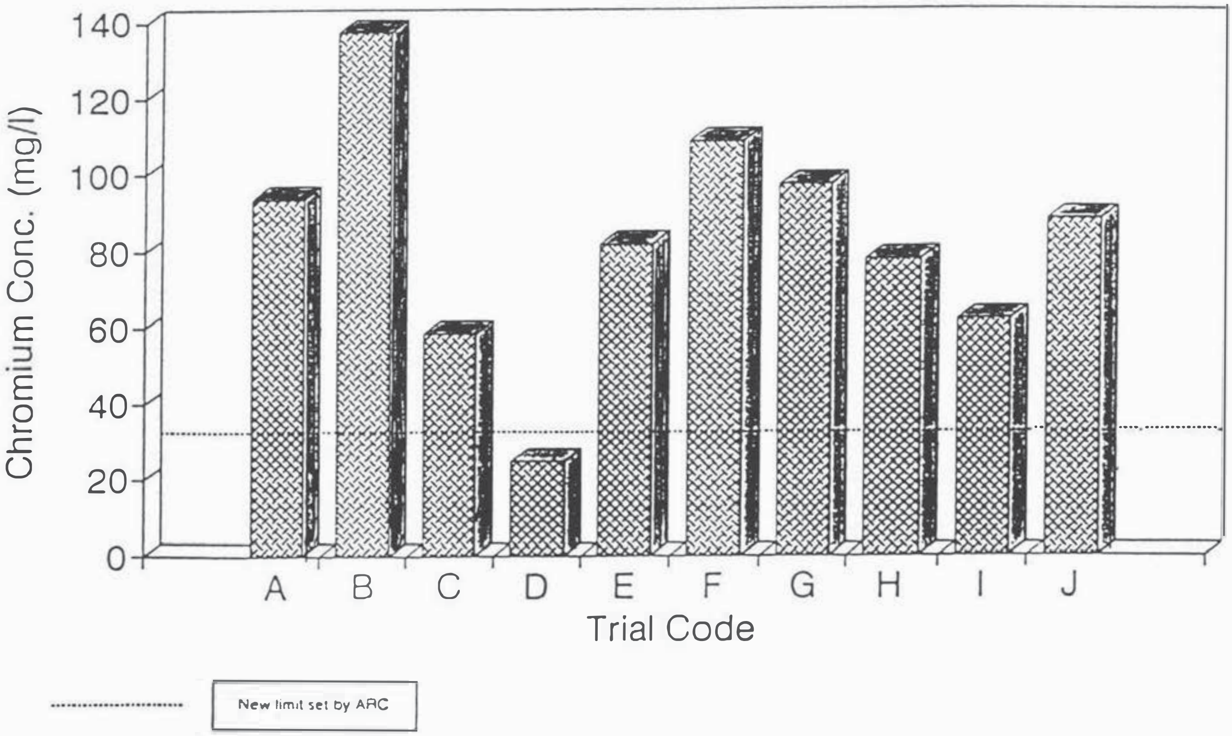


Figure 4.11: Combined effluent (high exhaustion trials)



From the tannery survey, Tannery with Code 8 satisfied the current limits (50 mg/l ARC) but would fail to the new limit (30 mg/l). Codes 4, 6 and 7 were bordering around the current limit. All other codes failed to meet the current limit by a factor of two.

From the high exhaust chrome systems Process Code D satisfied the current limit, Codes C and I were bordering around the current limit. All other codes failed to meet the limit by a factor of two.

Overseas, the discharge limits for chromium are more stringent (generally < 10 mg/l), hence all codes with current dilution ratios would fail to comply.

Percentage Chromium Loss During Post-tanning

The percentage of chromium lost from the wet blue material during processing was calculated from:-

- the total chromium (g) contained in the combined liquors
- the total chromium content (g) of the wet blue material

For the tannery survey, Tannery with Code 8 showed the least amount of chromium loss (3.3%). Next were Codes 7, 6 and 4 with approximately 4% chromium loss. All other tanneries had losses in the range from 7.0 - 8.9% .

For the high exhaustion chrome systems, Process Code D had the least amount of chromium loss (1.4%). All other Processes showed losses of chromium between 3 and 7%. The informations were presented in Figure 4.12 and Figure 4.13.

Figure 4.12: Percentage of chromium loss (post tanning processes) : commercial systems

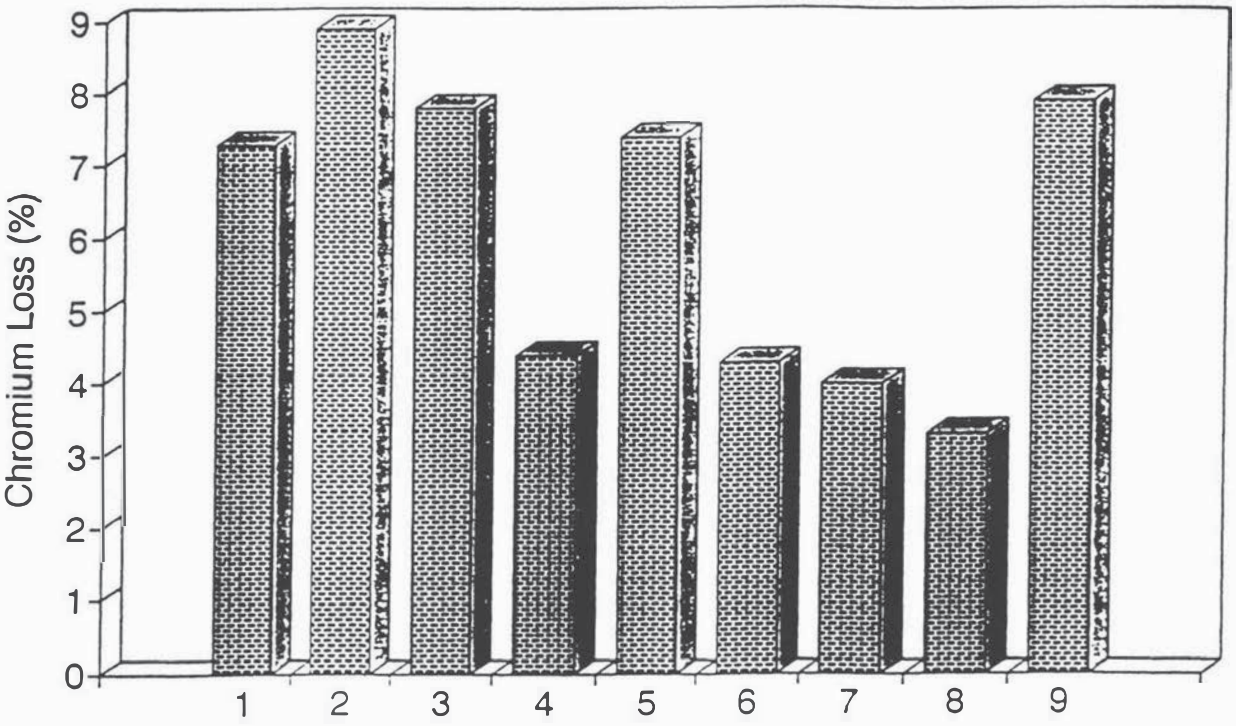
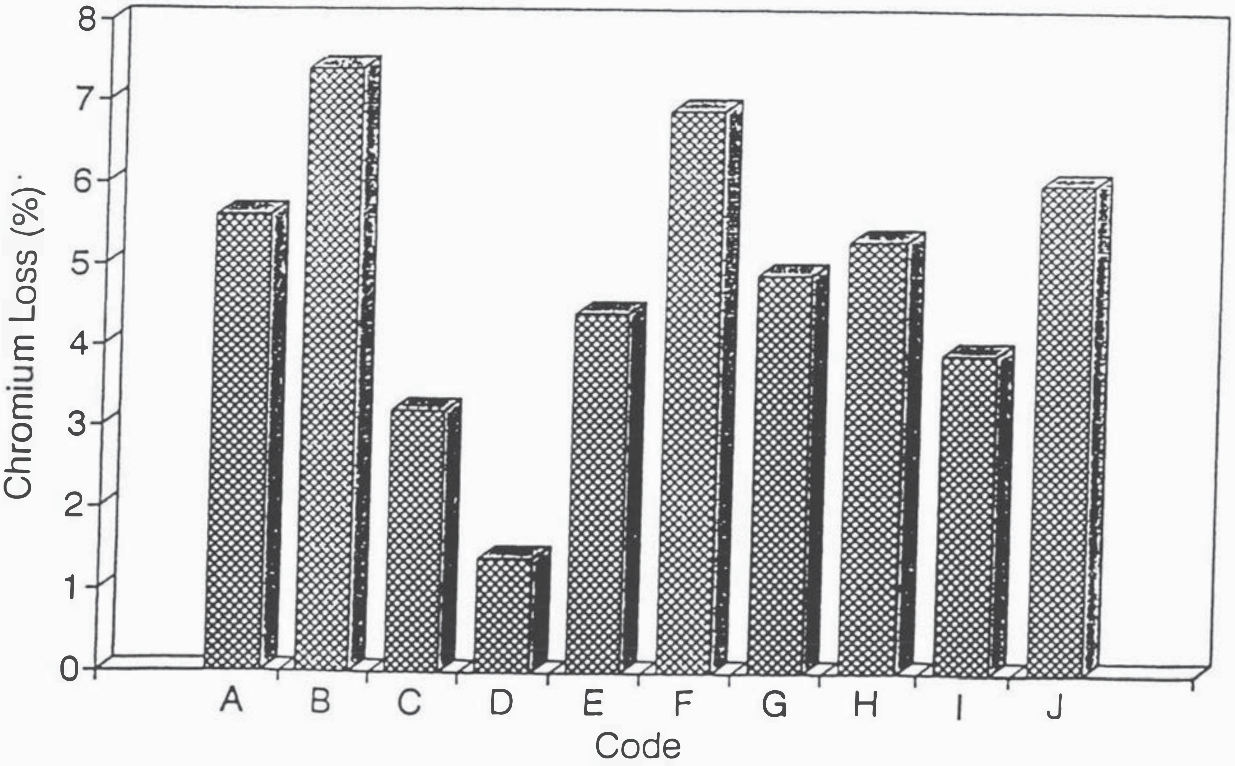


Figure 4.13: Percentage of chromium loss (post tanning process) : high exhaust systems



The results of tensile, tear and lastometer values are given in Tables 4.7, 4.8 and 4.9 respectively. There were no significant differences between the values obtained for LASRA standard (without oil) and high exhaust tanning systems. However, results obtained from leather processed with LASRA standard (with oil) were significantly better than all others. This showed the benefit of a small addition of oil in the tanning bath.

Table 4.7: Comparative tensile strength of chrome tanned crust leather from various chrome tanning systems

Treatments	Thickness, mm (Avg)	Breaking Load, N (Avg)	Tensile Strength, N/mm^2 (Avg)
A: LASRA standard (with oil)	2.00	428.5	21.6
B: LASRA standard (without oil)	2.30	347.2	15.3
C: Neosyn EE (Hodgson)	2.05	389.7	19.1
D: Baychrome CP (Bayer)	2.10	426.6	20.2
E: Cromeno A/FN (Rohm)	2.02	274.4	13.4
F: Feliderm CSN (Hoechst)	2.14	333.8	15.4
G: Uberol 8027 (Carpetex)	2.01	352.9	17.4
H: Oxazolidine E (Allied)	1.82	285.3	15.3
I: Sodium/Ammonium Salt of Isophthalic acid	2.04	293.7	14.3
J: Implenal DC Dicarboxylic acid (BASF)	1.90	239.1	12.6

Table 4.8: Comparative tear strength of chrome tanned crust leather from various chrome tanned systems

Treatments	Thickness, mm (Avg)	Breaking Load, N (Avg)	Tear Strength, N/mm (Avg)
A: LASRA standard (with oil)	2.05	216.0	104.3
B: LASRA standard (without oil)	2.40	198.7	83.0
C: Neosyn EE (Hodgson)	2.08	200.4	96.0
D: Baychrome CP (Bayer)	2.03	162.9	79.6
E: Cromeno A/FN (Rohm)	2.00	169.9	84.2
F: Feliderm CSN (Hoechst)	2.23	166.6	74.2
G: Uberol 8027 (Carpetex)	1.94	198.0	102.7
H: Oxazolidine E (Allied)	1.91	145.8	77.4
I: Sodium/Ammonium Salt of Isophthalic acid	2.11	161.9	76.3
J: Implenal DC Dicarboxylic acid (BASF)	1.90	157.2	81.9

Table 4.9: Comparative grain strength of chrome tanned crust leather from various chrome tanned systems

Treatments	Distension at Grain Crack, mm (Avg)	Load at Grain Crack, kg (Avg)
A: LASRA standard (with oil)	10.21	52.0
B: LASRA standard (without oil)	10.16	42.8
C: Neosyn EE (Hodgson)	9.08	43.5
D: Baychrome CP (Bayer)	8.91	39.7
E: Cromeno A/FN (Rohm)	7.99	27.7
F: Feliderm CSN (Hoechst)	10.47	36.2
G: Uberol 8027 (Carpetex)	9.93	42.8
H: Oxazolidine E (Allied)	8.90	40.0
I: Sodium/Ammonium Salt of lsophthalic acid	8.40	26.0
J: Implenal DC Dicarboxylic acid (BASF)	8.94	34.8

4.4.3 Lamb Skins

4.4.3.1 Visual Assessment of Crust

From the material obtained from various tanneries, considerable differences in the crust leather in terms of softness, handle, fullness and evenness of dyeing were noticed. These differences could be attributed direct to the differences in the chrome tanning at each tannery. The various wet blues processed at LASRA also showed significant differences. Mainly those high exhaust systems with masked tannages gave paler shades while others gave brighter colour. The Baychrome 2421 system in our exploratory trial gave fuller leather with some chrome spots. This might be due to over-basification as the end pH of the tanning bath was 4.65. This might have been due to the high pH(5.4) of Baychrome 2421 . In the trial where the starting pH was reduced from 2.85 to 1.4 as advised by the chemical supplier(Bayer), the chrome spots still persisted but to a lesser extent, even though the final pH of the tanning bath was 3.7. Preferred grain characteristics were found in the following systems:-

- 6% LASRA Standard Method
- Oxazolidine

- Neosyn EE
- Sodium/Ammonium Salt of Isophthalic Acid

4.4.3.2 Shrinkage Temperature and Quality

All wet blues gave satisfactory leather; all stood the boil except Baychrome 2420 which had a lower shrinkage temperature of 93 - 96°C.

4.4.2.3 Exhaustion Efficiency and Mass Balance for Chromium

The exhaustion efficiency and the mass balance for chromium for the various chrome tanning processes were as given in Table 4.10 and 4.11 .

Table 4.10 Mass balance for chromium and efficiency of chrome tanning systems of New Zealand Lamb skins

	Tanning process codes for chrome tanning systems of lamb skins				
	Tannery 1	Tannery 2	Tannery 3	Tannery 4	Tannery 5
Weight of limed pelt,Kg*	11.65	11.5	12	11.25	12.85
Moisture in pelt, %	70.64	70.64	70.64	70	70.64
Chrome offered%,(as Cr**),%	1.305	0.60928	0.9792	1.214	1.0625
Total Chromium,(as Cr),g	152.615	70.15	117.6	136.125	136.21
Chromium in exhaust, (as Cr**),g/l	2.5901	0.41349	1.641	1.752	1.555
Total Chromium in exhaust#,(as Cr),g	30.1735	4.715	19.68	19.68	20.05
Actual Chrome in wet blue after tanning,(as Cr**),%	2.795	1.92	3	3.27	2.985
Calculated Chrome in wet blue after tanning,(as Cr),g	0.84	0.5631	0.85	0.981	0.87579
Efficiency :calculated,%	64.36	92.42	86.73	81.08	82.43
:actual ,%	66.61	91.8	83.26	85.53	85.28

* Accuracy of the tannery balance : + or - 0.1 Kg.

**Accuracy of chrome determination : + or - 0.3%

Table 4.11 Mass balance for chromium and efficiency of chrome tanning systems of New Zealand Lamb skins

	Tanning process codes for chrome tanning systems of lamb skins								
	LASRA Standard		High Exhaust tanning systems						
	A	B	C	D	E	F	G	H	I
Weight of limed pelt,Kg*	10.2	10.2	10.2	10.2	10.2	10.2	11.5	10.5	11.5
Moisture in pelt, %	71	71	70.9	70.9	70.9	69.1	71.7	71.7	72.9
Chrome offered%,(as Cr**),%	1.07	0.89	0.82	0.82	0.82	0.80	0.82	0.82	0.89
Total Chromium,(as Cr),g	109.45	90.78	83.91	83.91	83.91	81.15	94.61	86.33	102.83
Chromium in exhaust, (as Cr**),g/l	0.78	0.45	0.19	0.43	0.53	0.56	0.29	0.24	0.2
Total Chromium in exhaust#,(as Cr),g	7.97	4.59	2.12	4.38	5.4	5.67	3.3695	2.4675	2.3
Actual Chrome in wet blue after tanning,(as Cr**),%	3.38	2.85	2.68	2.64	2.65	2.40	2.69	2.81	3.16
Calculated Chrome in wet blue after tanning,(as Cr),g	0.864	0.8265	0.78	0.77	0.77	0.74	0.76	0.98	0.86
Efficiency :calculated,%	91.6	93.26	95.12	94.00	93.9	93.03	91.62	96.76	95.99
:actual ,%	92.71	94.96	96.39	94.78	93.56	93.00	90.37	97.10	96.14

* Accuracy of the tannery balance : + or - 0.1 Kg.

The efficiency of the commercial chrome tannages was highest for tannery with Code 2 with 92% utilisation. This result fell between the two LASRA Standard Methods.

The efficiency of the high exhaust systems varied between 90 - 97%. The highest exhaustion was obtained with Baychrome 2420; the exhaust liquor had practically no chrome at all but the quality of the wet blue, as stated earlier was not as anticipated. The other high exhaust systems which followed Baychrome 2420 were Implenal DC, Sodium/Ammonium Salt of Isophthalic Acid, Oxazolidine E, Uberol 8027, Cromeno A/FN and Neosyn EE.

These results were very encouraging as some of these systems could satisfy the chrome limits for tannery effluents when normal dilution factors were taken into consideration. These findings were notably different from the results obtained from the studies on hide tannage[1]. In that study the claims that high exhaust systems could allow discharge of chrome liquors from hide tanneries without further treatment could not be confirmed.

4.4.3.4 Post-Tannage Process Liquors

All process liquors discharged during the post-tanning stages were as given in Table 4.12 and Figures 4.14 to 4.18.

Table 4.12: Chromium concentrations of post-tannage discharges

Tannery Code	Sammying	Washing	Retanning	Washing	Dye/Fatliquor	Wash
1	234.3	55.5	11.3	2.6	14.1	4.5
2	42.3	6.8	16.9	5.7	4.5	5.7
3	31.5	7.8	8.8	3.2	8.3	0.2
4	338.6	105.8	45.5	16.9	4.2	2.4
5	411.7	81.1	41.9	21.0	18.9	13.5

Values in mg-Cr/l

Figure 4.14: **Chromium release from commercial wet blue**

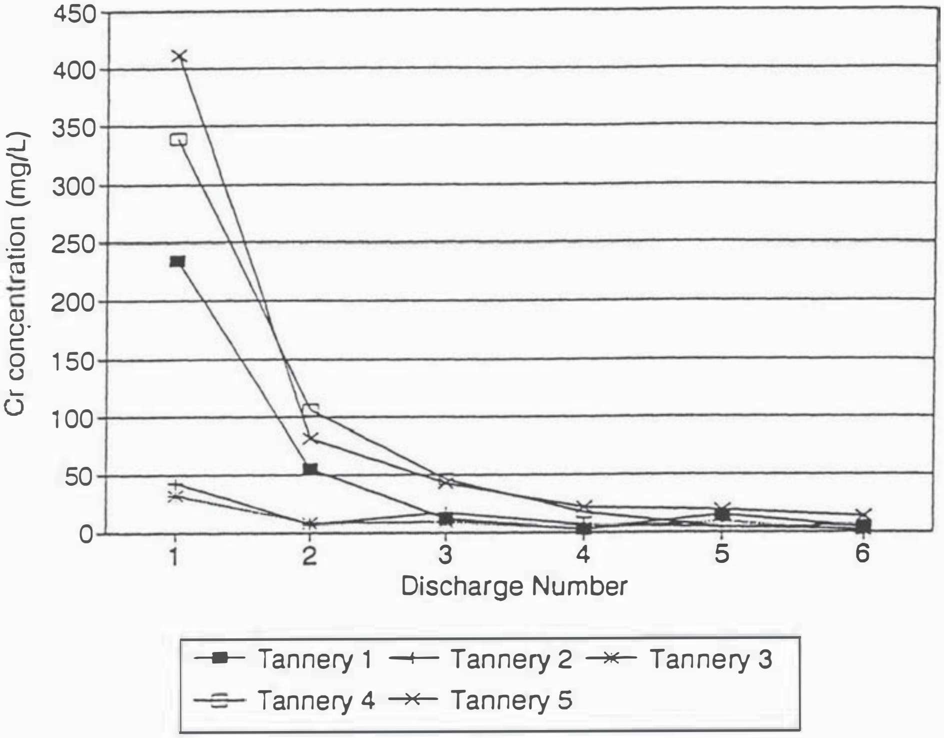


Figure 4.15: **Chromium release from high exhaust trials A to E**

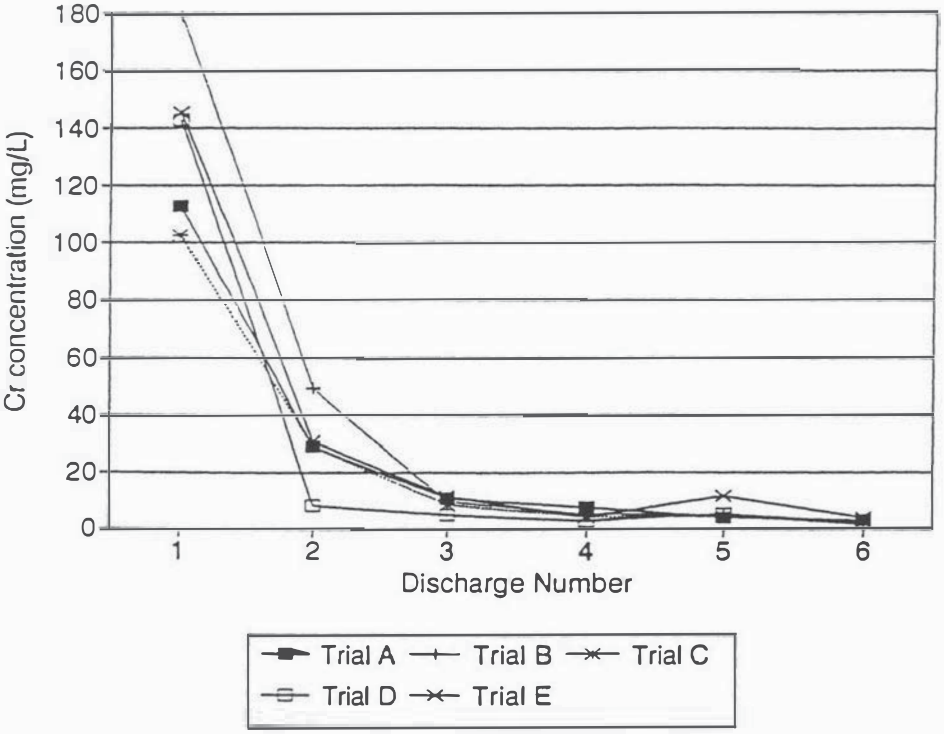


Figure 4.16: Chromium release form high exhaust trials F to I

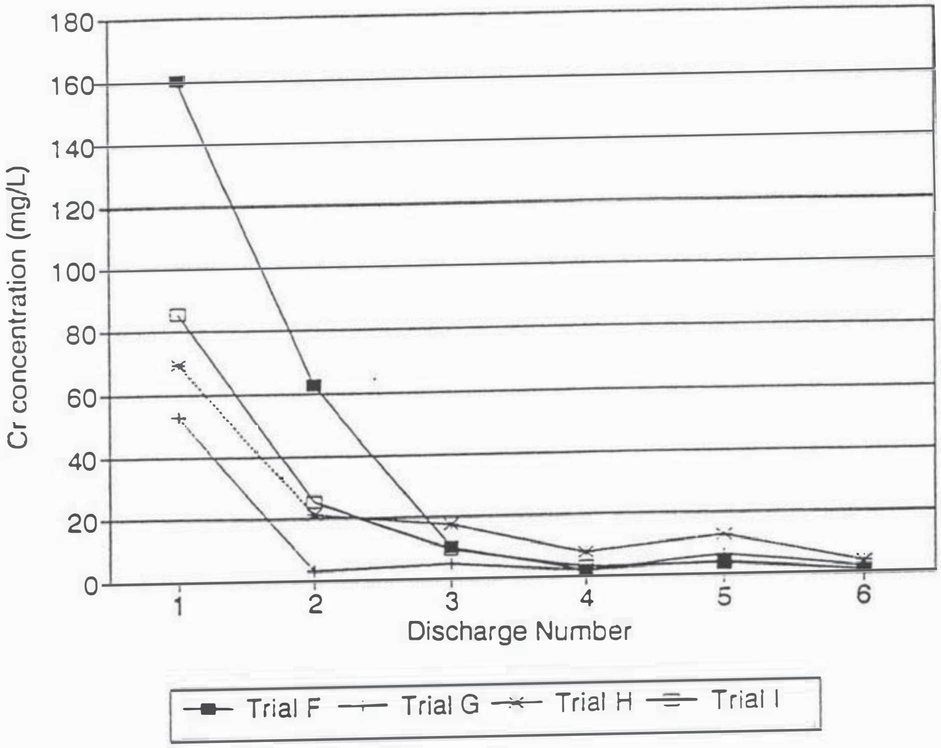


Figure 4.17: Total chromium released (tannery survey)

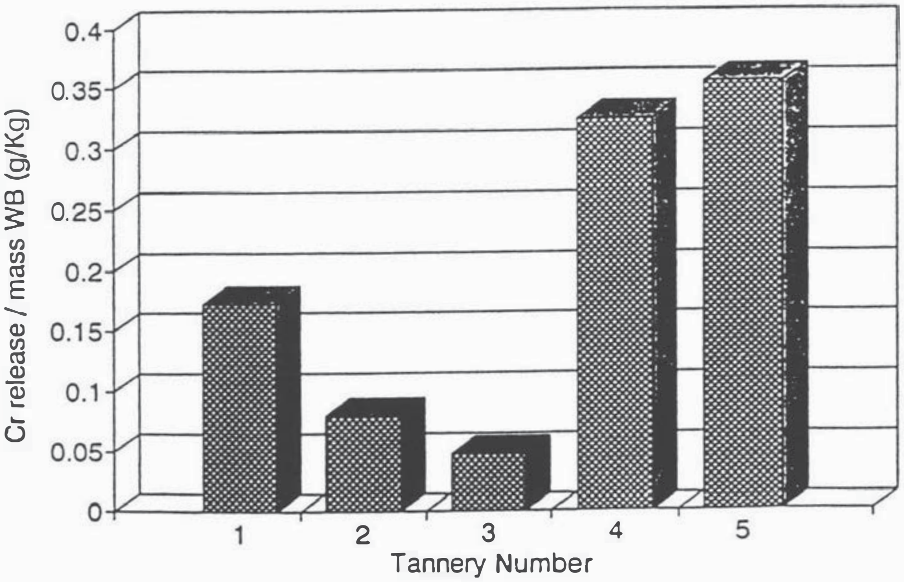
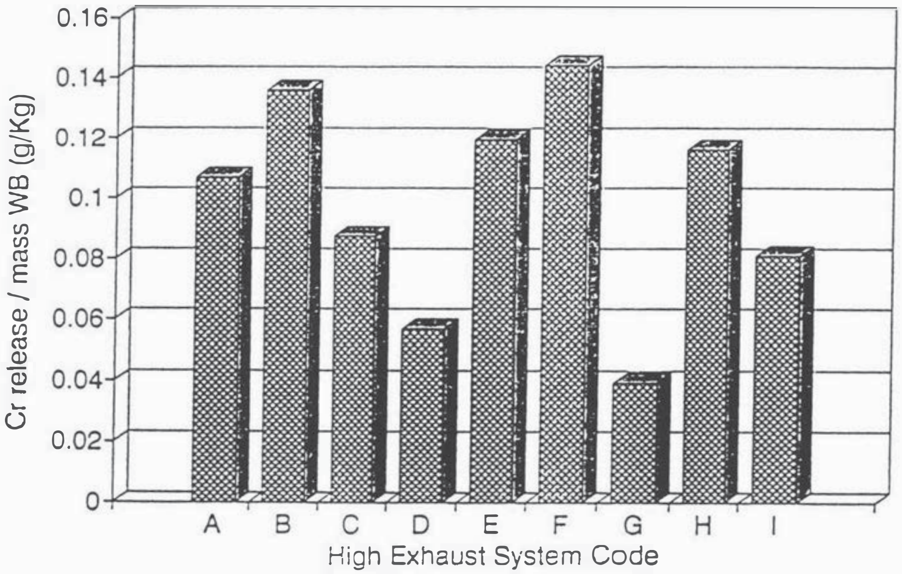


Figure 4.18: Total chromium released (high exhaust trials)



4.4.2.5 Evaluation of leachates from the post-tanning of high exhaust wet blue

The chromium levels of the high exhaust wet blue lamb skin materials are shown in Table 4.13.

Table 4.13: Chromium levels of wet blue lamb skins from high exhaust tanning trials

Process Code	Cr_2O_3 at Zero Moisture (%)
A (LASRA process 5% offer)	4.38
B (LASRA process 6% offer)	4.98
C	4.16
D	4.45
E	4.28
F	4.00
G	3.81
H	4.37
I	4.16

Table 4.14 showed the chromium concentration in the discharges from all post-tannage processing for each of the high exhaust chrome tanned materials.

Table 4.14: Chromium concentrations of discharges from the high exhaust tanning trials

Process Code	Sammying Discharge 1	Washing Discharge 2	Neutralising Retanning Discharge 3	Washing Discharge 4	Dye/Fatliquor Discharge 5	Wash Discharge 6
A	112.5	28.8	10.8	7.5	3.7	3.2
B	178.7	49.4	9.6	5.4	4.9	1.2
C	102.3	28.7	8.7	4.4	4.4	1.9
D	142.9	8.3	5.0	2.6	5.3	2.1
E	145.3	30.8	11.5	4.3	11.3	3.8
F	160.2	62.7	10.2	1.9	4.3	1.1
G	52.6	3.2	4.9	1.9	6.5	2.3
H	69.4	21.5	17.7	7.9	12.9	4.0
I	85.6	25.6	9.5	3.1	3.7	1.1

Values in mg-Cr/l

A large variation was observed in the chromium leaching characteristics between all five commercial processes. The least chromium leaching was observed with the wet blue of tannery 3, followed by tannery 2 and tannery 1. In terms of chrome loss during post-tannage expressed as a percentage of the wet blue chrome content, the commercial tannery produced material gave values ranging from 0.4 - 3.3%.

For the high exhaust systems, a significant variation also existed between the different options. Note again that systems A and B were not high exhaust processes, but were conventional tannages at different chrome offers. High exhaust system G gave the lowest amount of released chrome. It was interesting to note that tannery 3 achieved a similar, low level of chrome release to the best of the high exhaust systems studied in the trial. The high exhaust trials gave chrome loss results of 0.3 to 1.5% expressed on the original wet blue chrome content.

Chrome release results for tanneries 2 and 3 were comparable with the best results provided from the high exhaust trials. Chrome releases from the wet blue skins produced by tanneries 2 and 3 were characterised by the consistency throughout post-tannage. The results represented in graphical form showed no pronounced peaks for any of the post-tannage stage. This could be interpreted as progressive release of a small amount of unbound or weakly held chrome throughout the post-tannage operations. Results for tanneries 4 and 5 and to a greater extent tannery 1 showed pronounced peaks at the first wash stage of post-tannage. This suggested that these tannages resulted in a greater quantity of unbound chrome that was released simply by water washing rather than as a consequence of chemical treatment.

Comparison of these chrome release patterns with those derived on 2.0 mm bovine wet blue showed distinct differences. Total chrome loss from the commercially produced ovine material was of the same order as the loss on the commercially produced wet blue bovine product, however, the significant release of chrome from the wet blue lamb skins occurred at the onset whilst it occurred progressively from the wet blue hides. This suggested that structural differences determine release rates of unfixed material. It indicated however that improved end-of-tannage washing might achieve more on the ovine than on the bovine wet blue.

Results for the high exhaust systems showed a marked and uniform distinction from the majority of the currently used commercial tannages. Chrome release for all high exhaust wet blue was low and quite regular throughout post-tannage. The high exhaust wet blue did not show a pronounced release of chrome at the first wash stage. These characteristics were of course consistent with the principles of high chrome exhaustion and the fact that exhaustion was achieved by higher orders of fixation rather than any increase in the absorption of unbound or weakly bound chrome.

Results of the two LASRA tannages, designated A and B showed the further advantages of a lower chrome offer. As well as the nearly 17% saving in chrome offer, using 5% chrome powder rather than 6% gave a decreas in the release of the chrome during post-tanning.

The conventional chrome tannage at the reduced offer of 5% gave chrome release figures that were consistent with the best results achieved on high exhaust material. The indications from this were that high exhaustion and a lower offer gave compound advantages.

The study has shown that chrome release from wet blue lamb skins during retannage/ fatliquoring/dyeing could be substantially reduced through the application of high exhaustion tanning technology and by the use of lower amount of chrome.

4.4.3.6 Physical Properties

Physical test results are given in Tables 4.15, 4.16, 4.17 and 4.18. These results showed little difference between the various systems as far as physical properties were concerned. All leathers would satisfy normal requirements for nappa garment leather stipulated in the European Commission guide lines for such leather.

Table 4.15: Tear strength of chrome tanned New Zealand lamb skins

Treatments	Thickness, mm	Breaking Load, N		Tear Strength, N/mm	
	avg	Perpendicular avg	Parallel avg	Perpendicular avg	Parallel avg
Commercial Tanneries					
Code 1	1.3	48	43	38	32
Code 2	1.2	67	62*	56	49
Code 3	1.4	59	50	43	35
Code 4	1.35	63	58	49	42
Code 5	1.15	43*	41	40	36
LASRA Standards					
6% chrome offer	1.15	51	38	45	36
5% chrome offer	1.25	58	46	46	35
High Exhaust Chrome Systems with 4.6% Chrome Offer					
Oxazolidine E	1.3	57	50	45	40
Cromeno A/FN	1.05	46	36	44	34
Neosyn EE	1.2	60	49	50	40
Baychrome 2420	1.1	53	47	49	43
Repeat	1.15	50	43	42	40
Uberol 8027	1.1	49	43	46	39
Sodium/Ammonium Salt of Isophthalic Acid	1.35	57	54	44	39
Implenal DC	1.55	75*	67*	49	42

Table 4.16: Grain strength of chrome tanned New Zealand lamb skins

Treatments	Distension at Grain Crack, mm avg	Load at Grain Crack, kg avg
Commercial Tanneries		
Code 1	8.7*	27.7
Code 2	10.3	41.5
Code 3	9.5	32.0
Code 4	9.5	35.5
Code 5	10.1	33.7
LASRA Standards		
6% chrome offer	9.1	29.0
5% chrome offer	9.7	38.3
High Exhaust Chrome Systems		
Oxazolidine E	9.4	37.0
Cromeno A/FN	9.4	30.5
Neosyn EE	9.2	34.2
Baychrome 2420	9.5	33.7
Repeat	9.1	30.8
Uberol 8027	9.9	33.0
Sodium/Ammonium Salt of Isophthalic Acid	9.3	32.0
Implenal DC	10.5*	45.8

* Values are significantly different ($p < 0.05$) from LASRA Standard (5% chrome offer)

Table 4.17: Tensile strength of chrome tanned New Zealand lamb skins

Treatments	Thickness, mm	Breaking Load, N		Tensile Strength, N/mm^2	
	avg	Perpendicular avg	Parallel avg	Perpendicular avg	Parallel avg
Commercial Tanneries					
Code 1	1.4	1.52	175.2*	11.0	12.9*
Code 2	1.3	220	271.8	15.8	22.5
Code 3	1.5	187	230.7	12.3	15.3
Code 4	1.65	221	249.3	13.1	16.5
Code 5	1.2	198	204.5	16.5	16.6
LASRA Standards					
6% chrome offer	1.2	166	192.8*	12.8	17.5
5% chrome offer	1.45	191	280.8	12.7	19.5
High Exhaust Chrome Systems with 4.6% Chrome Offer					
Oxazolidine E	1.25	189	257.2	15.3	20.0
Cromeno A/FN	1.2	148	207.3	12.7	17.1
Neosyn EE	1.35	185	253.0	13.7	19.2
Baychrome 2420	1.15	161	218.8	14.6	18.3
Repeat	1.1	142	178.3*	18.1*	21.2
Uberol 8027	1.25	169	194.0*	13.2	16.7
Sodium/Ammonium Salt of Isophthalic Acid	1.45	191	210.3	12.4	14.8
Implenal DC	1.6	271*	299.7	16.9	18.7

* Values are significantly different ($p < 0.05$) from LASRA Standard (5% chrome offer)

Table 4.18: Elongation at break of chrome tanned New Zealand lamb skins

Treatments	Thickness mm	Percent Elongation at Break # Perpendicular avg	Parallel avg
Commercial Tanneries			
Code 1	1.4	78.0	67.0*
Code 2	1.3	96.0	74.7
Code 3	1.5	91.0	72.7
Code 4	1.65	82.7	72.0
Code 5	1.2	93.0	63.0*
LASRA Standards			
6% chrome offer	1.2	92.0	61.7
5% chrome offer	1.45	111.0	78.7
High Exhaust Chrome Systems			
Oxazolidine E	1.25	99.7	72.3
Cromeno A/FN	1.2	105.3	68.7
Neosyn EE	1.35	107.7	71.0
Baychrome 2420	1.15	91.0	74.0
Repeat	1.1	69.5	80.8
Uberol 8027	1.25	80.3	63.3
Sodium/Ammonium Salt of Isophthalic Acid	1.45	81.3	73.0
Implenal DC	1.6	90.3	72.3

* Values are significantly different ($p < 0.05$) from LASRA Standard (5% chrome offer) control

4.5 Experimental Series B : Reduced Chrome Offer

On the basis of these results, we carried out a further series of high exhaust tanning trials using the best five systems to explore the potential advantages to be gained from the use of only 4% Tannachrome S. The systems explored were those based on Oxazolidine E, Cromeno A/FN, Uberol 8027, the LASRA modification and 6% Baychrome 2420 (readjusting the pickle pH to 2.0 - 2.2). The shrinkage temperatures of the wet blue leathers produced from these trials were as follows:-

Oxazolidine E system	111°C
Cromeno A/FN system	106°C
Sodium/Ammonium Salt of Isophthalic Acid	105°C
Uberol 8027 system	110°C
Baychrome 2420 system	99°C

Table 4.19 gives the efficiency of chrome exhaustion for these high exhaustion lower chrome tanning systems. The efficiency of the Oxazolidine E and Baychrome 2420 systems did not change whereas the three other systems showed further improvements beyond those shown in the first trials.

Table 4.19: Chrome exhaustion of various chrome tanning systems on New Zealand lamb skins

Treatments	Efficiency of Tanning %*
High Exhaust Chrome Systems	
4% Tannachrome S	
Oxazolidine E	93.1
Cromeno A/FN	89.7
Sodium/Amm.Salt of Isophthalic Acid	98.1
Uberol 8027	96.6
6% Baychrome 2420	99.9

* Efficiency of tanning was calculated from the combined chrome in the tanning exhaust and first wash liquor

It should be noted that these figures do not include the chrome lost to effluent during sammying, washing and retannages. Neither do they take into account the final dilution that will normally take place in a tannery before the effluent is discharged. Assuming a dilution of 30 times per kg of lamb pelts processed (in contrast to 12 times per kg of hides), mainly due to aqueous degreasing of pelts, many of these chrome tanning systems would give very low chrome levels in the final effluent.

Tables 4.20, 4.21, 4.22 and 4.23 give the results of the physical tests. Once again there was little difference between the various sets of physical properties and these crust leathers would all satisfy the requirements for garment nappa prescribed in the European Commission guide line for such leather.

Table 4.20: Tear strength of chrome tanned New Zealand lamb skins

Treatments	Thickness, mm avg	Tear Strength, N/mm	
		Perpendicular avg	Parallel avg
High Exhaust Chrome System			
4% Tannachrome S			
Oxazolidine E	1.32	40	37
Cromeno A/FN	1.35	38	33
Sodium/Ammonium Salt of Isophthalic Acid	1.22	43	40
Uberol 8027	1.15	40	34
6% Baychrome 2420	1.16	37	33

Table 4.21: Tensile strength of chrome tanned New Zealand lamb skins

Treatments	Thickness, mm avg	Tensile Strength, N/mm^2	
		Perpendicular avg	Parallel avg
High Exhaust Chrome System			
4% Tannachrome S			
Oxazolidine E	1.38	10	13
Cromeno A/FN	1.40	11	12
Sodium/Ammonium Salt of Isophthalic Acid	1.31	12	15
Uberol 8027	1.23	11	13
6% Baychrome 2420	1.23	12	12

Table 4.22: Elongation at break of chrome tanned New Zealand lamb skins

Treatments	Thickness, mm avg	Elongation at Break, %	
		Perpendicular avg	Parallel avg
High Exhaust Chrome System			
4% Tannachrome S			
Oxazolidine E	1.38	125	90
Cromeno A/FN	1.40	104	84
Sodium/Ammonium Salt of Isophthalic Acid	1.31	98	91
Uberol 8027	1.23	106	96
6% Baychrome 2420	1.23	98	36

Table 4.23: Grain strength of chrome tanned New Zealand lamb skins

Treatments	Distension at Grain Crack, mm avg	Load at Grain Crack, kg avg
High Exhaust Chrome System		
4% Tannachrome S		
Oxazolidine E	9.6	28.3
Cromeno A/FN	9.2	24.6
Sodium/Ammonium Salt of Isophthalic Acid	9.0	24.3
Uberol 8027	9.8	24.8
6% Baychrome 2420	9.4	24.0

4.6 Conclusion

4.6.1 Hides

All high exhaust systems gave better exhaustion, particularly Baychrome CP, Neosyn EE, Oxazolidine E, Cromeno A/FN, Uberol 8027 and Feliderm CSN, giving about 10 - 12% more chrome exhaustion. But it was also found that the efficiency of conventional chrome tanning could also be improved to 86% by using a reduced chrome oxide offer, down to 1.5% and using 0.5% Tanbase, and maintaining end temperatures to 43°C. Compared to conventional efficiency of 70 - 75% of chrome tanning for an offer of 1.8 - 2.0%, this increase is very significant. It was clear that the difference of efficiency between our control with 1.5% Cr_2O_3 with oil against all high exhaust systems (1.25% Cr_2O_3) was not more than 6 - 8%.

The results obtained from this trial show that there is a large variation in the amount of chromium released from wet blue hides sourced from all of the bovine wet blue tanners in New Zealand. There is a large variation in the amount of chromium released from wet blue hides previously tanned using a selection of high exhaust tanning aids. The percentage chromium lost from the wet blue during post-tanning ranges from 3.3 - 8.9% for New Zealand wet blue tanners, and 1.4 - 6.9% for wet blues produced in the high exhaust chrome trials (LASRA). The standard LASRA process lost 7.4%, with the addition of oil the amount lost was reduced to 5.6%.

The combined effluents from one tannery sample and one high exhaust tanning process will meet the current discharge limits for chromium (50 mg - Cr/l) in most areas of New Zealand. All others were either bordering or exceeding the limits. Therefore, tanners should review if they should use high exhaust chrome and precipitate or recycle this residual chrome, or just use a standard system with lower chrome offer with parameters of tannage which improve exhaustion. The economy of the process would determine the choice. The present technology of producing chrome tanned leather from cow hides needs considerable improvement to pass modern environmental standards.

4.6.2 Lamb Skins

The study has shown that wet blues from New Zealand tanneries differ significantly in terms of chrome release. In terms of meeting typical tradewaste discharge limits for chromium (30 mg/l), tanneries 3 and 2 would comply; their overall discharge would range between 10 - 20 mg Cr/l. The remaining tanneries would exceed the limit.

With the high exhaust trials all discharges would easily comply with the limit. System G would produce wastewater with a final chromium level under 10 mg/l. With the two LASRA methods, system B (6% chrome powder offer) would produce a wastewater with a chromium level of about 30 mg/l and System A (5% chrome powder offer) a chromium level of about 20 mg/l.

These studies have also shown that New Zealand lamb skins could be processed with 4% Tannachrome S in place of 6% commonly used in the trade without any adverse effect on the quality of the final leather. In conjunction or replaced by high exhaust systems the chrome utilisation would markedly improve.

The adoption of systems that give improved chrome usage and chrome retention would be beneficial to both the producer and the user of the wet blue lamb skins.

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CHAPTER 5

NOVEL TECHNIQUE OF CHROME TANNING OF LAMB SKINS

5.0 INTRODUCTION

New Zealand lamb skins are presently exported in the pickled condition, following a standard paint, liming, deliming, bating and pickling process. These pickled skins are then mostly chrome tanned after degreasing. Considerable amounts of research have been conducted at New Zealand Leather and Shoe Research Association (Inc) and all over the world on various depilatory and appropriate preservation pickling systems[1-8], but very few publications relate to pickling as an aid to chrome tanning of New Zealand lamb skins.

"Pickling" in general was thought to be essential for chrome tanning for the following reasons:-

(a) to bring the pH of the skins below 3 which was thought to be more conducive for chrome tanning, and

(b) to help in better and uniform fixation and penetration of chrome tanning agents into the skins.

Unfortunately, most of the studies on pickling as preparation for chrome tanning were based on steer hides or calf skins[9-12] and hardly any publication could be traced which provided basic data on New Zealand lamb or sheep skin. While the chemical significance of lowering the pH before chrome tanning to around 3 could be appreciated, the penetration argument has no relevance to thinner lamb or sheep skins. On the other hand, strong acid and salt pickling dissolved considerable amounts of skin-protein resulting in loss of shrinkage temperature and strength of the final leather. It was noticed that the shrinkage temperature of raw New Zealand lamb skin, when fresh, was around 55 - 56°C but this dropped to 42 - 44°C when these skins were stored in the pickled condition for a long period. This fall was attributed to the loss of protein through hydrolysis in the acid medium. Bowes & Mitton[13] also showed that this skin deterioration occurred faster when storage temperature rose above 30°C. As this temperature increased skin soluble nitrogen content increased, skin shrinkage temperature and tear strength decreased.

Cooper[14] based on her studies, on the effect of storage of pickled pelt up to 65 weeks, showed that at 30°C the shrinkage temperature of pickled lamb skin fell from 56°C to 42°C and the ratio of soluble protein increased from about 5 to 15. Obviously, the effect would be more serious for delicate skins like lamb skins but might not be that detrimental for hides of higher animals like cow and buffalo.

Another problem of the present system was the use of lime and stronger alkali, like caustic soda in the lime-paint. The higher concentration of alkali caused excess swelling to the skin structure, dissolved the intermittent fat layer and separate skins into two distinct layers, particularly at the butt and neck region. When lime was used, this might be partially linked to the skin substrate and partially dissolved in the water present in the skin or deposited between the fibres in the form of undissolved lime. It would be necessary then to removal all calcium salts before the pelts entered pickling otherwise poorly soluble calcium sulphate would be precipitated within the pelt which would be difficult to remove afterwards. But it would not be easy to remove the lime which would be bound to the skin chemically. The process of deliming would be much easier and faster without lime as alkali derived from sodium sulphide, ie. sodium hydroxide would be very soluble and could be removed easily.

5.1 The Novel Chrome Tanning Process

With these two points in mind, a novel tanning system without any lime in depilation, and completely omitting the pickling process was developed. The tanned skin could be preserved for a longer period for export or processed further into finished leather without any problem. If needed, very rapid one day painting to chrome tanning could be carried out to optimise production time with considerable economic gain

A brief description of this novel process is given below:-

Stock	New Zealand lamb skin, green or wet salted
Soaking	Normal
Paint	180 g/l sodium sulphide solution
	450 - 500 g/skin application rate
	Pile flesh to flesh for 2 hours
	Dewool
	Weigh slats
Drum	60% water at 25°C
	Run 20 minutes
	Adjust sodium sulphide content to 1.2% w/v as usual
	Run (overnight if required) at 5 minutes/hour
	Next day, check for proper liming and wash out until clear
	Drain
Delime	25% water at 30°C
	2% ammonium chloride or sulphate
	0.4% hydrogen peroxide (100 vol)
	Run 20 minutes
	Check pH 8.0 - 9.0
add	0.1% Tryptec bate
	80% water at 35°C
	Run 40 minutes

	Check cross-section for complete deliming with phenolphthalein Check bating Drain
Wash	80% water at 20°C Run 15 minutes Repeat washing thrice Flesh Weigh All percentages are based on this fleshed weight
Degrease	Follow any standard solvent or aqueous degreasing system Drain
Chrome Tan	40% brine (5% salt solution) Run 10 minutes Check S G-6° Be
add	4 - 5% chrome powder 25/33 Run 1 - 2 hours Leave overnight at 40°C, if possible running 10 minutes/hour Normally no basification would be required but 0.15 - 0.2% sodium bicarbonate would be sufficient to raise pH to 3.6-3.8 if required.

It might be possible to reduce the duration of the liming process from the normal 16 hours to a much shorter period with the addition of an enzyme like Alcalase while drumming the slat at 28°C and then degreasing and chrome tanning could be completed in the same day. Tanning trials were conducted with four dozen New Zealand lamb skins, one dozen for each of the following treatments and their physical and chemical properties assessed:-

A Standard Quikpul paint, overnight liming and standard pickle-chrome tanning with 5% chrome powder (25% Cr_2O_3, 33% basic)

B Quikpul with only 16° Be sodium sulphide solution, overnight liming without lime, chrome tanned without pickle

C Quikpul as B; only three hours liming, chrome tanned without pickle

D Quikpul with 240 g/l sodium sulphide solution for one hour only, then processed as C

5.2 Results of Small Scale Trials

5.2.1 It was noticed that this no-pickle process gave about 16.6% better chrome uptake in leather than that was obtained with the standard chrome tanning process with an offer of 5% chrome powder 25/33. Table 5.1 below showed the improvement of the chrome content and the physical properties of the leather against conventionally tanned leather.

Table 5.1:Comparative properties of chrome tanned crust New Zealand lamb skin with or without pickling

Characteristics of the Leather	Standard Lime Pickle-Chrome - Control	No Lime - No Pickle Chrome Tanned		
	A	B	C	D
Chrome Content (as Cr_2O_3) on moisture free basis, percent	4.12	4.94	4.73	4.74
Percent increase of chrome uptake over control	-	19.9	14.8	15.04
Average increase over control, percent	-	16.58	-	-
Tear Strength (IUP/8)				
Breaking Load, N				
- parallel	36	48	50	48
- perpendicular	45	54	58	54
Tear Strength, N/mm				
- parallel	38	60	51	50
- perpendicular	43	64	55	53

Tensile Strength (IUP/6)				
Breaking Load, N				
- parallel	238	293	297	214
- perpendicular	129	152	179	140
Tensile Strength, N/mm^2				
- parallel	19	28	23	18
- perpendicular	10	14	13	11
Elongation at Break, % (IUP/6)				
- parallel	75	71	79	70
- perpendicular	196	189	178	172
Lastometer Test (IUP/9)				
Distention at grain crack, mm	12	14	12	12
Load at grain crack, kg	25	27	26	25
Double Hole Stitch (ASTM D4705-87)				
Tear strength, N	89	104	121	103

A Standard Quikpul paint, overnight liming and standard pickle-chrome tanning with 5% chrome powder (25% Cr_2O_3, 33% basic)

B Quikpul with only 16° Be sodium sulphide solution, overnight liming without lime, chrome tanned without pickle

C Quikpul as B; only three hours liming, chrome tanned without pickle

D Quikpul with 240 g/l sodium sulphide solution for one hour only, then processed as C

The variation of strength noted above occurred on skins that were freshly pickled with less acid and salt, and tanned without storage. The differences could be more significant if these skins had gone through preservation pickle and were stored for some longer period as would normally happen to New Zealand lamb skins which are exported. Further, the skins which were from these no pickle tannages were fuller, tighter and had finer grain characteristics.

The main features of the tanning system were as follows[15]:-

- no pickling
- degreasing at high pH after deliming, without any pretanning
- chrome tanning at high pH after deliming without any pickling, masking or basification

The main advantages of this system were:-

- high exhaustion of chrome
- fuller leather with finer grain
- improved tensile and tear strength
- minimum environmental impact of chrome tanning
- cost saving, both for tanning and after treatment of effluent

5.3 Large Scale Trials

Two large scale trials each with ten dozen lamb skins were conducted with the help and active participation of three companies. The details were as given below:-

5.3.1 Experimental Trial 1

The carbon dioxide delimed and bated pelts were collected from the co-operating fellmongery and examined at the New Zealand Leather and Shoe Research Association (Inc).

The skins were found to contain relatively heavy amounts of flesh. The pH of the delimed pelts was 8.90 and the cross-section of the pelts at the thickest part, when tested with phenolphthalein, gave a pink colour at the centre, indicating that they were not completely delimed.

These skins could not be fleshed in the pilot tannery with Turner fleshing machine (Type 205) without damaging the grain. It was therefore decided to proceed with aqueous degreasing and chrome tanning with unfleshed skins. The process of degreasing and tanning were as given below. Only 4.6% chrome tanning powder (Tannachrome S) was used for tanning at pH 8-9.

Stock	Delimed pelt
	Flesh and weigh
Degrease	3% Tergolix CA
	100% water at 32°C
	Run 30 minutes
add	150% water at 40°C
	Run 30 minutes
	Drain
Wash	150% water at 32°C
	Run 10 minutes
	Drain
Wash	150% water at 40°C
	Run 10 minutes
	Drain
Re-degrease	3% Tergolix CA
	150% water at 32°C
	Run 35 minutes
	Drain
Wash	150% water at 32°C
	Run 25 minutes
	Drain
Wash	150% water at 32°C
	Run 10 minutes
	Drain

Wash	150% water at 40°C
	Run 10 minutes
	Drain
	Check pH - ~8.0
Chrome Tan	5% salt
	100% water at 32°C
	Run 10 minutes
add	4.6% chrome powder
	Run overnight
	Check pH - 3.6

5.3.2 Results and Discussion on Trial 1

There was no problem in chrome tanning without pickling or basification. The end pH of chrome tanning was 3.6 and the leather stood the boil test. The trial showed, once again, the technical possibility of chrome tanning with lower chrome offer and without pickling. But the analysis of chrome and grease content, as given in Table 5.2, showed clearly that it was essential to flesh the skins before degreasing. There seemed to be a good correlation between the chrome and fat content of the wet blue, with a coefficient of correlation of 0.86, ie. the higher the fat content, the lower the chrome uptake by the pelt (see Figure 5.1).

Figure 5.1: Chrome and grease content of lambskin

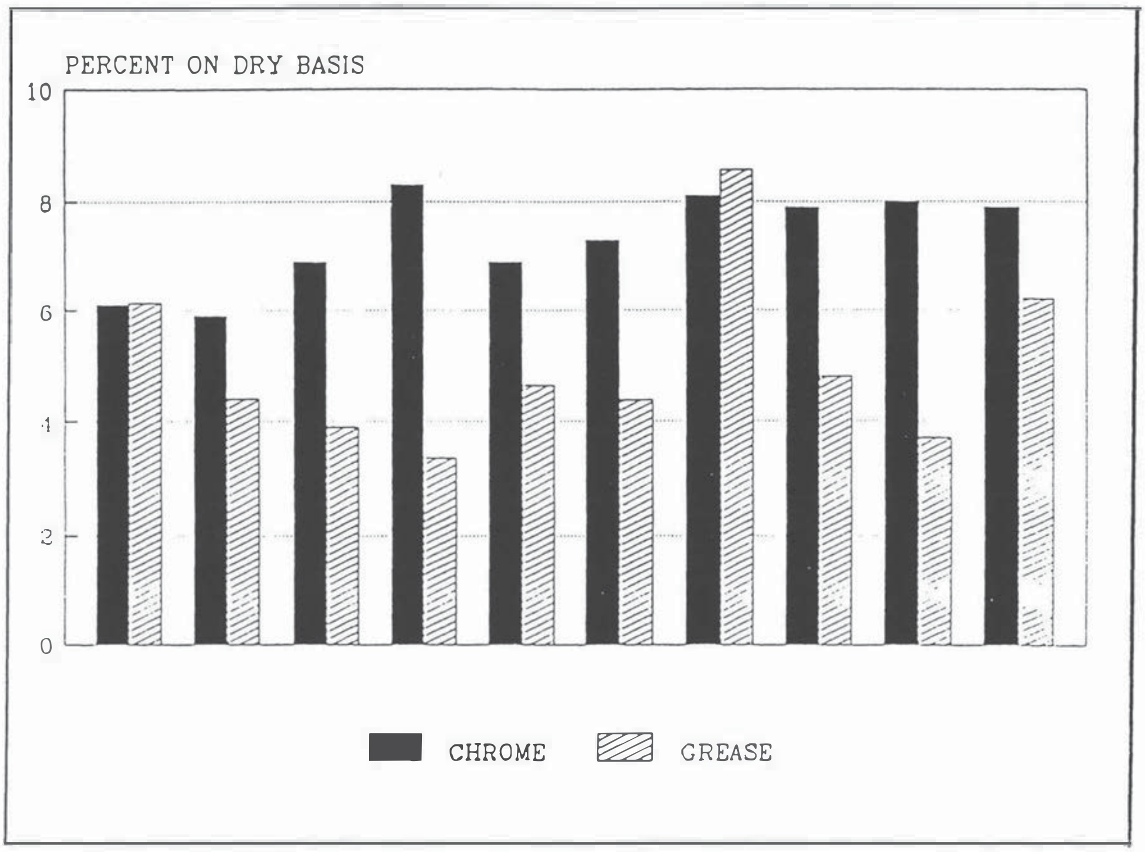


Table 5.2:Chrome and fat content of chrome tanned lamb skins

Skin No.	Chrome Content (% as Cr_2O_3 at 0% moisture)	Fat Content (% at 0% moisture)
1	5.12	24.01
2	4.74	19.94
3	5.99	14.01
4	5.76	13.86
5	5.69	19.00
6	4.46	35.80
7	4.66	31.72
8	5.29	17.77
9	4.69	27.61
10	5.87	17.83
Average	5.23	22.15
Standard Deviation	0.57	7.44

Two dozen pelts from the same delimed lot which were collected from the same fellmongery after pickling were also tanned; One dozen of these pelts were fleshed at this pickled stage and the other dozen kept without fleshing. All these skins were then degreased following the same method followed for delimed skins, repickled and chrome tanned with 5% chrome tanning powder (Tannachrome S).

On comparative assessment, it was found that the wet blue skins from the no-pickle system were considerably shrunken, particularly when there was adherent flesh. The leather also looked considerably fuller compared to those processed from pickled pelts. The pickled/tanned skins looked much more spread out whether they were fleshed or unfleshed. When comparing fleshed vs unfleshed skins, in both systems of tannage the fleshed skins were considerably flatter and bigger. The skins from the delimed/tanned system were considerably fuller than those from the pickle/tan system. The chrome and fat contents of the two systems were as given in Table 5.3.

Table 5.3: Chrome and fat content in lamb skin

	Fat (% dry weight)	Chrome Content (as Cr_2O_3 at 0% moisture)	Chrome Utilisation (%)
Pickle/tan system	18.2	3.31	74.21
Nopickle/tan system	28.2	4.97	86.43

These chrome tanned skins were then shaved to 1.0 mm and retanned together following the same process and crusted out. Samples from the official sampling position were then tested for all physical properties and results are given in Tables 5.4, 5.5, 5.6 and 5.7.

Table 5.4:Comparative grain strength on New Zealand lamb skins with or without pickling

Skin No.	Distention at Grain Crack (mm)	Load at Grain Crack (kg)
No pickle/tan		
1	10.47	29
2	11.16	30
3	10.26	26
4	10.25	20
5	10.13	20
6	10.85	30
Average	10.52	25.8
Standard Deviation	0.40	4.75
Pickle/tan		
1	10.30	26
2	9.14	13
3	10.17	29
4	10.07	27
5	9.54	22
6	10.92	26
Average	10.02	23.9
Standard Deviation	0.62	5.59

Table 5.5: Comparative tear strength of New Zealand crust lamb skins with or without pickling

Skin No.	Thickness (mm)	Tear Strength (N/mm)
No pickle/tan		
1	1.12	24.9
2	1.03	39.4
3	1.02	38.4
4	1.03	21.6
5	1.16	30.3
6	1.05	32.0
Average	1.07	31.1
Standard Deviation	0.07	7.09
Range	-	21.6 - 39.3

Pickle/tan		
1	1.27	29.6
2	1.04	19.2
3	1.11	35.3
4	1.15	37.1
5	1.04	33.8
6	1.11	28.9
Average	1.12	30.7
Standard Deviation	0.09	6.44
Range	-	19.2 - 37.0

Table 5.6:Comparative tensile strength of New Zealand crust lamb skin with or without pickling

Skin No.	Thickness (mm)	Tensile Strength (N/mm^2)
No pickle/tan		
1	1.16	127.3
2	1.06	175.2
3	1.06	168.2
4	1.05	82.0
5	1.19	86.0
6	1.04	130.4
Average	1.10	128.2
Standard Deviation	0.06	44.0
Range	-	81.9 - 175
Pickle/tan		
1	1.28	134.7
2	0.94	65.3
3	1.16	154.6
4	1.17	169.1
5	1.07	147.5
6	1.16	106.6
Average	1.13	129.6
Standard Deviation	0.11	38.0
Range	-	65.2 - 169

Table 5.7: Comparative elongation at break of New Zealand crust lamb skin with or without pickling

Skin No.	Thickness (mm)	Elongation at Break (%)
No pickle/tan		
1	1.16	95
2	1.06	112
3	1.06	94
4	1.05	97
5	1.19	126
6	1.04	97
Average	1.10	103
Standard Deviation	0.06	13
Pickle/tan		
1	1.28	89
2	0.94	77
3	1.16	96
4	1.17	103
5	1.07	89
6	1.16	111
Average	1.13	94
Standard Deviation	0.11	12

Even with the degreasing problem it was evident from the results that the no pickle system gave stronger leather than the pickle/tan system. This also confirmed earlier finding. The following could be concluded from this trials:-

- The delimed pelts should be fleshed well before degreasing, otherwise loss of area might result.
- The quality of present prefleshing should be improved.
- Aqueous degreasing agents should be carefully examined for their efficiency in comparison to solvent degreasing and their environmental impact reviewed.

5.4 Experimental Trial 2

5.4.1 *Details of the Industrial Experiment*

A second trial was conducted with the objective of studying the effect of fleshing on:-

- chrome uptake of wet blue
- grease removal
- area yield
- leather quality
- physical properties

The experimental design for the ten dozen lamb skin trial was as follows:-

- **Treatment A**

  One good prefleshing only

  Green fleshed at the sheepskin tannery but no fleshing after deliming
- **Treatment B**

  One good prefleshing plus another good fleshing after deliming

  Green fleshed at the sheepskin tannery and fleshed again after deliming at the wet blue pelt tannery
- **Treatment C**

  One regular fellmongery prefleshing plus another good fleshing after deliming

  Green fleshed at the fellmongery and fleshed again after deliming at the wet blue pelt tannery

200 skins were collected from a meat plant and two thirds of the skins were green fleshed in a sheepskin tannery, leaving one third unfleshed. These skins were then brought to the fellmongery and the unfleshed skins

were prefleshed on their Andar prefleshing machine. Therefore there were three sets of pelts, two sets fleshed at the sheepskin tannery and the other set prefleshed at the fellmongery. All of these skins were then processed together up to CO_2 deliming and bating. These were then taken to the wet blue pelt tannery for further processing. Two sets, one prefleshed at the fellmongery and the other at the sheepskin tannery were fleshed keeping the other set without a second fleshing.

All these skins were then aqueous degreased and chrome tanned together without pickling or masking with 5% chrome tanning powder. No basification was done.

The skins were separated in three sets. The average shrinkage temperatures of the three lots were as given in Table 5.8.

Table 5.8:Shrinkage temperature

Treatments	Shrinkage Temperature
A	110°C
B	117°C
C	117°C

The areas of all these skins were measured and skins graded for smoothness of grain. Ten random neck samples were taken from each set and their chrome and fat contents determined following the official methods the International Union of Leather Technologists and Chemists. The wet blue was then taken to the finished leather tannery for commercial grading before shaving and retanning.

The shaving of wet blue to standard thickness, would of course, minimise the difference due to initial fleshings but to examine the final quality of leather, all skins were processed following a normal commercial process. It was found earlier that to obtain a comparable crust, 50% less retanning agent was required but this had to be ignored and no adjustment for the inherent fullness obtained with this no-pickling tanning system was made in the recipe to retannage. In actual production this factor should also be considered for obtaining better leather at lower cost. Three dozen of similar commercial wet blue were also processed for comparison. The crust leather was also selected again before finishing into commercial nappa leather.

5.4.2 Results and Discussions on Trial 2

The results are given in Tables 5.9, 5.10, 5.11, 5.12 and 5.13.

Table 5.9:Area and yield of wet blue lamb skins

	Treatment A	Treatment B	Treatment C
Average area per skin (sq ft)	9.20	9.16	9.06
Average weight per skin (kg)	2.47	1.95	2.02
Average yield per skin (sq ft/kg)	3.72	4.70	4.48

Table 5.10:Percent distribution of flatness of wet blue lamb skins

Grades of Wet Blue (based on grain flatness)	Treatment A	Treatment B	Treatment C
1 (best)	5.5	19.3	12
2	18.5	36.8	22
3	24.1	28.1	36
4	27.8	14	24
5	24.1	1.8	6

Table 5.11: Percent distribution of various grades of wet blue lamb skin

Commercial Grades of Wet Blue Lamb skins	Treatment A	Treatment B	Treatment C
Nappa			
- heavy	20.4	24.6	26.0
- light	1.8	5.2	4.0
- total	22.2	29.8	30.0
Mottle			
- heavy	3.7	-	2.0
Third			
- heavy	63.0	57.9	66.0
- light	9.3	5.3	2.0
- total	72.2	63.1	68.0
Fourth	1.8	7.0	-
Numberof Skins	54	57	50

Table 5.12:Chemical analysis of wet blue lamb skins

	Treatment A	Treatment B	Treatment C
Moisture (%)	81.2	82.2	82.3
Chrome Content (as Cr_2O_3)*	6.7	7.3	7.8
Fat Content (%)*	9.3	5.0	7.5
Efficiency of Tanning (5)	86.2	93.8	96.1

* Based on zero percent moisture

Table 5.13:Percent distribution of various grades of crust leather

Grades of Crust Leather	Treatment A	Treatment B	Treatment C
Nappa Selection			
- heavy, A	5.5	3.7	-
- heavy, B	18.5	22.2	28.0
- light, B	3.7	3.7	4.0
- total	27.8	29.6	32.0
Thirds Selection			
- heavy, E	63.0	62.9	68.0
- light, E	9.36	7.5	-
- total	72.2	70.4	68.0
Number of Skins	54	54	50

When compared with three dozen crust skins of normal production, it was found that the skins from the no-pickle/tanning system were more uniform and deeper in shade and gave fuller leather with better grain characteristics. The area of the finished nappa leather was measured . Table 5.14 indicated the benefits of a good fleshing system on grade and yield of nappa leather.

Table 5.14:Area yield of finished nappa leather (sq ft)

Grades of Finished Lamb skins	Treatment A	Treatment B	Treatment C
Nappa Selection			
- heavy, A	16.3	24.3	-
- heavy, B	80.2	96.2	119
- light, B	6.6	19.4	12.7
- total	103.1	139.9	131.7
Thirds Selection			
- heavy, E	259.8	263.2	243.6
- light, E	28.9	19.4	4.9
- total	288.7	282.6	248.5
Total	391.8	422.5	380.2
Yield (sq ft/skin)	7.53	7.82	7.6

Ten skins from each of the three sets of finished nappa were selected at random and physical tests done on samples cut from the official sampling position and following relevant physical test methods of the International Union of Leather Technologists and Chemists. The results are given in Tables 5.15, 5.16, 5.17 and 5.18. The values are similar but still indicative of the benefits of better fleshing systems.

Table 5.15:Effect of different fleshing systems on double hole stitch tear strength

	Thickness (mm)	Stitch Tear Strength (N)
Treatment A		
Average	1.08	91.0
Standard Deviation	0.16	29.5
Range	0.82 - 1.41	26.5 - 116.0
Treatment B		
Average	1.16	95.5
Standard Deviation	0.13	32.9
Range	0.93 - 1.33	39.5 - 140.0
Treatment C		
Average	1.12	95.6
Standard Deviation	0.11	23.0
Range	0.88 - 1.26	54.0 - 121.0

Table 5.16:Effect of different fleshing systems on grain strength (ball burst)

	Distention at Grain Crack (mm)	Load at Grain Crack (kg)
Treatment A		
Average	9.44	18.1
Standard Deviation	0.42	5.7
Range	8.9 - 9.95	6.0 - 26.0
Treatment B		
Average	9.61	20.5
Standard Deviation	0.80	7.2
Range	8.24 - 10.87	8.0 - 31.0
Treatment C		
Average	9.67	21.6
Standard Deviation	0.74	4.3
Range	8.14 - 10.45	15.0 - 30.0

Table 5.17: Effect of different fleshing systems on tear strength

	Parallel		Perpendicular		Tear Strength	
	Thickness (mm)	Breaking Load (N)	Thickness (mm)	Breaking Load (N)	Parallel (N/mm)	Perpendicular (N/mm)
Treatment A						
Average	1.18	48.3	1.18	52.2	38.4	42.3
Standard Deviation	0.16	13.72	1.06	14.68	12.04	12.59
Range	0.95 - 1.33	18.0 - 55.6	0.83 - 1.43	20.6 - 62.3	16.6 - 49.4	19.7 - 56.2
Treatment B						
Average	1.20	50.9	1.19	52.2	38.2	43.3
Standard Deviation	1.13	16.20	0.12	14.68	11.44	17.96
Range	0.95 - 1.33	25.3 - 68.3	0.92 - 1.34	20.6 - 62.3	23.5 - 52.4	26.9 - 59.5
Treatment C						
Average	1.20	54.5	1.19	56.7	45.4	47.6
Standard Deviation	0.12	7.19	0.12	11.03	6.03	9.29
Range	0.92 - 1.32	44.3 - 66.3	0.94 - 1.31	33.6 - 69.6	33.7 - 55.5	20.0 - 70.4

Table 5.18: Effect of different fleshing systems on tensile strength

	Parallel		Perpendicular		Tensile Strength	
	Thickness (mm)	Breaking Load (N)	Thickness (mm)	Breaking Load (N)	Parallel (N/mm)	Perpendicular (N/mm)
Treatment A						
Average	1.12	120.7	1.15	87.8	11.0	7.7
Standard Deviation	0.15	47.55	0.15	32.56	4.52	2.73
Range	0.87 - 1.46	41.0 - 189.0	0.90 - 1.47	39.6 - 133.3	3.4 - 16.4	3.1 - 11.64
Treatment B						
Average	1.20	126.11	1.19	97.1	10.3	8.1
Standard Deviation	0.11	69.81	0.09	41.01	5.33	3.36
Range	0.96 - 1.36	30.6 - 209.3	0.98 - 1.29	33.0 - 147.3	4.7 - 17.2	2.8 - 12.23
Treatment C						
Average	1.19	129.4	1.20	98.4	11.0	8.31
Standard Deviation	0.13	39.48	1.20	37.34	3.33	3.14
Range	0.92 - 1.33	67.3 - 192.6	0.92 - 1.31	51.6 - 154.6	5.2 - 15.9	4.05 - 12.3

5.5 Extension of the Novel Principle to Pickled Lamb Skin Tanning

Conventionally aqueous degreasing is done on pickled pelts. The pelts are pretanned with aldehydes to increase the thermal stability so that degreasing can be carried out at higher temperature. Normally a degreasing temperature which is 20°C lower than the shrinkage temperature of the pretanned pelts could safely be employed.. This however need to initially lift the pH of the pickle pelts from pH 2.0 to pH 4.5 - 6.5 to improve the efficiency of the pretanning agent and then readjust the pH to pH 3.0-3.5 before chrome tanning. Glutaraldehyde is a common agent for such pretannage. DasGupta[16] published results of his comparative studies of aqueous degreasing of lamb skins with glutaraldehyde and oxazolidine A which showed that fat removal and strength properties with oxazolidine A was better than that with glutaraldehyde. Many other pretanning agents, like glyoxal, oxazolidine E and tetrakishydroxyl methyl phosphonium sulphate may also be used. The extension of ThruBlu process of chrome tanning provided an option to eliminate repickling of the degreased pelts with acids and salts.

5.5.1 Chrome Tanning of Degreased Lamb Skins with or without Repickling:

4 dozen pickled lamb skins were taken and divided at random in to 4 sets of one dozen each. One set, Set A was degreased and chrome tanned following conventional chrome tanning after bringing down the pH to 3.0 after degreasing with formic acid. Set B and Set C were pretanned with 3% Oxazolidine A and 3% Oxazolidine E respectively, degreased and then chrome tanned without repickling where as Set D was pretanned with 3% Oxazolidine A , degreased with Set B but chrome tanned after repickling as the control(Set A). Composite samples, taking equal amount of chrome tanned pelts from the neck area of the twelve skins of each set, were analysed for chrome and fat content. The results are given in Table 5.19.

Table 5.19:Comparative fat and chrome content of New Zealand Lamb Skins

	Set A	Set B	Set C	Set D
Fat content, percent				
a. before degreasing	20.8	26.1	20.2	26.2
b. wet blue	2.9	1.5	1.7	1.3
Chrome content, as Cr_2O_3, % Moisture free basis	3.8	4.2	3.7	3.8

Having seen the benefit of such pretannage with Oxazolidine A for both grease removal and chrome absorption by lamb skin, this chrome tanning trial without repickling were repeated three times against a standard control with one dozen pickled pelt per lot. The results of chrome in the exhaust were as given in Table 5.20.

Table 5.20: Chrome content of oxazolidine A pretannage and high pH chrome tanning

	Control	Trial-1	Trial-2	Trial-3
Chrome offered, as Cr_2O_3	138.4	127.2	129.4	128.8
Chrome in wet blue, as Cr_2O_3, % moisture free basis	3.54	3.72	3.74	3.72
Chrome in tanning exhaust bath, as Cr_2O_3, mg/l	213.7	76.7	73.6	52.2

These wet blue skins were washed with 200% water at 30^{O}C with 0.2% Nonionic wetting agent(Teric GN9 - Ex.ICI Plc,Australia) for 30 min. to find out how much chrome were leached out from these wet blue skins. The results were as given in Table 5.21.

Table 5.21:Leaching behaviour of wet blue lamb skins pretanned with Oxazolidine A

		Oxazolidine A Pretan		
	Control	**Trial-1**	**Trial-2**	**Trial-3**
Weight of wet blue, kg	7.3	7.3	7.8	7.6
Chrome in wet blue, as Cr_2O_3, moisture free basis, %	3.54	3.72	3.74	3.72
Chrome in leach liquor, ppm	17.32	10.95	10.86	8.75
Total chrome leach liquor, mg	108.04	84.68	80.30	62.78
Percent of chrome in leather	0.042	0.031	0.028	0.023

The leaching of chrome from such pretanned leather with Oxazolidine was reduced by an average of 36 percent from the chrome tanned control wet blue.

Thus the concept of novel chrome tanning without pickling were successfully extended to develop a new option for chrome tanning of New Zealand lamb skins where the pickled pelts could be pretanned with 3% Oxazolidine A or Oxazolidine E and degreased successfully at low temperature of 35°C with aqueous degreasing agents. Such degreased skins could then be chrome tanned at high pH without any repickling to give high exhaustion of conventional chrome tanning agents. No masking and basification were also required. The leaching characteristics of such pretanned wet blue were also better than the conventional wet blue.

5.6 Suggested Mechanism

Gustavson[17] and Thomas and Kelly[18] have shown that the removal of the amino groups from collagen by the deamination caused a considerable decrease in chrome fixation and suggested that the coordination of the amino group was a factor in chrome fixation. Theis and Kleppinger[19] reported that formaldehyde pretannage lowered the chrome fixation. But, Fein, Filachione, *et al*[20] reported that the chrome tanned leather pretanned with glutaraldehyde gave 4.0% Cr_2O_3 compared to 3.44% for the untreated chrome control. Apart from higher chrome fixation, they also obtained 7°C higher shrinkage temperature for such pretanned leather than that was obtained for the control. According to their study, the fixation of aldehyde and chrome at pH 4.0 were independent of each other. DasGupta[21] recently also reported that there were no decrease in chrome content of leather due to the pretannage with glutaraldehyde (Relugan GT 50 of BASF), oxazolidine (Oxazolodine A of Angus Chemicals), glyoxal (Relugan LD6167 of BASF) and tetrakis hydroxy methyl phosphonium sulphate (Albrite AD of Albright and Wilson). The effect of such pretannages on the chrome content of wet blue, pH, shrinkage temperature and the exhaustion rate during the chrome tannage were as given in Figures 5.2, 5.3, 5.4 and 5.5.

Figure 5.2: Effect of pretannage on chrome content of wet blue

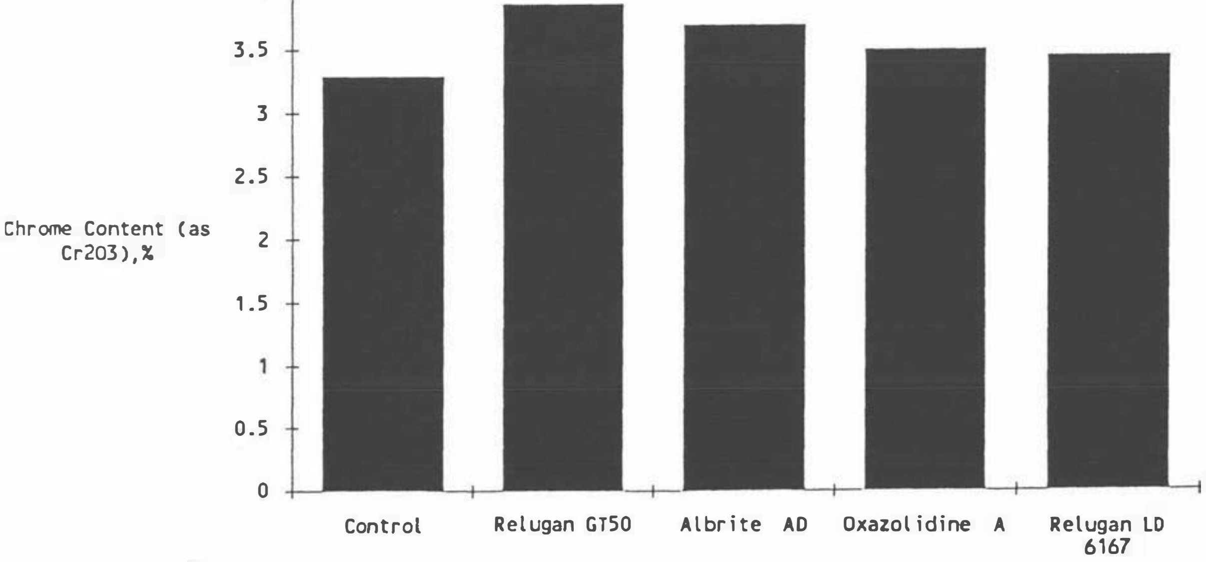


Figure 5.3: pH profile during chrome tannage of pretanned pelts

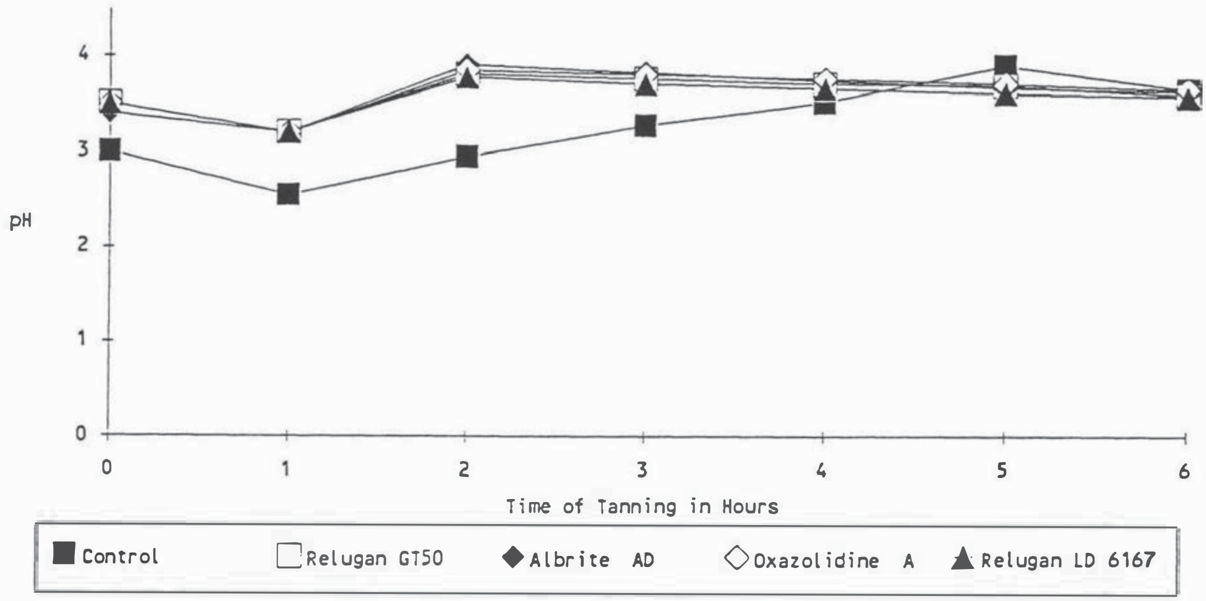


Figure 5.4: Shrinkage temperature of chrome tanned skins

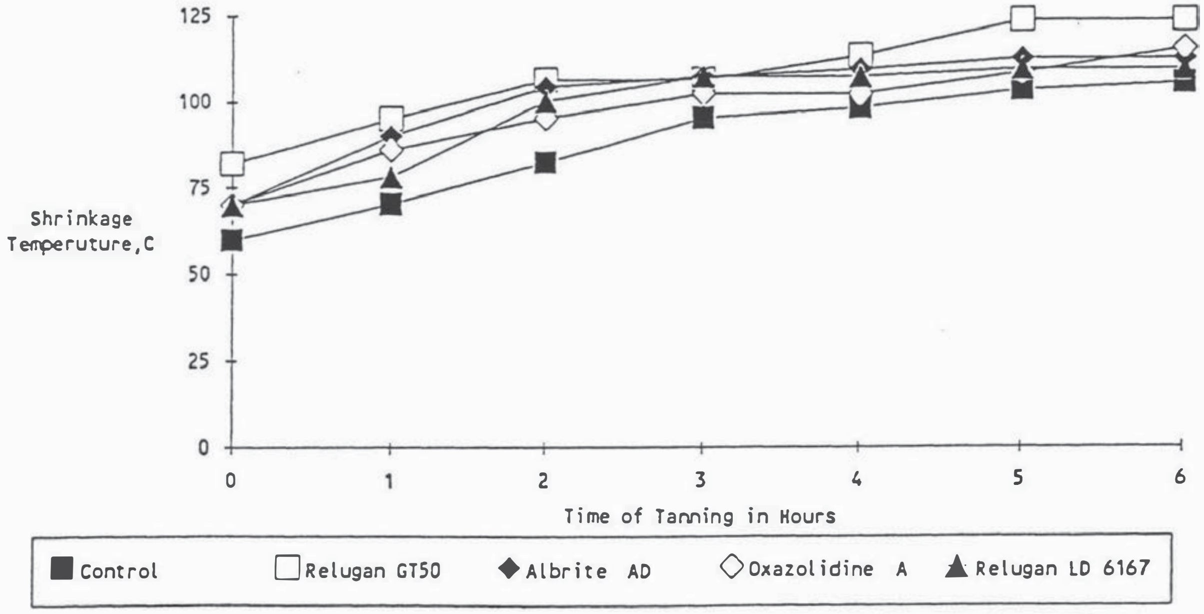
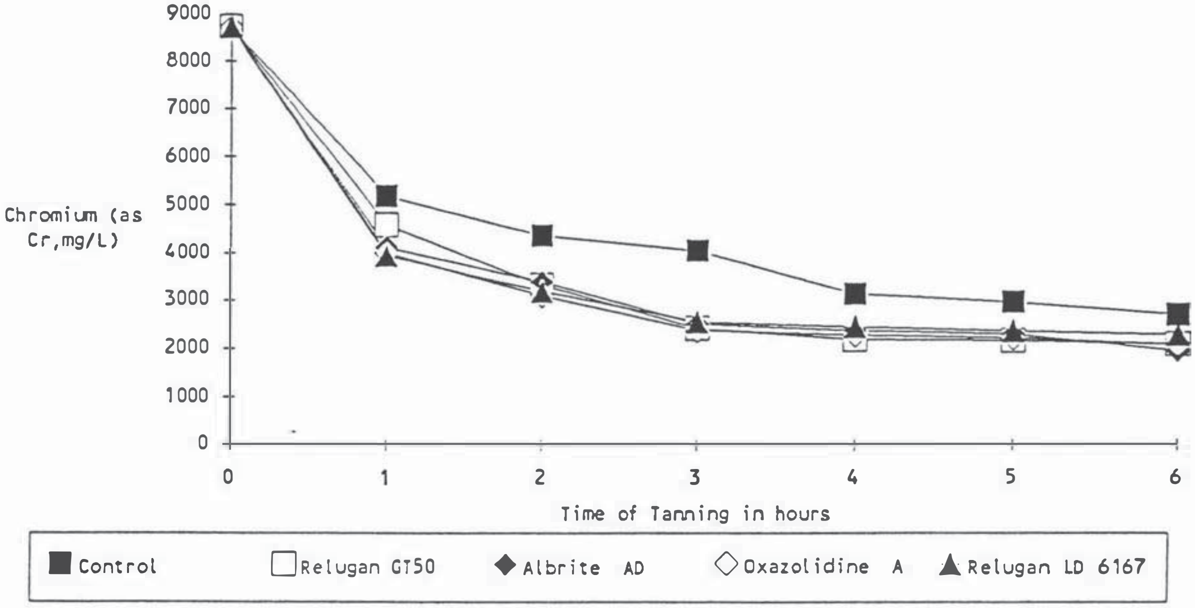


Figure 5.5: Rate of exhaustion of chrome of pretanned skins



At high pH the amino groups were responsible for the additional fixation of chromium. Further, the reaction of the aldehydes or oxazolidine with the basic groups might be associated with the lowering of the isoelectric point of collagen. The isoelectric point of limed collagen is around 4.7. Pretannage with oxazolidine or other aldehydes could drop the isoelectric point of collagen and this could also increase chrome fixation due to the increased availability of carboxylic acid groups. It might be pointed out that Mizutani, Mohri and Okada[22] also noted that the shrinkage temperature of chrome tanned leather was higher with the pretreatment with aldehydes than the control, and the tanned leather had also more uniform distribution of chrome. This also supported the proposed view. It was therefore postulated that at high pH the anionic and nonionic species of basic chrome sulphate reacted with the non carboxylic groups of collagen and when the pH dropped to pH 3 to 4 due to the acidity of the tanning agent, the cationic chrome complexes reacted with the carboxylic groups of the collagen. This suggested mechanism was in line with the view expressed by Erdmann[23].

5.7 Conclusion

The “no pickle” rapid chrome tanning system worked satisfactorily in larger scale trials and confirmed our earlier small scale work.

The efficiency of chrome tanning was considerably improved by the no-pickle system. The quality and strength of finished leather was also improved.

The trial re-established the importance of good fleshing for lamb skin tanning before degreasing. Good fleshing was directly related to good degreasing and improved chrome uptake. Quality and yield of final leather was also largely dependent on good fleshing.

Aqueous degreasing at the delimed stage gave satisfactory leather and worked better than at the pickle stage. Attempts should be made to improve the efficiency of aqueous degreasing.

Concept of “no-pickle” chrome tanning could be extended to pickle lamb skin to tan these skins after degreasing without repickling with acids to bring down the pH to 3.0.

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CHAPTER 6

NOVEL POLYMERIC CHROME TANNING SYSTEMS

6.0 INTRODUCTION

Chapter 2 have shown that the commercial basic chromium sulphate tanning agent contained various species of chrome complexes and considerable amount of sodium sulphate. Gustavson[1] had shown that presence of sodium sulphate reduced the amount of cationic complexes and increased the corresponding amount of nonionic complexes. His studies[2] with phthalate masked chromium sulphate also showed the significant reduction of cationic complexes. Both of these factors considerably slowed down the chrome tanning process at the normal pH (2.5-4.0) of conventional chrome tanning. Mohri, Mizutani,Arima & Okada[3] have shown that 0.15 equivalent of salt per g of hide lead to decrease in chrome uptake by hides and recommended higher pickle pH and lower salt for improved chrome uptake in leather. Therefore, to improve the exhaustion and to minimise the environmental impact of chrome tanning due to salt discharge, an attempt was made to reduce the sodium salt in the chrome tanning agent.

6.1 Reduction of Sodium Sulphate

Commercial sulphur dioxide reduced 33% basic chromium sulphate solutions, containing about 12-15% Cr_2O_3 were obtained from Chrome and Chemicals (New Zealand) Limited, Auckland, New Zealand. The sodium sulphate was removed by simply crystallising out these at low temperature. These chrome solutions were cooled in stages first to 5- 7°C, filtered and then further cooled to - 10°C and refiltered to remove sodium sulphate crystals. Table 6.1 would clearly show that by this simple system more than 70% of the sodium salt could be removed from commercial chrome tanning agent.

Table 6.1: Reduction of sodium sulphate from commercial chrome tanning solutions

Batch No.	pH of Liq	Chrome Content (% Cr_2O_3)	Na_2SO_4 Content (%)	Salt Removal (%)
493	2.46	11.90	9.78	
After Salt Removal	2.29	13.83	2.88	70.56
339	2.49	11.96	9.91	
After Salt Removal	2.23	15.14	2.72	72.56
202	2.45	11.24	9.70	
After Salt Removal	2.25	13.02	3.02	68.87

The partly salt free chrome sulphate solution when separated in cationic exchange resin, Dowex 50W x 8 (Sodium form) and anionic exchange resin, Dowex 1X8-50 and actual amount of chrome determined by Atomic Absorption Spectrophotometer gave us the following values for each fractions:-

Anionic complex:	6.1%
$[Cr(SO_4)_2]^-$	
Nonionic complex:	14.5%
$[Cr(OH)SO_4]^0$	
Cationic complexes:	
$[Cr(SO_4)]^+$	10.2%
$[Cr(OH)_2SO_4Cr]^{2+}$	13.5%
$[Cr]^{3+}$ and $[Cr(OH)SO_4Cr]^{3+}$	39.6%
$[Cr(OH)_2Cr]^{4+}$ and $[Cr(OH)_2Cr(OH)_2Cr]^{5+}$	16.1%
	100%

This values roughly showed similar effect of salt on the composition of chrome complexes as suggested by Gustavson[2]. The separated species when concentrated or dried by freeze -drying technique were found to be stable as long as pH remained constant. Ageing or freeze drying of separated samples did not alter their character significantly. This incidentally was also noticed by Takanouchi[4]. When 0-4N HCl were used as eluent, better separation were obtained than 0-5N NaCl, but highly acidic eluents could not be used to determine their tanning reactivities since very low pH mitigates against reaction between cationic complexes and collagen carboxyl groups. Therefore, all tanning trials were done with fractions separated with 0-5N NaCl eluent and concentrated by freeze-drying technique.

6.2 Reactivity of Various Chrome Complexes

Tanning trials were carried out with pickled lamb skins at pH 3.0 to 4.0, using various fractions of the separated complexes. While Takenouchi[5,6] used constant pH and hide powder, we conducted our trials on lamb skins and varying the pH from initial pH 3.0 to a final pH 4.0 to simulate actual commercial tanning practice. Thermal stability comparisons (a measure of cross-linking) of separated complex fractions against the standard chrome tanning compound were carried out and utilisation of the chrome was determined by measuring the chrome in the residual chrome exhaust of the tanning baths with Atomic Absorption Spectrophotometer. Table 6.2 and Table 6.3 gives the result of trials with anionic fraction and combined anionic and nonionic fractions respectively.

Table 6.2: Comparative tanning power of anionic complex and chrome control

Time (h)	Treatment	pH	Shrinkage Temp °C
3.5	Control	2.65	74.5
	Anionic	2.80	52
4.5	Control	3.91	82
	Anionic	4.03	53
22	Control	2.65	100
	anionic	4.00	62

Table 6.3: Comparative tanning power of anionic and nonionic complex and chrome control

Time (h)	Treatment	PH and Shrinkage Temperature, Ts °C			
		1st Set		2nd Set	
		pH	Ts °C	pH	Ts °C
4	Control	2.68	68	2.15	69
	Anionic + Nonionic	2.52	48	2.05	49
6	Control	3.52	82	3.95	78
	Anionic + Nonionic	4.03	65	3.82	54
22	Control	3.75	89	3.90	94
	Anionic + Nonionic	3.68	80	3.91	91

Utilisation of Chrome:

Control	74.48%
Anionic and Nonionic	54.42%

It was clear from these tables that while anionic chrome complexes had practically no tanning power, nonionics have considerable lower tanning power than control. Similar tanning trials were also conducted with various cationic complexes and we found that the affinity of complexes with skin collagen increased with the cationic charge of the complexes upto^{4+}, and then no further increase in affinity with higher charges than 4^+ were noticed as will be clear from results given in Table 6.4.

Table 6.4: Effect of cationic complexes on the tanning

Treatments	Time/Shrinkage Temperature, Ts °C					
	4 hours		6 hours		22 hours	
	pH	Ts °C	pH	Ts °C	pH	Ts °C
Fraction 2 (1+)	1.38	48	3.60	55	3.82	74
Fraction 3 (2+)	3.49	58	3.98	68	3.64	74
Fraction 4 (3+)	3.46	68	3.55	74	4.02	76
Fraction 5 (4+)	3.48	70	3.88	72	3.82	79
Fraction 6 (5+)	3.40	74	4.02	73	4.00	80

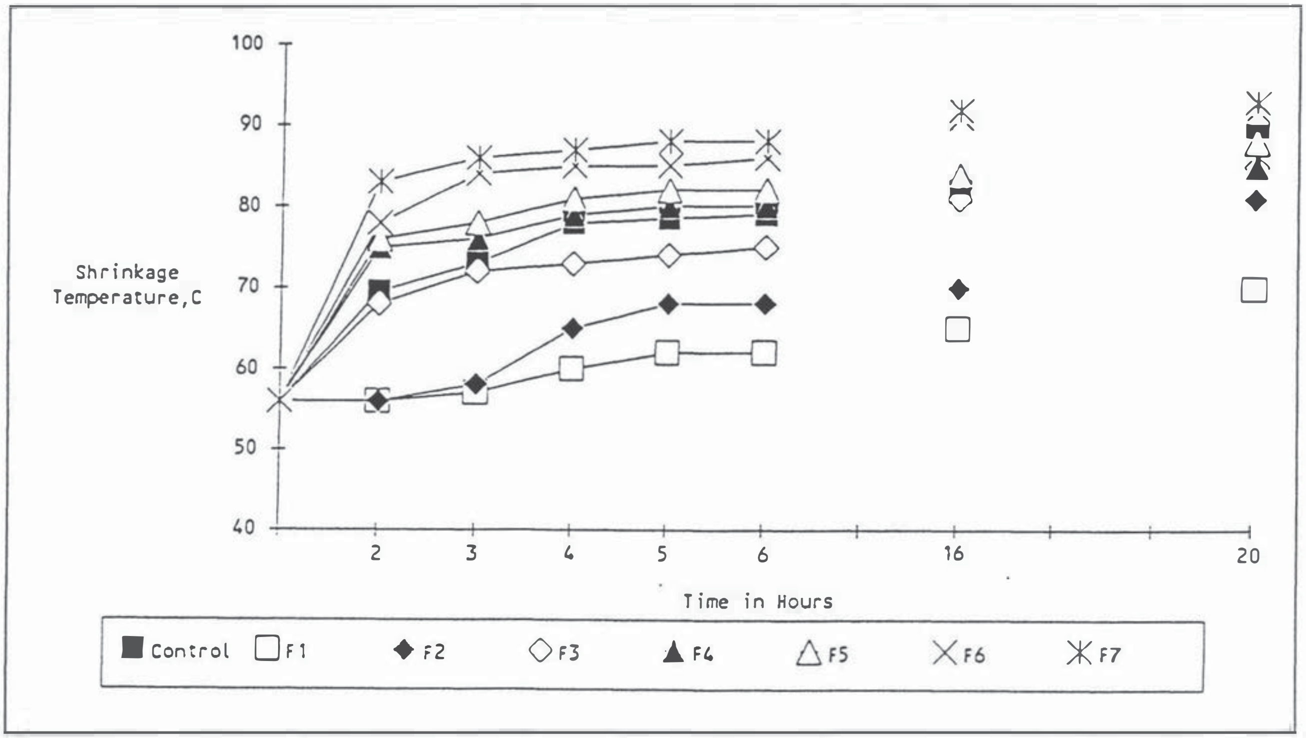
The reactivity of the combined cationic chrome complexes were then studied against standard chrome control on similar pickled and degreased lamb skins and it was found this combined fraction tanned leather rapidly and more efficiently. The exhaustion of chrome, established through the analysis of chrome in the exhaust chrome liquor with Atomic Absorption Spectrophotometer, in three separate trials, were as follows:-

	Control	**Cationic Complexes**
	65.43%	89.04%
	75.04%	98.65%
	74.48%	95.65%
Average:	72.25%	95.11%

These were excellent chrome exhaustion figures compared to standard chrome tanning agents. The quality of leather was also very satisfactory.

We have also studied the effect of three temperatures, namely 20, 30 and 40°C and found that higher the temperature better the exhaustion. But higher charge cationic complexes are very reactive even at low temperature and therefore the effect of temperature is rather minimal on them. Similarly, anionic complex did not have significant improvement of their tanning power even at higher temperature up to 40°C. Anionic, nonionic and cationic complex with (1+) always gave lower shrinkage temperature than control. Further, until the pH was raised nonionic complexes also did not show any tanning power. Figure 6.1 shows the typical reactivity of various fractions at 30°C. Similarly we also studied the effect of pH. We noticed that pH is the main factor of chrome tanning. The higher the pH, the higher the fixation of chrome. This was also noticed by Takata, Shirai and Okada[7] who reported that the reactivity of chromium complex to collagen increased as the charge of the complex increased and the fraction of $(Cr)^{+5}$ possessed a specifically strong affinity to collagen.

Figure 6.1: Effect of temperature on the shrinkage temperature of lamb skin (30°C)



Separate tanning trials conducted each with one dozen of lamb skins with 5% Tannachrome S (25% Cr_2O_3, 33% Basic) at 20, 30, 40 and 50°C showed that higher temperature gave higher chrome exhaustion and lower yield of final leather as would be clear from the results given in Table 6.5 and Table 6.6. The quality of leather was also inferior. Therefore we thought that a temperature of 35-40°C would be optimum for the chrome tanning of lamb skin to maintain its quality and yield. All our subsequent tanning studies were therefore conducted at temperature not exceeding 40°C.

Table 6.5: Effect of tanning temperature on area yield

Tanning Temperature	Pickle Pelt Area sq ft	Wet Blue Area sq ft	% of pelt	Crust Area sq ft	% of pelt
20°C	7.67	7.55	98.5	6.70	87.5
30°C	7.83	7.57	96.7	6.77	8.5
40°C	8.40	8.02	95.5	7.18	85.6
50°C	8.35	7.90	94.8	6.87	82.5

Table 6.6: Effect of tanning temperature on chrome exhaustion

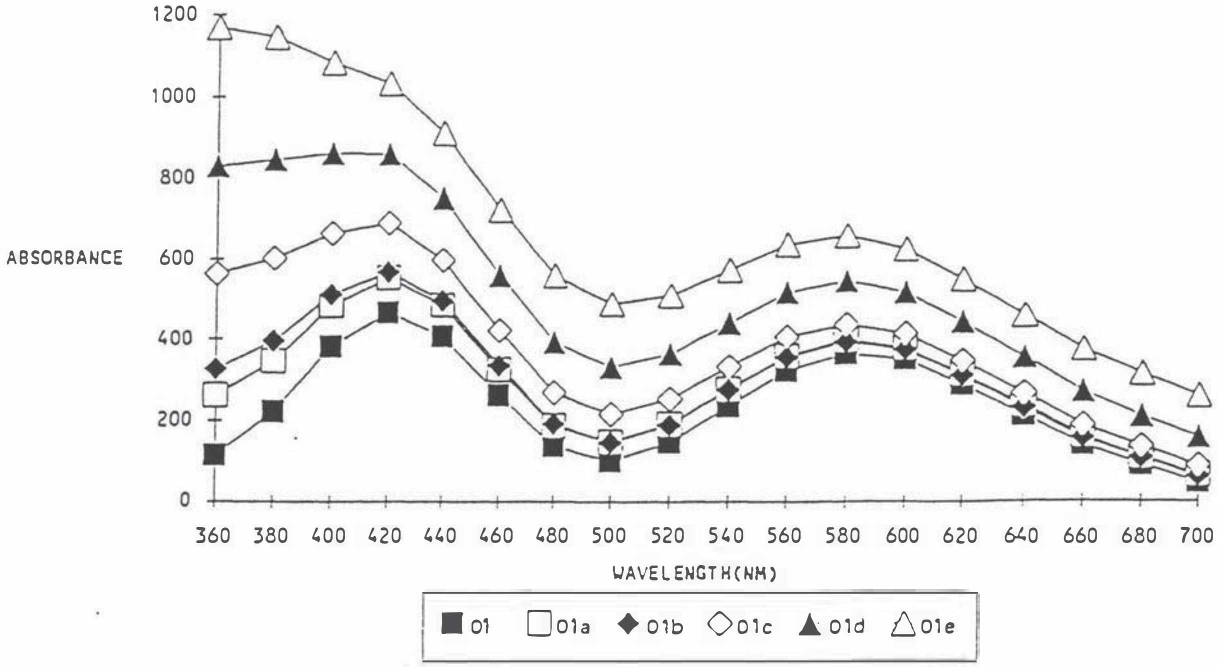
Temperature of Tanning	Chrome Content (as Cr_2O_3), %	Efficiency of Tanning, %	Quality
20°C	3.3	74.85	Best
30°C	3.55	79.40	Best
40°C	3.70	93.68	Good
50°C	3.81	97.98	Fair with draw

In an attempt to improve the exhaustion of chrome during chrome tannage, it might be worthwhile to remove part of the sodium salt and the less active component, like anionic and nonionic complexes from the commercial chrome sulphate liquor before it comes to tanners. But, removal of less reactive complexes was found to be very difficult and cumbersome. Therefore, alternative devises like enrichment or modification of chrome complexes with agents like carboxylic acids or polymer were investigated.

6.3 Polymer Modification of Chromium complexes

Attempts were made to modify chrome tanning agents with polycarboxylic acids without much success as reported in chapter III. We initially tried with different amount of polyamide to establish the nature of the complex. The spectrum of the complex given in Figure 6.2 indicates bridging similar to the acetate, phthalate and oxalate complexes, quite different from formate which gives mainly an increase in amplitude in 580nm.

Figure 6.2: Effect of polyamide addition on the chromium sulphate complex

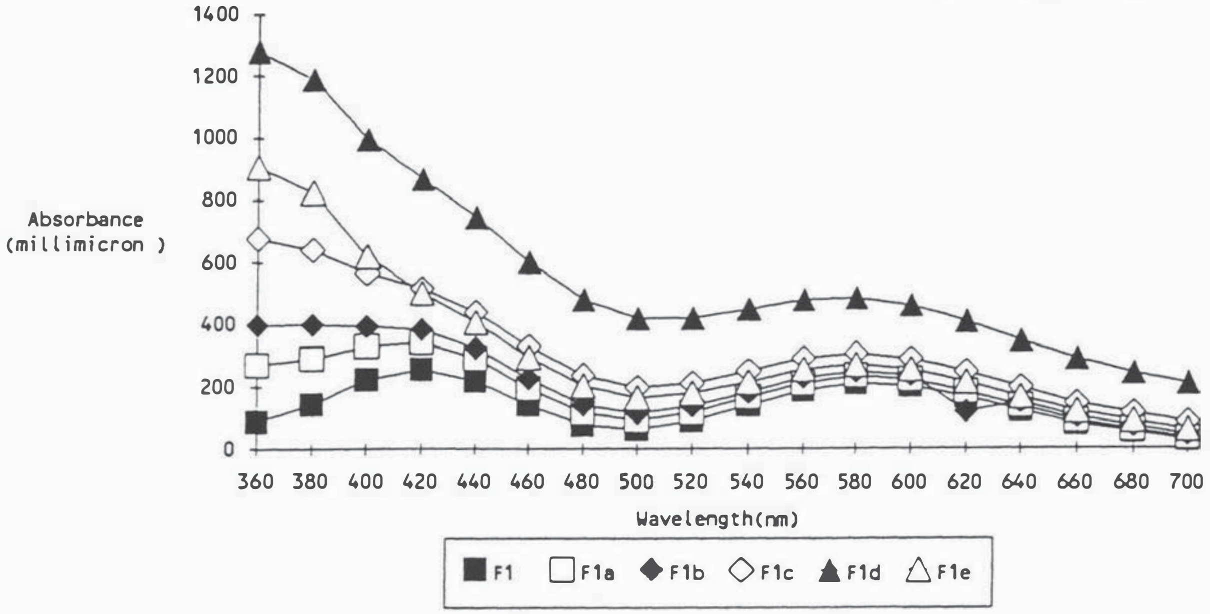


O1 = No resin.

O1a= 0.25g resin/mol Cr_2O_3
O1b= 0.50g resin/mol Cr_2O_3
O1c= 0.75g resin/mol Cr_2O_3
O1d= 1.00g resin/mol Cr_2O_3
O1e= 1.25g resin/mol Cr_2O_3

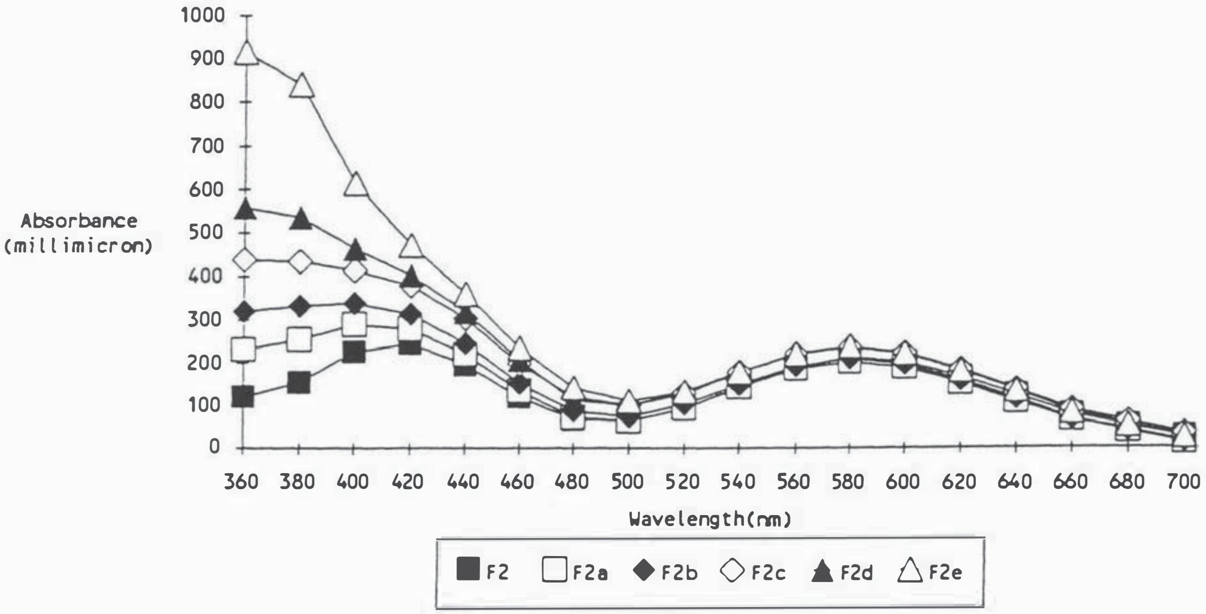
To understand the mechanism more thoroughly, each separated fraction of the chromium sulphate was similarly reacted with 0.25 to 1.25g of polyamide per mole of Cr_2O_3. Figures 6.3, 6.4, 6.5, 6.6, 6.7 and 6.8 illustrates these results.

Figure 6.3:Effect of polamide on chrome complex (fraction 1 - anionic)



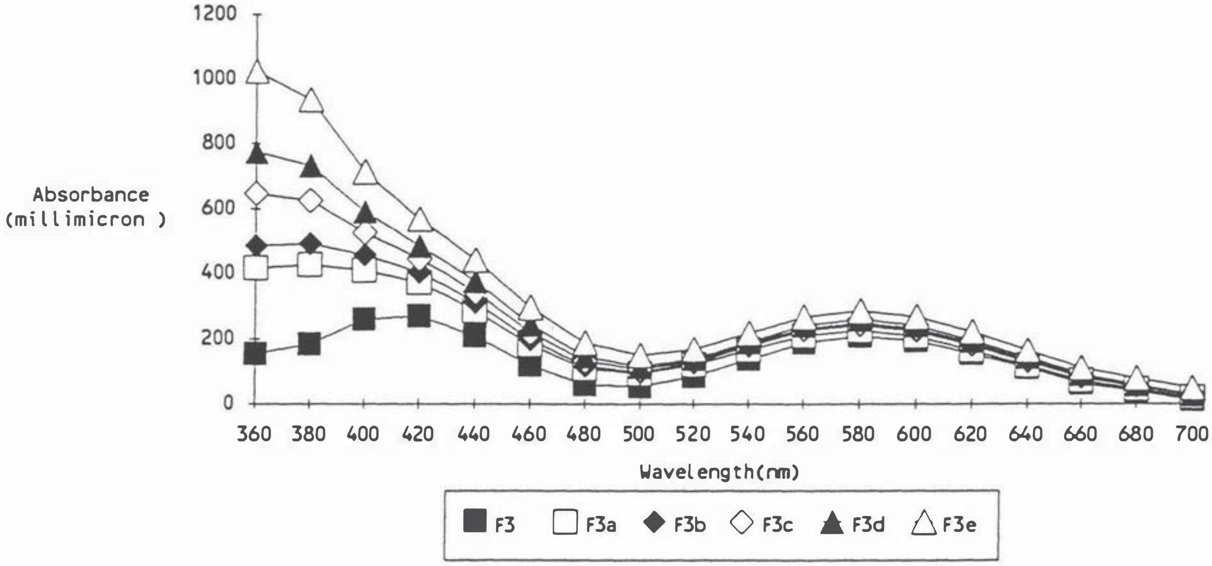
F1 = No resin
F1a = 0.25g/mol Cr_2O_3
F1b = 0.50g/mol Cr_2O_3
F1c = 0.75g/mol Cr_2O_3
F1d = 1.00g/mol Cr_2O_3
F1e = 1.25g/mol Cr_2O_3

Figure 6.4:Effect of polamide on chrome complex (fraction 2 - nonionic)



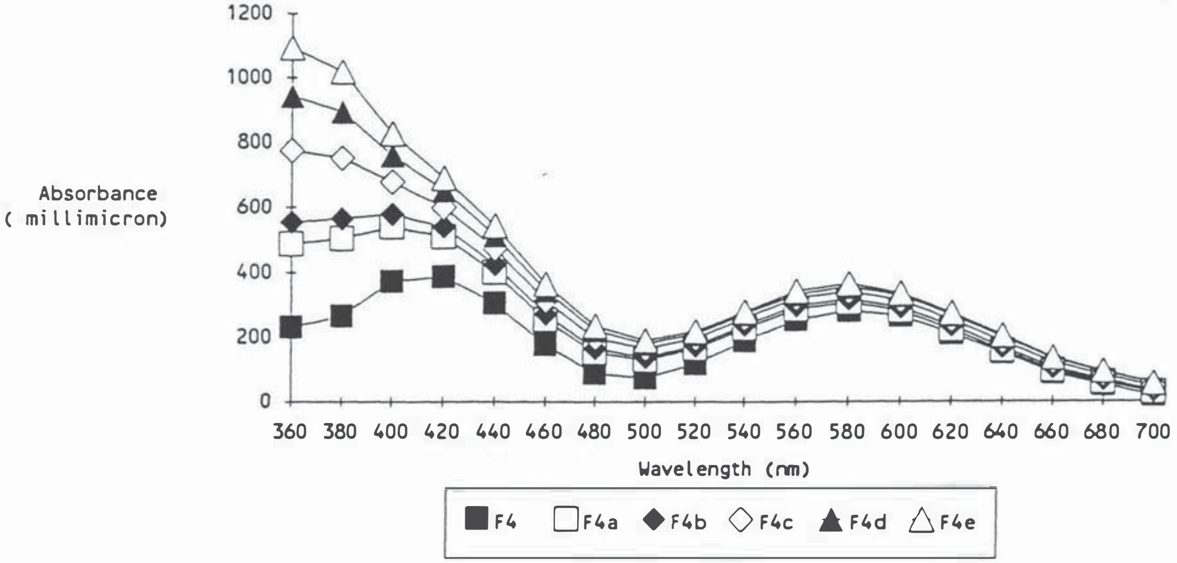
F2 = No resin
F2a = 0.25g/mol Cr_2O_3
F2b = 0.50g/mol Cr_2O_3
F2c = 0.75g/mol Cr_2O_3
F2d = 1.00g/mol Cr_2O_3
F2e = 1.25g/mol Cr_2O_3

Figure 6.5:Effect of polamide on chrome complex {fraction 3 - cationic (1^+)}



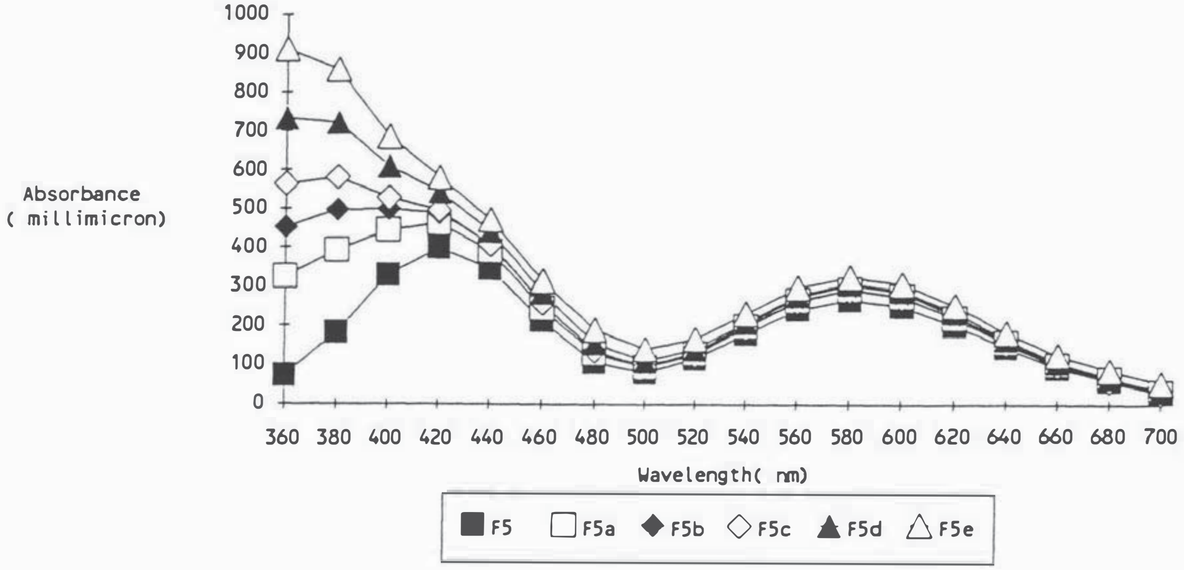
F3 = No resin
F3a = 0.25g/mol Cr_2O_3
F3b = 0.50g/mol Cr_2O_3
F3c = 0.75g/mol Cr_2O_3
F3d = 1.00g/mol Cr_2O_3
F3e = 1.25g/mol Cr_2O_3

Figure 6.6:Effect of polamide on chrome complex {fraction 4 - cationic (2^+)}



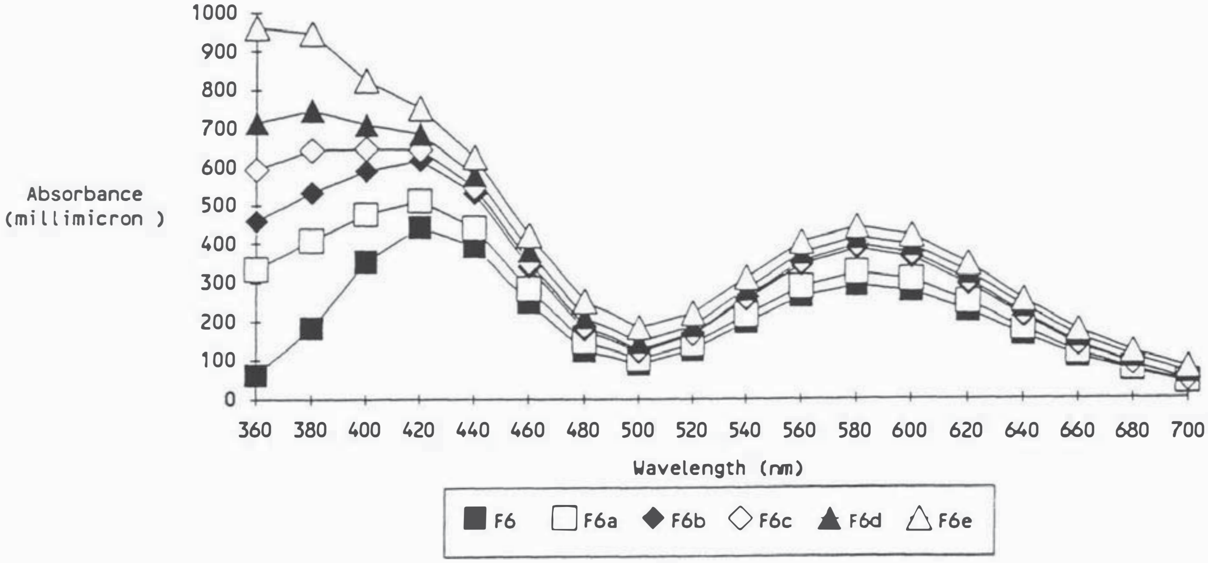
F4 = No resin
F4a = 0.25g/mol Cr_2O_3
F4b = 0.50g/mol Cr_2O_3
F4c = 0.75g/mol Cr_2O_3
F4d = 1.00g/mol Cr_2O_3
F4e = 1.25g/mol Cr_2O_3

Figure 6.7:Effect of polamide on chrome complex {fraction 5 - cationic (3^+)}



F5 = No resin
F5a = 0.25g/mol Cr_2O_3
F5b = 0.50g/mol Cr_2O_3
F5c = 0.75g/mol Cr_2O_3
F5d = 1.00g/mol Cr_2O_3
F5e = 1.25g/mol Cr_2O_3

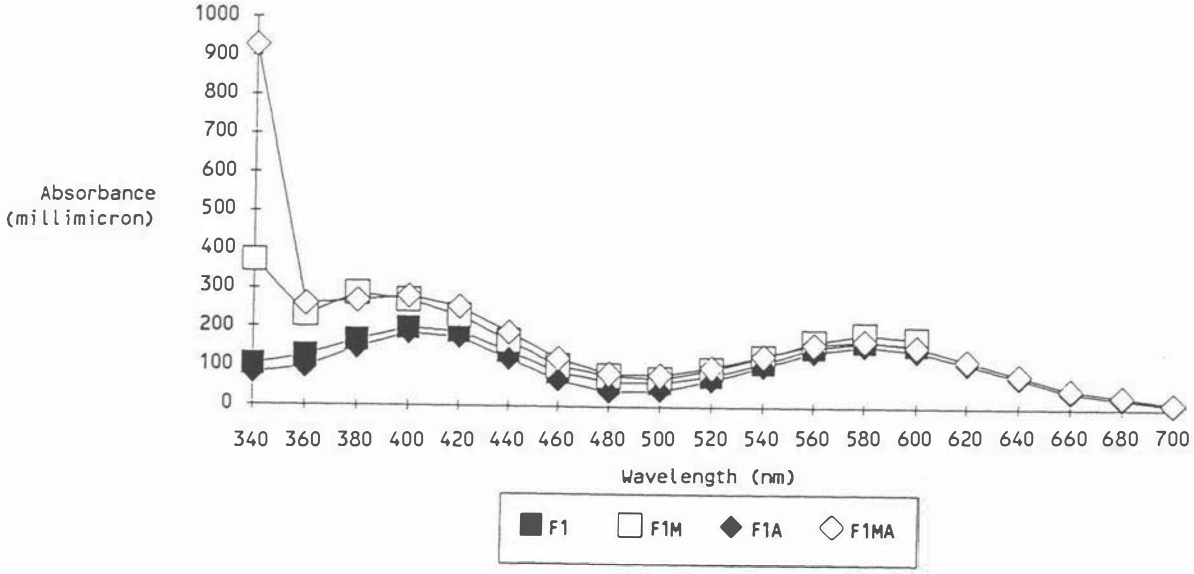
Figure 6.8:Effect of polamide on chrome complex {fraction 6 - cationic (4^+ and above)}



F6 = No resin
F6a = 0.25g/mol Cr_2O_3
F6b = 0.50g/mol Cr_2O_3
F6c = 0.75g/mol Cr_2O_3
F6d = 1.00g/mol Cr_2O_3
F6e = 1.25g/mol Cr_2O_3

From the analysis of the spectrum of these fractions and their modified fractions, this can be concluded that all but the anionic complexes form bridging complexes of chromium to certain aspect like the phthalate. We have also studied the effect of ageing for six months on various fractions thus separated from commercial basic chrome sulphate tanning solutions, containing about 15 % Cr_2O_3 (33% basicity) and their polyamide modified fractions and found that there were no significant changes in these fractions due to ageing as would be clear from their spectrum before and after ageing as given in Figures 6.9, 6.10, 6.11, 6.12, 6.13, 6.14 and 6.15.

Figure 6.9: Effect of ageing on the chrome complex : fraction 1 and its polyamide modified fraction



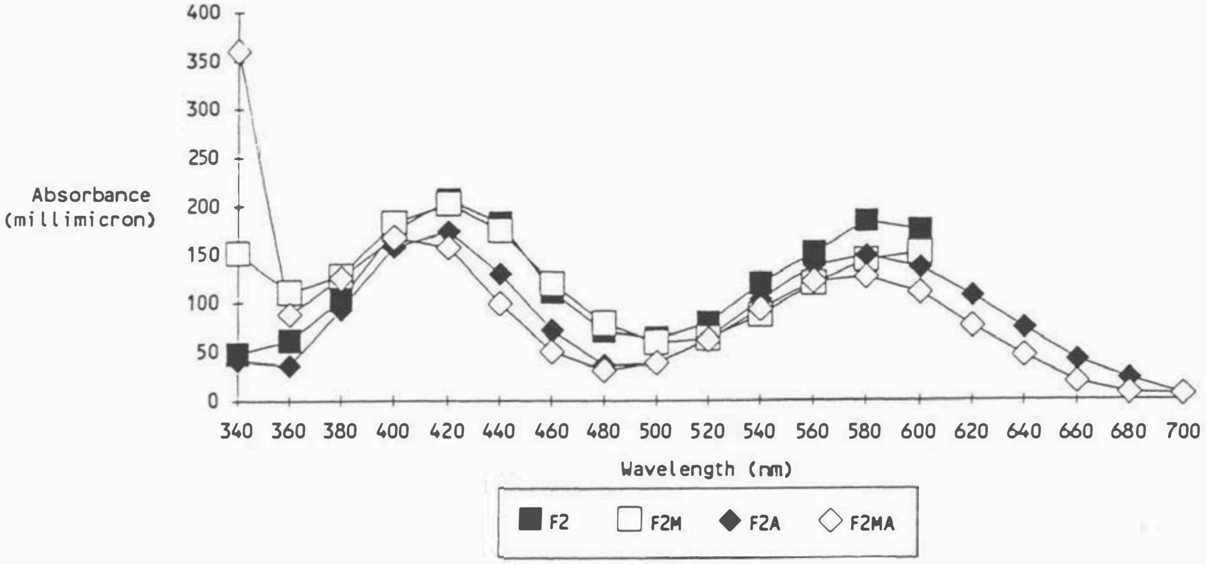
F1 = Fraction 1 before ageing.

F1A= Fraction 1 after ageing.

F1M= Fraction 1 modified, before ageing.

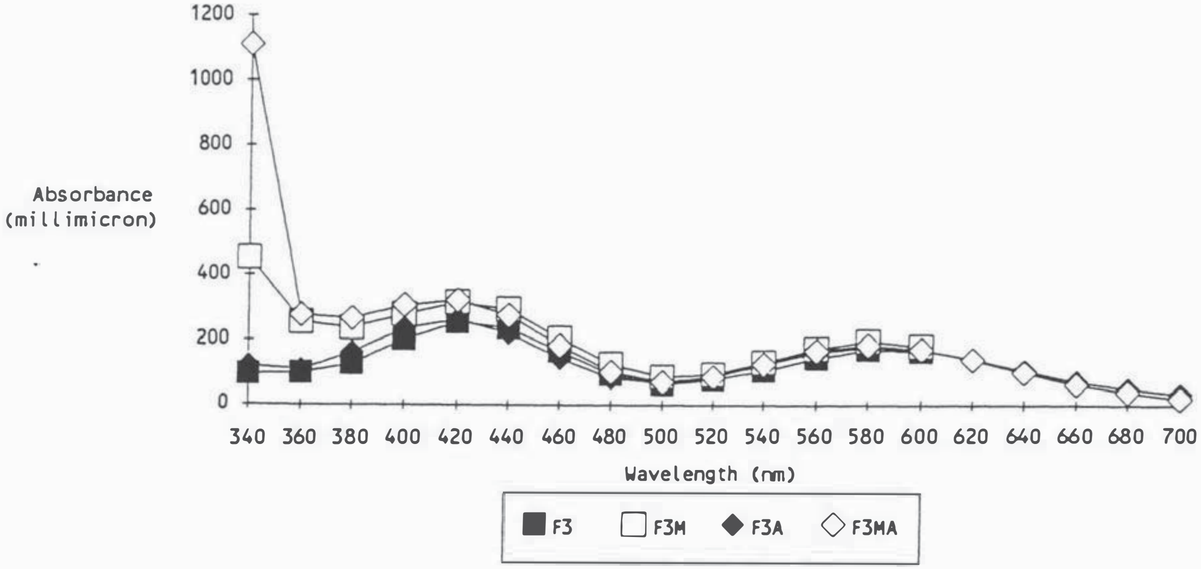
F1MA= Fraction 1 modified after ageing.

Figure 6.10: Effect of ageing on chrome complex : fraction 2 and its polyamide modified fraction



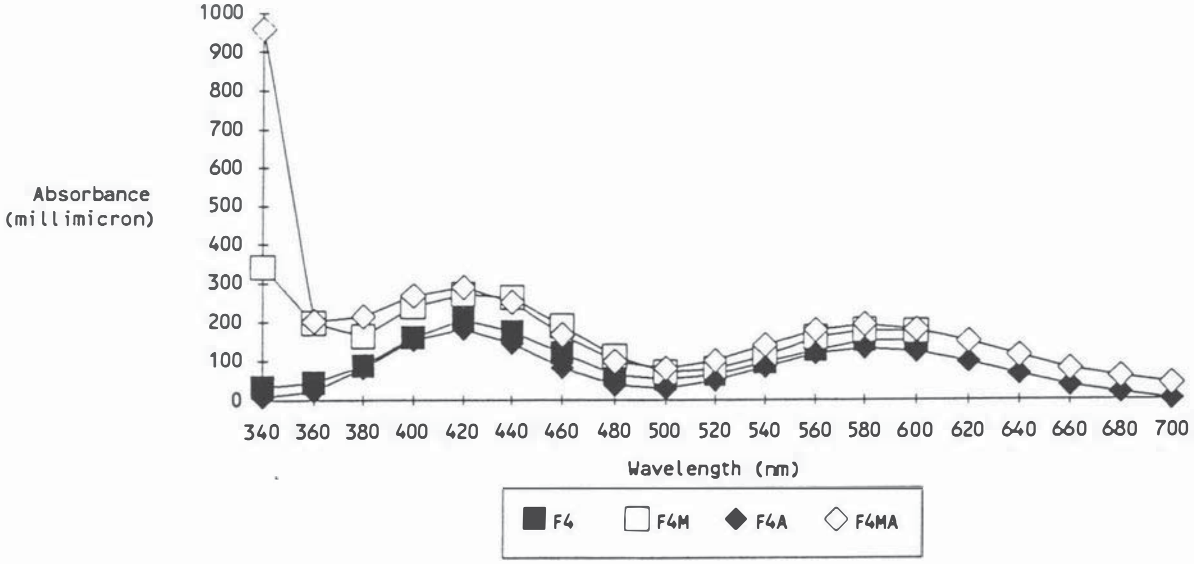
F2 = Fraction 2 before ageing.
F2A = Fraction 2 after ageing.
F2M = Fraction 2 modified, before ageing.
F2MA = Fraction 2 modified, after ageing.

Figure 6.11: Effect of ageing on chrome complex : fraction 3 and its polyamide modified fraction



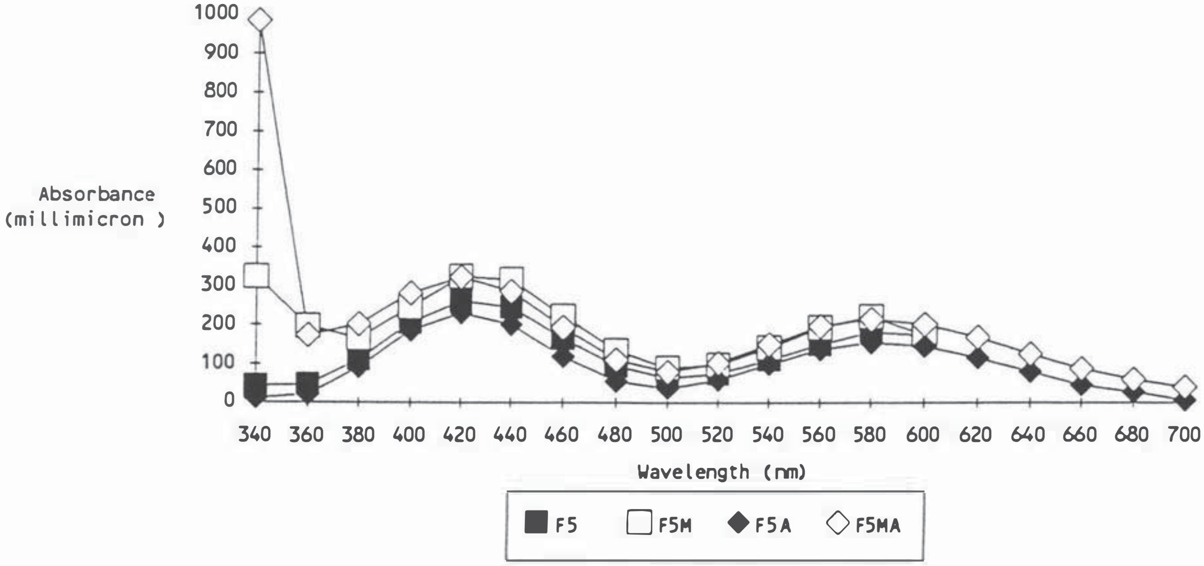
F3 = Fraction 3 before ageing.
F3A = Fraction 3 after ageing.
F3M = Fraction 3 modified, before ageing.
F3MA = Fraction 3 modified, after ageing.

Figure 6.12: **Effect of ageing on chrome complex : fraction 4 and its polyamide modified fraction**



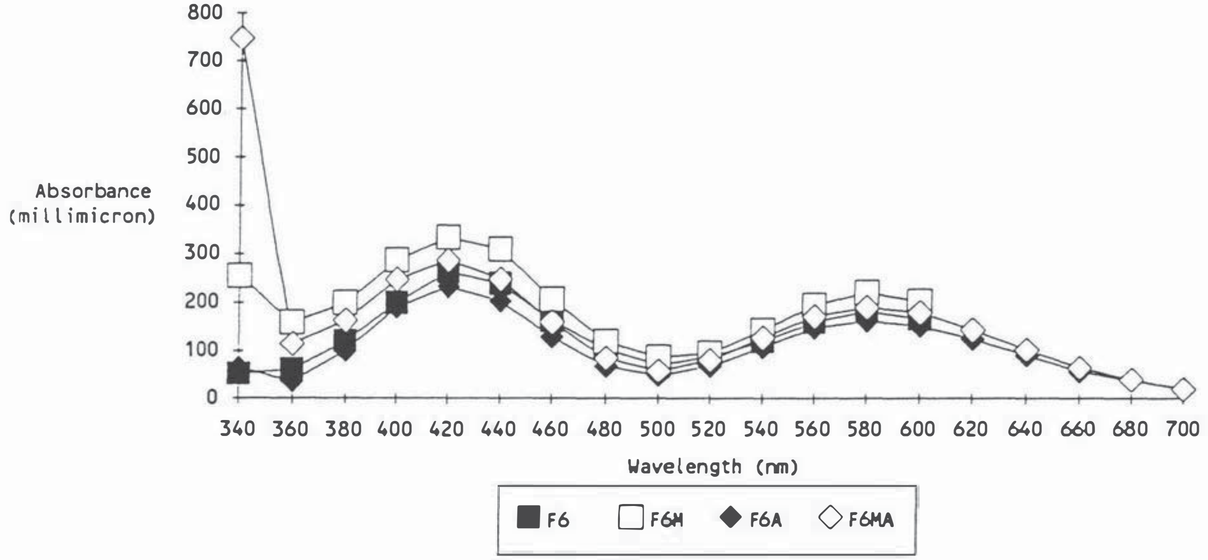
F4 = Fraction 4 before ageing.
F4A = Fraction 4 after ageing.
F4M = Fraction 4 modified, before ageing.
F4MA = Fraction 4 modified, after ageing.

Figure 6.13: **Effect of ageing on chrome complex : fraction 5 and its polyamide modified fraction**



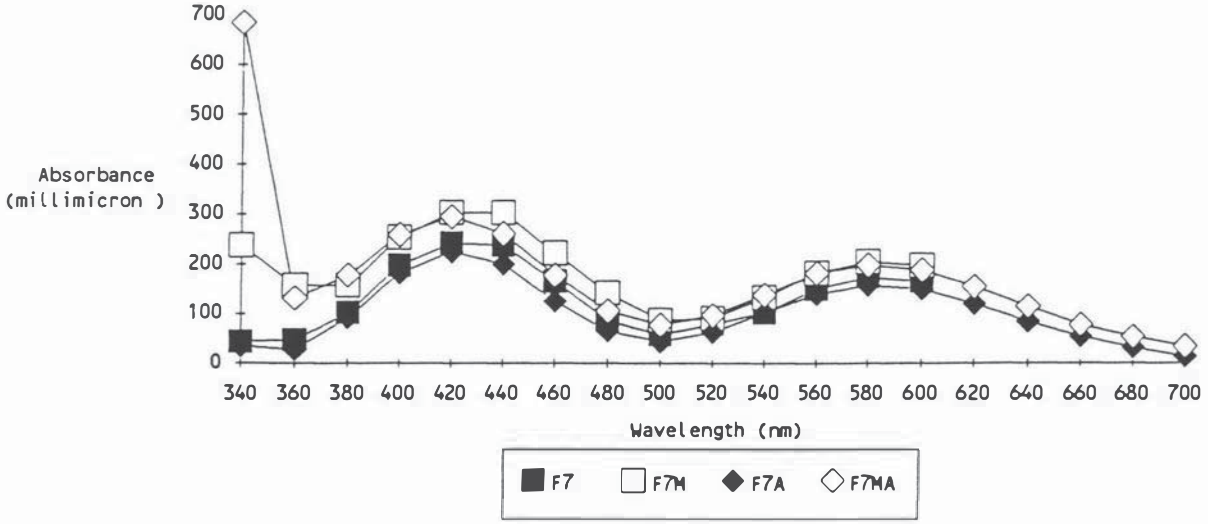
F5 = Fraction 5 before ageing.
F5A = Fraction 5 after ageing.
F5M = Fraction 5 modified, before ageing.
F5MA = Fraction 5 modified, after ageing.

Figure 6.14: Effect of ageing on chrome complex : fraction 6 and its polyamide modified fraction



F6 = Fraction 6 before ageing.
F6A = Fraction 6 after ageing.
F6M = Fraction 6 modified, before ageing.
F6MA = Fraction 6 modified, after ageing.

Figure 6.15: Effect of ageing on chrome complex : fraction 7 and its polyamide modified fraction



F7 = Fraction 7 before ageing.
F7A = Fraction 7 after ageing.
F7M = Fraction 7 modified, before ageing.
F7MA = Fraction 7 modified, after ageing.

6.4 Tanning Trials with Chrome/Polyamide Complex

Match pair, small scale tanning trials with this chrome/Polyamide complex at normal tanning pH 3.0 against standard chrome tanning agent were conducted on pickled New Zealand lamb skins. The results of such trials given in Table 6.7 indicated improvement of chrome exhaustion.

Table 6.7:Comparative tanning characteristics of chrome/polyamide complex and standard chrome tanning agent

Time (hours)	Control		Chrome/polyamide complex	
	pH	Shrinkage temperature °C	pH	Shrinkage temperature, °C
0	3.2	52	3.2	52
1	2.72	74	2.69	74
2	2.7	79	2.68	81
Basify : add 0.5% tanbase				
3	4.02	88	3.85	87
5	3.68	94	4.4	93
23	3.93	110	4.3	110
Chrome content of Leather (as Cr_2O_3 on moisture free basis), %		3.54		3.73
Chrome utilisation, %		73.5		87.9
Leaching Property : (Cr/100 g Wetblue), g		0.05		0.02

Therefore, large scale trials were conducted on pickle lamb skins. All these skins were then crusted out following a standard retanning process. All these skins were then tested for the following parameters against the control:-

1. Chrome Content (as Cr_2O_3), (IUC/8)
2. Shrinkage Temperature, °C, (IUP/16)
3. Distention at Grain Crack, (IUP/9)
4. Load at Grain Crack, (IUP/9)
5. Tear Strength, (IUP/8)
6. Tensile Strength, (IUP/6)
7. Elongation at Break, (IUP/6)
8. Colour Values,(CIELAB).

These results are summarised in Table 6.8.

Table 6.8: Comparative properties of lamb skins tanned with standard chrome tanning agent and chrome/polyamide

Properties	Standard Control	Polymer Modified
1. Chrome content, (as Cr_2O_3), moisture free basis, %	3.6	3.76
2. Shrinkage temperature, C	Both stood boil 109	110
3. Distention at grain crack (IUP/9), mm	10.12	9.95
4. Load at grain crack (IUP/9), kg	23.33	22.93
5. Tear strength (IUP/8), N/mm	33.38	31.98
6. Tensile strength (IUP/6), N/mm^2	14.55	13.6
7. Elongation at break (IUP/6), %	62	57
8. Colour values (CIELAB)		
L	20.34	20.54
a	0.76	0.63
b	0.63	0.13
ΔE	75.52	75.32

* No significant difference in physical properties between the two sets

This was clear that this system gave slightly better chrome exhaustion and shrinkage temperature, keeping all other physical properties similar to the commercially acceptable control.

Similar big scale trials were then conducted with bovine hides and all these tests were done on these matched hides. In addition, we also conducted stratigraphic analysis (layerwise distribution) of chrome within these full substance hides. The results are given in Table 6.9.

Table 6. 9: **Comparative properties of side leather tanned with standard chrome tanning agent and chrome/polyamide complex**

Properties	Standard Control	Polymer Modified
1. Chromecontent,(as Cr_2O_3), moisture free basis, %		
Layer 1 (grain)	3.69	3.6
Layer 2 (mid grain)	3.47	3.3
Layer 3 (middle)	3.3	2.93
Layer 4 (mid flesh)	3.27	2.75
Layer 5 (flesh)	3.38	3.2
Average	3.24	3.2
2. Shrinkage temperature, C	Both stood boil	
Layer 1 (grain)	109	105
Layer 2 (mid grain)	109	107
Layer 3 (middle)	108	109
Layer 4 (mid flesh)	108	116
Layer 5 (flesh)	106	116
3. Distention at grain crack (IUP/9), mm	9.97	9.64
4. Load at grain crack (IUP/9), kg	44	46
5. Tear strength (IUP/8), N/mm		
Parallel	69	71
Perpendicular	77.2	77.3
6. Tensile strength (IUP/6), N/mm^2		
Parallel	12	13.3
Perpendicular	13.2	16.8
7. Elongation at break (IUP/6), %		
Parallel	69	78
Perpendicular	71	71
8. Grainbreak (SATRA scale)	1	1
9. Colour values (CIELAB)		
L	48.3	49.32
a	23.83	23.65
b	31.51	31.61
ΔE	61.63	60.86

* No significant difference in physical properties between the two sets

We noticed slight lower chrome content in the middle layer with this novel chrome complex, even though the total chrome content in the hides were similar. The strength of the leather tanned with the novel complex were slightly better and colour obtained with the same dye was also better. However, we did not obtained significant improvement in the chrome exhaustion on these type of ovine leather at the conventional pH of the tanning.

Ion exchange separation of this polyamide modified chrome complex ,following procedure as indicated before, we obtained the result given in Table 6.10 which seems comparable to that reported by Gustavson[2]. This might explain why we did not obtained significant improvement in the chrome exhaust at lower pH of chrome tanning.

Table 6.10:Distribution of complexes in polymer modified basic chrome sulphate solution

	Original	After Modification	Phthalate[2] Masked
Anionic Complex	6.15%	12.03%	5%
Nonionic Complex	14.52%	37.50%	50%
Cationic Complexes	79.33%	50.47%	45%

Comparative trials were therefore, conducted on pickled lamb skins at higher pH after pretanning and degreasing the skin as given in Chapter 5, and compared with the conventionally degreased and chrome tanned control. The results showed considerable differences in chrome uptake and the rate of tanning at higher pH, tanning was very fast and was completed within 2h where as normal control took 4h. The details of the tanning profile of pH, shrinkage temperature and exhaustion are shown in Figures 6.16, 6.17 and 6.18. The mass balance of chromium and the efficiency of chrome tanning with this polyamide-chrome complex as given in Table 6.11 would clearly show the significant improvement in the exhaustion of chrome. This was 98.7% against 84.9% for standard chrome control. Their comparative physical properties indicated in Table 6.12 showed no significant difference from the commercially acceptable control.

Figure 6.16:pH profile of chrome tanning bath tanned with poly/chrome complex and Tannachrome S

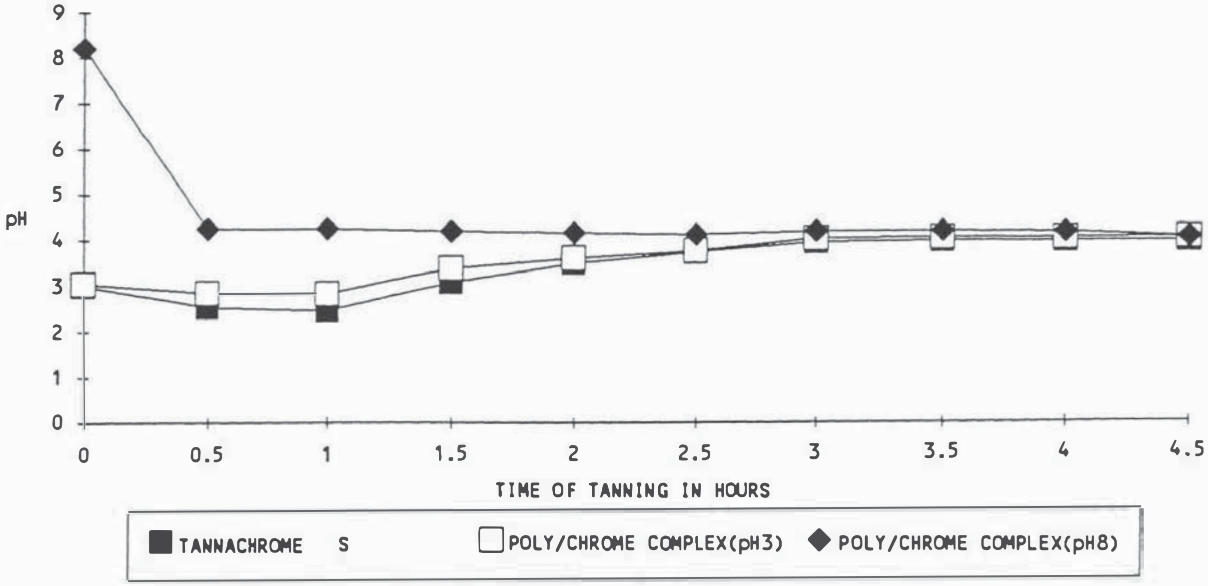


Figure 6.17:Shrinkage temperature of lamb skin tanned with poly/chrome complex and Tannachrome S

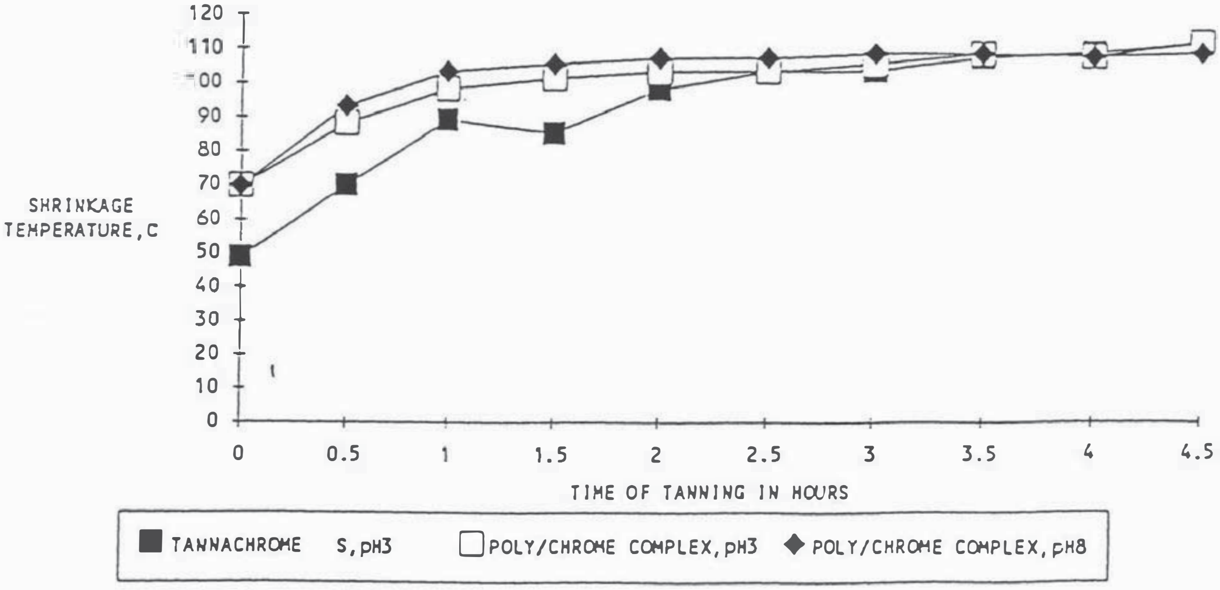


Figure 6.18: Rate of exhaustion of chrome (as Cr_2O_3) during tanning with poly/chrome complex and Tannachrome S

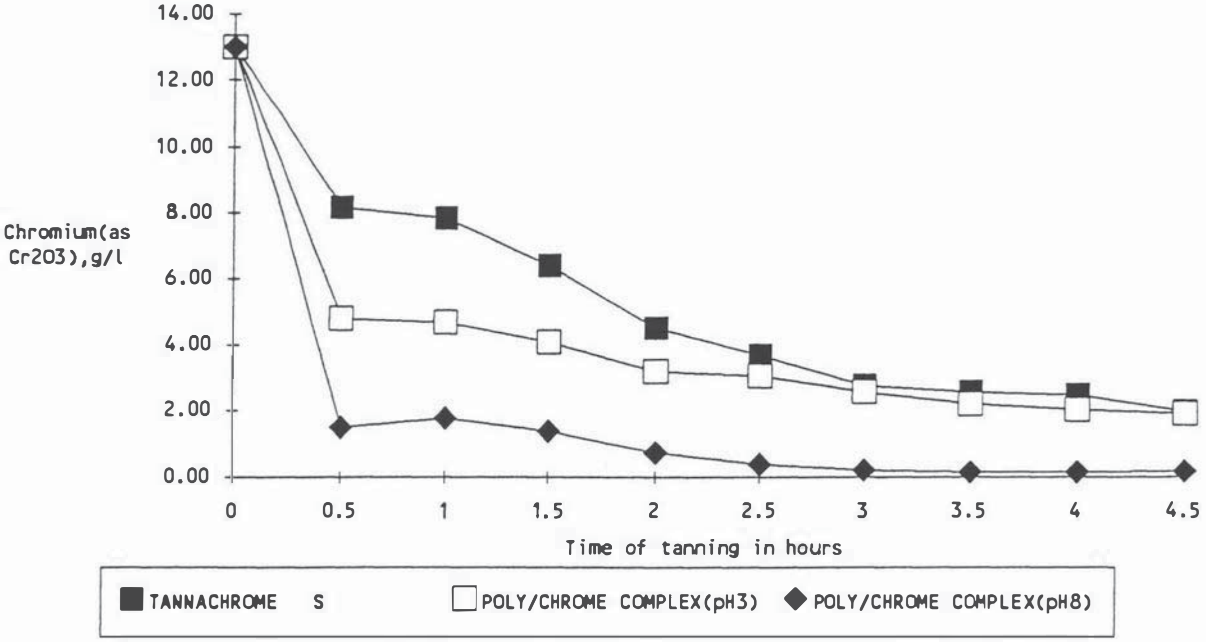


Table 6.11 Mass balance of chromium and efficiency of chrome tanning system tanned with standard chrome powder and polyamide/chrome complex

	Standard Chrome powder (Tannachrome S)	Polyamide/Chrome complexes	
		pH 3.0	pH 8.0
Weight of pelt,Kg*	4.0	3.85	4.05
Moisture inpelt,%	62.30	62.00	63.00
Chrome offered,(as Cr**),%	0.88	0.88	0.88
Total chromium,(as Cr),g	35.36	34.03	35.80
Chromium in exhaust,(as Cr**),g/l	1.33	1.29	0.13
Total chromium in exhaust,g	5.32	4.96	0.53
Actual chrome in wet blue, moisture free basis,(as Cr**),%	1.96	1.97	2.35
Calculated chromium in wet blue, after tanning,(as Cr),g	0.74	0.75	0.87
Efficiency : calculated,%	84.09	85.22	98.86
Actual ,%	84.95	85.42	98.52

* Accuracy of the tannery balance: + or - 0.1kg.

** Accuracy of chrome determination: + or - 0.03%

Table 6.12:Comparative physical properties of lamb skin

Properties	Chrome/Polyamide Tanned		Chrome Control
	Standard pH	High pH	
1. Shrinkage Temperature (IUP/16), °C	108	107	108
2. Distentionat Grain Crack(IUP/9), mm	8.75	8.81	8.88
3. Load at Grain Crack (IUP/9), kg	24.26	26.25	23.01
4. Tear Strength (IUP/8), N/mm	38.17	36.00	37.68
5. Tensile Strength (IUP/6), N/mm^2	13.01	12.33	12.25
6. Elongation at Break (IUP/6), %	62.4	64.5	64.6
7. Colour Values (CIELAB)			
L	62.57	63.14	64.59
a	- 5.44	- 8.82	- 7.52
b	- 6.09	- 3.80	- 4.55
ΔE	34.31	33.97	32.40

* No significant difference in physical properties. Colour lighter for the control

To verify the fact that this low chrome in exhaust liquors were not merely due to the high pH chrome tanning and to establish the impact of this polyamide -chrome complex on the exhaustion of chrome, we again tanned three comparative sets of lamb skin, six skins each, one degreased and tanned at conventional pH 3.0, the other two sets of lamb skins were pretanned and degreased and then tanned at pH 7.2 with the standard chrome tanning agent and polyamide-chrome complex respectively. The results and the details of the tanning profile of pH, shrinkage temperature and exhaustion are given in Figures 6.19, 6.20 and 6.21. Figure 6.22 gives an actual picture of the exhaust liquors which more clearly allows to visualise the dramatic difference of chrome discharge between the conventional and the novel chrome tanning systems.

Figure 6.19: pH profile of chrome tanning bath tanned with poly/chrome compex and Tannachrome S

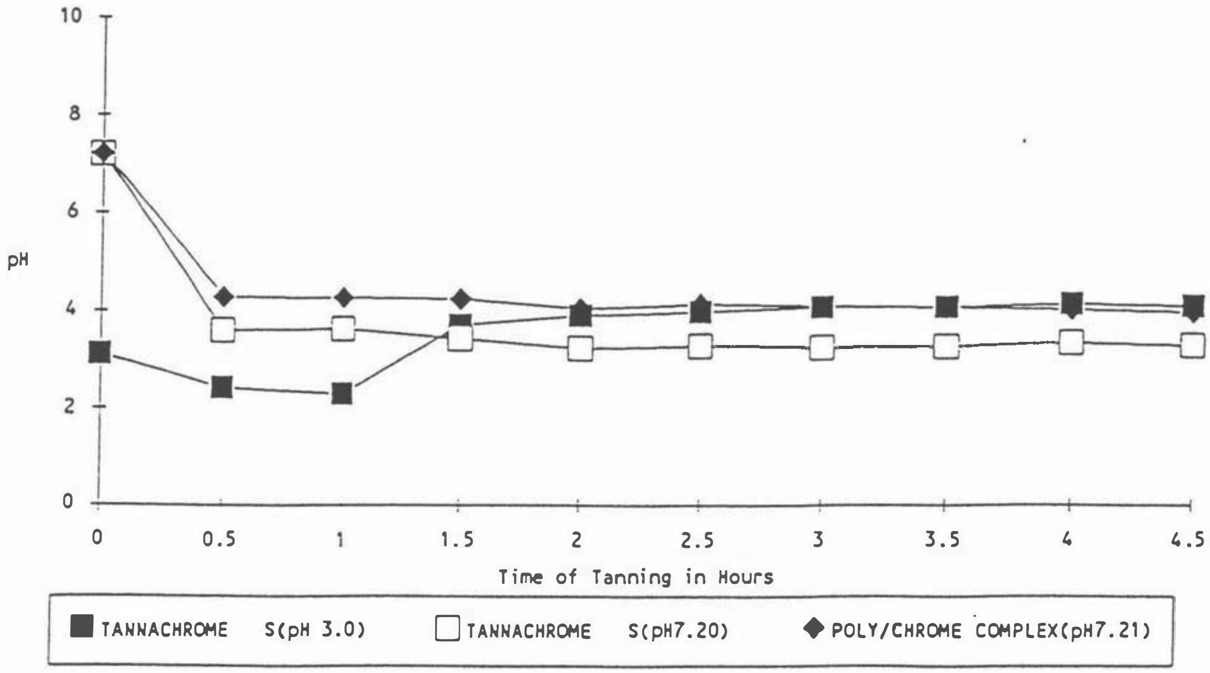


Figure 6.20:Shrinkage temperature of lamb skin tanned with poly/chrome complex and Tannachrome S

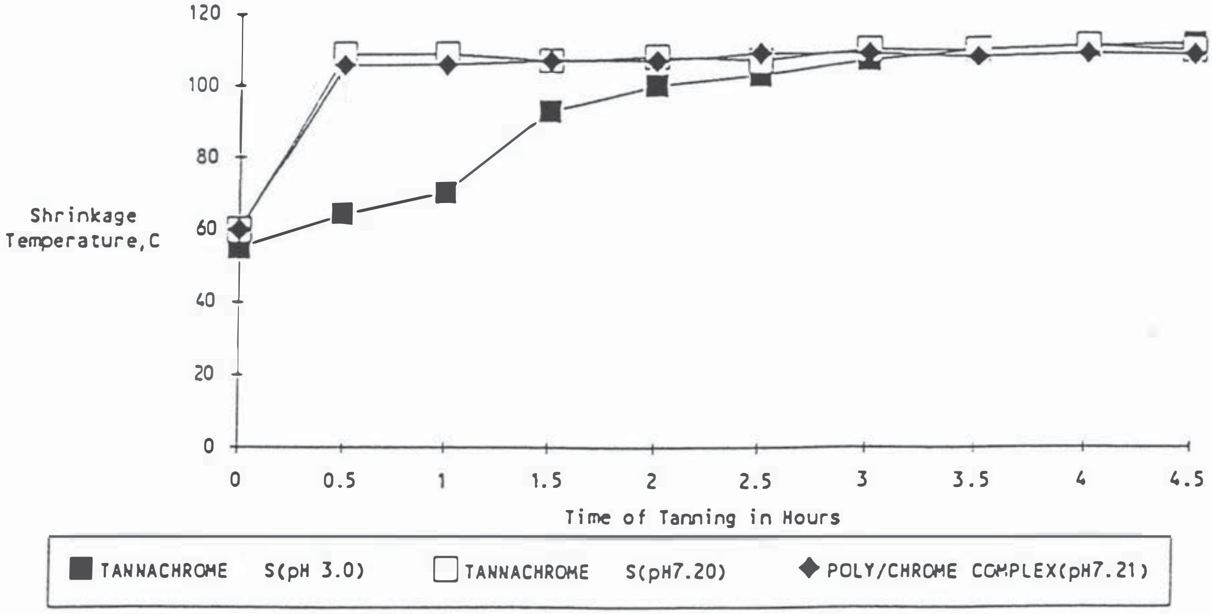
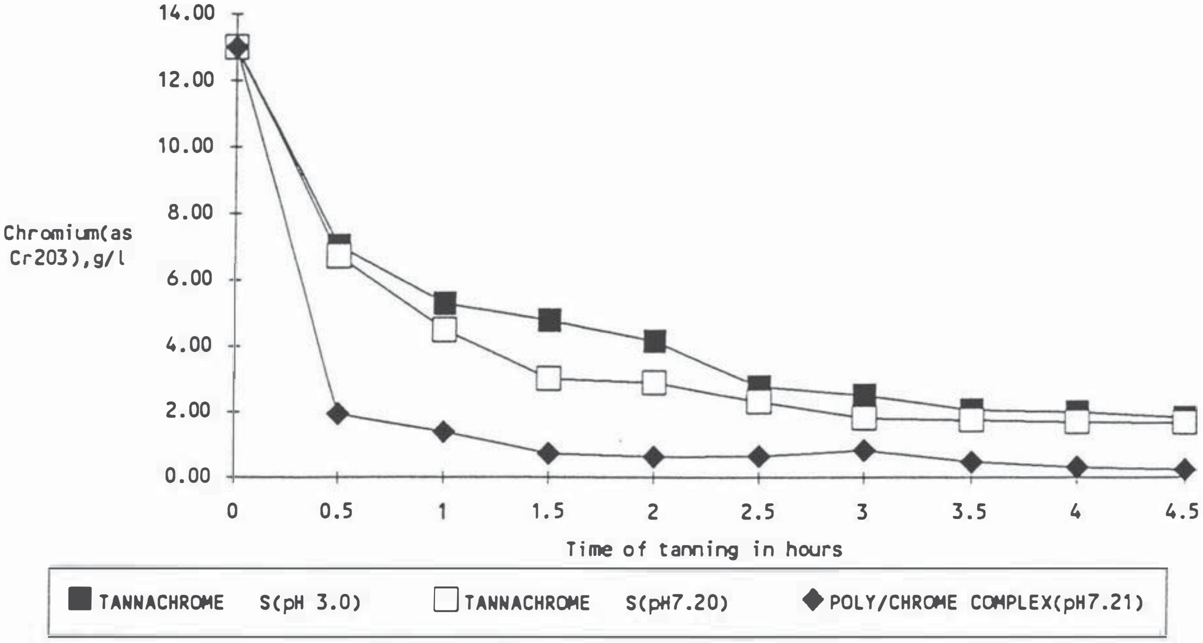


Figure 6.21:Rate of exhaustion of chromium (as Cr_2O_3) during tanning with poly/chrome complex and Tannachrome S



The mass balance of chromium and the efficiency of chrome tanning were as given in Table 6.13. The results confirmed our earlier findings that polyamide-chrome complex considerably improved the exhaustion and rate of chrome tanning. Once again the efficiency of chrome tanning with polyamide-chrome complex was 98.2% against 87.2% for the standard chrome tanning agent at pH 7.2

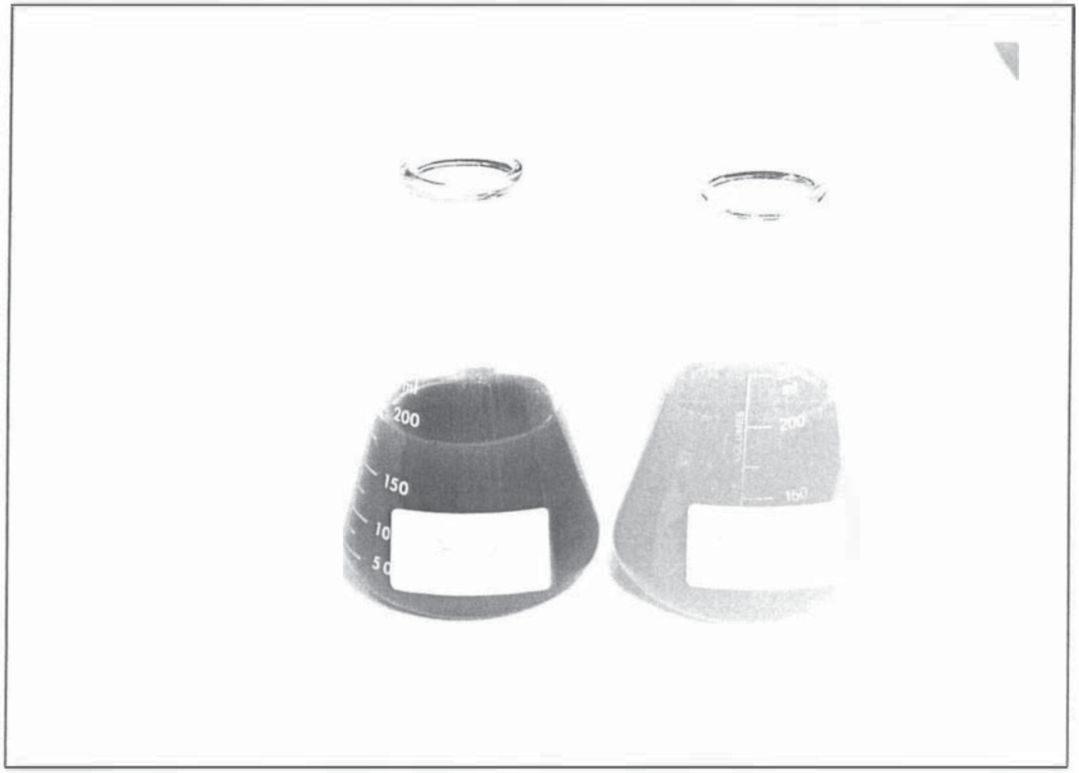
Table 6.13 Mass balance of chromium and efficiency of chrome tanning system tanned with standard chrome powder and polyamide/chrome complex

	Standard Chrome powder (Tannachrome S)		Polyamide/Chrome complexes
	pH 3.0	pH 7.2	pH 7.2
Weight of pelt,Kg*	7.15	6.75	6.25
Moisture inpelt,%	62.30	62.30	63.00
Chrome offered,(as Cr**),%	0.88	0.88	0.88
Total chromium,(as Cr),g	63.21	59.67	59.35
Chromium in exhaust,(as Cr**),g/l	1.24	1.14	0.16
Total chromium in exhaust,g	8.87	7.70	1.00
Actual chrome in wet blue, moisture free basis,(as Cr**),%	1.99	2.04	2.35
Calculated chromium in wet blue, after tanning,(as Cr),g	0.75	0.77	0.87
Efficiency : calculated,%	85.27	87.50	98.50
Actual ,%	85.97	87.10	98.31

* Accuracy of the tannery balance: + or - 0.1kg.

** Accuracy of chrome determination: + or - 0.03%

Figure 6.22:Exhaust liquors form conventional and novel tanning systems



The physical properties of the leather when compared with conventional chrome tannage and those chrome tanned at high pH were similar or better as could be seen from the Table 6.14.

Table 6.14:Comparative physical properties of lamb skin

Properties	Chrome Tanned Leather		Chrome/Polyamide Complex
	Standard pH	High pH	High pH
1. ShrinkageTemperature (IUP/16), °C	111	110	110
2. Distention at Grain Crack (IUP/9), mm	8.61	9.07	9.22
3. Load at Grain Crack (IUP/9), kg	21.87	26.84	26.34
4. Tear Strength (IUP/8), N/mm	29.41	37.19	38.35
5. Tensile Strength (IUP/6), N/mm^2	33.37	33.30	38.13
6. Elongation at Break (IUP/6), %	55.8	62.8	59.0
7. Colour Values (CIELAB)			
L	50.92	46.46	48.26
a	- 3.20	- 2.88	- 2.89
b	- 6.49	- 5.56	- 5.83
ΔE	45.61	49.88	48.13

* No significant difference in physical properties. Colour lighter for the control

6.5 Conclusion

In conclusion, therefore, this could be suggested that such a complex apart from reacting with the carboxyl group of skin collagen, also reacted with the non carboxyl groups through hydrogen or coordinate bonds. This might support the idea of Erdmann[8] that tanning process was a stepwise reaction and the initial hydrogen bonds or salt links might be gradually transformed into coordinate bonds with the carboxylic group of collagen to give stabler leather.

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CHAPTER 7

SUMMARY AND RECOMMENDATIONS

7.0 SUMMARY

7.1 Commercial chrome tanning systems gave about 75-85% chrome utilisation, causing environmental problems for the leather industry. Following the state of the art technology, with the reduction of chrome offer, lower float, higher temperature and pH of tanning, and using improved masking and basifying agents, this absorption of chrome could be improved to 85-90%. At present, internationally about 400,000 tons of chrome tanning agents were used annually. This means that about 60,000 tons of chrome tanning agents remained unutilised during the main chrome tanning and might be discharged annually to the environment if no recycling or treatment is done at the tannery.

7.2 The aim of the study was to look afresh into the basic tanning system. The three alternative approaches were explored to improve the chrome exhaustion during the tanning itself to minimise its environmental impact. The idea was to develop a clean technology rather than to create pollution and treat that pollution at the end of the processing.

7.2.1 Improvement of the classical system through the addition of auxiliary chemicals during tanning

Here the possibilities of improving the availability of carboxylic groups for better fixation of chrome were explored. Various chemicals including two patented by the author were used (chapter 4). The improvement in the chrome exhaustion was found in the range of 90 to 94%. This even though minimised the amount of chrome in the exhaust liquors could not eliminate the need of further treatment of the waste liquor before discharge into the water system of the area.

7.2.2 Changing the present technology of tanning

This approach helped to develop a novel chrome tanning technology for New Zealand lamb skin eliminating conventional pickling process. According to this novel tanning system, delimed lamb pelts were degreased at high pH and chrome tanning conducted at that high pH (pH 6.5 to 8.5) without any acid-salt pickling. No basification of chrome during tanning was also required. Higher and faster chrome fixation with 95-97% exhaustion efficiency were obtained (Chapter 5). According to the proposed theory, the skin collagen released more carboxylic groups at high pH, due to the upward shift of the iselectric point of the collagen, which became available for higher chrome fixation. Further, initially chrome, particularly the nonionic and anionic chrome species of the commercial basic chrome sulphate tanning agent, were fixed at the non carboxylic groups of the skin collagen. This might later be converted to a more stable linkage with the carboxylic acid group of the collagen when the pH of the tanning bath dropped to 3.5. In practice, the drop of pH of the system occured due to residual acidity of the chrome tanning agent and no addition of acid was required.

7.2.3 Changing the chrome complex itself

This extensive study of the chrome complex (Chapter 3 and Chapter 6) showed that the commercial sulphur dioxide reduced basic chrome sulphate solution (12-15% Cr_2O_3, 33% basic) had the following composition:

Complexes	**Commercial Chrome Tanning Agent**	
	Full Salt	**Partly Salt Free**
Anionic: $[Cr(SO_4)_2]^-$	5.0%	6.0%

Nonionic:	27.0	14.5
$[Cr(OH)SO_4]^0$		
Cationics:		
$[CrSO_4]^+$	12.8%	10.2%
$[Cr(OH)_2SO_4Cr]^{2+}$	18.1%	13.5%
$[Cr]^{3+}$ and		
$[Cr(OH)SO_4Cr]^{3+}$	13.4%	39.6%
$[Cr(OH)_2Cr]^{4+}$ and		
$[Cr(OH)Cr(OH)_2Cr]^{5+}$	23.7%	16.2%

This values clearly showed that partly salt free chrome tanning agents had higher percentages of cationic species of chrome complexes with higher cationic charge. This therefore explained why partly salt free chrome tanning agents gave better chrome fixation. 70% sodium sulphate from commercial chrome tanning agent could be removed by simple crystallisation at low temperature. This reduced the salt discharge from chrome tanning and minimised the environmental impact of chrome tanning.

7.2.4 Reactivity of Chrome complexes

The reactivity of the separated nonionic, anionic and cationic species of the chrome tanning agent towards skin collagen were established. It was found that at normal pH of chrome tanning (pH 2.5-4.0), anionic species had no tanning power where as the nonionic complexes only tanned at higher pH and took longer period to tan with poor exhaustion rate. The affinity of cationic complexes increased with the increase in the cationic charge of the complexes up to $(Cr)4^+$. No further increase in the affinity with higher charges than $(Cr)4^+$ were noticed. This confirmed the views of the Japanese researchers[1] who first suggested that differential absorption of cationic chromium complexes take place during chrome tanning against the conventional view that charge had no role in chrome tanning. It was found that there was practically no effect of ageing on the structure of the separated species of the chrome complexes. It was also noticed that higher the temperature of tanning, higher was the efficiency of chrome exhaustion but the quality of the leather became poorer above 40°C.

7.2.5 Chrome-Polyamide complex

A novel chrome complex was developed (Chapter 6). The spectrum of the complex showed considerable increase in amplitude at 420nm indicated bridging similar to the acetate, phthalate and oxalate complexes, quite different from formate which mainly gave an increase in amplitude at 580nm. Six month ageing study with this complex and complexes of polyamide with various separated chrome species showed that there were no significant changes in the complexes due to ageing. Ion exchange separation of this chrome-polyamide complex showed that this complex had ionic species distribution nearer to phthalate masked basic chrome sulphate as found by Gustavson[2].

7.2.6 Tanning Characteristics of Chrome-Polyamide complex

Trials with pickled lamb skins and side leather at lower pH like the conventional chrome tannage (Chapter 6) showed slightly better chrome exhaustion for lamb skin but no significant improvement for side leather. The physical properties of the side and lamb skins were satisfactory. But when lamb skins were tanned according to the novel chrome tanning process (Chapter 5), significant improvement in chrome exhaustion was obtained. The exhaustion of chrome was 99% and leather stood boil in two hours, shortening the chrome tanning process considerably. The properties of the finished leather was found similar when compared with the conventional accepted commercial leather was found satisfactory. The objective to develop a chrome tanning system with minimum environmental impact was achieved. The theory of such a successful tannage was postulated. The nonionic chrome fraction of the chrome-polyamide complex was fixed with the non-carboxylic group of skin collagen at high pH through hydrogen bond and as the pH of the tanning bath came down to pH 3.5, carboxylic acid group of the collagen reacted with the cationic complexes. This stepwise tanning reaction also supported the views of Erdmann[3] who also suggested that such initial hydrogen bond or salt links might gradually be transformed into coordinate bonds with the carboxylic group of collagen to give stabler leather.

7.3 Recommendations

7.3.1 New Zealand lamb skin might be chrome tanned after deliming and degreasing without acid -salt pickling with conventional 33% basic chrome sulphate liquor or powder, following the novel tanning technique to obtain a tanning efficiency of 97% and to minimise the environmental impact of chrome tanning.

7.3.2 New Zealand lamb skin might be chrome tanned after deliming and degreasing without acid-salt pickling with Chrome-polyamide complex, following the novel tanning technique to obtain about 99% chrome exhaustion. This will minimise the environmental impact of chrome tanning significantly.

7.3.3 Those tanners who have no access to green lamb skins and have to process pickled pelts, pretanning of lamb skins before degreasing would continue to be the only option. The principle of this no-pickle novel chrome tanning system might still be applied to this pretanned skins.

Chrome tanning might be successfully carried out after degreasing without readjusting the pH of the tanning bath to 3.0-3.5 with acid and tanning completed without further basification. This would minimise significantly the chrome in the waste tan liquor.

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APPENDIX A

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