THEORETICAL ASPECTS OF THE REACTION OF ZIRCONIUM COMPOUNDS AND VEGETABLE TANNINS WITH THE CHROMIUM-COLLAGEN COMPLEX.

by

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SUMMARY

Studies have been made of the reactions which take place when zirconium compounds and vegetable tannins react with chromium tanned leather, in order to elucidate the mechanisms of the reactions which occur on retannage. Statistical procedures have been used in all investigations because of the variable nature of the substrate, and computer techniques have been applied to the repetitive statistical computations.

Although chromium and vegetable tannages are well understood, further information on the reaction of zirconium with collagen was necessary before attempting to interpret the results of the studies of combination tannages with chromium, and this has been obtained by a comparative study of the reactions of chromium and zirconium with modified collagen. It is concluded that the mechanism of the reaction of basic zirconium sulphate with collagen is multipoint attachment of the tanning material by residual valency forces, although charge effects with basic groups may be supplementary. Zirconyl chloride reacts with carboxyl groups but does not form satisfactory, stable cross-links with collagen. Further evidence for this theory was obtained from the investigation of the reaction of zirconium compounds with chromium tanned collagen. Zirconyl sulphate does not interfere with effective chromium tannage and therefore can have little affinity for the carboxyl groups on the protein, but it displaces chromium complexes loosely held by auxiliary valencies without reducing the shrinkage temperature of the chromium leather. Zirconyl chloride, although only fixed to a limited extent, apparently forms co-ordination compounds with the carboxyl groups, disrupting the chromium tannage because there is an over-all loss of hydrothermal stability. There is no evidence that zirconium co-ordinates with, or releases acid from chromium-collagen complexes, since combination chromium/zirconium tanned leathers are stable on storage.

Retannage of chromium tanned leather with vegetable tanning materials generally results in loss of strength and a product which tends to deteriorate on ageing. Lower initial strength is probably due to the increased avidity of chromium tanned pelt for vegetable tannins, resulting from the liberation of internally neutralised reactive sites which are not normally

available in vegetable tannage, and from the co-ordination of vegetable tannins and non-tannins to the chromium complex with the displacement of sulphate radicals. From a study of the retannage of chromium tanned modified collagen, it appears that basic groups probably play an important part in the rapid absorption of vegetable tannin. These reactions result in overloading of the fibre and an increased number of cross-links, both of which tend to produce weak leather. Deterioration with age is primarily a hydrolytic degradation of the protein which is catalysed by acid liberated from the chromium complexes by the entry of vegetable tannins, those factors which favour the formation of acid causing greater and more rapid deterioration.

Increase in the quantity of chromium in the leather increases the number of potential binding sites for vegetable tannin, and there is increased prospect of sulphate displacement and increase in acidity. Increase in the degree of vegetable retannage increases the tendency of vegetable tannins to enter the chromium complexes, displacing sulphate with release of strong acid — hydrolysable tannins with their high content of dissociating groups are particularly active in this respect, and also tend to cause detannage. It has been shown that both the tannins and the non-tannins of mimosa extract are capable of forming co-ordination compounds with chromium. Modification of the chromium-collagen complex by incorporation of substances which react preferentially with the chromium and resist the penetration of vegetable tannins into the complex inhibits the development of acidity on ageing and a more durable product results. However, under moderate conditions of moist heat, the application of competing complexing agents is ineffective in preventing deterioration, since, although there is a reduction in the development of strong acid when these materials are used, the weak acid which is liberated tends to have an adverse effect on the leather fibre.

Conclusive evidence for the existence of chromium loosely bound by secondary valency forces in chromium tanned leather has been shown by studies of tannages with modified collagens, and also by the fact that both basic zirconium sulphate and vegetable tannins displace chromium from chromium tanned leather without affecting the hydrothermal stability.

The practical applications of these findings has enabled satisfactory methods for the manufacture of good quality leather to be formulated. These have been confirmed in practical tanning trials and recommended methods are given. In Volume 2 are given the details of the technological work which forms the basis of the above.

Three aspects of this work are of special importance, namely, (a) the reasons for, and methods of minimising the weakness of chrome-retan leathers and their deterioration on ageing, (b) evidence from which the mechanism of zirconium tannage can be deduced, and (c) evidence for the existence of weakly bound chromium which does not contribute to the hydrothermal stability of chromium tanned leather.

CHAPTER 1

INTRODUCTION

The chemistry of the reactions with collagen of both chromium compounds and vegetable tannins has been very extensively studied, and there is overwhelming evidence that chromium tannage is primarily the result of the co-ordination of chromium compounds with the carboxyl groups of reactive side-chains of collagen[1-3], whereas secondary valency forces, particularly hydrogen bonds are chiefly responsible for the major portion of vegetable tannin fixation[4-9]. In each case, tannage is effected by the formation of cross-links between adjacent polypeptide chains in collagen fibres[2,10,11], the former by means of a limited number of strong bonds, whereas the latter is dependent on multipoint fixation without specifically involving particular reactive sites.

The position with zirconium is less clear. Despite extensive investigations into some aspects of the chemistry of zirconium compounds relating to their combination with collagen[12,13], the mechanism of the reaction between zirconium and collagen is still not fully understood. While zirconium is classed as a mineral tanning agent, McLaughlin and Theis[14] questioned the inclusion of zirconium in this group, and more recently the individuality of zirconium has been recognised[11,15]. Studies have shown that although zirconium tannage is metallic in character, it appears to have much in common with vegetable tannage. There is evidence to show that while carboxyl groups are not involved in tannage with zirconium sulphate[12,16], zirconium is dependent to some extent on reaction with the amino groups[17], although potentiometric[18] and electrophoretic[12,13] studies give no evidence of a co-ordination reaction between zirconium and amino groups, nor is zirconium in aqueous solution bound to organic radicles through nitrogen[19]. On the other hand, zirconyl chloride readily forms co-ordination compounds with carboxylic acids, yet it is a poor tanning agent[18]. This is further evidence that co-ordination of carboxyl groups in collagen does not play a significant part in tannage with zirconium.

The study of the fixation of zirconium by chemically modified collagens has yielded contradictory results which may, in part, be due to

differences in the experimental techniques used by several authors[17,20]. Yet it is considered that this would be a valuable means of determining whether particular reactive groups on the protein are responsible for the fixation of zirconium, as is the case with chromium, and this approach is to be used as part of the present study.

Since zirconium salts in solutions of high acidity are predominantly anionic[21], their reaction with charged basic groups to form salt links may reinforce the combination by multipoint attachment involving residual valency forces which is regarded as the main mechanism of reaction[12,16]. In addition to fullness and softness, the zirconium tanned leather and vegetable retanned chromium leather show the same structural features under the electron microscope; the individual fibrils are filled out and broadened, the fibril network is opened out and the spaces between the fibrils are filled with a dense non-fibrous material[22]. Whilst the interaction of zirconium with collagen is thought to involve multipoint attachment by means of residual valency forces, Ranganathan and Reed[23] infer that H-bonding plays no part in zirconium fixation. Electron micrographs suggest that aggregates of zirconium complexes are deposited on and between the fibres, but no explanation to account for the increase in hydrothermal stability is given, although they agree that, whilst zirconium is metallic in nature, the resulting leather has more in common with vegetable tanned leather than with chromium tanned leather. Metelkin, Zaides and Kuz'mina have studied the reaction of raw hide, silk fibroin and polyamide 6 with ammonium zirconyl sulphate, and noted that the amount of bound zirconium was five times as great for raw hide as for fibroin and about ten times as great as for polyamide 6[24]. They concluded that zirconium compounds may react with the amino and peptide groups of the protein. Thus the chemical properties and physical characteristics of zirconium tanned leather resemble in many respects those of leathers containing vegetable tannins. The important aspects of the chemistry and tanning action of zirconium salts has been reviewed by the author[16].

Since zirconium tanning salts, like vegetable tannins, are known to have filling properties, it is not surprising that each of these two

classes of tanning materials has been used in combination with chromium to effect improvements in the otherwise empty pure-chrome leathers.

Although full-chrome leathers possess a number of very desirable properties, this type of leather, particularly when made from inferior hides, is not entirely satisfactory for modern usage owing to lack of both tightness and uniformity. On the other hand, although vegetable tanned leathers are full and uniform, and easily embossed, they lack thermal stability. It was natural, therefore, that combinations of these two tanning procedures should have been attempted. It was hoped that the resulting leather would have the desirable properties afforded by both processes, namely, the strength, heat resistance and springiness of the chromium tannage, and the fullness and tightness of the vegetable tannage. In practice, the result has been a compromise. Lightly retanned leathers retain most of the properties of full-chrome leather, and heavily retanned leathers approach more nearly the character of vegetable tanned leather. Hence the interest in zirconium retannages which, it was hoped, would retain the mineral character of the leather; but these retannages were comparatively recently introduced, and vegetable retannages are still of greater commercial interest. Thus in this thesis a comparison of the effects of retanning chromium tanned leather with zirconium compounds and vegetable tannins is made in addition to studying the reactions which occur in retanning.

Important investigations of the reaction of vegetable tannins with chromium tanned pelt had been made by Gustavson[25] as early as 1927, and by Page and Holland[26] in 1932, prior to the general introduction of the retan process, yet these observations were largely disregarded by many manufacturers. It is well known that the two tannages are not mutually exclusive, and that chromium tanned skin has greater affinity for vegetable tannins than has native hide. This has been clearly demonstrated by work on hide powder by van Vlimmeren[27], Kanagy[28], and Amos and his co-workers[29,30]. In an attempt to obtain the greater plumpness, fullness, tightness and uniformity resulting from retannage, tanners were tempted to use ever-increasing quantities of retanning material, with the result that the fibre was often overloaded and weak leather was produced. Moreover, Wilson, Roddy, Mann and their co-workers[31-35] had

discovered that this type of leather was unstable and deteriorated on storage. It is important, therefore, to examine chrome-retan leather from two points of view: the influence of various factors on the initial strength of the leather, and the ageing characteristics of the leather.

The Reaction of Vegetable Tannins with the Chromium-Collagen Complex

(a) The Displacement of Sulphate Groups

In addition to observations from laboratory experiments, the difficulties and drawbacks that are encountered in commercial production of chrome-retan leather, and in pilot plant studies of this tanning process, give indications of reactions that have taken place. The investigation of fresh and aged leathers may also yield valuable information on the subject. Reports of the examination of unserviceable leather have shown that the pH was substantially lower than the minimum specified and that these leathers had become more acid on storage[34-36], an observation which was confirmed by an examination of a representative selection of men's shoe upper leather in 1954[37]. Since the leather had been stored in acid-free atmospheres, the extra acidity must have been generated within the leather itself. Most workers were of the opinion that the increased acidity resulted from the reaction of vegetable tanning extracts with the chromium compound in the leather, in which components of the extract entered the chromium complex and displaced sulphate groups. Gustavson[38], and Amos and Thompson[30], consider that the displacement of sulphate groups is caused mainly by non-tannins in the extract. On the other hand, Kubelka[39], Williams-Wynn and Shuttleworth[40], and Bowes, Moss and Young[41], have shown that the acidity of basic chromium sulphate solutions was increased when pure tannin was admixed. Furthermore, when purified mimosa tannin was reacted with chromium tanned hide powder, considerably more sulphate was found in the spent retan liquors than in the controls treated with water adjusted to the same pH[40]; the increase in sulphate corresponded to an immediate increase in acidity of the liquors. Lasserre[42] has also observed that the pH of chromium tanned leather falls quickly during retannage, and the major changes have taken place within 24 hours of manufacture, but these effects were dependent on the type of vegetable tannin. The drop in pH was

rapid and large with chestnut, but less with sulphited quebracho or mimosa extract. Moreover, the effect of the reaction of various vegetable tannins with chromium salts has a strong correlation with the effect on chromium tanned leather. It is concluded that both the tannins and the non-tans in vegetable tanning materials interact with chromium, liberating sulphate[41].

(b) The Displacement of Chromium

Chromium displacement from chromium tanned collagen by vegetable tanning extracts has received some attention, but the investigation of this reaction is complicated by the insolubility of some of the vegetable tannin-chromium complexes and the amount of soluble chromium in spent retan liquors is not a reliable guide to the extent of detannage[43]. Nevertheless, the presence of chromium in exhausted retan liquors indicates that detannage may have occurred, although it is likely that the chromium held at single sites would be more easily stripped than the compounds forming cross-links between adjacent polypeptide chains, and dechroming would have to be extensive before hydrothermal stability was affected. Feher and Kerese[44-46] discovered that (a) the rate of chromium displacement was affected by the kind of retanning agent, (b) increased extraction was found at low pH, (c) masking had only a slight influence on extraction, and (d) stripping being initially rapid chromium extraction could be reduced only by considerably shortening the tanning period. Quebracho removed very little chromium, but syntans and lignosulphonates had a strong leaching action[46]. Similar observations were made by Erdi[47] and Ferebauer[48], with the further observation that ageing in the blue increased the leather's resistance to dechroming.

Amos and Thompson[30] reported that in mimosa retannages, chromium displacement was caused by reaction between ionised non-tannins and the chromium complexes, and by hydrogen ion. Nayudamma and Koteswara Rao[49] found that myrobalans was a much more efficient agent than mimosa for stripping chromium, claiming that the chromium content of leather had been reduced by 10% and 2%, and the shrinkage temperature lowered by 16° and 0°C respectively. This was after rather drastic treatment. Bowes[43] examined the effect of prolonged treatment

of three vegetable tanning materials (mimosa, myrobalans and sulphited quebracho) on chromium tanned hide at elevated temperature, and found that all three extracted appreciable amounts of chromium and caused falls in shrinkage temperature of up to 25°C. Most of the detannage occurred in the first few days, and both losses of chromium and falls in shrinkage temperature increased with increase of the temperature of extraction and with fall in pH. Myrobalans was the most effective in extraction of chromium and in reduction of shrinkage temperature, whereas sulphited quebracho had the least effect. The small effect of sulphited quebracho is surprising because work with other compounds containing the sulphonic acid group, as for example syntans[44,48,49], and recent work on sulphited mimosa[50] have shown not only that chromium was more easily displaced than when these reactive groups were absent, but also that there was a significant reduction in shrinkage temperature.

Boratynska Targowska and Targowski[51] reported that plant tannins and also synthetic tannins can displace chromium salts from tanned leather, the amount of chromium displaced depending on the duration of the subsequent tanning with plant tannin and on the type of tannin. The displacement activity of the tannins decreased in the order chestnut > spruce > mimosa > quebracho, but plant extracts other than tannins (non-tannins) can also displace chromium from combination with collagen. In this respect mimosa non-tannins are particularly effective in stripping chromium, possibly as a result of the relatively large amount of amino- and imino-acids which have been shown to be present in mimosa extract[52].

All of the above work was conducted using very long floats, extended tanning periods and an extremely high retan to collagen ratio. Under these conditions, even if the reactions were feeble, displacement must have been considerable and far in excess of that which would occur under normal tannery conditions. However, it is obvious that those factors which favour displacement of the chromium are also those that result in increased acidity, and it is possible that part of the chromium displacement is due to the increased acidity. Nevertheless, most of the displacement seems to be the result of complex formation between the

vegetable tannin and the chromium. This suggests that a certain degree of detannage must occur, but if shrinkage temperature is taken as a criterion of stability there is little correlation between loss of hydrothermal stability and chromium displacement, except under abnormal conditions.

(c) The Influence of Masking Agents

The increase in acidity in chrome-retan leather is undoubtedly a chemical process involving the displacement of sulphate groups from the chromium-collagen complexes by components in the vegetable tanning extract. The addition of complexing agents before retannage should, therefore, reduce this reaction by themselves displacing the sulphate, forming stable compounds which are more resistant to vegetable tannins. Organic acids limit the increase in acidity which follows the addition of polyphenolic substances to chromium solutions[40], confirming work reported by Otto[53].

Formate is one of the most commonly used masking agents but it forms relatively weak complexes. Nevertheless, pH stability and resistance to sulphate displacement during retanning was markedly better than when unmasked chromium compounds had been used[40]. In determining the conditions for the precipitation of vegetable tannins by chromium salts, Bowes and co-workers[41] discovered that tannins can apparently displace acetate from the chromium complex but not the more strongly complexing citrate anion. While formate masking of chromium tanning liquors does ensure a more even distribution of chromium through the thickness of pelt, and hence prevents overloading of the grain, the more strongly complexing agents such as phthalate and sulphophthalate afford an even greater degree of protection as mentioned by Shuttleworth and co-workers[54]. In this connection Lasserre and Paviot[55] maintain that it is necessary to use only a small amount of mild alkali such as sodium bicarbonate when neutralising with masking agents to obtain low-acidity retanned leather, whereas chromium tanned leather had to be neutralised to an equilibrium pH in excess of 5.5 if only sodium bicarbonate was used, to ensure a retanned leather with a pH higher than 3.5.

(d) The Influence of the Degree of Retannage

No specific study of the effect of the degree of retannage has been made, but the influence of increasing the level of vegetable retannage of chromium tanned leather can be inferred from the results of the examination of commercial leathers[37]. Thus, on average, the heavily retanned leathers were more acid and tore more easily than those which were lightly retanned, but this aspect is in need of more thorough investigation. It is possible that the lower strength of the heavily retanned leathers can be explained by the increased overall degree of tannage, since it has been shown that the strength of collagen and leather fibres was decreased by tannage and by increasing level of tannage, regardless of type[56,57].

(e) The Ageing Characteristics of Chrome-Retan Leather

Work previously discussed relating to the examination of aged leather[32,34] has shown that chrome-retan leather is relatively unstable, and mention was made of a fall in pH in those leathers that had lost strength on storage. Lollar[58] states that leather is most stable in the pH range 3 to 6, and that stability is lost if changes occur to either extreme of acidity or alkalinity. Bowes and Raistrick[59] showed that, with fall in pH of chrome-retan leather, strength losses increased progressively, increasing sharply below pH 4. Burton and Vivian[60] suggested that one of the causes of weakness in chrome-retan leather was acidity from sulphuric acid released from chromium complexes during or after the retannage. However, Kendall and Williams-Wynn[61] have shown that sound retan leather is not weakened by treatment with sulphuric, lactic or acetic acid solutions at pH 2.5, but this does not preclude the catalytic action of acid in promoting hydrolytic instability.

The observed facts concerning the deterioration of chrome-retan leather are consistent with slow changes which might arise from the liberation of strong acid from the chromium-collagen complex, as vegetable tannins entered the complex and displaced sulphate, leading to the hydrolytic degradation of the protein, and it is probable that moisture plays an important part in the process. Bowes[62] has shown that with increasing humidity of storage the number of N-terminal residues

of the skin protein increased, although above pH 4,0 relatively few N-terminal residues were liberated. As the pH fell there was a sharp increase, the major part of the increase occurring between pH 3,5 and 3,0, but in atmospheres of 40% r.h. and less, very few N-terminal residues were liberated even at pH 2,5, thus confirming the effect of moisture on storage. When serious deterioration had taken place as evidenced by an increase in acidity and a reduction in strength, the presence of protein degradation products could often be detected[35,40]; at this stage the pH of the leather began to rise.

On behalf of the United States Department of Agriculture, Bowes and associates have made a fundamental study of the mechanism of the deterioration of leather fibres, and details are given in the final report published in 1963[62]. Although the terms of reference of this project were very wide, the work included an investigation of chrome-retan leather. A comprehensive range of leathers was studied and the report shows that exposure to moist heat can lead to the deterioration of most types of leather, and that both degradation of the protein and changes in the tanning agent seem to be involved. Moreover, the poor resistance of vegetable-chromium combination tanned leathers to moist heat became increasingly obvious as the work progressed. In most cases the pH of these leathers fell during storage and there were decreases in shrinkage temperature of up to 20°C. These changes on storage suggested that there was interaction between the vegetable tannin and chromium, leading first to displacement of sulphate groups from the chromium complex and then of protein carboxyl groups leading to detannage. That such interactions can occur have been amply demonstrated[41,43], but quantitative assessment of the degree to which interaction occurred and the factors affecting it were more difficult to establish[62]. The interaction is likely to cause deterioration in three ways : by increase in acidity, by removal of chromium from combination with protein and by the formation of gummy precipitates in the interstices of the fibrils which will tend to cause crackiness.

The Reaction of Zirconium with the Chromium-Collagen Complex

Since the reaction of zirconium with collagen is imperfectly understood, the study of the interaction of zirconium with chromium tanned pelt has received little attention. Superficially zirconium salts resemble vegetable tannins in their action with collagen, but many of the recommended methods for their use have been obtained empirically[63], and the mode of reaction is only suggested by inference. Unfortunately the methods used to establish the mechanism of vegetable tannage[7-9] are not applicable to zirconium. The lack of solubility of zirconium salts in organic solvents excludes the application of extraction studies to this tanning system, and additional work using alternative methods is required to gain further evidence from which the mechanism of reaction with skin protein can be deduced.

No evidence is available from the literature to suggest the mechanism of the reaction of zirconium with chromium tanned collagen. Vivian[64] has made some tentative suggestions and concludes from work using ion exchange resins that it appears probable that there is an interaction between chromium and zirconium species that would play a part in zirconium retannage of chromium tanned leather. On the other hand he also states that chromium and zirconium tannages are independent of each other, zirconium leather fixing just as much chromium as normal hide and the same holds for the reverse combination tannage.

Several communications dealing with the technological aspects of chromium-zirconium combination tannages have appeared[63-68]. From these it seems that the ionic nature of the zirconium tanning compound may be of importance since masking with citric acid, which produces anionic zirconium complexes, increased the fixation of zirconium and resulted in higher hydrothermal stability. On the other hand, zirconium in combination with chromium seems to act more as a filler than as a tanning agent, because strength characteristics are not adversely affected as would be expected from a higher degree of tannage[56,57].

The purpose of the work presented in this thesis is to make a thorough and quantitative investigation of the reaction of zirconium compounds and vegetable tannins with chromium tanned leather, with a view to suggesting possible reaction mechanisms, and to determining satisfactory procedures for the production of strong, durable chrome-retan leathers.

CHAPTER 2

METHODS AND PROCEDURES

2(a) Statistical Plans

In modern scientific investigations, especially when dealing with materials of biological origin, statistical methods are indispensable, and Mitton[69] has demonstrated the advantages which statistics can offer when applied to experimentation in leather science. The factorial design of experiment is particularly suitable for investigations of tannery processes, because leather manufacture is a delicately balanced succession of treatments each of which depends upon the other. This experimental design enables a large number of factors, whose effects are to be determined, to be included in the same experiment, resulting in (a) much greater efficiency, and (b) information on the extent to which the factors interact[70]. Moreover, an accurate estimate of the magnitude of error variance can be made which is necessary in order to apply an exact test of significance. Thus, 5% level of significance means that the effect has a probability of 1 in 20 of being due to chance; 1% and 0.1% mean 1 chance in 100 and 1000 respectively. In all the work reported in this thesis 5% is taken as the limit of significance. Significance levels are denoted by asterisks.

Between 5% and 1%	Probably significant, denoted by *
Between 1% and 0.1%	Significant, denoted by **
Less than 0.1%	Highly significant amounting almost to certainty, denoted by ***.

Experiments involving many factors may require some time to be taken in the search for suitable designs, but the planning of experiments has been greatly facilitated by the publication of tables of designs of factorial experiments[71]. These tables have been used to obtain the following experimental plans used in this work.

(i) Half-replicate design - 32 treatment combinations. This statistical plan involved six factors each at two levels with ABCDEF as defining contrast. Since this design was used for experiments involving hide powder, no blocks were necessary and the number of degrees of freedom that could be used for error estimations increased to 13. Moreover there were no first-order interactions confounded with blocks.

(ii) Quarter-replicate design - 64 treatment combinations. This statistical plan involved six factors, but two were at four levels, each formally equivalent to two two-level factors, thus it was a 2^8 factorial design with ACDEG and BCDFH as generators of defining contrasts. No first-order interactions were confounded with blocks, the experiments being conducted on hide powder.

(iii) Half-replicate design - 128 treatment combinations. This plan involved six factors as above, but, since the specimens were to be cut from hide, the samples had to be cut in blocks and the treatments so allocated to samples that the desired comparisons would not be influenced by differences between whole blocks; only in this way could accurate assessments be made. Thus this experiment was planned as a 2^8 design with ABCDEFGH as defining contrast, the samples being cut in eight blocks of 16 samples each. No first-order interactions were confounded with blocks and there were 71 degrees of freedom for error.

(iv) Quarter-replicate design - 128 treatment combinations. This plan involved seven factors, two of them double factors; thus this experiment was a 2^9 design with ADEFGH and BCDEGJ as generators of defining contrasts, the samples being cut in eight blocks, resulting in 60 degrees of freedom for error, and no first-order interactions were confounded with blocks.

(v) Quarter-replicate design - 256 treatment combinations. This plan involved eight factors, two of them double factors; thus this experiment was a 2^{10} design with ADEGHJ and BCFGHK as generators of defining contrasts, the samples being cut in 16 blocks of 16 samples. No first-order interactions were confounded with blocks and there were 168 degrees of freedom for error.

All of the technological work and the scientific studies of tanning processes have been based on statistical principles using the above factorial designs, or the results of experiments have been subjected to an analysis of variance using standard procedures[72]. The majority of the factorial designs involved 128 treatment combinations, and the mathematical manipulation of the numerical assessments is repetitive and time-consuming. Thus, when computer facilities became readily available,

computer programmes were written to perform the calculations most frequently required.

2(b) Computer Programmes

A programme, written in Manchester Auto-Code[73,74], was prepared for the ICT 1301 computer at Rhodes University to handle the statistical computations of experiments involving 128 treatment combinations, and to determine significance levels. By suitable modification this programme performed similar calculations for experiments involving 64 treatment combinations. A copy of the print-out of the programme appears in the Appendix. Selection of appropriate switches on the console instructed the computer to print fixed point numbers or to give the print-out in floating point form. An example of a typical result sheet is given in the Appendix.

In view of the very large number of significant interactions involving both double factors which had to be interpreted, an additional programme was written to handle this particular back-calculation. The print-out is the standard tabulation and the numbers are in floating point form. A copy of the print-out of this programme, and an example of a typical back calculation are given in the Appendix.

2(c) Preparation of Pure Tannin

Pure polyphenolic wattle tannins were obtained from commercial mimosa extract by Roux's method[75]. In brief the method is as follows: A clarified solution of the commercial extract was vigorously stirred and an excess of a 10% solution of lead acetate was slowly added to precipitate the tannin. The lead tannate was centrifuged down and washed with small quantities of water to remove the non-tannins and excess lead acetate. The precipitate was suspended in water and dilute sulphuric acid added with continuous stirring. This liberated the tannin, precipitating the lead sulphate which was centrifuged off. The pH of the solution was raised to between 4,0 and 4,1 by the careful addition of approximately 0,2 N sodium hydroxide solution. The solution was taken to complete dryness under reduced pressure and extracted with absolute ethanol which took up the tannin and left a residue of the salt. The

latter was separated off by centrifuging, and the clarified liquid concentrated and evaporated to dryness under reduced pressure. The purified tannin fraction remaining had the following analysis on the dry solids basis, as determined by the official hide powder method of analysis[76].

Tannins	97.91%
Non-tans	2.09%

2(d) Preparation of Pure Chromium Tanning Solutions

Commercial chromium tanning salts are obtained by the reduction of sodium dichromate with organic substances, and the oxidation products combine with chromium to form partially masked compounds. Since the effect of masking was to be studied, it was essential that pure solutions be used to which known amounts of masking agents could be added. Thus chromium tanning compounds were prepared in the laboratory by SO_2 reduction of pure potassium dichromate.

(i) 33% Basic chromium sulphate. This was prepared by the reduction of potassium dichromate with sulphur dioxide. 194 g. reagent grade potassium dichromate was dissolved in 500 ml. of water, and into this solution sulphur dioxide was passed until the chromium was completely reduced to the trivalent form (checked with diphenylcarbazide[77]). Excess SO_2 was expelled by boiling, and when cool the solution was made to 1 l. This solution contained 10.0% Cr_2O_3 w/v and was 33% basic.

(ii) Formate masked 33% basic chromium sulphate. To 250 ml. of the above solution was added 11.2 g. of sodium formate dissolved in 25 ml. of water. The solution was boiled to reduce the volume to about 200 ml., cooled and made to 250 ml. This solution contained 10% of Cr_2O_3 w/v, and had 1 mole of formate per mole of Cr_2O_3.

(iii) 50% Basic chromium sulphate. 23.8 g. of $Na_2CO_3.10H_2O$ dissolved in 25 ml. of water was slowly added to 250 ml. of the 33% basic chromium sulphate solution with constant stirring and gentle boiling. After the final addition, the solution was boiled to reduce the volume to about 200 ml., cooled and made to 250 ml. This solution contained 10.0% of Cr_2O_3 w/v, and was 50% basic.

(iv) Formate masked 50% basic chromium sulphate. A solution of 11.2 g. of sodium formate plus 23.8 g. of $Na_2CO_3.10H_2O$ in 40 ml. of water was slowly added to 250 ml. of the 33% basic chromium sulphate solution with constant stirring and gentle boiling. After the final addition the solution was boiled to reduce the volume to about 200 ml., cooled and made to 250 ml. This solution contained 10.0% of Cr_2O_3 w/v, had 1 mole of formate per mole of Cr_2O_3 and was 50% basic.

2(e) Modification of Collagen Substrates for Tanning Experiments

Thoroughly degreased freeze-dried goatskin corium and acetone dehydrated sheepskin were used when intact skin was required, otherwise standard hide powder (lots C 17 and C 20) was used. Appropriate quantities were chemically modified in one of the following ways, which are well established methods for treatment of protein.

(i) Esterification. Acid catalysed methanol was used to esterify the collagen under the conditions suggested by Fraenkel-Conrat and Olcott[78], and Burton, Danby and Sykes[79]. 25 g. of dry pelt was treated with 400 ml. of methanol made 0.1 N with concentrated hydrochloric acid. The reaction took place in stoppered bottles with intermittent shaking for 8 days. On completion of the treatment, the methanol was drained off and the product was placed in 10% sodium chloride solution for 24 hours and then neutralised to pH 3.7 with sodium hydroxide. When the product had reached equilibrium, it was washed in 3 changes of 5% salt solution and then in water until free from salt, and finally dehydrated with acetone. This treatment resulted in the introduction of 0.70 m. moles methoxyl/g. protein.

(ii) Deamination. Rehydrated pelt was treated with sodium nitrite in acid solution under the conditions suggested by Bowes and Kenten[80]. 25 g. of air dry pelt were soaked in distilled water for 24 hours, drained then treated with 25 g. of sodium nitrite in 125 ml. of water followed by the addition of 25 ml. of glacial acetic acid. The mixture was agitated intermittently and kept in a stoppered brown glass container in the dark. The process was repeated 4 times at 12 hour intervals when the pelt was rinsed in water, washed to remove acid in several changes of 10% sodium chloride solution, then in running water

until free from salt, and finally dehydrated with acetone. This treatment reduced the amino groups from 0.36 to about 0.04 m. moles/g. collagen.

(iii) Carboxylation. Bowes version[81,82] of the process developed by Fraenkel-Conrat and co-workers[83,84] was used for this modification. 25 g. of air dry pelt was soaked in water for 24 hours, drained, then treated with 400 ml. of water, 8 g. formaldehyde, 12 g. sodium chloride, 8 g. sodium bicarbonate and 3 g. glycine. The reaction proceeded with continuous agitation for the first 24 hours and with intermittent agitation for 48 hours, maintaining the pH at 8.3 by the careful addition of sodium hydroxide. The product was washed in several changes of 3% salt solution and then in water until free from salt, and finally dehydrated with acetone. The carboxyl groups were increased to approximately 1.85 m. moles/g. protein.

(iv) Acetylation. Vacuum dried collagen was treated with a mixture of acetic acid and acetic anhydride under the conditions recommended by Green, Ang and Lam[85]. 25 g. of hide powder, dried over P_2O_5, was treated with 200 ml. of a mixture of equal parts of acetic anhydride and glacial acetic acid. The reaction took place in stoppered bottles with intermittent shaking for 8 days. The liquid was drained off and the product exhaustively extracted with acetone and finally air dried. After 2 treatments, the total acetyl content of the pelt was 1.42 m. moles/g. collagen.

2(f) Small Scale Tannages

(i) Reaction of Mineral Tanning Salts with Modified Collagen. Weighed samples of air-dry collagen of known moisture content were wet back in a large volume of water, and the pH frequently adjusted to 3.0 with either hydrochloric or sulphuric acid, depending on the type of tanning salt to be used. After 24 hours the acidified pelt was transferred to specimen tubes and the appropriate volume of 1 molar salt (sodium chloride or sodium sulphate) solution added; this volume was equivalent to 800% of the dry pelt weight and contained either 0.5 or 2.5 equivalents of organic acid per mole of chromium or zirconium used in the subsequent tannage. After 6 hours agitation in the pickle, 1000% on dry collagen weight of a 0.5 M solution of 50% basic tanning salt was added, (solid

basic zirconium sulphate was used with an appropriate volume of water). The final concentration of mineral was 0.25 M and the large float ensured that the "spent" solution would still contain a relatively high concentration of tanning material. Reaction was allowed to proceed for 64 hours with continuous agitation. On completion of the tannage, the leather was pressed in a Carver laboratory press to remove most of the uncombined tanning material, then washed for 24 hours in water prior to drying, analysis, and test.

(ii) Reaction of Zirconium with Chromium Tanned Collagen. Weighed quantities of hide powder were wet back in 800% of water for 16 hours and a vacuum drawn to expel air. Appropriate quantities of salt were added to each sample so that in the final float (when pickle acid and mineral tanning agents had been added) the concentration was 1 M. After 1 hour's continuous agitation, sulphuric acid solution was added so that the equilibrium pH at the end of 24 hours was 4.0. To the pickled pelt in shaker bottles was added appropriate quantities of the stock chromium tanning solutions in water to give a final float volume of 1000% and a chromium concentration of 4% or 7% Cr_2O_3 on collagen. Reaction was allowed to proceed for 72 hours, the final pH being in the vicinity of 3.7, when the spent liquor was squeezed from the pelt which was aged in the blue for 5 days.

The chromed collagen was washed in water, and the relevant portions reacted with a large excess of glutaraldehyde for 48 hours. This pelt was washed to remove free aldehyde. The pretanned pelt was floated in 800% of water which contained 1.0 equivalents of citric acid per mole of zirconium (where appropriate) and immediately sufficient dry zirconium salt plus 700% of water were added to give a final mineral concentration of 0.25 M. After 36 hours reaction with continuous agitation, the pelt was pressed in a Carver press, washed, dried, and analysed as above.

(iii) Reaction of Vegetable Tannins with Chromium Tanned Collagen. Weighed quantities of hide powder and acetone dehydrated sheepskin pieces (normal or modified) were prechromed as in (ii) above. This chrome tanned collagen was aged in the blue for at least 1 week

and stored in plastic bags in a refrigerator at 4 °C.

The pelt from each tannage was suspended in water and the pH adjusted to 5.5 by adding sodium bicarbonate. Neutralisation was deemed to be complete when the pH of the liquor changed by not more than 0.1 of a pH unit after 30 minutes' continuous agitation. The liquor was drained off and the leather squeezed before being washed twice with water.

The neutralised tanned hide powder and pelt were subdivided into 8 equal portions and transferred to bottles for the retannage, each bottle containing 3 of the sheepskin pelt pieces as well as the hide powder. The quantity, temperature, pH, type of vegetable tanning material and type of pelt as determined by the appropriate factors in the plans of the experiments were adopted. The float in each case was 1000%, the volume being made up by the addition of water adjusted to the same temperature and pH. The reaction was allowed to proceed for 2 hours at the end of which time the liquor was expressed and kept for analysis, the tanned hide powder being washed twice with 1000% of water to remove uncombined tannin, squeezed and dried at 40°C in an air oven. When dry the pelt was thoroughly conditioned (3 weeks) in the standard atmosphere, subdivided into groups, and transferred to specimen bottles preparatory to testing or ageing.

(iv) General Procedures for Tanning Experiments. The details for the various stages in the manufacture of leathers were specified in the statistical plans of the various experiments. To avoid complications due to thickness, calfskins were used for the chromium-zirconium combination tannages, but for other tannages bovine hide split in lime was used. The requisite number of samples (usually 128 in 8 blocks of 16) were cut from the limed pelt, washed in a drum to remove free lime and raise the temperature, delimed with the appropriate material for 30 minutes at 35°C when pancreatic enzyme bate was added and agitation continued for a further 30 minutes.

This pelt was pickled in approximately 1M salt solution by the addition of acid (usually sulphuric) and reaction continued for 1 hour. At this stage chrome liquor was added together with additives where

necessary, and agitation continued for 4 hours. Reaction continued in the static solution over-night with a final agitation for 1 hour during which time the pH was raised to 3.7, if necessary.

The blue leather was usually aged for 24 hours, (although in some cases zirconium was added to the spent chromium liquor), after which the appropriate retan treatments were performed. The goods were always fatliquored (because this has a profound effect on physical properties), dried under tension, staked, and redried before conditioning, ageing and testing.

(v) Ageing. The natural ageing of leather samples and tanned pelt was conducted by exposure to the standard atmosphere ($20^{\circ} \pm 2^{\circ}C$ and $65 \pm 2\%$ r.h.)[86] for the appropriate period (usually 8 months).

Accelerated ageing was carried out by exposing the specimens to an atmosphere saturated with water vapour and maintained at $48^{\circ}C$ for 3 weeks[87,88]. The container was ventilated at weekly intervals and a small beaker of toluene was included to prevent mould growth. At the end of the ageing period the specimens were dried in an air oven at $40^{\circ}C$ for 16 hours and reconditioned in the standard atmosphere for at least 48 hours, prior to analysis and test.

2 (g) Titration Curves of Vegetable Tannins

25 ml. aliquots of clarified solutions of the vegetable tannins (chestnut, mimosa, myrobalans and quebracho) containing 2% soluble solids, were passed through cation exchange resins in the hydrogen form. The resin columns were thoroughly eluted with distilled water and the effluent made up to 200 ml. These solutions were titrated with standard 0.1 N NaOH, and the titration curves plotted after allowing for the dilution effect.

2(h) Analytical Procedures

Where possible the analyses and tests carried out on the leather or pelt were as specified in the "Official Methods of Analysis" of the Society of Leather Trades' Chemists. Other methods or modifications of the official methods are detailed below.

(i) Estimation of Methoxyl Groups. This estimation was carried out by the general method of hydrolysis with hydriodic acid, the liberated methyl iodide being absorbed by the bromine/acetic acid reagent of Vieboch and Brechner[89] whence it was estimated iodometrically. The apparatus used was similar to the commercial Clerk-Zeisel apparatus.

20-60 mg. of the methoxy compound (esterified collagen) was accurately weighed into the flask, and 5 ml. of iodine-free hydriodic acid (sp.gr. 1.7) was added. The scrubber contained 2 ml. of 20% acidified cadmium sulphate solution and 1 ml. of a heavy aqueous suspension of red phosphorus. The absorption unit contained 10 ml. of 10% potassium acetate in glacial acetic acid, to which was added 15 drops of washed, iodine-free bromine. A slow stream of carbon dioxide was passed through the apparatus prior to and during the reaction. Heat was applied to the flask so that the reflux line was at the base of the condenser for 25 minutes, after which it was heated more strongly to complete the reaction. The apparatus was then disconnected and the absorbers washed into a conical flask containing 5 ml. of 25% sodium acetate solution and the volume made up to about 125 ml. with distilled water. Pure concentrated formic acid was added dropwise (10 drops) to decompose the excess bromine, the operation being complete when the colour was discharged. The flask was then well shaken to remove any bromine vapour which may have been present. After adding potassium bromide and 20 ml. 2 N sulphuric acid, the distillate was titrated with standard 0.05 N sodium thiosulphate to the normal end-point for an iodine titration.

(ii) Estimation of Total Acetyl. Approximately 0.5 g. of dried (103°C in an air oven) acetylated collagen was accurately weighed into a flask and heated with 50 ml. of 2 N sulphuric acid under reflux for 2 hours. The mixture was then distilled in a current of steam until its volume had been reduced to about one-half and about 500 ml. had been collected in the receiver. The distillate was titrated with 0.05 N sodium hydroxide, and from the result was subtracted the small value given by a blank obtained by a similar hydrolysis and distillation of unacetylated collagen.

(iii) Free Sulphate in Leather and Spent Liquors. The sulphate was extracted from the leather by weighing 1.5 g. of the ground leather into a tube, adding 50 ml. of a 0.1 N KCl solution and wetting thoroughly by drawing a vacuum, then shaking mechanically for 24 hours. The pH of the slurry was measured before filtering through a No.41 filter paper, discarding the first 5 ml. of the filtrate and determining sulphate in aliquots of the remainder. The following method was applicable to both the extract of leather and the spent retan liquors.

Sulphate was determined in the liquors and in the 0.1 N KCl extracts of the leather by a micro-titration technique[90], using Thorin[91], and more recently Sulphanazo III[92] as indicator, the titrant being 0.01 N $Ba(ClO_4)_2$ in 50% alcohol solution. An aliquot of standard sulphuric acid was added to the extracts of leather because of the small quantity of sulphate present, and the titration performed in 50% alcohol solution.

(iv) pH and $[H^+]$. As mentioned above, the pH was determined on the 0.1 N KCl extract of the leather, and hydrogen ion concentration calculated where necessary.

(v) Extractable Tans. In the earlier work (Chapter 4(a) and 4(b)) the uncombined and weakly bound tannins were extracted from ground leather by cold Soxhlet extraction with azeotropic methyl ethyl ketone which has been shown to remove uncombined tannins as effectively as aqueous acetone[93]. Recently the superiority of aqueous dioxan as an extraction medium for vegetable tannins has been demonstrated[7], and this solvent was used to extract tannins from powdered leather by a shake method[7,8].

(vi) Chromium in Leather and Spent Liquors. Chromium in the leathers was determined, employing Method No. 4 of the "Official Methods of Analysis", 1951[94], using the mixture of perchloric and sulphuric acids for destroying the protein and oxidising the chromium. A modification of the above method was used for determining chromium in the spent retan liquors. For this determination a large aliquot of the liquor was taken, a few drops of concentrated sulphuric acid added and the total reduced considerably in volume. When only a few ml. remained, 10 ml. of concentrated nitric acid was added followed by 15 ml. of the

perchloric-sulphuric acid oxidising mixture and the reaction completed at the boil. The remainder of the determination was carried out as specified for leather.

(vii) Zirconium in Leather Approximately 0.5 g. of the zirconium compound (leather) was weighed into a 100 ml. Kjeldahl digestion flask and 10 to 15 ml. of the perchloric/sulphuric acid digestion mixture (see Method (vi) above) and 15 ml. of concentrated nitric acid were added. The mixture was heated gently to digest the organic matter then more strongly until fumes of perchloric acid were given off. The contents of the flask were cooled, diluted with about 50 ml. of approximately 1.0 N hydrochloric acid and boiled for 5 minutes. When cool, the solution was transferred to a 250 ml. volumetric flask and made up to the mark with distilled water.

The phosphate precipitation method[95] was used. An aliquot of the filtered zirconium solution containing about 0.1 g. of zirconium was diluted to about 100 ml. and sufficient sulphuric acid added so that the solution contained about 15% by volume. 50 ml. of a 10% solution of diammonium hydrogen phosphate was added and the resulting solution digested at 50°C for several hours and allowed to cool over-night. The precipitate was filtered into a tared, ignited Gooch crucible, washed with a cold 5% solution of ammonium nitrate, ignited at 900°C, and weighed as ZrP_2O_7.

In certain cases, where no interfering substances were likely to be present, zirconium was determined by weighing about 0.5 g. of the ground, well washed leather into platinum crucibles, ashing at a temperature of 900°C for 2 hours, and weighing the residue as ZrO_2.

2(j) Physical Testing

(i) Measurement of Shrinkage Temperature. Where possible the shrinkage temperature was measured in water using the official method[96]. Where shrinkage temperatures were higher than could be measured on this apparatus, T_s was determined by heating thoroughly wetted samples in liquid paraffin as heat transfer medium. The values thus obtained were the same as the corresponding values in water[97].

(ii) Measurement of Tearing Load. The official method using the simplified specimen pattern was used[98].

(iii) Measurement of Distension and Strength of Grain by Ball Burst Test. These assessments, commonly known as the Lastometer extension and load at grain crack, were obtained using the official method[99].

CHAPTER 3

CONTRIBUTION TO THE STUDY OF THE REACTION OF ZIRCONIUM WITH THE CHROMIUM-COLLAGEN COMPLEX

The reactions of vegetable tannins and chromium compounds with collagen have been extensively studied and the mechanisms of these two tannages are well established[1-9]. Thus from observations of combinations of these two tanning systems it is possible to speculate on the manner in which these two tannages might interact. In the case of zirconium insufficient information regarding its combination with collagen is available to establish a reaction mechanism. Thus before attempting to study the reaction of zirconium with the chromium-collagen complex, it has been necessary to obtain further information on the reaction of zirconium with collagen, and this has been achieved by a comparative study of the tannage of chemically modified collagen by both chromium and zirconium.

3 (a) The Effects of Organic Acids on the Fixation of Chromium and Zirconium by Chemically Modified Collagen [100]

The reaction of zirconium with collagen appears to be different from the reaction of chromium, although both are regarded as mineral tanning agents. Investigations into the theory of masking have been of considerable importance in elucidating the mechanism of chromium tanning, and it is thought that the essential reaction is the formation of a co-ordination compound involving the side chain carboxyl groups of collagen and basic chromium salts[101-103]. Masking reduces the rate of reaction of the chromium with pelt and strong complexing agents inhibit the reaction altogether by competing with the protein carboxyl groups and preventing permanent fixation. Confirmation of the importance of the carboxyl group in chromium tanning has come from studies of the tanning of various chemically modified collagens[104-106], where low fixation with no increase in hydrothermal stability has been observed only in tannages of esterified or decarboxylated collagen.

Zirconium is also capable of forming co-ordination complexes with a variety of organic acids[107-109], but the available literature on

the reactions of zirconium with collagen[17,109,110], provides evidence which indicates that co-ordination of the carboxyl groups is of less importance than in chromium tanning. Carboxylic acids readily form co-ordination compounds with zirconium oxychloride, yet this salt is a poor tanning agent[18]; this is further evidence that co-ordination of carboxyl groups in collagen plays no significant part in the tannage. Moreover, masking of zirconium salts with organic acids is not effective in reducing the reactivity of zirconium and promoting its penetration into pelt as is the case with chromium, but the rapid increase in particle size of the zirconium complex in the presence of masking agents[111,112] may disguise their true effects.

The purpose of the present investigation is to clarify the position, by comparing the effect of a variety of organic acids on the fixation of chromium and zirconium by a number of collagen substrates, which had been chemically treated to inactivate the various polar side chains. In an investigation of this nature, certain compromises have to be made in order to obtain comparative results. Hence, although the optimum effects of the masking agents would have been achieved at a pH of 3.5 to 4.0, this would have caused precipitation of many of the zirconium salts. Optimum fixation of zirconium is at pH 1.0, where chrome fixation is negligible. If, however, the pelt has been subjected to an equilibrium pickle, zirconium tannage can take place at pH values as high as 3.0[113]. This pH was therefore chosen for the pickle pH as an acceptable compromise in the present work. In addition, maximum effects of masking agents are obtained if the organic acid and the mineral salt are allowed to react together prior to tanning. However, the use of organic acids in the pickle is an alternative which is sufficiently effective to warrant commercial recommendation, and this technique has been used in the present investigation. After adjustment to pH 3.0 with mineral acid, the pelt was brought to equilibrium at pH 3.0 with a solution of partially neutralised organic acid.

In practice it has been found that chromium and zirconium sulphates are superior to the corresponding chlorides as tanning agents; a comparison of these two mineral acid salts has therefore also been included in the present investigation.

The substrates used in this investigation had the following general composition, having been characterised by direct analysis, by analysis of acid/base binding characteristics, and by reference to published analyses of collagen.

Table 3(a), I
Active Side Chains in Chemically Modified Collagen

Modification	m.-moles/g. protein		
	Carboxyl	Amino	Hydroxyl
Nil (control)	1.05	0.34	1.74
Esterification	0.35	0.34	1.74
Acetylation	1.02	0.00	
Carboxylation	1.85		

Eight carboxylic acids were used in this work. Table 3(a), II lists the acids and their pK values. Stock solutions of these acids were prepared and adjusted to pH 3.0 by the addition of potassium hydroxide. At the concentration levels used, some of the acids were not completely soluble, and aliquots of well mixed slurries were taken for making up the pickle liquors.

Table 3(a), II
Acid pK Values of the Masking Agents[114]

Organic Acid	pK_1	pK_2	pK_3
Formic acid	3.69		
Butyric acid	4.81		
α-amino-n-butyric*	2.5		
ε-amino-n-caproic*	4.3		
Lactic	3.81		
Citric	3.07	4.73	5.41
Oxalic	1.19	4.21	
Adipic	4.43	5.41	

* from Cohn and Edsall[115]

The results of the fixation of metal, and the rise in shrinkage temperature of the collagen (ΔT_s) are presented in Tables 3(a), III and 3(a), IV respectively. An analysis of variance[72] was carried out on the results obtained in this work, but since no duplicate analyses and shrinkage temperature determinations were made, the high order

TABLE III

Fixation of Tanning Agent in mg. Atoms Metal/Gram Protein

CHROMIUM TANNAGE.

Organic Ligand.		Normal Collagen.		Esterified Collagen.		Carboxylated Collagen.		Acetylated Collagen.	
Type	Equiv. ligand/mole Cr.	Cl	SO_4	Cl	SO_4	Cl	SO_4	Cl	SO_4
Nil	—	1·16	1·64	0·58	0·69	1·28	1·84	0·91	0·90
Formic	0·5	0·69	1·22	0·29	0·43	1·20	1·32	0·63	0·55
	2·5	0·50	0·52	0·09	0·17	0·91	0·85	0·47	0·33
Butyric	0·5	0·67	1·18	0·27	0·45	0·98	1·26	0·59	0·60
	2·5	0·61	0·68	0·49	0·61	1·09	1·06	0·64	0·43
α-NH_2	0·5	0·95	1·26	0·34	0·44	0·91	1·22	0·63	0·53
Butyric	2·5	0·32	0·26	0·12	0·08	0·48	0·33	0·36	0·14
ϵ-NH_2	0·5	0·55	1·12	0·25	0·31	0·78	0·84	0·41	0·45
Caproic	2·5	0·25	0·24	0·07	0·09	0·49	0·43	0·12	0·11
Lactic	0·5	0·98	1·46	0·48	0·42	1·28	1·42	0·67	0·58
	2·5	0·36	0·47	0·13	0·15	0·68	0·73	0·29	0·22
Citric	0·5	0·41	1·08	0·22	0·43	0·81	1·26	0·19	0·28
	2·5	0·06	0·12	0·12	0·15	0·13	0·21	0·03	0·06
Oxalic	0·5	1·12	1·50	0·54	0·69	1·46	1·59	0·85	0·75
	2·5	0·01	0·01	0·08	0·06	0·01	0·01	0·02	0·02
Adipic	0·5	0·56	1·29	0·45	0·50	1·22	0·82	0·60	0·47
	2·5	0·47	0·65	0·24	0·23	1·06	0·87	0·63	0·29

Differences to be significant must be greater than 0·35 at 5% level of confidence.
0·47 at 1% „ „
0·61 at 0·1% „ „

ZIRCONIUM TANNAGE.

Organic Ligand.		Normal Collagen.		Esterified Collagen.		Carboxylated Collagen.		Acetylated Collagen.	
Type	Equiv. ligand/mole Zr.	Cl	SO_4	Cl	SO_4	Cl	SO_4	Cl	SO_4
Nil	—	1·52	2·66	1·21	5·19	1·39	1·16	0·98	2·67
Formic	0·5	2·66	3·19	2·00	2·40	1·70	1·01	1·67	2·13
	2·5	2·15	2·09	0·93	1·19	1·25	1·64	1·42	1·18
Butyric	0·5	2·33	3·09	1·91	2·83	2·08	1·06	1·54	2·16
	2·5	0·44	1·35	1·45	1·85	0·85	1·75	1·37	1·08
α-NH_2	0·5	1·15	1·76	0·65	0·89	0·70	1·27	0·92	0·73
Butyric	2·5	1·01	0·70	0·38	0·48	0·52	0·68	0·90	0·24
ϵ-NH_2	0·5	1·35	3·06	1·23	2·16	0·98	1·31	0·71	1·61
Caproic	2·5	1·90	1·86	0·31	0·81	1·32	1·24	0·98	0·70
Lactic	0·5	2·46	3·10	1·97	2·56	1·73	1·80	1·55	2·20
	2·5	1·98	1·89	0·94	1·25	0·81	1·45	0·86	0·92
Citric	0·5	2·01	3·16	1·13	2·73	0·40	1·28	1·40	2·16
	2·5	0·11	0·75	0·12	0·44	0·09	0·54	0·07	0·73
Oxalic	0·5	2·26	3·68	1·30	2·26	0·94	0·98	0·84	1·02
	2·5	0·18	0·13	0·11	0·12	0·18	0·12	0·03	0·11
Adipic	0·5	1·30	2·43	1·21	1·59	0·86	1·16	0·95	1·68
	2·5	1·39	4·93	1·29	1·44	1·10	0·64	1·41	1·09

Differences to be significant must be greater than 1·45 at 5% level of confidence.
1·93 at 1% „ „
2·51 at 0·1% „ „

TABLE IV

Increase in Shrinkage Temperature of Tanned Proteins

CHROMIUM TANNAGE.

Organic Ligand.		Normal Collagen.		Esterified Collagen.		Carboxylated Collagen.		Acetylated Collagen.	
Type	Equiv. ligand/mole Cr.	Cl	SO_4	Cl	SO_4	Cl	SO_4	Cl	SO_4
Nil	—	63	69	24	24	52	62	56	66
Formic	0·5	43	54	14	15	49	55	53	46
	2·5	33	40	10	8	56	56	46	45
Butyric	0·5	48	51	17	20	52	56	54	38
	2·5	36	41	17	20	46	42	53	44
α-NH_2	0.5	50	62	16	13	48	53	46	43
Butyric	2·5	34	39	16	6	39	31	33	22
ϵ-NH_2	0·5	46	49	11	13	44	45	38	38
Caproic	2·5	28	30	8	1	29	33	19	18
Lactic	0·5	59	67	25	18	46	55	56	52
	2·5	40	42	14	10	39	48	54	50
Citric	0·5	32	61	18	16	35	51	40	54
	2·5	2	10	3	4	7	8	7	8
Oxalic	0·5	47	52	15	17	47	55	50	46
	2·5	0	0	0	0	4	0	7	2
Adipic	0·5	51	58	16	23	51	56	46	39
	2·5	33	61	14	17	50	57	58	57

Differences to be significant must be greater than 15 at 5% level of confidence.
20 at 1% „ „
26 at 0·1% „ „

ZIRCONIUM TANNAGE.

Organic Ligand.		Normal Collagen.		Esterified Collagen.		Carboxylated Collagen.		Acetylated Collagen.	
Type	Equiv. ligand/mole Zr.	Cl	SO_4	Cl	SO_4	Cl	SO_4	Cl	SO_4
Nil	—	8	42	21	37	0	18	24	32
Formic	0·5	14	42	25	33	7	14	21	27
	2·5	24	37	17	23	12	20	19	22
Butyric	0·5	36	41	25	35	8	16	22	31
	2·5	28	36	19	27	7	16	22	18
α-NH_2	0.5	7	32	18	20	3	17	20	19
Butyric	2·5	12	23	15	13	6	20	17	14
ϵ-NH_2	0·5	7	37	18	30	0	16	20	21
Caproic	2·5	20	34	23	18	8	21	21	19
Lactic	0·5	13	40	21	33	7	19	21	32
	2·5	18	37	19	23	15	21	22	22
Citric	0·5	15	41	22	36	16	18	24	29
	2·5	1	21	0	9	3	12	0	13
Oxalic	0·5	11	44	17	32	12	16	16	21
	2·5	0	0	0	0	0	0	0	0
Adipic	0·5	18	37	25	30	6	17	22	33
	2·5	14	39	29	28	14	15	32	23

Differences to be significant must be greater than 10·6 at 5% level of confidence.
14·1 at 1% „ „
18·4 at 0·1% „ „

interactions had to be used as an estimate of the error, so the differences which are required for statistical significance are unduly large. Nevertheless, despite the large error term, all main effects and most first-order interactions proved to be highly significant.

(i) Chromium. Detailed examination of the results shows that all of the pelt treatments affected chromium fixation very significantly, but only esterified collagen significantly reduced the increase in hydrothermal stability. Carboxylation increased the chromium fixation, but there was no corresponding large rise in ΔTs, probably a reflection of the logarithmic nature of the ΔTs/fixed chromium relationship, and the high initial shrinkage temperature of the untanned carboxylated pelt.

Esterification, even though not complete, brought about a very large drop in the amount of chromium fixed and a correspondingly large decrease in ΔTs. The effect on both properties supports previous conceptions that the increased hydrothermal stability following chromium tannage is due to the formation of a co-ordination complex involving the ionised carboxyl group. Acetylation has brought about an appreciable reduction in chromium fixation, but again in agreement with previous work, there was no decrease in ΔTs. Since the $-COO^-$ groups are unaffected by this treatment, this is further confirmation of the hypothesis that only the formation of a co-ordination bond between chromium and the protein carboxyl groups can confer the large increase in hydrothermal stability which is the predominant characteristic of chromium tanning. The chromium which is attached to other centres apparently has a negligible effect on the hydrothermal stability of the protein.

On the whole, sulphate was a slightly superior tanning agent to chloride, but the difference was more evident in the fixation of the chromium than in the increase in hydrothermal stability; this is thought to be due to the greater stability of the olated group in the presence of sulphate. The addition of the large amount of masking agent (2.5 equiv./mole Cr) as against the small amount (0.5 equiv./mole Cr) was effective in reducing both chromium fixation and ΔTs. This agrees with the general conception of masking put forward by Thorstensen[116] who defines masking agents as materials which when added to chromium solutions reduce their tanning power.

In the experimental technique employed, no pH adjustments were made, and the masking acids were added to the pelt in the pickle. Hence their effectiveness would probably be at a minimum. However, the oxalate and citrate ions are such strong complexing agents that they virtually prevented chromium fixation when present in a high molar ratio. The mono-carboxylic and amino acids follow a very similar pattern and the weak mono-carboxylic acids tended to be the more effective in inhibiting chromium fixation. The strong complexing action of the polybasic citric and oxalic acids has been mentioned, and the formation of five-membered rings involving one chromium atom is suggested as the reason for the high complex stability with corresponding low chromium fixation. The action of the adipic acid is contrary to what might be expected from consideration of the published work of Holland[117], who found that adipic acid increased chromium fixation, and he attributed this to chain formation in which each of the widely separated $-COO^-$ groups formed a co-ordination compound with different chromium complexes. In the present work, the adipate did not show this effect and behaved more like a mono-carboxylic acid. It is possible that this was a pH effect and that only at higher pH values does increased chromium fixation occur.

(ii) Zirconium. Carboxylation and acetylation resulted in a considerable decrease in the amount of zirconium sulphate fixed compared with the amount fixed by normal collagen. These treatments also considerably reduced the ΔT_s, particularly in the carboxylated collagen. Carboxylation and acetylation are achieved at the expense of amino groups, thus it appears that amino groups may play an important part in the fixation of zirconium sulphate to hide protein, yet there is no evidence that amino groups co-ordinate to zirconium in aqueous media[19]. On the other hand, esterification increased the amount of zirconium fixed by the collagen but there was no corresponding increase in the ΔT_s. It seems, therefore, that the carboxyl group is not an important site for binding zirconium sulphate to collagen, confirming the author's earlier work[12].

Zirconium chloride, by contrast, reacted quite differently with the modified proteins. In this case the carboxyl group seemed to be a supplementary binding site for zirconium as illustrated by the lower amount

of zirconium fixed by esterified collagen and, relative to zirconium in sulphate solution, a greater amount fixed by carboxylated collagen. This confirms results from a study of the reaction of zirconium salts with model substances containing the reactive groups which are present in skin protein[18]. Nevertheless, the picture is not at all clear, but bearing in mind the large particle size of zirconium compounds in solution[111, 112], steric effects must influence the results. Despite the large amount of zirconium fixed from chloride solution by various modified collagens, less hydrothermal stability was imparted by chloride salts than by sulphate salts. Thus, contrary to the generally accepted reaction in chrome tanning, co-ordination of carboxyl groups to zirconium does not confer a large increase in hydrothermal stability.

The effect of the masking agents on the zirconium fixation and the $\triangle$Ts was similar to that obtained with chromium. Oxalate and citrate form such strong complexes that the fixation of zirconium was virtually prevented when these ions were used in high molar ratio. Since the reduction in tanning ability is usually attributed to complex formation by the co-ordination of carboxyl groups to the metal, it seems that all the organic anions included in this study formed complexes with the zirconium. This is in direct contrast to the observations made from the tannages of modified collagen.

Discussion

Some aspects of the chemistry of zirconium and chromium compounds appear to be similar. For example, salts of both metals hydrolise in aqueous solution to produce basic compounds which polymerise to form polynuclear particles, and organic acid anions form co-ordination complexes with both of these metals. However, the above results indicate that zirconium tannage cannot be considered to have a similar mechanism to chromium tannage. Reaction of chromium with collagen undoubtedly involves the reaction of charged carboxyl groups on the protein with the metal to form a co-ordination complex. Zirconium sulphate on the other hand, seems to have little affinity for carboxyl groups in the hide protein as distinct from those in simple organic acids, and appears to be dependent more on the amino groups for fixation and increase in hydrothermal stability. Fixation of the chloride salt which appears to

react with carboxyl groups is low. Nevertheless, acetylated collagen still fixes appreciable amounts of zirconium with a corresponding increase in shrinkage temperature, so that zirconium tannage cannot be limited to amino groups alone and if, as seems likely, the mechanism of the reaction is multi-point attachment of the tanning material by residual valency forces, the physical properties of zirconium particles in solution would play an important role in the tanning process. The reduction in the tanning power of many of the masked zirconium solutions may be a reflection not of the reduced reactivity of these compounds, but of the increase in particle size in the presence of these organic acids[12], with consequent restriction or prevention of penetration into hide.

It is suggested that, at the pH of 3.0 used for this experiment, the carboxylic groups of the protein were able to compete much less successfully with co-ordination sulphate groups attached to the olated zirconium complex by six-membered ring formation, than with the monodentate chloride groups. In general, the tendency of zirconium to form complexes of large particle size with increase of pH restricts the choice of pH of tannage to the region where relatively few of the carboxylic groups of the protein are ionised, as compared with basic chromium salts which remain soluble at pH values favourable to co-ordination with ionised carboxyl groups of the protein side chains.

3(b) The Effect of Chromium Pretreatment on the Fixation of Zirconium by Collagen

The results of the investigation described above support previous opinions of the mechanism of chromium tanning, but, in the case of the zirconium tannages, apparently contradictory evidence has been obtained. Thus the fixation of zirconium by collagen pre-reacted with chromium may yield information from which the mechanism of zirconum fixation can be deduced. Moreover, combined chromium/zirconium tannages are of commercial importance, and information regarding the reaction of zirconium with the chromium-collagen complex will be of both theoretical and practical value.

Since amino groups appear to be of importance in fixing zirconium to hide protein, pretreatment with chromium should increase the reactivity of zirconium with collagen by increasing the availability of these reactive sites. Similarly, these reactive sites are important in aldehyde tannage[118], and confirmation of their importance in zirconium tanning may be obtained by treatment of the chromium tanned collagen with aldehyde before retanning with zirconium. Glutaraldehyde was chosen because it is reactive over a wide pH range[119], whereas formaldehyde requires pH values for effective reaction which are excessively high for stable chromium tanned leather.

As previously stated, zirconium sulphates and zirconium chlorides appear to react differently, and examples of both of these groups have been included for study. Moreover, the presence of citrate has been claimed to assist the tannage[108,120], and masking with this compound increases the anionic nature of zirconium in solution leading to the possibility of electrovalent bonds with positively charged groups on the hide protein[12,110]. Therefore this factor was also included in the investigation.

The experiment was planned as a $\frac{1}{2}$ replicate of a 2^6 factorial design, giving a total of 32 treatment combinations. The factors varied and the levels of the factors were as follows:

Table 3(b), I

Fixation of Chromium and/or Zirconium by Collagen at pH 3.0 in mg. atoms metal/g. protein and the Corresponding Increase in Shrinkage Temperature

Chromium Fixation

Zirconium salt offered***	Quantity of Chromium Offered***		
	Nil	4% Cr_2O_3	Excess
none	0.00	0.54	1.64
$ZrOCl_2$	0.00	0.53	1.60
$ZrOSO_4$	0.00	0.37	1.20

Zirconium Fixation

Zirconium salt offered***	Quantity of Chromium Offered***		
	Nil	4% Cr_2O_3	Excess
none	0.00	0.00	0.00
$ZrOCl_2$	1.76	0.19	0.12
$ZrOSO_4$	2.91	1.51	1.12

Increase in Ts

Zirconium salt offered***	Quantity of Chromium Offered***		
	Nil	4% Cr_2O_3	Excess
none	0	48	67
$ZrOCl_2$	11	40	49
$ZrOSO_4$	42	48	65

A. Quantity of chromium offered

(1) 4% Cr_2O_3 on collagen
a large excess

B Basicity of chromium salt

(1) 33% basic chromium sulphate
b 50% basic chromium sulphate

C Masking of chromium salt

(1) not masked
c formate masked, 1 mole formate/mole Cr_2O_3

D Aldehyde pretreatment for zirconium tannage

(1) none
d chromed collagen reacted with excess of glutaraldehyde

E Type of zirconium salt

(1) zirconyl chloride
e zirconyl sulphate

F Masking of zirconium tannage

(1) not masked
f citrate masked, 0.5 equiv. citrate/mole ZrO_2.

A series of blank determinations were made to obtain levels of chromium and zirconium fixation and hydrothermal stability of the collagen in the absence of the alternative mineral tanning agent.

The results of the fixation of metal and increase in shrinkage temperature are presented in Table 3(b), 1. The quantity of chromium attached to the collagen was virtually unaffected by the after-treatment with zirconyl chloride, but the chromium content was markedly reduced when zirconyl sulphate was offered. By contrast, the shrinkage temperature of the zirconyl chloride treated leather was considerably lower than the un-retanned chromium leathers, notwithstanding the high chromium content, whereas the hydrothermal stability of the zirconyl sulphate treated leathers was maintained despite a marked reduction in the chromium content. Obviously the pelt tanned with an excess of chromium fixed a large amount of chromium, and there was a correspondingly large increase in shrinkage temperature.

Zirconium fixation was distinctly reduced by chromium

Table 3(b), II

Fixation of Chromium and/or Zirconium by Collagen in mg. atoms metal/g. protein, and the Corresponding Increase in Shrinkage Temperature

Chromium Fixation

Zirconium salt offered***	Pretannage ***		
	None	Chromium	Chromium + Aldehyde
None	0.00	1.10	1.09
$ZrOCl_2$	0.00	1.12	1.00
$ZrOSO_4$	0.00	0.81	0.75

Zirconium Fixation

Zirconium salt offered***	Pretannage***		
	None	Chromium	Chromium + Aldehyde
None	0.00	0.00	0.00
$ZrOCl_2$	1.76	0.17	0.15
$ZrOSO_4$	2.91	1.41	1.22

Increase in Ts

Zirconium salt offered***	Pretannage*		
	None	Chromium	Chromium + Aldehyde
None	0	57	59
$ZrOCl_2$	11	43	46
$ZrOSO_4$	42	56	57

pretannage, the zirconyl chloride being particularly adversely affected. Although the fixation of zirconium from zirconyl sulphate solutions was lower on the chromium pretanned pelt than on untreated collagen, the differences were not as marked, and the influence of the increased fixation of zirconyl sulphate relative to zirconyl chloride must be taken in relation to the chromium contents of the various groups of leathers. Thus it is seen that little zirconyl chloride was fixed by chromium tanned collagen and the chromium content was scarcely affected, yet there was a marked reduction of hydrothermal stability. On the other hand appreciable quantities of zirconyl sulphate were fixed by prechromed pelt; some of the chromium was displaced, but there was no significant change in the shrinkage temperature of the leather.

Glutaraldehyde treatment of the chromium tanned leather prior to the zirconium retannage significantly influenced the results which are presented in Table 3(b) II. The aldehyde had no stripping action on the chromium, but when the aldehyde treated leathers were subsequently retanned with zirconium, the chromium content of the leathers was reduced to a greater extent than the chromium tanned leathers which had not received the aldehyde treatment. The zirconyl chloride did not affect the chromium content of the leather unless glutaraldehyde preceded the zirconium retannage. The interesting aspect of this observation was that although the chromium content of the leathers without glutaraldehyde was not reduced by the zirconyl chloride retannage, the shrinkage temperature was markedly reduced. The zirconyl sulphate retannage caused considerable displacement of chromium, the loss of chromium in the chromium and the chromium-plus-glutaraldehyde pretanned pelts being 27% and 31% respectively. However, this loss of chromium was not accompanied by a reduction in shrinkage temperature.

Zirconium fixation was considerably decreased by pretreatment with chromium and the aldehyde tannage of the chromium leather further reduced the take-up of zirconium. This effect was particularly noticeable in the case of the zirconyl sulphate retannage, although with zirconyl chloride chromium pretreatment had so drastically reduced the zirconium fixation that no further reduction due to the aldehyde could be expected. The reduction in fixation of zirconium resulting from the glutaraldehyde

Table 3(b), III

Fixation of Chromium and/or Zirconium by Collagen in mg. atoms metal/g. protein, and the Corresponding Increase in Shrinkage Temperature

Chromium Fixation

Zirconium salt offered***	Zr Masking	
	None	Citrate
None	1.09	1.09
$ZrOCl_2$	1.09	1.04
$ZrOSO_4$	0.79	0.76

Zirconium Fixation

Zirconium salt offered***	Cr collagen		Normal collagen	
	Zr Masking***		Zr Masking***	
	None	Citrate	None	Citrate
None	0.00	0.00	0.00	0.00
$ZrOCl_2$	0.15	0.16	1.52	2.01
$ZrOSO_4$	1.42	1.22	2.66	3.16

Increase in Ts

Zirconium salt offered***	Cr collagen		Normal collagen	
	Zr Masking*		Zr Masking*	
	None	Citrate	None	Citrate
None	58	58	0	0
$ZrOCl_2$	44	45	8	15
$ZrOSO_4$	54	58	42	41

treatment of the chromium leather did not influence the hydrothermal stability of the leathers. The cross-linking effect of the aldehyde[121-123], must compensate for the loss of chromium and the reduction in zirconium fixation.

The effect of the masking of the zirconium tanning salts with citrate is shown in Table 3(b), III. Treatment of the chromium tanned collagen with zirconyl chloride had no effect on the chromium content of the leather, but when the zirconium salt was citrate masked the chromium content of the leathers was slightly reduced. The chromium content of the leathers retanned with zirconyl sulphate was substantially reduced, but masking had no significant effect. As previously mentioned the hydrothermal stability of the zirconyl chloride treated chromium tanned leather was lower than the untreated leather and the presence of citrate had no measurable effect. Treatment of the chromium tanned leather with zirconyl sulphate slightly reduced the shrinkage temperature, but if the zirconium salt was masked with citrate no difference in the shrinkage temperature could be detected.

Zirconium fixation was substantially lower on chromium tanned collagen than on normal collagen, particularly in those leathers retanned with zirconyl chloride, and citrate masking had no significant effect. In those leathers retanned with zirconyl sulphate, citrate masking further reduced the fixation of zirconium, and this is in direct contrast to the effect of citrate masking on the fixation of zirconyl sulphate by normal collagen. The lower fixation of zirconium from the masked zirconyl sulphate together with the low chromium content of these leathers did not result in reduced hydrothermal stability, the shrinkage temperature being higher than that of the equivalent leathers retanned with unmasked zirconyl sulphate in which both the chromium and the zirconium content were greater, and equal to the pure chromium tanned pelt.

It is interesting to note that neither the basicity nor formate masking of the chromium tanning salt has influenced these results.

Discussion

Of the two zirconium tanning salts investigated, zirconyl chloride was the more adversely affected by pretreatment of the skin protein with chromium, although the amount of zirconyl sulphate fixed was also reduced by this treatment. It appears, therefore, that the chromium occupied sites on the collagen which would normally fix zirconyl chloride, and other sites on the protein are not of major importance in fixing zirconium from zirconyl chloride solution. The amount of zirconium fixed by chromium tanned pelt was less than 7% of that fixed by normal collagen. The fixation by chromium tanned pelt of zirconium from zirconyl sulphate solution was still substantial, although the amount was reduced to about 40% of the potential. Thus in tanning with zirconyl sulphate, sites occupied by chromium account for only part of the fixation of zirconium. The aldehyde treatment of the chromium tanned leather still further reduced the fixation of zirconium from zirconyl sulphate solutions, indicating that the aldehyde occupied sites which were auxiliary binding sites for the zirconium in this system, but not in chloride solution. Although citrate masking increased the fixation of zirconium by normal collagen, the reverse was the case when chromium tanned collagen was the substrate.

The average increase in shrinkage temperature by treatment with chromium was 58^{o}C, but this increased hydrothermal stability of the collagen was considerably reduced when the pelt was retanned with zirconyl chloride, although the over-all chromium content had not been reduced. Thus the chromium-collagen complex must have been modified by treatment with zirconyl chloride although very little of this zirconium reagent was fixed. The shrinkage temperature of the chromium tanned collagen was not affected when zirconyl sulphate was used in retannage, notwithstanding a large reduction in the chromium content of the leather. Appreciable quantities of zirconium were fixed under these conditions. Treatment of the chromium tanned collagen with glutaraldehyde before zirconium retannage resulted in both lower chromium contents and reduced zirconium fixation, but this was not accompanied by a loss in hydrothermal stability.

These results are consistent with the view that zirconyl

chloride, which appears to depend upon reaction with carboxyl groups for combination with collagen, takes the place of chromium compounds when these are temporarily released from co-ordination to the protein. Whilst this does not necessarily displace chromium from collagen it does cause disruption of the cross-linking of the chromium tannage resulting in unipoint fixation of both chromium and zirconium with consequent loss of hydrothermal stability. Zirconyl sulphate, which has little affinity for the carboxyl groups on the protein, does not disrupt the chromium tannage but evidently displaces chromium complexes loosely held by auxiliary valencies which do not contribute significantly to the high level of hydrothermal stability conferred by co-ordination. The reaction of the glutaraldehyde which blocked the reactive basic groups reduced the take up of zirconyl sulphate at these sites, but because of the effective cross-linking action of this aldehyde, the effect on hydrothermal stability is masked. The aldehyde pre-retannage did not affect the fixation of zirconyl chloride, another indication that amino groups are not important in tannage with this salt.

3(c) The Reaction of Zirconium with Chromium Tanned Pelt [120, 124, 126, 127]

Use is made of the plumping action of zirconium for retanning chromium tanned pelt[63, 125]. This procedure produces leather which has several advantages over the conventional chrome-retan leather. Chief among these are its storage stability, an all-mineral tannage with better dyeing properties, and very pale coloured leather which forms an excellent base for pastel shades. However, numerous disadvantages of the process are to be recognised: apart from the high cost of zirconium tanning materials, drawbacks include the difficulty in obtaining zirconium and fatliquor penetrations, and the harsh feel of the leather.

Woodroffe[63] has recommended a procedure which works well in practice, but no systematic study of the factors has been made. Difficulties with penetration are no longer a problem[112], but the efficacy of various suggested factors were yet to be proved, and the following experiment was undertaken to investigate the zirconium retannage of chromium tanned leather, to verify the recommended conditions.

The experiment was planned as a 1/4 replicate of a 2^9 factorial design, giving a total of 128 treatment combinations. The factors varied and the levels of the factors were as follows:

A Quantity of chromium offered

(1) 0.5% Cr_2O_3 as 33% basic chromium salt
a 2.0% Cr_2O_3 as 33% basic chromium salt

B Presence of chromium stable fatliquor in chrome tannage

(1) none
b 1% of a suitable sulphited oil

C Pre-retan addition of masking agent for zirconium

(1) none
c 0.8 equiv. or 0.5 equiv. citrate/mole ZrO_2

D Quantity of zirconium offered

(1) 1.25% ZrO_2 as 45% basic salt
d 2.0% ZrO_2 as 45% basic salt

EF Addition of oil during zirconium tannage

(1) none
e 1% cationic fatliquor
f 0.5% cationic fatliquor plus 0.5% raw oil
ef 1% raw oil emulsified with a non-ionic surface active agent

GH Addition of syntan after zirconium tannage

(1) none
g 1% neutralised syntan
h 1% replacement type white syntan
gh 1% complex basic aluminium salt

J Neutralising material

(1) 2% sodium bicarbonate
j 1% sodium acetate plus 1% sodium bicarbonate.

The general procedure for the preparation of the leathers is given in Chapter 2, but details are given in a separate publication[120], and these, together with the results of technological importance are given in Vol. 2, p. 1 and 20.

Certain properties, namely, stiffness, thickness, looseness of the grain, colour, and extractable fats and oils are only of technological interest; of greater importance to the subject under investigation are those properties which give some measure of the reaction between zirconium and prechromed pelt. Moreover, the effect of ageing is likely to be of interest and the ageing characteristics of the leathers were determined after storage both in the standard atmosphere and at elevated temperature and humidity.

The chromium content of the leathers was obviously influenced by the quantity of chromium offered, but the degree of retannage with zirconium sulphate had no significant effect. Thus stripping of chromium during the retannage did not appear to be serious, although no direct measure of chromium displacement was made. Apart from the increased zirconium content with increase in the amount of zirconium offered, it is interesting to note that the presence of citric acid increased the fixation of this metal, but only when the small amount of zirconium was offered as shown in Table 3(c), I.

Table 3(c), I
Zirconium Content, % ZrO_2

Pre-retan addition	Quantity of Zirconium offered		Mean
	1.25% ZrO_2	2.0% ZrO_2	
none	1.67	3.47	2.57
1% citric acid	1.93	3.45	2.69
Mean	1.80	3.46	2.63

Retannage with zirconium reduced the shrinkage temperature, the increased effect of the higher level of retannage being particularly noticeable in leathers with a high chromium content. Thus the shrinkage temperature of the lightly prechromed leathers fell by only 0.5°C on increasing the quantity of zirconium offered, but the difference was more than 2°C in leathers containing the large amount of chromium. The shrinkage temperature was also affected by the pre-retan addition of citric acid which prevented a large fall in hydrothermal stability. The effect of citric acid addition is evident in Table 3(c), II.

Table 3(c), II
Shrinkage Temperature, °C

Pre-retan addition***	Quantity of Zirconium offered*		Mean
	1.25% ZrO_2	2.0% ZrO_2	
none	97.4	94.7	96.1
1% citric acid	98.1	98.3	98.2
Mean	97.8	96.5	97.2

A high shrinkage temperature does not necessarily correspond with a high zirconium content, and as previously mentioned, loss of chromium is not significant. Thus the nature of the chromium-collagen complex must be altered by retannage with zirconium. It is of considerable importance to note that shrinkage temperature of the leathers did not alter materially on ageing.

The pH values of the unaged leathers in themselves are not of great importance because they can easily be altered by subsequent treatments. Very small differences were noted, increased acidity of the leathers being attributed to increase in the quantity of chromium and zirconium offered, and the presence of citric acid, the range of pH values being between 4.12 and 4.45, with an average of 4.32. After ageing at elevated temperature and humidity the average pH had fallen to 4.16 and after natural ageing to 4.18. These differences of about 0.15 of a pH unit in that pH range constitute a negligible change in acidity.

All the leathers prepared in this experiment possessed very good physical properties, the average values being: slit tear strength,

516 lb./in.; lastometer load at grain crack, 2875 lb./in.; and lastometer extension at grain crack, 12.0 mm. These figures are in line with what would be expected for good quality full-chrome leather, and considerably in excess of average physical test results of conventional chrome-vegetable retan leather. Thus retannage of chromium tanned leather with zirconium appears to have no serious drawbacks as far as quality is concerned. On ageing, the deterioration was no more than is expected of full-chrome leather, thus there is no evidence of a subsequent reaction involving complex formation between zirconium and the chromium-collagen complex. Moreover, with increasing zirconium content deterioration was reduced, indicating increased stability with increasing degrees of retannage, even under the most rigorous ageing conditions.

In a subsequent experiment[126,127], the effect of different zirconium compounds was studied in combination tannages with chromium or as a retannage on chromium tanned leather. Other factors which are known to affect leather quality, but which are unconnected with the reaction of zirconium or chromium with pelt, were included in this experiment which was planned as a 1/4 replicate of a 2^{10} factorial design, giving 256 treatment combinations. The factors varied and the levels of the factors were as follows:

A Duration of liming

(1) ordinary sulphide lime
a ordinary lime plus 3 days in white lime

BC Deliming material

(1) 1% ammonium chloride
b 1.5% ammonium sulphate
c 1% formic acid
bc 1% acetic acid

D Quantity of chromium offered

(1) 1.5% Cr_2O_3 as 33% basic chromium salt
d 2.5% Cr_2O_3 as 33% basic chromium salt

E Period at which zirconium tannage was applied

(1) during chromium tannage
e after chromium tannage in a fresh float

FG Type of retanning material

(1) none
f 1% Al_2O_3 as complex aluminium salt
g 1% ZrO_2 as 45% basic salt
.fg 1% ZrO_2 as 45% basic salt containing silica

H Addition of cationic fatliquor during retannage

(1) none
h 1% neatsfoot oil emulsified with a cationic/nonionic emulsifier

J Type of neutralising material

(1) 1% sodium bicarbonate
j 1% sodium acetate plus 1% sodium bicarbonate

K Type of final fatliquor

(1) 4% neatsfoot oil emulsified with a cationic/nonionic emulsifier
k 5% sulphated neatsfoot oil plus 2% nonionic surface active agent on oil weight.

Details of the preparation of the leathers are given in a separate publication[126], and these together with the results of technological importance are given in Vol. 2, p. 28 and 42. As mentioned in the previous section, a large number of properties were measured and these are fully discussed in the section referred to above. For the purposes of this dissertation mention will be made of only those properties which gauge the extent of reaction of the mineral tanning agents and pelt.

The amounts of mineral tanning agent (aluminium or zirconium) offered in addition to the chromium were less than in the previous experiment and consequently the amount in the leather was less. Moreover, the method of application was different and the chromium content of the pelt was generally higher. Thus the results of the two experiments are not directly comparable.

The chromium contents of the leathers given the two levels of chromium were 2.20% and 3.13% Cr_2O_3, and the combination tannages with zirconium or aluminium whether in the chromium tannage or as a retannage had no significant influence on these values. The leathers retanned with the aluminium salt had an average Al_2O_3 content of 1.04%, and those retanned with the two zirconium salts had ZrO_2 contents of 0.95% and 1.00% respectively; the level of pretannage with chromium

did not affect the uptake of these metals.

The shrinkage temperature of the leathers was considerably increased by the combination of chromium and aluminium, but the hydrothermal stability tended to be reduced if the leathers were retanned with zirconium. This effect is shown in Table 3(c), III.

Table 3(c), III
Shrinkage Temperature, °C

Retannage**	Retanning Material***				Mean
	None	Al_2O_3	ZrO_2	ZrO_2+SiO_2	
during Cr	117	126	119	116	120
after Cr	115	120	112	111	114
Mean	116	123	116	114	117

Of particular interest was the fact that the shrinkage temperatures were consistently higher if the zirconium or aluminium tanning agents were added in admixture with the chromium than if they were applied subsequently as a retannage. Furthermore, the hydrothermal stability of the leathers did not alter on ageing.

The pH values of the leathers varied between 3.69 and 3.81, only the type of neutralising material having a significant effect between these narrow limits. Moreover, on ageing the pH dropped by not more than 0.2 of a unit, and this small increase in acidity could not be attributed to any of the factors.

The physical properties of these leathers, namely slit tear, 475 lb./in.; lastometer load at grain crack, 2072 lb./in. and lastometer extension, 10.7 mm., were very good, and the ageing characteristics of the zirconium combination tanned leathers were excellent, but the aluminium combination tannages deteriorated more than the full-chrome. The average losses on natural ageing were: slit tear, 0.52%; lastometer load, 0.05%; and lastometer extension, 3.36%. These losses are so insignificantly small that they can be disregarded and are indicative of the excellent storage stability of these leathers.

Discussion

The most interesting effect and one of considerable theoretical importance was the reduction in shrinkage temperature when chromium tanned leather was retanned with zirconium. In general, increased fixation of tanning material resulted in greater hydrothermal stability as was found in the combination chromium-aluminium tanned leathers, but the reverse was the case in the combination chromium-zirconium tanned leathers.

Also of considerable importance was the fact that the physical properties of chromium tanned leathers were not seriously affected by retannage with zirconium, and that no deterioration occurred on ageing. Although the change in shrinkage temperature on retanning suggests an interaction of zirconium with the chromium-collagen complex, this reaction must be completed during the retannage because there was no evidence of further interaction on storage. Thus these combination tanned leathers, once formed, must be perfectly stable. These results are consistent with the theory that, whereas vegetable tannins displace sulphate groups from the chromium complex with release of acid, which hydrolyses the protein on ageing under humid conditions, zirconium compounds displace chromium complexes without the formation of acid.

CHAPTER 4

CONTRIBUTION TO THE STUDY OF THE REACTION OF VEGETABLE TANNINS WITH THE CHROMIUM-COLLAGEN COMPLEX

4(a) The Reaction of Mimosa Extract with Chromium Tanned Collagen[128]

The development of acidity in chrome-retan leather on ageing indicates that the reaction of the vegetable tanning material with the chromium-collagen complex is not completed during the normal period of retannage for upper leather, and slow reactions must take place after the completion of the tannage. Thus, although the reaction is slow in air-dry leather, the reaction can be accelerated if the leather is kept moist, a result confirmed by artificial ageing treatments at high humidity[87,129-131], and by the fact that exclusion of moisture reduces the deterioration on ageing[88]. Several workers attribute this reaction to the action of the non-tannins on the chromium complex[29,30,38], although others have shown that interaction occurs between chromium and both the non-tannins and the tannins of vegetable tanning extracts[39-41,43,132]. Thus there may be some fractions in mimosa extract that react rapidly with the chromium-collagen complex and others that react more slowly, but it is probable that there is a mass-action relationship and that the rate of reaction is rapid at first but becomes slower with time.

The purpose of the present investigation was to study the effect of various factors in the manufacture of chrome-retan leather on the sulphate and chromium displacement, and the development of acidity and the fixation of tannins during the manufacture of leather and on storage. Two parallel experiments were conducted, in each case the same amounts of tannins were offered to the chromium tanned pelt but in one case it was added as purified tannin having an analysis of 97.91% tannin, and in the other as whole extract having an analysis of 76.36% tannin on a dry solids basis.

The experiments were planned as 1/4 replicates of a 2^8 factorial design, giving a total of 64 treatment combinations. The factors varied and the levels of the factors were as follows:

A Quantity of chromium offered

(1) 4% Cr_2O_3 on collagen (0.53 mg.atoms/g. collagen)
a 7% Cr_2O_3 on collagen (0.92 mg.atoms/g. collagen)

B Basicity of chromium salt

(1) 33% basic chromium sulphate
b 50% basic chromium sulphate

C Masking of chromium salt

(1) not masked
c formate masked, 1 mole formate/mole Cr_2O_3

DE pH of retannage

(1) pH 3.0
d pH 4.0
e pH 6.0
de pH 8.0

FG Quantity of mimosa tannins offered

(1) none
f 4% tannin on collagen
g 8% tannin on collagen
fg 16% tannin on collagen

H Temperature of retannage

(1) 20°C
h 35°C

1. Analysis of Spent Retan Liquors

(i) Chromium content was determined on each liquor, the results being recorded as mg. atoms Cr/g. collagen.

Very little chromium was found in the liquors, the average amount stripped by the purified tannins being only about 0.5% of the chromium present in the pelt, and 1.1% of the chromium was stripped by the whole extract. The most important factor in determining the amount of chromium in the liquors was the level of chromium offered. Smaller amounts of chromium were displaced from the pelt which was offered the low level of chromium, whereas considerably more was stripped from the highly tanned pelt. The effect of tannins and whole extract is shown in Table 4(a), I, the greater activity of the whole extract probably resulting from the weakly acid non-tannins.

Table 4(a), III

Displaced Chromium in Retan Liquors

10^3 mg. atoms Cr/g. collagen

	pH of Retannage***				
	3.0	4.0	6.0	8.0	Mean
pure tannin	3.53	2.53	1.99	1.32	2.34
whole extract	6.70	4.76	4.82	3.79	5.01

Table 4(a), IV

Displaced Chromium in Retan Liquors

10^3 mg. atoms Cr/g. collagen

	Level of Retannage**				
	nil	4% tans	8% tans	16% tans	Mean
pure tannin	0.97	2.41	2.50	3.36	2.34
whole extract	0.96	5.42	6.42	7.26	5.01

Table 4(a), I
Displaced Chromium in Retan Liquors
10^3 mg. atoms Cr/g. collagen

	Quantity of Chromium Offered***		
	4% Cr_2O_3	7% Cr_2O_3	Mean
pure tannin	0.76	3.92	2.34
whole extract	3.01	7.03	5.01

Masking reduced the displacement of the chromium at the high level of chromium tannage, but the effect, although significant, was relatively small. Of greater significance was the fact that the leathers tanned with 50% basic chromium sulphate were more resistant to displacement by mimosa tannins and extract than those tanned by the 33% basic salt, and this effect is shown in Table 4(a), II. This is probably the result of the greater stability of the masked or higher basicity chromium salts.

Table 4(a), II
Displaced Chromium in Retan Liquors
10^3 mg. atoms Cr/g. collagen

	Basicity of Chromium Salt***		
	33% basic	50% basic	Mean
pure tannin	3.01	1.68	2.34
whole extract	6.18	3.86	5.01

Of almost equal importance was the pH of retannage; the lower the pH, the greater the quantity of chromium in the liquor, the amount of chromium stripped at pH 3 being considerably higher than at other pH levels, see Table 4(a), III. Thus it is obvious that some chromium was stripped even at high pH, but this was mainly associated with the high level of retannage, the high pH probably promoting complex formation between the tannin and the chromium. The effects of the four levels of retannage are given in Table 4(a), IV, which shows that as expected the amount of chromium displaced increased with increase in the level of retannage.

The temperature of retannage had no significant influence on the results.

Table 4(a), V

Free Sulphate in Retan Liquors

10^2 m. moles SO_4/g. collagen

Pure Tannin	Level of Retannage***				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	0.55	0.67	0.85	1.00	0.77
4	0.57	1.00	0.87	1.20	0.91
6	0.57	1.15	1.32	1.85	1.22
8	0.60	1.10	1.55	2.50	1.44
Mean	0.57	0.98	1.15	1.64	1.08

Whole Extract	Level of Retannage***				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	0.60	0.41	0.62	0.66	0.58
4	0.66	0.85	1.06	1.27	0.96
6	0.60	0.87	1.25	1.76	1.12
8	0.60	1.16	1.76	3.00	1.63
Mean	0.62	0.82	1.18	1.68	1.07

(ii) Free sulphate was determined and recorded as m. moles SO_4 per gram of collagen. The average amount of sulphate in the liquors was not dependent on whether the pelt had been retanned with pure tannin or with whole extract; in each case the sulphate in the retan liquors was slightly in excess of 1.0×10^{-2} m. moles SO_4/g. collagen.

More sulphate was found in the liquors after retanning the pelt with the higher chromium content***, the average values being: low chrome, 0.89; high chrome, 1.29×10^{-2} m. moles SO_4/g. collagen. More sulphate was also given with the unmasked chromium***, the average values being: unmasked, 1.19; masked, 0.96×10^{-2} m. moles SO_4/g. collagen. In the absence of tannin, pH of treatment had no significant influence on the amount of sulphate in the liquors, but with increasing amounts of tannin and with increasing pH of retannage, progressively more sulphate was found in the liquors. This effect is given in Table 4(a), V, from which the influence of the type of retanning material can also be gauged.

(iii) pH values of the liquors were measured immediately after expressing from the hide powder, greater acidity being found in those liquors from the pelt tanned with the high level of chromium*** (low chrome, pH 5.1; high chrome, pH 4.7), from the pelt tanned with low basicity chromium ***, (33% basic chromium, pH 4.6; 50% basic chromium pH 5.2), and from pelt tanned in unmasked chromium liquors *** (not masked, pH 4.6; formate masked, pH 5.2). Increasing the level of retannage increased the acidity of the liquors, but at the lower pH levels of retannage the increase in acidity was more marked, see Table 4(a), VI, from which will be seen the insignificant effect of the purity of the retanning material.

Table 4(a), VI
pH of Spent Retan Liquors

Pure Tannin	Level of Retannage ***				
pH of Retannage ***	Nil	4% tans	8% tans	16% tans	Mean
pH 3	4.8	4.4	4.1	3.9	4.3
4	5.4	4.8	4.6	4.0	4.7
6	5.6	5.1	5.2	4.9	5.2
8	5.7	5.5	5.3	5.0	5.4
Mean	5.4	5.0	4.8	4.5	4.9

Whole Extract	Level of Retannage ***				
pH of Retannage ***	Nil	4% tans	8% tans	16% tans	Mean
pH 3	4.8	4.4	4.3	4.2	4.4
4	5.2	5.0	4.9	4.8	5.0
6	5.2	5.2	5.1	5.0	5.1
8	5.5	5.4	5.3	5.2	5.4
Mean	5.2	5.0	4.9	4.8	5.0

2. Assessments of Unaged Leathers

(i) Fixation of vegetable tanning material was determined by reference to the weight yield relative to collagen and the results are recorded as g. tannin/100 g. collagen.

Increasing the amount of tannin offered increased the amount of tanning material taken up by the pelt. Comparison of the figures for the pure tannin and whole extract, Table 4(a), VII, shows that the amount of tannin absorbed by the chromium tanned pelt was greater when the purified tannin was used as the retanning material - less tannin was fixed from whole extract although the same quantity of tannins was offered in each case. The fact that the values for tannin fixed are not zero when no tannin was offered is indicative of the imprecise nature of this assessment. The negative values in fact show there was a small loss.

Table 4(a), VII
Tannin Fixed (g. tannin/100 g. collagen)

	Level of Retannage***				Mean
	Nil	4% tans	8% tans	16% tans	
pure tannin	- 0.6	4.0	6.4	12.4	5.6
whole extract	- 0.4	3.0	4.8	13.2	5.1

Almost double the amount of tannin was fixed by the pelt offered the higher amount of chromium, the amounts of tannin fixed from pure tannin being slightly higher than from whole extract, see Table 4(a), VIII. Masking of the chromium pretannage reduced the fixation of tannins by the pelt, the effect being the same whether pure tannin or whole extract was used, as shown in Table 4(a), IX. Formate probably competed with tannin for co-ordination sites on the chromium, accounting for the above effect of masking.

Table 4(a), VIII
Tannin Fixed (g. tannin/100 g. collagen)

	Quantity of Chromium Offered***		Mean
	4% Cr_2O_3	7% Cr_2O_3	
pure tannin	3.9	7.3	5.6
whole extract	3.9	6.3	5.1

Table 4(a), IX
Tannin Fixed (g. tannin/100 g. collagen)

	Masking of Chromium***		Mean
	Not masked	Formate masked	
pure tannin	7.0	4.2	5.6
whole extract	6.6	3.6	5.1

(ii) Extractable tannin increased with increasing amount of vegetable tannin offered but this result was considerably influenced by the pH at which the retannages were performed. The results for the two types of retanning material (pure tannin or whole extract) are shown in

Table 4(a), X

Extractable Tannin in Unaged Leathers

g. tannin/100 g. collagen

Pure Tannin	Level of Retannage***				
pH of Retannage**	nil	4% tans	8% tans	16% tans	Mean
pH 3	0.03	0.53	1.19	4.80	1.64
4	0.02	0.50	1.06	3.71	1.32
6	0.03	0.46	0.77	2.14	0.85
8	0.03	0.39	0.67	1.95	0.76
Mean	0.03	0.48	0.92	3.14	1.14

Whole Extract	Level of Retannage***				
pH of Retannage*	nil	4% tans	8% tans	16% tans	Mean
pH 3	0.05	1.09	2.09	5.32	2.14
4	0.04	0.80	1.69	3.94	1.62
6	0.05	0.50	1.30	3.30	1.29
8	0.04	0.56	1.32	3.24	1.29
Mean	0.05	0.76	1.60	3.95	1.59

Table 4(a), X, from which it will be seen that more tannin was loosely bound if the leathers had been retanned with whole extract than if they were retanned with pure tannin. The non-tannins probably react preferentially, with the result that less tannin is irreversibly fixed. pH had no significant effect on the fixation of vegetable tanning material, yet this factor was highly significant in relation to the amount of tannin extracted by solvent. Thus with increasing acidity more tannins were free to be extracted and the high pH of retannage resulted in high levels of irreversibly bound tannin, as would be expected from the greater reactivity of ionised groups in the tannin.

The amount of extractable tannin was greater at the lower level of chromium tannage than at the high; less tannin was extracted from pelt tanned with low basicity chromium than from that tanned with the high basicity chromium; and less was extracted from the unmasked chromium tanned pelt than from the masked. These effects are shown in Tables 4(a), XI, XII and XIII which indicate the effect of the purity of the vegetable tanning materials. The significance of these differences is much reduced in the case of the whole extract.

Table 4(a), XI
Extractable Tannin in Unaged Leathers

g. tannin/100 g. collagen

	Quantity of Chromium Offered**		
	4% Cr_2O_3	7% Cr_2O_3	Mean
pure tannin	1.35	0.93	1.14
whole extract	1.85	1.34	1.59

Table 4(a), XII
Extractable Tannin in Unaged Leathers

g. tannin/100 g. collagen

	Basicity of Chromium*		
	33% basic	50% basic	Mean
pure tannin	0.93	1.35	1.14
whole extract	1.53	1.65	1.59

Table 4(a), XIV

Increase in Shrinkage Temperature, ^{o}C

Pure Tannin	Level of Retannage***				
Chromium offered***	nil	4% tans	8% tans	16% tans	Mean
4% Cr_2O_3	51	56	61	62	57
7% Cr_2O_3	63	64	65	66	64
Mean	57	60	63	64	61

Whole Extract	Level of Retannage***				
Chromium offered***	nil	4% tans	8% tans	16% tans	Mean
4% Cr_2O_3	55	56	57	60	57
7% Cr_2O_3	61	63	64	66	63
Mean	58	59	61	63	60

Table 4(a), XIII
Extractable Tannin in Unaged Leathers

g. tannin/100 g. collagen

	Masking of Chromium***		
	Not masked	Formate masked	Mean
pure tannin	0.87	1.34	1.14
whole extract	1.55	1.63	1.59

(iii) Chromium content of the leathers was determined as mg. atoms of chromium/g. of collagen.

The amount of chromium offered obviously had a considerable influence on the results*** (low chromium, 0.37; high chromium, 0.65 mg. atom Cr/g. collagen). The more basic tannage fixed more chromium*** (33% basic chromium, 0.46; 50% basic chromium, 0.51 mg. atom Cr/g. collagen). This assessment was too insensitive to detect differences due to the other factors.

(iv) Shrinkage temperature increased considerably with increasing degree of retannage when the pelt had been pretanned with the low level of chromium, but the increase was not as marked when the larger amount of chromium had been offered, showing that the high chromium content gave better hydrothermal stability. The effect of the type of retanning material on this interaction is given in Table 4(a), XIV.

Higher increases in shrinkage temperatures were obtained from the highly basic liquors* (33% basic chromium, $\Delta Ts = 60^{\circ}C$; 50% basic chromium, $\Delta Ts = 62^{\circ}C$) and from the masked chromium tannages* (unmasked, $\Delta Ts = 59^{\circ}C$; masked, $\Delta Ts = 62^{\circ}C$).

(v) pH values of aqueous extracts of the leathers showed that increased acidity resulted when the high level of chromium was used in tanning*** (low chromium, pH 4.2; high chromium, pH 3.7), when low basicity liquors were used*** (33% basic chromium, pH 3.8; 50% basic chromium, pH 4.1), and if the leathers were unmasked*** (unmasked, pH 3.8; masked, pH 4.1).

Increasing the amount of tannin offered increased the acidity of

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Table 4(a), XV

pH of Unaged Leathers

Pure Tannin	Level of Retannage***				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	3.9	3.4	3.2	3.0	3.4
4	4.4	3.9	3.5	3.3	3.8
6	4.4	4.2	4.0	4.0	4.2
8	4.7	4.4	4.3	4.3	4.4
Mean	4.4	4.0	3.8	3.7	4.0

Whole Extract	Level of Retannage***				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	3.9	3.7	3.7	3.6	3.7
4	4.2	4.0	4.0	3.9	4.0
6	4.2	4.0	4.0	4.1	4.1
8	4.5	4.2	4.2	4.1	4.3
Mean	4.2	4.0	4.0	3.9	4.0

the leather particularly if the retan liquors were acidifed before use, see Table 4(a), XV, but the effect of pH of treatment had no marked effect if the leathers were not retanned. Table 4(a), XV also shows the insignificantly small effect due to the type of retanning material.

(vi) Free sulphate extracted from the leathers was greater when the higher amount of chromium was used in the pretannage, especially with low basicity liquors and when the chromium liquors were unmasked. The effects of these factors and the purity of the vegetable retanning materials are shown in Tables 4(a), XVI, XVII and XVIII. These results show that the masked and more basic chromium tannages, containing less sulphate, are more stable.

With increasing levels of retannage increasing amounts of sulphate were liberated except when the retannage was conducted under very acid conditions. Thus from Table 4(a), XIX, it is seen that relatively large amounts of sulphate were free in the lightly retanned or full-chrome pelt, free sulphate decreasing with increasing tannin offered at the low pH level, whereas under the more normal conditions of pH of retanning little displacement occurred at the low level of retannage, but considerable amounts of free sulphate were found at the higher levels of retannage. The pH effect is also most interesting. Apart from the abnormally low pH of 3, the lower pH values result in less sulphate displacement than the higher. Thus there is probably an optimum pH level at which sulphate displacement is at a minimum, but these values must be considered in relation to the pH values and ageing characteristics of the leathers.

Table 4(a), XVI

Free Sulphate in Unaged Leathers

10^2 m. moles SO_4/g. collagen

	Quantity of Chromium Offered**		Mean
	4% Cr_2O_3	7% Cr_2O_3	
pure tannin	8.8	17.9	13.4
whole extract	8.4	15.2	11.8

Table 4(a), XVIII

Free Sulphate in Unaged Leathers

10^2 m. moles SO_4/g. collagen

	Masking of Chromium**		
	not masked	formate masked	Mean
pure tannin	16.9	9.8	13.4
whole extract	14.0	9.5	11.8

Table 4(a), XIX

Free Sulphate in Unaged Leathers

10^2 m. moles SO_4/g. collagen

Pure Tannin	Level of Retannage**				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	13.8	11.3	7.3	3.5	9.0
4	4.8	4.5	5.8	11.5	6.7
6	3.0	9.5	25.5	28.5	16.6
8	10.5	18.0	22.0	34.3	21.2
Mean	8.0	10.8	15.2	19.5	13.4

Whole Extract	Level of Retannage**				
pH of Retannage***	nil	4% tans	8% tans	16% tans	Mean
pH 3	11.9	11.0	8.0	2.9	8.4
4	4.1	3.6	10.4	12.4	7.6
6	6.6	8.7	15.5	26.5	14.3
8	4.6	11.6	15.2	35.0	16.6
Mean	6.8	8.7	12.3	19.2	11.8

Table 4(a), XVII
Free Sulphate in Unaged Leathers
10^2 m. moles SO_4/g. collagen

	Basicity of Chromium*		
	33% basic	50% basic	Mean
pure tannin	14.9	11.8	13.4
whole extract	15.6	7.9	11.8

Discussion

The results indicate that chromium was displaced during the retanning treatments whether purified tannin or whole extract was used, and although a small amount of chromium was found in the liquor obtained after treating neutralised chromium tanned pelt with water, the quantity of chromium in the spent retan liquors increased progressively as the quantity of tannin offered increased. Thus the mimosa tannins undoubtedly had a stripping and solubilising action on the chromium complexes in the leather although more chromium was displaced by the whole extract than by the pure tannin. Two possible reasons can be advanced to explain the increased reactivity of the whole extract on retannage. The leathers retanned with extract were offered a greater total of soluble solids than when purified tannin was used, and therefore are likely to have shown greater chromium displacement, but more probably the non-tannins, which include a significant quantity of ionisable groups[52], were largely responsible for the increased effect. Another important observation was that masking and increase in basicity of the chromium reduced the displacement of the chromium, which indicates that the masked chromium-collagen complexes and those of greater basicity were more stable and therefore resistant to the action of vegetable tannin.

In the same way, the amount of sulphate in the spent retan liquors increased with the amount of tannin offered, although in this case there was no significant difference between the retannages using purified tannin or the whole extract. However, of equal importance was the pH at which the retannages were effected, the higher pH resulting in increased sulphate displacement. It is interesting to note that the amount

of sulphate in the tannin-free liquors was almost constant, regardless of pH, which indicates that this quantity was ionic whereas the tannins displaced complexly bound sulphate groups.

Analysis showed that the pH values of the aqueous extracts of the leathers were considerably less than the pH of the spent retan liquors, in some cases by as much as 1 pH unit. Since the fall in pH can be attributed to the acidity developed by the displacement of sulphate, the sulphate displacement after retanning, (during cessing and drying) must be considerable. This is exactly what was found, about 10 times more free sulphate being extracted from the leather than was present in the spent retan liquors. With the exception of the very low pH of retannage, the amount of sulphate extracted from the unaged leathers increased with increasing degree of retannage, from which it is evident that the vegetable tannin reacted with the chromium complexes by displacing sulphate. If the retannage was conducted with liquors adjusted to pH 3.0 (the chromium tanned pelt being neutralised to pH 5.5), increasing the tannin content of the retan liquors caused a reduction in the quantity of free sulphate extracted from the leather, which may be explained as follows.

Addition of solutions of tannin at pH 3.0 to a system at pH 5.5 yields final pH values which vary depending on the tannin concentration. Reference to the pH values of aqueous extracts of the leathers (Table 4(a), XV) shows that tannins buffer the system, the larger quantity of tannin maintaining a relatively greater acidity than the weaker tannin solutions, and hence the ionisation of the tannin in the strong solution was less than in the more dilute solutions. Since it is likely that only ionised tannins (and non-tannins) co-ordinate with the chromium with displacement of sulphate, the greatest amount of sulphate is liberated by those solutions containing the largest number of ionised species. Thus, at pH 3, less sulphate was displaced by the 16% tannin solution than by the weaker tannin solutions, because fewer ionised groups were present in the former, more concentrated solution.

The tannin extracted with azeotropic methyl ethyl ketone can be considered to be that part which is either deposited within the pelt structure or loosely bound to reactive sites on the protein, but not readily

removed by water since the leathers were well washed before drying; the unextracted portion is thought to be the more firmly bound tannin which has complexed with the chromium compounds. pH of retannage has had a very considerable influence; the higher the pH, the greater the amount of irreversibly fixed tannin. Although more tannin was fixed by pelt with the higher level of chromium tannage, both increase in basicity and masking of the chromium complex resulted in a decrease in the amounts of tannin fixed. This is further evidence that the reaction of tannins with chromium compounds was reduced when the stability of the chromium was enhanced through increased olation or the presence of a masking agent giving stronger complexes than sulphate. It is obvious that the chromium complexes were by no means saturated with tannins at the levels of retannage used in this experiment, since increasing the amount of tannin offered resulted in increasing amounts of unextractable tannin. It is surprising therefore that, at the 2% level of retannage, not all of the tannin was irreversibly fixed, and this indicates that some of the tannin must have been bound at sites on the protein before it had an opportunity to react with the chromium.

This experiment has shown that when purified polyphenolic tannins were used, the results were qualitatively similar to those using whole extract. Thus it is obvious that the tannins definitely reacted with the chromium-collagen complexes displacing sulphate which caused the fall in pH so well known to chrome-retan leather manufacturers. In certain respects, the reaction of the chromium-tanned pelt with mimosa extract had a greater effect than when the purified tannins from the same extract were used, and in contrast to the opinion of other workers[29,38], it is concluded that both the tannins and the non-tannins react with the chromium complexes. This is not without some justification on theoretical grounds since mimosa extract is relatively pure, i.e. it has a high tannin to non-tannin ratio, and much of the non-tannin consists of polyphenolic molecules too small to tan but capable of the normal chemical reactions.

Previous work has shown that leathers containing both vegetable tannin and chromium deteriorate more readily than leathers tanned with either of these materials alone, particularly if they are stored under warm,

humid conditions[32,34,59,87,88,129,130,132,133], and many of the tannage factors which are of importance in the manufacture and storage stability of chrome-retan leather have been elucidated[88,132,134]. The majority of these observations have been made on leathers from statistically planned laboratory and pilot plant experiments, from which certain deductions were made regarding the reaction mechanisms[40]. Nevertheless, these observations can be only a guide, since, in the systems studied, the materials used were by no means pure, and the minor components might influence the reactions to a greater extent than their proportions in the mixtures would suggest. Thus this present investigation was extended to study the effect of treatment variables on storage stability.

4(b) The Ageing Characteristics of Chromium Tanned Collagen Retanned with Mimosa Extract[133]

Bowes[62] has shown that hydrolytic breakdown of the polypeptide chains occurs when collagen is stored under warm, moist conditions. Such breakdown is increased by increase in acidity, rise in temperature, and increase in moisture content. Since tanning agents reduce hydrolytic breakdown, chromium being particularly effective in forming stable cross-links between the polypeptide chains, it seems strange that chromium tanned collagen should become so unstable when retanned with vegetable tanning materials. This dual tannage might be expected to increase rather than reduce the storage stability of the leathers, especially since the shrinkage temperature of the chromium tanned leather is increased on retannage, signifying an increase in the degree of cross-linking. It has been suggested that with combination tanned leathers, there is interaction between the vegetable tannins and the chromium complex leading to increased acidity and displacement of chromium from the protein, both of which could promote degradation of the protein.

While this accounts for the lack of storage stability, there are conflicting opinions expressed in the literature regarding the components of the vegetable tanning extracts which are responsible for the reaction with the chromium complexes. A fundamental study[41,43,135] of the reaction of mimosa extract and other reagents with chromium tanned pelt has shown that ionically bound sulphate was displaced by mimosa extract to a much greater extent than by pyrogallol, and that prolonged treatment of chromium tanned leather in solutions of vegetable tanning extracts resulted in losses of chromium and falls in shrinkage temperature which varied depending on the retanning material. Nevertheless, no attempt had been made to determine which component of the extracts was effective in this respect. The results indicated that the non-tannins may be most important in lowering the shrinkage temperature on ageing, since the vegetable extract with the highest proportion of non-tannins (myrobalans) had the greatest effect, and that with the lowest proportion of non-tannins (sulphited quebracho) had the least effect. In this work an attempt has been made to determine which component of mimosa extract is chiefly responsible for the slow reactions which take place on storage, and the

importance of various factors in promoting or retarding the effects.

Specimens of the leathers which had been examined and discussed in the previous section were stored and aged under the following conditions of temperature and humidity:-

Storage A	48°C, 100% r.h., 3 weeks
Storage B	48°C, 65% r.h., 3 weeks
Storage C	20°C, 100% r.h., 8 months
Storage D	20°C, 65% r.h., 8 months

At the end of each storage period the leathers were dried and conditioned, then assessed for pH of aqueous extract, free sulphate, extractable tans and shrinkage temperature, and the results are recorded and compared with the results for unaged leathers. Thus, this report deals with the changes which have occurred during storage under various conditions of temperature and humidity.

(i) <u>pH values</u> of aqueous extracts of the leathers showed that the greatest increase in acidity occurred in those leathers stored in a warm, moist atmosphere, and the least in the leathers stored at normal temperature and humidity. The average changes in pH for the four storage conditions were:

	pure tannin	whole extract
48°C, 100% r.h., 3 weeks	0.16 pH unit	0.17 pH unit
48°C, 65% r.h., 3 weeks	0.05 pH unit	0.04 pH unit
20°C, 100% r.h., 8 months	0.14 pH unit	0.16 pH unit
20°C, 65% r.h., 8 months	0.07 pH unit	0.08 pH unit

and since the original average pH of the leathers was 3.96 and 4.0 respectively, these changes do not constitute a dangerous increase in acidity. The importance of moisture is convincingly illustrated by these results; it is possible that even smaller changes would have been brought about if the humidity at which the leathers were stored had been lower than that of the standard atmosphere.

The pH differences for the two groups of leathers, one tanned with purified polyphenolic tannins and the other with whole extract, were almost identical, indicating that the changes that had occurred on storage took place to the same degree whether non-tannins were present in the system or not.

Whilst these average differences in acidity are not great, certain

Table 4(b), I

Change in pH on Storage

	Level of Retannage				Mean
	nil	4% tans	8% tans	16% tans	
Original pH	4.37	3.99	3.77	3.70	3.96
pH after storage at 48°C, 100% r.h.	4.31	3.83	3.57	3.49	3.80
pH after storage at 48°C, 65% r.h.	4.41	3.90	3.67	3.60	3.90
pH after storage at 20°C, 100% r.h.	4.32	3.88	3.62	3.50	3.83
pH after storage at 20°C, 65% r.h.	4.35	3.94	3.69	3.57	3.89

Table 4(b), II

Change in pH on Storage

	Masking		Mean
	none	formate	
Original pH	3.80	4.11	3.96
pH after storage at 48°C, 100% r.h.	3.69	3.90	3.80
pH after storage at 48°C, 65% r.h.	3.78	4.01	3.90
pH after storage at 20°C, 100% r.h.	3.64	4.03	3.83
pH after storage at 20°C, 65% r.h.	3.69	4.07	3.89

Table 4(b), III

Change in pH on Storage

	Level of Chrome		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original pH	4.30	3.61	3.96
pH after storage at 48°C, 100% r.h.	4.18	3.41	3.80
pH after storage at 48°C, 65% r.h.	4.29	3.52	3.90
pH after storage at 20°C, 100% r.h.	4.20	3.45	3.83
pH after storage at 20°C, 65% r.h.	4.25	3.52	3.89

of the factors investigated influenced the results, and some quite large variations were noted. The most significant differences were due to the level of retannage, whereas the full chrome leathers were hardly affected. These results are shown in Table 4(b), I, for the leathers retanned with the purified extract.

Another interesting effect was the influence of masking on the pH of the leathers after storage. Where the leathers had been stored at elevated temperature, and especially at high humidity, the presence of formate resulted in a greater increase in acidity, but when the leathers had been stored at normal temperatures, masking resulted in less acid being formed. These results are given in Table 4(b), II from which it will be seen that although in some cases the differences were greater, the pH values of the leathers containing formate were consistently higher than those of the unmasked leathers.

The greater the chromium content the greater the amount of acid developed on storage. Thus, after storage at 48°C and 100% r.h. it was found that the pH of the leathers pretanned with 4% Cr_2O_3 was reduced by only 0.12 of a unit, whereas leathers pretanned with 7% Cr_2O_3 showed a change in pH of 0.20. Although the changes after storage under the other conditions were not as great, the higher chrome content always resulted in the development of more acid, giving final pH values which are recorded in Table 4(b), III.

Thus it is seen that a high chromium content and a high degree of retannage resulted in increased acid development under all conditions of storage, and the presence of a masking agent was beneficial if the leathers were stored at normal temperatures; at elevated temperature formate resulted in greater acid development. When whole extract had been used for retanning, a slight but insignificantly greater increase in acidity occurred, the differences between this series and the series retanned with the purified polyphenolic fraction being of the order of 0.01 of a pH unit.

(ii) Free Sulphate in the leather, which was extracted by shaking with a solution of potassium chloride, increased by about 10% after storage at elevated temperature and humidity, but at the lower

Table 4(b), IV

Change in Free Sulphate on Storage

10^2 m. moles SO_4/g. collagen

	Level of Chrome		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original free SO_4	8.8	17.9	13.4
Free SO_4 after storage 48°C, 100% r.h.	9.5	19.6	14.6
Free SO_4 after storage 48°C, 65% r.h.	9.8	19.3	14.5
Free SO_4 after storage 20°C, 100% r.h.	9.0	18.5	13.7
Free SO_4 after storage 20°C, 65% r.h.	9.1	18.7	13.9

Table 4(b), V

Change in Free Sulphate on Storage

10^2 m. moles SO_4/g. collagen

	Level of Retannage				Mean
	nil	4% tans	8% tans	16% tans	
Original free SO_4	8.0	10.8	15.2	19.5	13.4
Free SO_4 after storage 48°C, 100% r.h.	9.0	11.9	16.4	21.1	14.6
Free SO_4 after storage 48°C, 65% r.h.	9.0	11.8	16.3	21.0	14.5
Free SO_4 after storage 20°C, 100% r.h.	8.0	11.2	15.9	20.6	13.7
Free SO_4 after storage 20°C, 65% r.h.	8.1	11.3	15.8	20.7	13.9

temperature the increase in the sulphate was negligible. The average differences in free sulphate for the four storage conditions are given below, the results being given as m. moles SO_4/g. collagen.

	pure tannin	whole extract
48°C, 100% r.h., 3 weeks	12.1×10^{-3}	19.4×10^{-3}
48°C, 65% r.h., 3 weeks	11.8×10^{-3}	16.7×10^{-3}
20°C, 100% r.h., 8 months	4.0×10^{-3}	4.7×10^{-3}
20°C, 65% r.h., 8 months	5.0×10^{-3}	2.1×10^{-3}

Thus it is obvious that the higher temperature has resulted in greater displacement of sulphate especially at the higher humidity. The high humidity at the low temperature has not caused much increase in the free sulphate. Changing the retanning material from pure tannin to whole extract has resulted in an increase in the amount of free sulphate produced on storage at the higher temperature, but the very small quantities produced at the lower temperature are insignificant and the differences between the two series under these conditions are probably not real.

The greatest increase in free sulphate occurred in those leathers pretanned with the higher level of chromium, the average results for the leathers retanned with pure tannin at the 4% Cr_2O_3 level are: 7.3, 10.0, 2.0 and 2.5×10^{-3} m. moles SO_4/g. collagen for the four storage periods respectively, and at the 7% Cr_2O_3 level are: 16.9, 13.6, 6.0 and 7.7×10^{-3} m. moles SO_4/g. collagen under the same storage conditions. These figures result in the values of free sulphate given in Table 4(b), IV, and since this factor has the same influence in the leathers retanned with whole extract, the results presented in the table are representative of both series.

The basicity of the chromium tanning compound was important only when the leathers were stored at normal temperatures. Under these conditions the high basicity chromium tannage resulted in less sulphate development than was found in the leathers given the more acid tannage. However, this factor did not result in a significant difference when the leathers were stored at elevated temperature. Thus the average increases in free sulphate in the leathers tanned with the 33% basic chrome compound were: 10.6, 11.8, 8.6 and 8.7×10^{-3} m. moles SO_4/g. collagen and for the 50% basic tannages 13.6, 11.8, 3.3 and 3.2×10^{-3} m. moles SO_4/g. collagen for the four storage periods respectively.

The increase in free sulphate was greater for the retanned leathers than for the full-chrome leathers, although the latter showed an appreciable increase in free sulphate when stored at elevated temperature. These results are given in Table 4(b), V, for each of the four storage periods.

Although there was an appreciable increase in the amount of free sulphate that could be extracted from the leathers that had been retanned with the whole extract, the tannage factors that have been considered gave similar effects to those reported above for leathers retanned with purified polyphenolic material. Thus the two series of leathers behaved similarly on storage, the greater effect of the former presumably being due to the additive presence of non-tannins.

(iii) The Amount of Extractable Tans was reduced on storage, bigger differences being found for the long period ageing at normal temperature than after the accelerated ageing at elevated temperature. The average differences in per cent extractable tans for the four storage periods are given below.

	pure tannin	whole extract
48°C, 100% r.h., 3 weeks	0.52	0.84
48°C, 65% r.h., 3 weeks	0.38	0.53
20°C, 100% r.h., 8 months	0.76	1.11
20°C, 65% r.h., 8 months	0.59	1.19

The above results indicate that more tannin was fixed when leathers were aged after retanning with whole extract than in those retanned with pure tannin. Since each series was retanned with equivalent amounts of tannin, the increased fixation is probably due to the greater amount of total solids offered with the whole extract compared with the purified fraction.

The amount of extractable tans fixed on storage depended on the degree of retannage. Obviously no tans could be extracted from the full-chrome leathers and very little extra tannin was fixed in the lightly retanned leathers since most of the tannin was fixed at the time of retannage. With increasing amounts of tannin offered, there was an increase in the amount of tannin fixed on storage, but this was dependent on the pH of retannage. At the higher pH values the amount of tannin fixed on storage was less than at the lower pH values. This interaction

Table 4(b), VII

Change in Extractable Tans on Storage

g. tannin/100 g. collagen

	Level of Retannage				Mean
	nil	4% tans	8% tans	16% tans	
Original extractable tans	0.03	0.48	0.90	3.14	1.05
Ext. tans after storage 48°C, 100% r.h.	0.05	0.44	0.64	1.30	0.52
Ext. tans after storage 48°C, 65% r.h.	0.05	0.40	0.60	1.59	0.66
Ext. tans after storage 20°C, 100% r.h.	0.04	0.20	0.36	0.59	0.29
Ext. tans after storage 20°C, 65% r.h.	0.06	0.28	0.46	1.32	0.45

Table 4(b), VIII

Change in Extractable Tans on Storage

g. tannin/100 g. collagen

	pH of Retannage				Mean
	pH 3	pH 4	pH 6	pH 8	
Original extractable tans	1.47	1.21	0.78	0.70	1.05
Ext. tans after storage 48°C, 100% r.h.	0.56	0.55	0.47	0.48	0.51
Ext. tans after storage 48°C, 65% r.h.	0.77	0.74	0.59	0.55	0.66
Ext. tans after storage 20°C, 100% r.h.	0.28	0.31	0.29	0.23	0.28
Ext. tans after storage 20°C, 65% r.h.	0.61	0.44	0.34	0.38	0.44

is given in Table 4(b), VI for the leathers aged at 48°C and 100% r.h. The effect after the other storage periods, although different in magnitude, is essentially similar, and the results given in this table serve as an example.

Table 4(b), VI

Difference in Extractable Tans after Storage at 48°C, 100% r.h.

g. tannin/100g. collagen

pH of Retannage ***	Level of Retannage ***				Mean
	Nil	4% tans	8% tans	16% tans	
pH 3	-0.02	0.08	0.49	3.14	0.91
4	-0.02	0.04	0.35	2.29	0.66
6	-0.01	0.04	0.14	1.07	0.31
8	-0.02	0.02	0.04	0.87	0.22
Mean	-0.02	0.04	0.26	1.84	0.52

The change in extractable tans after the four types of ageing are given in Tables 4(b), VII and 4(b), VIII showing the effect of the degree of retannage and of pH of retannage respectively for the leathers retanned with pure tannins.

The amount of tannin extractable by aqueous methyl ethyl ketone was considerably reduced on ageing especially for the longer period at room temperature. This indicates that tannins fix progressively with time and even a considerable increase in temperature does not compensate for the shorter storage period. Although it has been shown that moisture plays an important part in the deterioration of leather on ageing[88], increase in the moisture content of the leather by storing the leather at high humidity has had little influence on the reactivity of the tannins in the leathers. Thus the fixation of tannin on storage is not significantly increased by increasing the humidity.

Although leathers with a high chromium content tended to fix more tannin during manufacture, leaving less unfixed tannin to be extracted with aqueous methyl ethyl ketone after storage, the difference between the extractable tans for the two levels of chromium tannage is not as marked, see Table 4(b), IX. However, an important factor with regard to the increased reactivity of the low level of chromium is the humidity at which

Table 4(b), IX

Change in Extractable Tans on Storage

g. tannin/100 g. collagen

	Level of Chrome		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original extractable tans	1.22	0.88	1.05
Ext. tans after storage 48°C, 100% r.h.	0.59	0.48	0.52
Ext. tans after storage 48°C, 65% r.h.	0.84	0.50	0.66
Ext. tans after storage 20°C, 100% r.h.	0.31	0.27	0.29
Ext. tans after storage 20°C, 65% r.h.	0.57	0.34	0.45

Table 4(b), X

Change in Extractable Tans on Storage

g. tannin/100 g. collagen

	Masking		Mean
	none	formate	
Original extractable tans	0.82	1.29	1.05
Ext. tans after storage 48°C, 100% r.h.	0.42	0.67	0.52
Ext. tans after storage 48°C, 65% r.h.	0.58	0.77	0.66
Ext. tans after storage 20°C, 100% r.h.	0.28	0.29	0.28
Ext. tans after storage 20°C, 65% r.h.	0.44	0.49	0.45

the leathers were stored. The humidity of storage had no significant influence on the reactivity of the leathers with the higher chromium content, but influenced the leathers tanned with 4% Cr_2O_3.

On storage, the leathers tanned with the masked chromium liquors fixed more tannin than those tanned with the unmasked liquors, although masking originally reduced the reaction of the tannin with chromed pelt, see Table 4(b), X. Thus, although masking inhibits the reaction, the fixation of tannin proceeds with time, and on storage the amount of unfixed, extractable tannin becomes reduced and more nearly equal for the two types of leather.

The longer the storage period the greater the amount of tannin fixed, and in the case of the 8 month ageing there was no difference in the extractable tannin between the masked and unmasked leathers. In this case the humidity of storage affected both types of leather equally.

The above figures are taken from the results of the reaction of purified tannin with chromium tanned collagen and, although they differ in magnitude from the results of the reaction of whole extract with chromium tanned collagen, the trends are similar in each case. Thus the two types of retanning materials are considered to be similar in their reaction with the chromium-collagen compound.

(iv) Shrinkage Temperature decreased by a maximum of not more than 2 degrees under any of the conditions of storage. The average differences in shrinkage temperature as a result of ageing were:

	pure tannin	whole extract
48°C, 100% r.h., 3 weeks	1.6°C	1.6°C
48°C, 65% r.h., 3 weeks	1.0°C	1.4°C
20°C, 100% r.h., 8 months	1.2°C	1.0°C
20°C, 65% r.h., 8 months	1.1°C	1.0°C

Since the original average shrinkage temperatures for the two series of leathers were 115°C and 114°C for those retanned with pure tannin and whole extract respectively, the fall in shrinkage temperature is not serious. Nevertheless some of the tanning variables are important in determining the extent of these changes.

Table 4(b), XI

Change in Shrinkage Temperature on Storage

	Level of Chrome		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original shrinkage temp.	111.4	118.5	115.0
Ts after storage 48°C, 100% r.h.	110.2	118.4	114.3
Ts after storage 48°C, 65% r.h.	109.4	118.4	113.9
Ts after storage 20°C, 100% r.h.	109.7	117.7	113.7
Ts after storage 20°C, 65% r.h.	110.1	117.6	113.8

Table 4(b), XII

Change in Shrinkage Temperature on Storage

	Level of Retannage				Mean
	nil	4% tans	8% tans	16% tans	
Original shrinkage temp.	111.4	113.7	117.1	117.7	115.0
Ts after storage 48°C, 100% r.h.	111.3	113.4	116.6	116.8	114.5
Ts after storage 48°C, 65% r.h.	110.8	112.9	116.0	116.0	113.9
Ts after storage 20°C, 100% r.h.	111.2	112.9	115.8	115.8	113.9
Ts after storage 20°C, 65% r.h.	111.2	112.6	115.9	115.9	113.9

The decline in hydrothermal stability was confined almost entirely to those leathers tanned with the lower level of chromium, and the changes in shrinkage temperature for the two levels of chromium tannage under the various conditions of storage are given in Table 4(b), XI. These figures represent an average fall in shrinkage temperature of 1,5°C for the 4% Cr_2O_3 chrome tannage and 0,6°C for the 7% Cr_2O_3 chrome tannage.

Only the highest degree of retannage resulted in a significant decrease in the shrinkage temperature on storage, although retannage with the other levels of tannin also resulted in small decreases. This effect was consistent under all ageing conditions as shown in Table 4(b), XII.

It will be seen that although the shrinkage temperature of the leathers retanned with the larger amounts of tannin tended to decrease more than that of the full-chrome or lightly retanned leathers, the higher shrinkage temperatures of the former were maintained relative to the latter.

Discussion

The changes in the properties of the leathers which have occurred on ageing throw important light on the mechanism of the reaction between vegetable tannin and chromed collagen. In the first place, chrome-retan leathers have become more acid on storage, whereas full-chrome leathers have shown little change in pH. In addition, the results show that the greater the degree of retannage the greater the increase in acidity. Modification of the chromium-collagen compound by altering the chromium content, or by masking the chromium tanning salt, influenced the behaviour on storage; the higher the level of chromium tannage the greater the increase in acidity, whereas masking reduced the development of acid.

The changes in acidity, as determined by the pH of aqueous extracts of the leathers, correspond fairly closely to the change in free sulphate, the greater the increase in acidity the greater the increase in free sulphate. Thus the development of acidity in leather on storage can be ascribed to the displacement of sulphate ions from the chromium-collagen compound. Since the amount of tannin that can be extracted

from the leathers decreased on storage, it can be implied that the displacement of the sulphate ions, and hence the increase in acidity, is due to the entry of the tannin into the chromium-collagen complex. Unfortunately this is not strictly true because the results from the different storage treatments show that the system chromium-collagen-vegetable tannin does not follow such a simple pattern.

Since the change in extractable tannin is greater after storage for 8 months at 20°C than after 3 weeks at 48°C, one would expect the change in free sulphate to follow the same pattern if tan fixation is due to complex formation with the chromium-collagen compound. However, this was not the case since the increase in free sulphate was greater after the short, high temperature storage than after the longer storage at room temperature. This indicates that the changes which take place in leather on ageing are different, depending on the conditions under which it is stored. Thus an accelerated ageing test based on exposing the leather to warm, humid conditions will not give entirely reliable results. Nevertheless, in wear, leather is frequently subjected to perspiration at body heat and a test at high temperature and high humidity may provide some evidence of the perspiration resistance of the leather, although other factors, such as the accumulation of perspiration residues, must also be taken into account.

The observation that, in most cases, the longer storage period, albeit at the low temperature, has resulted in greater differences in the chemical composition of the leathers than were found after three weeks at elevated temperature is difficult to explain, since the physical properties have been shown to be affected to approximately the same degree[87]. Since the development of acidity and the displacement of sulphate after storage for the longer time at the low temperature is less than after the warm, humid storage, the increased fixation of tan under the former conditions of ageing is probably not entirely due to the reaction with the chromium-collagen compound. It is thought that oxidation and condensation of the unbound tannin is partly responsible for the decrease in extractable tans under these conditions.

The picture is further complicated when masking agents are

used, since in leathers containing organic acid anions, storage under warm, humid conditions frequently caused greater deterioration than would be expected from the results after ageing under normal conditions of temperature and humidity. In the work reported above, the results show that on storage at elevated temperature formate masked chromium tanned pelt did fix more tannin than unmasked chromium tannages. However, this increase in fixation was not accompanied by an increase in free sulphate but the increase in acidity was greater than that obtained for normal leathers. Thus, whilst masking improved the storage stability of the leather at ordinary ambient temperatures, deterioration at the higher temperature was probably the result of the presence of free organic acid which had been displaced from the chromium complex, in addition to the hydrolytic degradation usually obtained under these conditions.

It is interesting that neither the pH of the mimosa extract used for retanning nor the temperature at which retannage was effected had influenced the storage stability of the leathers. In these experiments shrinkage temperature had not been greatly affected, and, since some of the conditions of storage were very rigorous, measurement of changes in this property do not appear to be a suitable means of determining deterioration on storage. The fact that the shrinkage temperature was maintained yet physical weakness resulted, indicates that detannage was not a serious cause of deterioration, and that the loss of strength must be the result of hydrolysis of the polypeptide chains.

When whole extract was used in place of the purified mimosa tannin some very interesting and significant observations could be made. It must be remembered that an equivalent amount of tannin was offered in each of the series, thus it is obvious that the leathers retanned with whole extract were offered a greater quantity of total solids, and, if the non-tannins in the extract take part in the reactions, the effects in the second series should be greater than in the first. This was generally the case although the influence of this factor on the pH of aqueous extract and on shrinkage temperature was negligible. However, the presence of the non-tannins has resulted in the increased displacement of sulphate, especially at elevated temperature. Thus it is evident that the non-tannins in mimosa extract also react with chromium tanned collagen.

In the reaction between mimosa extract and chromium tanned pelt the following are the important points:

1. The polyphenolic tannins react with the chromium-collagen compound, displacing sulphate which caused an increase in the acidity of the system.

2. The non-tannins also react in the same way and when a mixture of tannins and non-tannins was used the effect was slightly increased due to the presence of the non-tannins.

3. Increasing the degree of retannage increased the observed effects under all conditions of storage.

4. The higher the chromium content the greater the changes which occurred on storage.

5. A masked chromium tannage produced less acid on storage at normal temperatures but at elevated temperature and humidity the acidity was increased.

6. Storage under warm humid conditions for a short period was not exactly equivalent to long term storage at normal temperature and humidity.

It is concluded that both the tannins and the non-tannins are involved in the reaction of mimosa extract with chromium tanned leather, which confirms the deductions made from observations of pilot plant tannages and commercial leathers[40]. Detannage, in particular dechroming, does not appear to be an important contributory factor in the deterioration of chrome-retan leather on storage, but the chemical changes which occur are consistent with the hypothesis that the loss of strength is the result of the hydrolysis of the protein, catalysed by the acid liberated from the chromium-collagen complex by the entry of vegetable tannins and non-tannins into the complex.

4(c) The Reaction of a Selection of Vegetable Tanning Extracts with Chromium Tanned Collagen

Mimosa extract is a relatively pure vegetable tanning material in that it has a fairly high tannin/non-tannin ratio, while much of the non-tannins also consists of polyphenolic material. Although the results from the previous sections have shown that similar results were obtained whether the purified tannins or whole extract were used for retanning chromium tanned pelt, non-tannins are claimed to play an important part in retanning[30,38]. Since certain extracts are claimed to be superior to others for this purpose[41,46,51,136], these conclusions being based on chromium stripping[41,46,51] and other properties[136], a more quantitative assessment of their reaction with chromium tanned collagen was considered to be necessary. Four vegetable tanning extracts were selected for investigation, two being of the condensed variety (mimosa and quebracho), and two hydrolysable tannins (myrobalans and chestnut)[137]. Each group therefore consisted of one extract fairly rich in non-tannins and the other of a high tannin/non-tannin ratio. The analyses of the extracts used in this work were as follows:

Retanning Material	Tannin	Tan/Nontan Ratio	Insolubles
Chestnut extract	66.84	2.11	1.48
Mimosa extract	71.34	2.57	0.90
Myrobalans extract	60.42	1.93	8.28
Quebracho extract	84.35	5.71	0.88

The results are presented as percentage of dry solids content. Insoluble matter was removed by clarification of the liquors before use.

The results of acid-base titration of the vegetable tanning extracts used in this study are shown in Fig. 4(c),1 and the approximate content of functional groups titrating over the various pH ranges are indicated below:

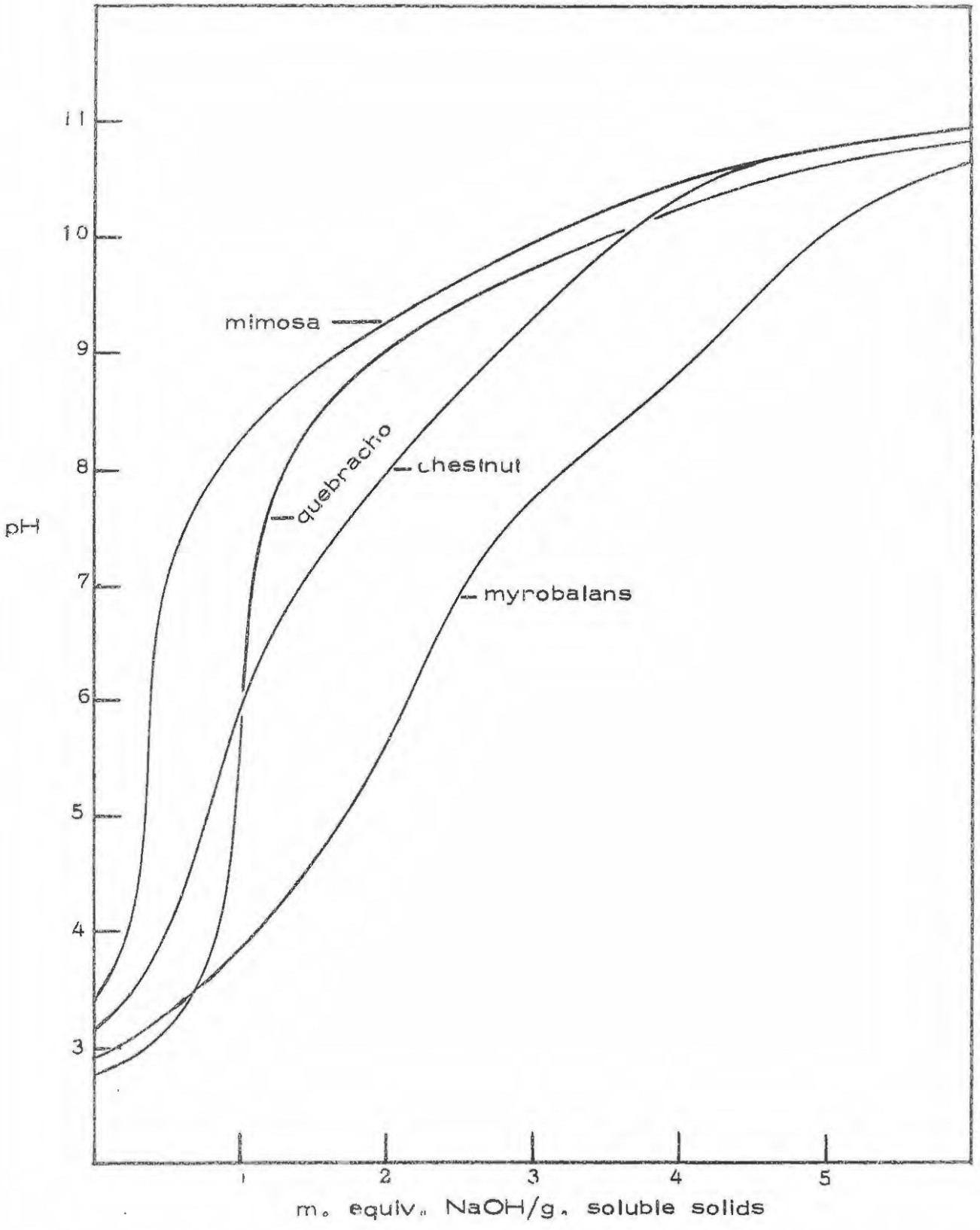

Figure 4(c), 1. Titration curves of vegetable tanning extract solutions after passage through cation exchange resins.

Approximate Content of Titrating Groups in Commercial Vegetable Tanning Extracts used in the Present Study

Vegetable Tanning Extract	Milli-equivalents ionic groups titrating per g. pH 2.5 to 6.5	pH 6.5 to 10.5	Total
Chestnut	1.2	3.0	4.2
Mimosa	0.4	3.6	4.0
Myrobalans	2.3	3.3	5.6
Quebracho	1.0	3.5	4.5

All values were determined on clarified solutions of the extracts after passage through cationic exchange resin. Quebracho extract contained 0.92 m. equivalents sulphonic acid groups.

Only about 0.35 m. equivalents/g. of ionic groups in mimosa extract titrated in the pH range of normal tannage (pH3.5 to 5.0), and this is partly accounted for (0.18 m. equivalents/g.) by the presence of amino- and imino-acids in the extract[52]. In the case of the other condensed tannin, quebracho, the titration curve revealed the presence of approximately 1.0 m. equivalent/g. of strong acid groups, the major portion of which is attributed to the presence of strong sulphonic acid groups introduced by treatment with bisulphite to confer solubility, the pKa value of which is about 3.1. Both of these extracts were comparable in showing evidence of an extensive range of titrating groups in the alkali pH region.

In the case of the hydrolysable tannins, the content of groups titrating in the acid range is considerable and particularly so in the case of myrobalans extract. The titration curves revealed the presence of about 2.3 m. equivalents/g. of weak acid groups with a pKa value of about 4.5 in myrobalans, and 1.2 m. equivalents/g. of acid groups, pKa approximately 3.8, in chestnut extract. The titration curves also showed evidence of an extended range of phenolic hydroxyl groups of ionic concentration equivalent to, but more acidic than those in the condensed tannins.

The vegetable tanning extracts were applied to chromium tanned pelt of different chromium contents, the chromium tanning salt being either

than from the low level, 1.01×10^{-3} mg. atoms chromium/g. collagen***, but masking and the higher basicity of the chromium tanning liquors made the chromium more resistant to leaching.

The type of retanning material also was of major importance; the high content of ionising groups probably accounting for the fact that myrobalans extract was the most efficient in stripping chromium from the pelt, whereas quebracho was only half as effective. In each case the lower pH of retannage resulted in the greater quantity of chromium in the liquor, as shown in Table 4(c), I.

Table 4(c), I
Displaced Chromium in Spent Retan Liquors
10^3 mg. atoms Cr/g. collagen

pH of Retannage*	Retanning Material**				Mean
	chestnut	mimosa	myrobalans	quebracho	
3.5	1.66	1.77	2.46	1.08	1.74
5.0	1.34	1.34	1.38	1.01	1.27
Mean	1.50	1.55	1.92	1.04	1.50

As expected, with increasing degree of retannage, the amount of chromium found in the retan liquors increased, and the effects of the different amounts and types of tanning extract are shown in Table 4(c),II.

Table 4(c), II
Displaced Chromium in Spent Retan Liquors
10^3 mg. atoms Cr/g. collagen

Level of Retannage***	Retanning Material**				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	1.08	0.78	1.32	0.86	1.01
4% tans	1.09	1.45	1.52	1.34	1.34
8% tans	1.47	1.61	1.84	0.94	1.47
16% tans	2.37	2.40	3.03	1.01	2.20
Mean	1.50	1.55	1.92	1.04	1.50

(ii) The free sulphate in the spent retan liquors is expressed in m. moles sulphate/g. collagen.

For this property the most important factors were the type and amount of vegetable retanning material used, and the pH at which the retannages were conducted. Thus the spent myrobalans liquors contained considerably more free sulphate than any of the other liquors, the mimosa retan liquors having the least, about one-sixth of the myrobalans. This effect is probably related to the relative amounts of ionising groups in the tannins. The effect on sulphate content of the different levels of retannage with each of the retanning materials is shown in Table 4(c), III.

Table 4(c), III

Free Sulphate in Spent Retan Liquors

10^2 m. moles SO_4/g. collagen

Level of Retannage***	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.15	0.30	0.20	0.35	0.25
4% tans	1.10	0.40	2.67	1.01	1.29
8% tans	1.55	0.60	6.07	2.59	2.70
16% tans	2.77	1.90	10.52	6.56	5.44
Mean	1.39	0.80	4.86	2.63	2.42

The higher the pH of retannage the larger the amount of sulphate in the spent retan liquors***, and this is consistent regardless of the type or amount of retanning material used, the average values being 1.71×10^{-2} m. moles SO_4/g. collagen and 3.23×10^{-2} m. moles SO_4/g. collagen for retannages at pH 3.5 and 5.0 respectively. Also, more sulphate was displaced from the leathers which had been tanned with the high level of chromium, 2.98×10^{-2} m. moles SO_4/g. collagen, compared with the low level of chromium tannage, 1.97×10^{-2} m. moles SO_4/g. collagen**.

(iii) The pH values of the spent retan liquors showed only small variations yet highly significant effects were noted. Of particular importance was the fact that the pH values of the myrobalans and the chestnut liquors were lower than either the mimosa or the quebracho liquors. Moreover, with increasing level of retannage the acidity of the liquors increased. This effect is shown in Table 4(c), IV.

Table 4(c), IV
pH Values of Spent Retan Liquors

Level of Retannage***	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	4.80	4.85	4.80	4.85	4.80
4% tans	4.55	4.65	4.50	4.85	4.65
8% tans	4.40	4.60	4.35	4.60	4.50
16% tans	4.10	4.25	4.10	4.40	4.20
Mean	4.45	4.60	4.45	4.70	4.55

Obviously those liquors adjusted initially to pH 3.5 showed lower pH values at the end of the retannage***, pH 4.40 as against pH 4.70 for leathers tanned at pH 5.0. Both the higher basicity*** and masking*** of the chromium liquors used in tanning resulted in higher pH values of the spent retan liquors: pH 4.65 compared with pH 4.45, and the leather with the lower chromium contents gave higher pH values: pH 4.65 compared with the highly chromium tanned leathers, pH 4.45**.

2. Analysis of Unaged Leathers

(i) Absorption of vegetable tanning material by the chromium tanned pelt increased as the level of retannage increased, but this was very dependent on the type of retanning material, see Table 4(c), V. It is obvious that quebracho fixed most readily, followed by myrobalans, whereas the fixation of both mimosa and chestnut was substantially less. The fact that the values in the table were not zero when no tannin was offered in retanning, shows the inexact nature of this determination, and the magnitude of these values is a measure of the accuracy that can be expected.

Table 4(c), V
Tannin Absorbed (g. tannin/100 g. collagen)

Level of Retannage***	Retanning Material**				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	- 0.5	0.5	- 0.3	0.7	0.1
4% tans	3.4	4.0	3.9	4.5	4.0
8% tans	6.3	5.5	7.0	7.0	6.4
16% tans	10.6	11.0	12.1	13.9	11.9
Mean	5.0	5.2	5.7	6.6	5.6

Leather with the greater quantity of chromium fixed more tanning material, 6.2% on collagen, compared with 5.0% fixed by the leather tanned with the lower level of chromium***; the 50% basic chromium tanned pelt fixed more than the 33% basic (6.4% and 4.8% tannin respectively)***, and masking of the chromium tanning compound reduced tannin fixation (formate masked, 5.1% tannin; unmasked, 6.1% tannin)*.

(ii) Extractable tannin, soluble in aqueous dioxan, increased as the level of retannage increased, the highest figures being for the myrobalans and quebracho retanned leathers, and the least being extracted from the chestnut retanned leathers. These results are given in Table 4(c), VI.

Table 4(c), VI
Extractable Tannin in Unaged Leather

g. tannin/100 g. collagen

Level of Retannage***	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.0	0.0	0.0	0.0	0.0
4% tans	0.4	0.5	0.6	0.6	0.5
8% tans	0.7	1.3	1.4	1.6	1.2
16% tans	1.9	3.3	5.5	4.2	3.7
Mean	0.8	1.3	1.9	1.7	1.4

More tanning material was extracted from the leathers offered the greater quantity of chromium than from those given a light chromium

tannage, but this was obviously dependent on the level of vegetable tannage, see Table 4(c), VII. Thus the increased absorption of tannin by the more heavily chromium tanned pelt cannot be ascribed entirely to reaction with the metal.

Table 4(c), VII
Extractable Tannin in Unaged Leather

g. tannin/100 g. collagen

Quantity of Chromium***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
4% Cr_2O_3	0.0	0.5	1.0	3.0	1.2
7% Cr_2O_3	0.0	0.5	1.5	4.5	1.7
Mean	0.0	0.5	1.2	3.7	1.4

(iii) The chromium content of the leathers was determined as mg. atoms of chromium/g. of collagen.

The only factors found to have a significant effect on the chromium content of the tanned collagen were those controlling the chromium tannage and these were all significant at the 0.1% level. Thus more chromium was found in the pelt if it had been offered the higher amount, 0.66 mg. atoms Cr/g. collagen, than if it had been offered the smaller amount, 0.41 mg. atoms Cr/g. collagen***. Tannage with the higher basicity chromium compound fixed more chromium, 0.58 mg. atoms Cr/g. collagen, than the low basicity, 0.49 mg. atoms Cr/g. collagen***, but masking reduced the fixation of chromium from 0.54 mg. atoms Cr/g. collagen to 0.52 mg. atoms Cr/g. collagen***.

(iv) Shrinkage temperature increased with increasing level of chromium offered***; when only 4% Cr_2O_3 was offered the average shrinkage temperature of the leathers was 99.8°C, but when the amount of chromium offered was 7% Cr_2O_3 the average shrinkage temperature was 117.0. However, retannage with vegetable tanning materials increased the shrinkage temperature, the hydrothermal stability increasing with increasing level of retannage as shown in Table 4(c), VIII. The lowest shrinkage temperature was given by myrobalans retannage, and this emphasises the difference between the condensed tannins and the

hydrolysable tannins. From the figures in the table it is obvious that the increase in shrinkage temperature resulting from retannage was higher for the condensed tannins (mimosa, $\Delta Ts = 3.4^{\circ}C$; quebracho, $\Delta Ts = 2.6^{\circ}C$) than for the hydrolysable tannins (chestnut, $\Delta Ts = 1.7^{\circ}C$; myrobalans, $\Delta Ts = 0.6^{\circ}C$).

Table 4(c), VIII
Shrinkage Temperature of Unaged Leathers, $^{\circ}C$

Level of Retannage***	Retanning Material**				
	chestnut	mimosa	myrobalans	quebracho	Mean
nil	107.0	106.0	107.5	107.0	106.9
4% tans	108.2	108.7	108.2	109.2	108.6
8% tans	108.5	109.2	107.0	109.0	108.4
16% tans	109.5	110.2	109.0	110.5	109.8
Mean	108.3	108.5	107.9	108.9	108.4

(v) The pH values of aqueous extracts of the leathers showed that retannage caused a marked increase in the acidity of the leathers, the acidity increasing with increasing level of retannage; an indication that sulphate displacement had occurred with the formation of strong acid. The pH was also affected by the type of retanning material, myrobalans causing the leather to be more acid and quebracho less acid than the average. The pH values for the different levels of the various retanning materials are given in Table 4(c), IX.

Table 4(c), IX
pH of Unaged Leathers

Level of Retannage***	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
nil	5.15	5.25	5.15	5.25	5.20
4% tans	4.80	4.70	4.60	4.75	4.70
8% tans	4.50	4.40	4.25	4.55	4.45
16% tans	4.05	4.25	3.95	4.50	4.20
Mean	4.60	4.65	4.50	4.75	4.65

Adjustment of the pH of the retanning material influenced the

pH of the leather, and as the level of retannage increased so the effect of the pH adjustment became more marked, but treatment of the chromium tanned pelt with water of the same pH values as the vegetable tanning liquors did not influence the pH of the leather. This effect is shown in Table 4(c), X.

Table 4(c), X
pH of Unaged Leathers

pH of Retannage***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
3.5	5.20	4.65	4.35	4.05	4.50
5.0	5.20	4.80	4.55	4.35	4.75
Mean	5.20	4.70	4.45	4.20	4.65

Leathers with the high chromium content were more acid, pH 4.50, than those with the low chromium content, pH 4.75***, but neither basicity nor masking of the chromium solutions used for tanning had an important influence on the pH of the unaged leathers.

(vi) Free sulphate was highest in the unretanned leathers, the amount decreasing on retannage and with increasing level of retannage. This indicates that sulphate must have been displaced during retannage. Moreover, the type of retanning material affected the amount of free sulphate in the leather, the amount in the myrobalans retanned leather being particularly low, and the highest amounts were found in the mimosa and the chestnut retanned leathers. This effect is shown in Table 4(c), XI.

Table 4(c), XI
Free Sulphate in Unaged Leathers
10^2 m. moles SO_4/g. collagen

Level of Retannage***	Retanning Material**				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	7.65	7.95	8.22	7.85	7.92
4% tans	7.62	7.62	7.27	8.02	7.63
8% tans	7.05	7.72	6.75	7.15	7.17
16% tans	7.22	6.35	5.12	5.05	5.93
Mean	7.38	7.41	6.84	7.02	7.16

Probably as the result of increased stability and competition from formate, masking of the chromium tanning salt reduced the amount of free sulphate in the leather, although this difference became less marked as the level of retannage increased, see Table 4(c), XII. At the highest level of retannage the amount of sulphate was equally low, irrespective of whether or not the pelt had been tanned with masked chromium compounds.

Table 4(c), XII
Free Sulphate in Unaged Leathers
10^2 m. moles SO_4/g. collagen

Masking of Chromium***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
not masked	8.45	7.90	7.57	5.89	7.45
formate masked	7.36	7.37	6.76	5.99	6.87
Mean	7.91	7.63	7.17	5.93	7.16

The high level of chromium pretannage resulted in considerably more free sulphate than when the leathers had been tanned with only 4% Cr_2O_3. However, at the high level, the higher basicity of the chromium tanning salt resulted in only a small reduction in the amount of free sulphate, whereas in those leathers tanned with the small amount of chromium, basicity had a marked effect, see Table 4(c), XIII.

Table 4(c), XIII
Free Sulphate in Unaged Leathers
10^2 m. moles SO_4/g. collagen

Basicity of Chromium Salt*	Quantity of Chrome Offered***		Mean
	4% Cr_2O_3	7% Cr_2O_3	
33% basic	6.54	8.74	7.64
50% basic	5.36	8.01	6.68
Mean	5.95	8.37	7.16

3. Analysis of Aged Leathers

(i) Increase in fixed tannins on ageing was higher if the leathers had been stored in a warm moist atmosphere than if they had been aged in the standard atmosphere, the increase in the solvent resistant tannin being greatest for the myrobalans and quebracho retanned leather and

least for the chestnut. These values are shown in Table 4(c), XIV in relation to the original solvent resistant tannin in the unaged leathers, and indicate the greater affinity of the quebracho tannin for chromium tanned pelt.

Table 4(c), XIV
Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
Original fixed tan	4.2	3.9	3.8	4.9	4.2
Increase on accel. age	0.4	0.9	1.3	1.2	0.9
Increase on nat. age	0.3	0.7	0.9	0.9	0.7

The increase in fixed tannin was dependent on the amount of tanhin offered and therefore also on the quantity of loosely held tannin, (see previous section). The effect of the amount of tannin offered on the increased fixation of the various tannins is given in Table 4(c), XV.

Table 4(c), XV
Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Level of Retannage***	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
nil	0.0	0.0	0.0	0.0	0.0
4% tans	0.0	0.2	0.2	0.3	0.2
8% tans	0.2	0.8	0.9	1.0	0.7
16% tans	1.2	2.6	4.3	3.5	2.9
Mean	0.4	0.9	1.3	1.2	0.9

Natural Ageing

Level of Retannage***	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
nil	0.0	0.0	0.0	0.0	0.0
4% tans	0.0	0.1	0.2	0.2	0.1
8% tans	0.2	0.7	0.6	0.9	0.6
16% tans	0.9	2.0	2.7	2.1	1.9
Mean	0.3	0.7	0.9	0.9	0.7

More tannin was fixed on ageing by the pelt that had been pretanned with the smaller amount of chromium than by that offered the larger amount. The solvent resistant tannin in the original unaged leathers together with the increase on ageing is shown in Table 4(c), XVI.

Table 4(c), XVI
Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

	Quantity of Chromium Offered**		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original fixed tans	3.8	4.5	4.2
Increase on accel. age	1.1	0.8	0.9
Increase on nat. age	0.8	0.6	0.7

Although, compared with the higher chromium content leather, the leather with the lower chromium content fixed more tannin on ageing, it still gave the lower value for total tannin fixation. This effect was dependent on the amount of vegetable tannin offered as shown in Table 4(c), XVII.

Table 4(c), XVII
Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Quantity of Chromium offered***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
4% Cr_2O_3	0.0	0.2	0.8	3.5	1.1
7% Cr_2O_3	0.0	0.1	0.6	2.3	0.8
Mean	0.0	0.2	0.7	2.9	0.9

Natural Ageing

Quantity of Chromium offered**	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
4% Cr_2O_3	0.0	0.2	0.7	2.2	0.8
7% Cr_2O_3	0.0	0.1	0.5	1.7	0.6
Mean	0.0	0.1	0.6	1.9	0.7

Table 4(c), XVIII

Fall in Shrinkage Temperature on Ageing, ΔTs, °C

Accelerated Ageing

Level of Retannage***	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.2	0.2	0.4	- 0.2	0.2
4% tans	- 0.5	- 1.7	0.7	0.2	- 0.3
8% tans	2.0	0.5	2.7	1.0	1.6
16% tans	4.7	1.7	3.5	0.2	2.6
Mean	1.6	0.2	1.9	0.3	1.0

Natural Ageing

Level of Retannage*	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	4.0	4.2	4.0	4.0	4.1
4% tans	3.7	2.2	5.7	0.5	3.1
8% tans	6.2	3.0	5.7	1.0	4.0
16% tans	3.2	2.5	5.5	0.5	2.9
Mean	4.3	3.0	5.2	1.5	3.5

(ii) Shrinkage temperature fell by an average of only 1°C on accelerated ageing, but by 3.5°C on natural ageing, the greatest loss of hydrothermal stability being shown by the myrobalans retanned leather. Moreover, the reduction in shrinkage temperature due to the quantity of vegetable tannin offered differed, depending on the method of ageing, see Table 4(c), XVIII. Thus on storage under moist, humid conditions increase in the amount of vegetable tannin caused an increase in deterioration, whereas under normal conditions the opposite was the case. It is interesting to note that neither condition of storage caused a significant loss of hydrothermal stability in leathers retanned with quebracho or mimosa; therefore the detanning effect of these vegetable tannins must be negligible.

Under natural ageing conditions the leathers with the high chromium contents deteriorated more than those with the low, but at elevated temperature and humidity the leathers with a low chromium content gained slightly in hydrothermal stability whereas the leathers with the high chromium content deteriorated, see Table 4(c), XIX.

Table 4(c), XIX
Fall in Shrinkage Temperature on Ageing, ΔTs °C

	Quantity of Chromium Offered		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original Ts	99.8	118.0	108.9
ΔTs accel. age	- 1.9	3.9	1.0
ΔTs nat. age	2.0	5.0	3.5

(iii) Increase in hydrogen ion concentration on storage was dependent on both type and amount of vegetable tannin offered. The most significant factor was the quantity of tannin in the leather, increase in acidity increasing with increase in degree of retannage. However, of greater importance was the effect of the type of vegetable retanning material, the chestnut and myrobalans extracts causing considerably more acid development than the mimosa or quebracho extracts, as shown in Table 4(c), XX in relation to the original hydrogen ion concentration.

Table 4(c), XXI

Increase in Acidity on Ageing, $\Delta [H^+] \times 10^5$

Accelerated Ageing

Level of Retannage***	Retanning Material**				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.50	0.25	0.50	0.25	0.37
4% tans	1.00	0.75	1.50	1.50	1.19
8% tans	3.75	1.50	3.00	2.25	2.62
16% tans	12.75	4.00	12.75	3.75	8.31
Mean	4.50	1.62	4.44	1.94	3.12

Natural Ageing

Level of Retannage***	Retanning Material***				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.00	0.00	0.00	0.00	0.00
4% tans	0.25	0.25	0.75	0.25	0.37
8% tans	1.25	0.75	1.50	0.50	1.00
16% tans	3.75	1.50	4.00	0.50	2.44
Mean	1.31	0.62	1.56	0.31	0.95

Table 4(c), XX
Increase in Acidity on Ageing, $\Delta[H^+] \times 10^5$

	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
Original $[H^+]$	2.34	2.19	3.24	1.70	2.37
$\Delta[H^+]$ accel. age	4.50	1.62	4.44	1.94	3.12
$\Delta[H^+]$ nat. age	1.31	0.62	1.56	0.31	0.95

Thus it is seen that not only is the myrobalans, and to a lesser extent the chestnut retanned leather more acid than the leathers retanned with either mimosa or quebracho extracts, but also the increase in acidity of these leathers on storage was greater. The detailed effects of the various retannages are shown in Table 4(c), XXI. The considerable effects of the myrobalans and chestnut retannages at the high levels of tannin offered, particularly after accelerated ageing should be noted.

The pH values of the retanning material were also important in determining the development of acidity on storage, the more acid the retannage the greater the increase in hydrogen ion concentration, and this effect was of increasing importance as the level of retannage increased, as shown in Table 4(c), XXII.

Table 4(c), XXII
Increase in Acidity on Ageing $\Delta[H^+] \times 10^5$

Accelerated Ageing

pH of Retannage**	Level of Retannage***				
	nil	4% tans	8% tans	16% tans	Mean
3.5	0.47	1.80	3.17	12.67	4.53
5.0	0.27	0.57	2.07	3.95	1.71
Mean	0.37	1.19	2.62	8.31	3.12

Natural Ageing

pH of Retannage**	Level of Retannage***				
	nil	4% tans	8% tans	16% tans	Mean
3.5	0.00	0.50	1.37	3.25	1.28
5.0	0.00	0.25	0.62	1.62	0.62
Mean	0.00	0.37	1.00	2.44	0.95

The greater activity of the chestnut and myrobalans is intensified

Table 4(c), XXIII

Increase in Acidity on Ageing, $\Delta[H^+] \times 10^5$

Accelerated Ageing

pH of Retannage**	Retanning Material**				
	chestnut	mimosa	myrobalans	quebracho	Mean
3.5	7.62	2.12	5.62	2.75	4.53
5.0	1.37	1.12	3.25	1.12	1.71
Mean	4.50	1.62	4.44	1.94	3.12

Natural Ageing

pH of Re tannage**	Retanning Material***				
	chestnut	mimosa	myrobalans	quebracho	Mean
3.5	1.62	1.00	2.12	0.37	1.28
5.0	1.00	0.25	1.00	0.25	0.62
Mean	1.31	0.62	1.56	0.31	0.95

at low pH of retannage and is particularly obvious in those leathers stored in a warm humid atmosphere, see Table 4(c), XXIII.

The development of acidity was greater if the leathers had been chromium tanned with the larger quantity of chromium, but the effect was mainly attributable to the formate masked chromium compounds, as shown in Table XXIV. This table shows that masking increases the acidity on storage, and that the effect is greatly enhanced under warm, moist conditions, when formate apparently cannot counter the complex forming tendency of the tannin.

Table 4(c), XXIV

Increase in Acidity on Ageing, $\Delta[H^+] \times 10^5$

Accelerated Ageing

Masking of Chromium	Quantity of Chromium Offered*		Mean
	4% Cr_2O_3	7% Cr_2O_3	
not masked	2.25	2.87	2.56
formate masked	2.00	5.37	3.68
Mean	2.12	4.12	3.12

Natural Ageing

Masking of Chromium *	Quantity of Chromium Offered*		Mean
	4% Cr_2O_3	7% Cr_2O_3	
not masked	0.81	0.95	0.88
formate masked	0.69	1.36	1.02
Mean	0.75	1.15	0.95

(iv) Increase in free sulphate on ageing increased with increasing level of tannin offered in retannage, the increase in sulphate being slightly greater on natural ageing than on accelerated ageing, but only for the myrobalans and quebracho retanned leathers. This interaction* is shown in Table 4(c), XXV. An important observation is that myrobalans retanned leather caused less sulphate displacement on ageing, particularly accelerated ageing, than the other retanning materials when the high level of retanning material was used, presumably because most of the displacement of sulphate had already occurred during retannage. No clear-cut distinction could be made between the other retanning materials.

The retannages conducted at the higher pH levels resulted in

Table 4(c), XXV

Increase in Free Sulphate on Ageing

10^2 m. moles SO_4/g. collagen

Accelerated Ageing

Level of Retannage***	Retanning Material				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.22	- 0.32	- 0.45	- 0.60	- 0.29
4% tans	0.20	0.47	0.37	0.37	0.35
8% tans	1.42	0.55	0.77	1.15	0.97
16% tans	1.62	1.85	1.37	1.52	1.59
Mean	0.86	0.64	0.51	0.61	0.66

Natural Ageing

Level of Retannage***	Retanning Material				Mean
	chestnut	mimosa	myrobalans	quebracho	
nil	0.20	- 0.22	0.20	- 0.17	0.00
4% tans	0.27	0.47	0.60	0.40	0.43
8% tans	1.20	0.55	1.02	1.42	1.05
16% tans	1.77	1.70	1.40	2.05	1.73
Mean	0.86	0.62	0.81	0.92	0.80

less SO_4 displacement on ageing, and this was particularly important with chestnut and myrobalans retannages as shown in Table 4(c), XXVI*. The difference in effect between the two ageing treatments was small, indicating that accelerated ageing gave similar effects to natural ageing.

Table 4(c), XXVI

Increase in Free Sulphate on Ageing

10^2 m. moles SO_4/g. collagen

Accelerated Ageing

pH of Retannage	Retanning Material				Mean
	chestnut	mimosa	myrobalans	quebracho	
3.5	1.27	0.85	0.74	0.70	0.89
5.0	0.46	0.42	0.30	0.52	0.42
Mean	0.87	0.64	0.52	0.61	0.66

Natural Ageing

pH of Retannage*	Retanning Material				Mean
	chestnut	mimosa	myrobalans	quebracho	
3.5	1.27	0.76	1.01	1.17	1.05
5.0	0.45	0.49	0.60	0.67	0.55
Mean	0.86	0.62	0.81	0.92	0.80

The influence of the pH of retannage is also of importance when the level of retannage is considered. Thus the sulphate liberated in the highly retanned leathers was greater if the retannages were conducted at low pH (3.5) than if the retanning extract had been adjusted to pH 5.0. This effect was similar under both conditions of storage, as shown in Table 4(c), XXVII.

Table 4(c), XXVII

Increase in Free Sulphate on Ageing

10^2 m. moles SO_4/g. collagen

Accelerated Ageing

pH of Retannage	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
3.5	- 0.22	0.52	1.07	2.19	0.89
5.0	- 0.35	0.19	0.87	1.00	0.42
Mean	- 0.28	0.35	0.97	1.59	0.66

Natural Ageing

pH of Retannage*	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
3.5	0.21	0.66	1.25	2.08	1.05
5.0	- 0.21	0.21	0.85	1.38	0.55
Mean	0.00	0.43	1.05	1.73	0.80

Discussion

Marked differences in the behaviour of the various retanning materials have been demonstrated, the greatest effects being due to the hydrolysable tannins in comparison with the condensed tannins. Myrobalans extract in particular has caused the greatest degree of sulphate displacement and chromium stripping as determined by analysis of the spent retan liquors. Moreover considerable additional free sulphate was found in the unaged myrobalans retanned leathers, although somewhat less than the free sulphate in the unaged leathers retanned with the other retanning materials. On ageing there was a smaller increase in free sulphate in the myrobalans retanned leathers compared with the other leathers, the amount liberated being almost independent of the conditions of ageing. Thus it is of interest to compare the total amounts of sulphate liberated from the chromium-collagen complex by each of the four retanning materials.

Total Free Sulphate from Retan Leathers

10^2 m. moles SO_4/g. collagen

Retannage	Free SO_4 in Retan Liquors	Free SO_4 in Unaged Leathers	Additional Free SO_4 in Aged Leather	Total Free Sulphate
nil	0.25	7.92	0.00	8.17
4% Chestnut tans	1.10	7.62	0.27	8.99
8% " "	1.55	7.05	1.20	9.80
16% " "	2.77	7.22	1.77	11.76
4% Mimosa tans	0.40	7.62	0.47	8.49
8% " "	0.60	7.72	0.55	8.87
16% " "	1.90	6.35	1.70	9.95
4% Myrobalans tans	2.67	7.27	0.60	10.54
8% " "	6.07	6.75	1.02	13.84
16% " "	10.52	5.12	1.40	17.04
4% Quebracho tans	1.01	8.02	0.40	9.43
8% " "	2.59	7.15	1.42	11.16
16% " "	6.56	5.05	2.05	13.66

Where considerable sulphate displacement had taken place during the retannage, the leathers contained less free sulphate, but nevertheless the myrobalans extract was considerably more reactive than the other tannins. However, this effect was not necessarily a characteristic of the hydrolysable tannins, since the quebracho retannages had liberated more sulphate than the chestnut. The greater reactivity of the myrobalans extract can be attributed to the high content of acidic groups relative to the other vegetable tanning materials, and the lower reactivity of the mimosa extract in the pH range studied can be similarly explained.

On the other hand, chromium displacement, although not a satisfactory measure of the reactivity of vegetable tannins with the chromium-collagen complex because of the insoluble nature of some of the products[62], has shown that quebracho was the least active. Thus although this vegetable tanning extract has caused considerable displacement of sulphate it has not caused extensive chromium solubilisation, whereas myrobalans extract has solubilised chromium and displaced much sulphate, indicating a significant degree of detannage. However, shrinkage

temperature is regarded as a better measure of effective tannage. Endorsement of the evidence for detannage by the greater displacement of chromium from the pelt by myrobalans extract, is given by the fact that this retannage gave the lowest increase in hydrothermal stability in the unaged leathers and on ageing the myrobalans retanned leather was less stable, showing a large fall in shrinkage temperature. By contrast, the leathers retanned with the condensed tannins and in particular quebracho extract showed a relatively high increase in hydrothermal stability and the fall in shrinkage temperature on ageing was negligibly small. These observations confirm the claim[43] that myrobalans extract was less satisfactory than sulphited quebracho or mimosa extracts for retanning, although the superiority of quebracho is questioned in the light of the greater displacement of sulphate caused by this vegetable retanning material.

The absorption of tanning material from clarified solutions of the vegetable tannin extracts was highest for quebracho and myrobalans and lowest for mimosa and chestnut, but much of the myrobalans extract taken up by the pelt was extractable by solvent. Thus the highest amount of fixed tanning material was taken up from quebracho extract solution and the least from myrobalans extract solution. On ageing, a further increase in fixed tannin occurred, the greatest increase being found in the myrobalans retanned leathers. Details of these effects are shown by the results of these assessments summarised below.

Tannin Fixation on Retannage and Ageing

g. tannin/100 g. collagen

Retannage	Tanning Material Absorbed	Fixed Tans	Increase in Fixed Tans on Ageing	Total Fixed Tans
4% Chestnut tans	3.4	3.0	0.0	3.0
8% " "	6.3	5.6	0.2	5.8
16% " "	10.6	8.7	0.9	9.6
4% Mimosa tans	4.0	3.5	0.1	3.6
8% " "	5.5	4.2	0.7	4.9
16% " "	11.0	7.7	2.0	9.7
4% Myrobalans tans	3.9	3.3	0.2	3.5
8% " "	7.0	5.6	0.6	6.2
16% " "	12.1	6.6	2.7	9.3
4% Quebracho tans	4.5	3.9	0.2	4.1
8% " "	7.0	5.4	0.9	6.3
16% " "	13.9	9.7	2.1	11.8

Thus although there is evidence from chromium and sulphate displacement that there was immediate interaction between the chromium tanned pelt and both myrobalans and quebracho extracts, in the case of the myrobalans it is obvious that mainly the small particle size non-tannins had reacted with the chromium complex because a large percentage of the tannins was extractable, whereas in quebracho it was the tannin that had reacted, most of the tannin being fixed. On ageing, further reaction had taken place with greater fixation of the myrobalans tannin. The greater reactivity of the quebracho relative to mimosa should also be noted and this is probably due to the presence of sulphonic acid groups in the former which impart greater complex forming tendency which is well established in sulphonic acid phenolic materials[176]. In this respect sulphited extracts based on condensed tannin types can be made to resemble hydrolysable tannins in their reaction with collagen[8], but the acidic groups are associated with the large particle size tannins and not the non-tannins. The mimosa and chestnut extracts occupy intermediate positions between myrobalans and quebracho in relation to the ageing characteristics of the leathers, and this can be attributed to the intermediate values of the tannin/non-tannin ratio. Thus extracts containing a high

percentage of non-tannins react rapidly with the chromium-collagen complex and little additional fixation of tannin occurs on ageing, but tanning extracts with a high tannin/non-tannin ratio react more slowly. Sulphited quebracho is anomalous in this respect in that the tannins carry charged ionic groups which form complexes with the chromium, but being relatively strong acid groups have little or no detanning effect, unlike the weak acid groups of the hydrolysable tannins.

The amount of tannin fixed was greater and the chromium and sulphate displacement increased as the quantity of tannin offered increased, but only at the low levels of retannage was the fixation on a quantitative basis. At the higher levels, exhaustion of the retan liquors was incomplete and of the tannin absorbed a significant part was extractable by aqueous dioxan, indicating a weak reaction with the chromed pelt. Unlike the vegetable tannin - collagen system where pH was found to have a marked effect on the solvent extraction of hydrolysable tannins[8], when the collagen had been modified by pre-reaction with chromium compounds, extraction, although much reduced, was not pH-dependent. Thus electrostatic repulsion of tannins ionically bound to basic groups as a result of the development of maximum negative charge on the protein carboxyl groups at elevated pH must be considerably reduced by blocking some of the carboxyl groups on chromium tannage. However, the effect is complicated by the fact that some of the tannin normally electrostatically attached to the protein at basic groups could have reacted with the chromium compound to form co-ordination complexes. The importance of the reactive sites on the protein is thus self-evident. The effect of masking of the chromium tanning compound has been to reduce vegetable tannin fixation, indirect evidence that the vegetable tanning extracts form co-ordination compounds with the chromium in chromium tanned pelt.

The chromium content of the retanned leathers, and the initial basicity and masking of the chromium compound are all important factors in determining the extent of reaction with vegetable tannins, and for completeness, a summary of the significant effects of the various factors on unaged leathers is presented in tabular form.

Factor	Level	Property				
		Chromium[1] Content	Fixed[2] Tans	Sulphate[3] Displaced	Ts, °C	pH
Quantity of Chromium	4% Cr_2O_3	0.41	3.8	7.92	99.8	4.75
	7% Cr_2O_3	0.66	4.5	11.35	118.0	4.50
Basicity of Chromium	33% basic	0.49	3.4	10.11		
	50% basic	0.58	5.0	9.15		
Masking of Chromium	not masked	0.54	4.7	9.92		
	formate masked	0.52	3.7	9.34		
Retanning Material	chestnut		4.2	9.77	108.3	4.60
	mimosa		3.9	8.21	108.5	4.65
	myrobalans		3.8	11.70	109.9	4.50
	quebracho		4.9	9.65	108.9	4.75
pH of Retannage	pH 3.5			8.87		4.50
	pH 5.0			10.39		4.75
Level of Retannage	nil		0.0	8.17	107.4	5.20
	4% tans		3.5	8.92	109.1	4.70
	8% tans		5.2	9.87	108.9	4.45
	16% tans		8.2	11.37	110.3	4.20

NOTE: 1. Chromium content is expressed in mg. atoms Cr/g. collagen.

2. Fixed tannin is expressed in g. tannin/100 g. collagen.

3. Sulphate displaced is expressed as 10^2 m. moles SO_4/g. collagen.

4(d) The Reaction of Vegetable Tannins with Chromium Tanned Modified Collagen

Important differences due to the effect of specific reactive groups of the protein on binding the hydrolysable tannins which have anionic character as well as phenolic hydroxyl groups, and the condensed tannins, have been discussed [8,9], and the observed affinity effects are readily explicable in terms of ionic binding, dipole attraction and hydrogen bond formation. Considerable differences in the reaction between chromium tanned collagen and the two classes of vegetable tanning materials have been shown in the previous section. Complex formation with the chromium-collagen compound occurred more readily with tannins possessing ionised dissociating groups than with mimosa extract, although in each case considerable sulphate displacement and increase in fixed tannin occurred on drying and on ageing. The increased affinity of vegetable tannins for chromium tanned pelt is thus attributed to the reaction between the chromium and the vegetable tannin, although the liberation of basic groups as a result of chromium tannage has been suggested as a possible alternative or additional binding site[138]. Vivian[139] showed that although increased reaction of tannin with collagen as a result of chromium pretannage involved protein groups made accessible by the formation of chromium-collagen complexes, the findings do not support Gustavson's theory that activated basic groups were involved. The relative importance of these two alternatives may be resolved by examination of the reaction of the two classes of vegetable tanning material with chromium tanned modified collagen.

The four protein substrates involved for study in this experiment were (a) standard, unmodified hide powder and acetone-dehydrated sheepskin pelt, (b) carboxylated hide powder and pelt in which the number of reactive side-chain carboxyl groups was increased at the expense of basic groups, (c) deaminated hide powder and pelt in which the basic groups were converted to hydroxyl, and (d) acetylated hide powder and pelt in which N-acetylation of the ε-amino groups of lysine and partial O-acetylation of the side chain hydroxyl groups had been effected. Characterisation of the substrates is given below:

Active Side Chains in Chemically Modified Collagen

Modification	m.moles/g. protein		
	Carboxyl	Amino	Hydroxyl
Nil (control)	1.05	0.34	1.74
Acetylation	1.02	0.00	0.66
Carboxylation	1.85	-	-
Deamination	1.05	0.05	-

Of the condensed tannins studied in the previous section, sulphited quebracho is atypical because of the presence of ionised sulphonic acid groups introduced by treatment with bisulphite to confer solubility and it thus resembles the hydrolysable tannins. Therefore mimosa extract was chosen to represent the condensed tannins. The hydrolysable tannins, chestnut and myrobalans, had similar characteristics, but the content of dissociating groups in the range of normal tannage pH was considerably greater for myrobalans than for chestnut, and since it was intended to emphasise the differences between the two classes of tannins, myrobalans was chosen as the representative of the hydrolysable tannins.

The type of collagen substrate and the class of tannin used in retanning were two of the factors included for study in the present experiment which was planned as a $\frac{1}{4}$ replicate of a 2^8 factorial design, giving a total of 64 treatment combinations. The factors varied and the levels of the factors were as follows:

AB Type of modified collagen

(1) normal collagen
a carboxylated collagen
b deaminated collagen
ab acetylated collagen

C Quantity of chromium offered

(1) 4% Cr_2O_3 on collagen (0.53 mg. atoms Cr/g. collagen)
c 7% Cr_2O_3 on collagen (0.92 mg. atoms Cr/g. collagen)

D Basicity of chromium salt

(1) 33% basic chromium sulphate
d 50% basic chromium sulphate

E Masking of chromium salt

(1) not masked
e formate masked, 1 mole formate/mole Cr_2O_3.

F Class of vegetable tannin

(1) condensed tannin (mimosa extract)
f hydrolysable tannin (myrobalans extract)

GH Quantity of tannins offered

(1) nil
g 4% tannin on collagen
h 8% tannin on collagen
gh 16% tannin on collagen

1. Analysis of Spent Retan Liquors

(i) The chromium content of each liquor is recorded as mg. atoms of chromium/g. collagen.

As could be expected, displacement of chromium from the protein on retanning was greater if the quantity of chromium offered had been high, but increase in the number of reactive sites on the protein through carboxylation reduced the tendency of the chromium to be stripped. Less chromium was stripped from the other chemically modified collagens, but this is probably related to the lower uptake of chromium by these protein substrates by removal of sites which bind chromium weakly. This effect is shown in Table 4(d), I.

Table 4(d), I
Displaced Chromium in Spent Retan Liquors
10^3 mg. atoms Cr/g. collagen

Quantity of Chromium***	Collagen Substrate***				
	normal	carboxylated	deaminated	acetylated	Mean
4% Cr_2O_3	1.88	0.73	1.00	1.39	1.25
7% Cr_2O_3	3.80	1.74	1.71	2.63	2.47
Mean	2.83	1.24	1.36	2.01	1.86

Due possibly to their effect on chromium complex stability, both masking and increase in the basicity of the chromium compound reduced the tendency of chromium to be displaced, the extent of this effect being shown in Table 4(d), II. As shown in the previous section, the hydrolysable tannin with its higher content of ionising groups displaced more

Table 4(d), II

Displaced Chromium in Spent Retan Liquors

10^3 mg. atoms Cr/g. collagen

Basicity of Chromium salt***	Masking of Chromium***		Mean
	not masked	formate masked	
33% basic	2.77	1.70	2.24
50% basic	1.62	1.35	1.49
Mean	2.20	1.53	1.86

Table 4(d), III

Displaced Chromium in Spent Retan Liquors

10^3 mg. atoms Cr/g. collagen

Retanning Material***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
mimosa	1.51	1.57	1.80	1.98	1.72
myrobalans	1.54	1.97	2.11	2.43	2.01
Mean	1.52	1.77	1.95	2.20	1.86

chromium from chromium tanned pelt than did the condensed tannin and this effect increased as the level of retannage increased, as shown in Table 4(d), III. Thus it is obvious that each of the factors has had a significant influence on this property.

(ii) The free sulphate in the spent retan liquors is expressed in m. moles sulphate/g. collagen.

As expected, more sulphate was displaced from leathers that had been tanned with the high level of chromium, 2.71×10^{-2} m. moles SO_4/g. collagen, compared with the low level of chromium tannage, 1.80×10^{-2} m.moles SO_4/g. collagen**, and less sulphate was displaced from the masked chromium complex, 1.91×10^{-2} m. moles SO_4/g. collagen than from the unmasked chromium, 2.60×10^{-2} m. moles SO_4/g. collagen*. In addition marked differences in the amount of sulphate displaced could be attributed to the protein substrate. Thus less sulphate was displaced from the chromium complex attached to the normal collagen than from the carboxylated, acetylated or deaminated collagens, the amount increasing in that order.

Collagen substrate**	Sulphate displaced
Normal	1.59×10^{-2} m.moles SO_4/g.
Carboxylated	1.83×10^{-2} m.moles SO_4/g.
Deaminated	3.09×10^{-2} m.moles SO_4/g.
Acetylated	2.52×10^{-2} m.moles SO_4/g.

This effect seems to be due to the type of linkage binding the chromium to the protein.

Of equal importance was the degree of retannage, the amount of free sulphate in the spent retan liquors increasing with increase in the quantity of tannin offered. As expected the more reactive myrobalans retannage was considerably more effective in displacing sulphate than was the mimosa retannage, as shown in Table 4(d), IV.

Table 4(d), IV

Free Sulphate in Spent Retan Liquors

10^2 m. moles SO_4/g. collagen

Retanning Material***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
Mimosa	0.24	0.27	0.59	1.91	0.75
Myrobalans	0.24	1.70	4.61	8.40	3.74
Mean	0.24	0.99	2.60	5.16	2.25

(iii) The pH values of the spent retan liquors showed only small variations, yet the differences were very significant. However, they are likely to be of little practical importance. In accordance with expectation, the spent retan liquors were more acid if the pelt had been pretanned with the high level of chromium, pH 4.29, than if the pelt contained less chromium, pH 4.37***. Pelt tanned with the higher basicity chromium resulted in higher pH values, pH 4.38, than if low basicity chromium had been used***, pH 4.28, and masking caused a considerable reduction in the acidity of the liquor, pH 4.46 compared with pH 4.20***.

Myrobalans retannage, with the greater content of carboxyl groups, caused lower pH values in the retan liquors, pH 4.24, than mimosa retannage, pH 4.42***, and the effect of retannage increased with increase in the amount of vegetable tanning extract offered. However, the effect of the degree of retannage was dependent on the protein substrate as shown in Table 4(d), V.

Table 4(d), V

pH Values of Spent Retan Liquors

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	4.07	4.44	4.62	4.45	4.39
4% tans	4.00	4.36	4.56	4.47	4.35
8% tans	3.95	4.32	4.55	4.46	4.32
16% tans	3.90	4.15	4.52	4.50	4.27
Mean	3.98	4.32	4.56	4.47	4.33

2. Analysis of Unaged Leathers

(i) Absorption of vegetable tanning material was difficult to determine because some of the modifications, notably acetylation, tended to denature the protein with consequent loss of hide substance. Thus there was not 100% recovery of the protein after pickling and chromium tanning. An estimate of the tannin fixation has been made, taking into account the loss of protein during processing. Thus it is of interest to note that both the carboxylated and the deaminated proteins fixed less tannin than either the normal, unmodified collagen or the acetylated collagen. This effect is shown in Table 4(d), VI in relation to the increasing level of tannin offered. It is suggested that this is due to the relative number of hydrogen bonding and chromium co-ordinating sites available to the tannin.

Table 4(d), VI
Tannin Absorbed (g. tannin /100 g. collagen)

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	0.0	0.0	0.0	0.0	0.0
4% tans	3.4	2.3	3.2	3.9	3.2
8% tans	6.6	3.7	5.5	6.4	5.5
16% tans	11.4	5.8	9.1	11.9	9.5
Mean	5.4	3.0	4.5	5.5	4.6

The effect of the modifications of the protein was also important when the type of vegetable retanning material was considered. Thus, although the absorption of both mimosa and myrobalans tannin was approximately equal on normal collagen, more myrobalans than mimosa was fixed by the carboxylated and the deaminated collagens although the amount of tannin absorbed in each case was less than by the normal collagen, as shown in Table 4(d), VII**. Slightly more mimosa than myrobalans tannin was taken up by the acetylated collagen but the amount absorbed was little different from the amounts absorbed by normal collagen. These differences may be related to both reactivity and steric hindrance effects.

Table 4(d), VIII

Extractable Tannin in Unaged Leather

g. tannin/100 g. collagen

Retanning Material	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
mimosa	1.4	0.3	2.3	3.6	1.9
myrobalans	2.5	0.8	1.7	2.9	2.0
Mean	2.0	0.5	2.0	3.2	1.9

Table 4(d), IX

Extractable Tannin in Unaged Leather

g. tannin/100 g. collagen

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	0.1	0.1	0.0	0.1	0.1
4% tans	0.7	0.3	0.7	0.9	0.6
8% tans	2.0	0.5	2.4	2.1	1.8
16% tans	5.0	1.3	4.9	9.8	5.2
Mean	2.0	0.5	2.0	3.2	1.9

Table 4(d), VII
Tannin Absorbed (g. tannin/100 g. collagen)

Retanning Material	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
Mimosa	5.5	2.5	4.2	5.8	4.5
Myrobalans	5.2	3.5	4.7	5.2	4.6
Mean	5.4	3.0	4.5	5.5	4.6

More tannin was absorbed by the pelt with the higher chromium content, 5.5 g./100 g. collagen, than by the pelt with the low chromium content, 3.6 g./100 g. collagen***.

(ii) Extractable tannin. The amount of tannin extractable by solvent from normal collagen was greater if the chromed pelt had been retanned with myrobalans than with mimosa, and this also applied to the carboxylated collagen, but on a smaller scale. On the other hand more mimosa tannin than myrobalans was extracted from the deaminated or acetylated pelt. These results are shown in Table 4(d), VIII**. These effects are likely to be related to the firmness of fixation of the tannins, giving varied solvent resistance.

The amount of extractable tannin in the leather increased as the amount of retanning material offered increased, but the amounts varied depending on the protein substrate, as shown in Table 4(d), IX***, due probably to variable extent of firmness of tan fixation by the different substrates.

(iii) The chromium content is expressed as mg. atoms of chromium/g. of collagen.

In addition to the factors controlling the chromium tannage, namely, the basicity and masking of the chromium compound and the quantity of chromium offered, the protein substrate considerably influenced the chromium content of the pelt. Thus while carboxylation slightly increased the fixation of chromium, both deamination and acetylation considerably reduced the chromium content, although this was evident mainly at the high level of chromium offered. This effect is shown in Table 4(d), X. These results are consistent with the theory of chromium

tannage [1-3], where chromium fixation is regarded to be co-ordination with the carboxyl groups, while the amino groups neutralise the displaced sulphate ions.

Table 4(d), X
Chromium Content of Tanned Collagen
mg. atoms Cr/g. collagen

Quantity of Chromium offered***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
4% Cr_2O_3	0.49	0.49	0.35	0.37	0.42
7% Cr_2O_3	0.67	0.69	0.44	0.48	0.57
Mean	0.58	0.59	0.39	0.43	0.50

As expected, more chromium was fixed if the chromium tanning salt was offered at an initial basicity of 50% than if the liquors were 33% basic, but masking reduced the uptake of chromium. This effect is shown in Table 4(d), XI.

Table 4(d), XI
Chromium Content of Tanned Collagen
mg. atoms Cr/g. collagen

Basicity of Chromium salt**	Masking of Chromium***		Mean
	not masked	formate masked	
33% basic	0.50	0.47	0.49
50% basic	0.51	0.51	0.51
Mean	0.50	0.49	0.50

(iv) Shrinkage temperature Because of the wide variation in the shrinkage temperature of the untanned substrate (normal collagen, Ts = 54°C; carboxylated collagen, Ts = 74°C; deaminated collagen, Ts = 58°C; and acetylated collagen Ts = 39°C) the hydrothermal stability of the leathers is best considered as the increase in shrinkage temperature resulting from the various tannage factors. The results are reported as the increase in shrinkage temperature relative to the appropriate untanned collagen, i.e. ΔTs. The chromium content of the leather had a marked influence on the shrinkage temperature rise, but neither the basicity nor

masking of the chromium influenced this property. The effect of chromium pretannage was consistent on each of the collagen substrates as shown in Table 4(d), XII. Thermal stability is believed to be due mainly to bridging of protein chains, and it is evident that this has been most effective in the case of the normal collagen despite the greater fixation of chromium by the carboxylated collagen.

Table 4(d), XII
Increase in Ts due to Tannage, °C

Quanty of Chromium offered**	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
4% Cr_2O_3	56.4	41.9	45.6	44.7	47.1
7% Cr_2O_3	60.4	42.9	53.6	47.0	51.0
Mean	58.4	42.4	49.6	45.8	49.0

The type of retanning material had no significant influence on the shrinkage temperature of the retan leathers, but with increasing quantity of vegetable tannin offered there was a corresponding increase in hydrothermal stability. However, retannage of the chromium tanned acetylated collagen did not cause a significant change in shrinkage temperature as shown in Table 4(d), XIII. These results are probably indicative of the extent of bridging of protein chains.

Table 4(d), XIII
Increase in Ts due to Tannage, °C

Level of Retannage*	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	55.7	41.2	45.5	46.7	47.3
4% tans	56.2	41.0	45.5	46.7	47.4
8% tans	59.5	43.5	52.7	44.5	50.0
16% tans	62.0	43.7	54.7	45.5	51.5
Mean	58.4	42.4	49.6	45.8	49.0

(v) The pH values of aqueous extracts of the leathers showed that all factors had a highly significant effect on this property. The substrate was important, the highest pH being shown by the carboxylated pelt and the lowest by normal collagen. The values are as follows:***

Collagen Substrate	pH of Unaged Leathers
Normal	4.55
Carboxylated	4.81
Deaminated	4.69
Acetylated	4.67

Each of the factors controlling the chromium tannage was important in deciding the pH of the leather, being significant at the 0.1% level. Thus leather with the higher chromium content was more acid, pH 4.59, than the leather with the low chromium content, pH 4.79***; leathers tanned with chromium with an initial basicity of 50% had a pH of 4.76 compared with the pH of 4.62 in the 33% basic tannage***; masking of the chromium liquors resulted in a leather with higher pH, 4.84, compared with the unmasked tannage which had a pH of 4.54***.

The acidity of the leather increased with increasing level of retannage, this effect being greater for the myrobalans retannage than for the mimosa retannage as shown in Table 4(d), XIV.

The results are all in the expected direction, being related to the acidity contributed by the displacement of sulphate groups attached to the chromium bound to the protein.

Table 4(d), XIV
pH of Unaged Leathers

Retanning Material***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
Mimosa	5.02	4.83	4.73	4.60	4.79
Myrobalans	5.03	4.57	4.39	4.36	4.59
Mean	5.03	4.70	4.57	4.47	4.69

Table 4(d), XVI

Free Sulphate in Unaged Leathers

10^2 m. moles SO_4/g. collagen

Masking of Chromium***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
not masked	10.87	10.12	9.76	9.85	10.15
formate masked	7.70	8.14	7.89	6.81	7.63
Mean	9.28	9.13	8.82	8.33	8.89

Table 4(d), XVII

Free Sulphate in Unaged Leathers

10^2 m. moles SO_4/g. collagen

Collagen Substrate***	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
normal	11.17	10.70	10.27	10.47	10.65
carboxylated	8.77	8.62	8.92	8.52	8.71
deaminated	7.55	7.65	6.95	5.77	6.98
acetylated	9.65	9.55	9.15	8.55	9.22
Mean	9.28	9.13	8.82	8.33	8.89

(vi) Free sulphate in the unaged leathers was higher in leathers containing more chromium, 9.78×10^{-2} m. moles SO_4/g. collagen, than in leathers tanned with the small amount of chromium, 7.99×10^{-2} m. moles SO_4/g. collagen***. In addition both masking and increase in basicity of the chromium liquors reduced the amount of free sulphate in the leathers, but masking had a much greater effect on the 50% basic liquors than on the 33% basic liquors. The values of this interaction are given in Table 4(d), XV.

Table 4(d), XV
Free Sulphate in Unaged Leathers
10^2 m. moles SO_4/g. collagen

Basicity of Chromium salt**	Masking of Chromium***		Mean
	not masked	formate masked	
33% basic	10.27	8.08	9.17
50% basic	10.04	7.18	8.61
Mean	10.15	7.63	8.89

The free sulphate in the leathers decreased as the level of retannage increased, the amounts being considerably lower in the leathers tanned with the masked chromium compound than in the unmasked chromium tanned leathers. This effect is shown in Table 4(d), XVI. The effect of the increasing level of retannage was also modified by the collagen substrate. Thus although there was a general decrease in the free sulphate with increasing level of retannage, this is not apparent for the carboxylated pelt, as shown in Table 4(d), XVII. Moreover, it will be seen that the free sulphate in the leathers from the modified collagens, especially the deaminated collagen, was lower than in leathers from the normal collagen. These results are related to displacement of sulphate from the chromium complex.

3. Analysis of Aged Leathers

(i) Increase in fixed tannins on ageing was greater if the leathers had been stored in a warm, humid atmosphere, than if they had been stored in the standard atmosphere, but in most cases similar trends were observed. Under each of the two storage systems marked differences in

Table 4(d), XVIII

Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	0.0	0.0	0.0	0.0	0.0
4% tans	0.2	0.1	0.4	0.3	0.2
8% tans	1.0	0.2	1.4	1.5	1.0
16% tans	3.8	0.6	3.5	4.7	3.1
Mean	1.3	0.2	1.3	1.6	1.1

Natural Ageing

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	0.0	0.0	0.0	0.0	0.0
4% tans	0.3	0.1	0.3	0.3	0.2
8% tans	1.0	0.2	1.0	1.1	0.8
16% tans	3.3	0.5	2.4	3.4	2.4
Mean	1.1	0.2	0.9	1.2	0.8

the fixation of tannins due to the type of collagen were noted, the retanned carboxylated pelt fixing much less than any of the other protein substrates. This is obviously related to the lower amount of tannins absorbed during retanning. In Table 4(d), XVIII are presented the results of the effect of ageing on the fixation of tannins by each of the modified collagens.

The fixation of mimosa and myrobalans tannin on ageing was not greatly different if the retannages were effected on a substrate of chromium pretanned normal collagen, or carboxylated collagen, but considerably more mimosa tannin than myrobalans tannin was fixed by the deaminated and especially the acetylated collagens. The results are given in Table 4(d), XIX for each of the two ageing systems. Deamination and acetylation reactions, particularly the latter, tend to denature the protein with the possibility of more reactive sites for hydrogen bonding being made available. The un-ionised mimosa tannin may be free to re-orientate and become fixed during ageing, whereas the myrobalans having ionised groups which are weakly directional, may not be able to re-orientate to the same extent, with the result that the hydrolysable tannin does not increase its resistance to solvent extraction to the same extent as the condensed tannins. The observed results may be the result of oxidation/polymerisation reactions but these are unlikely to account for the large differences between the two tannins on ageing.

Table 4(d), XIX

Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Retanning Material**	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
Mimosa	1.3	0.1	1.4	2.3	1.3
Myrobalans	1.3	0.3	1.2	1.0	0.9
Mean	1.3	0.2	1.3	1.6	1.1

Natural Ageing

Retanning Material**	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
Mimosa	1.1	0.1	1.0	1.5	0.9
Myrobalans	1.1	0.3	0.8	0.9	0.8
Mean	1.1	0.2	0.9	1.2	0.8

Leathers with the lower chromium content fixed more tannin on ageing than the leathers tanned with the high level of chromium, and this

was consistent regardless of the ageing conditions as shown in Table 4(d), XX. This is probably the result of the greater initial fixation of tannin by the highly chromium tanned pelt with the result that there was less free tannin to fix on ageing.

Table 4(d), XX

Increase in Fixed Tannin on Ageing

g. tannin/100 g.collagen

	Quantity of Chromium Offered		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original fixed tans	3.2	4.9	4.05
Increase on accel. age	1.3	1.0	1.15
Increase on nat. age	0.9	0.8	0.85

The basicity of the chromium tanning compound also influenced the fixation of tannin on ageing, a greater increase being recorded in the leathers tanned with the 50% basic chromium than in the 33% basic chromium tanned leathers. However, as shown in Table 4(d), XXI this effect was evident at only the high level of retannage. This was probably the result of the greater amount of unfixed tannin in the heavily retanned 50% basic chromium tanned pelt.

Table 4(d), XXI

Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Basicity of Chromium salt**	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
33% basic	0.0	0.3	1.2	2.5	1.0
50% basic	0.0	0.3	1.0	3.9	1.3
Mean	0.0	0.3	1.1	3.2	1.1

Natural Ageing

Basicity of Chromium salt**	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
33% basic	0.0	0.3	0.9	1.9	0.8
50% basic	0.0	0.2	0.7	2.8	0.9
Mean	0.0	0.2	0.8	2.4	0.8

As has already been mentioned, increase in the level of retannage has resulted in an increase in the amount of tannin fixed on

ageing, but this was not as great with the myrobalans retannage as with the mimosa retannage, the differences being particularly evident at the higher levels of retannage. This effect is shown in Table 4(d), XXII. As mentioned above, this probably is connected with the charge effect on the myrobalans tannin.

Table 4(d), XXII
Increase in Fixed Tannin on Ageing

g. tannin/100 g. collagen

Accelerated Ageing

Retanning Material**	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
Mimosa	0.0	0.3	1.2	3.6	1.3
Myrobalans	0.0	0.2	0.9	2.8	1.0
Mean	0.0	0.3	1.1	3.2	1.1

Natural Ageing

Retanning Material**	Level of Retannage***				
	nil	4% tans	8% tans	16% tans	
Mimosa	0.0	0.2	0.9	2.7	0.9
Myrobalans	0.0	0.2	0.7	2.1	0.7
Mean	0.0	0.2	0.8	2.4	0.8

(ii) Shrinkage temperature fell on ageing by an average of 2.8°C under warm, humid storage, and by 2.1°C on natural ageing, but the collagen substrate considerably influenced the extent to which the hydrothermal stability changed on ageing. Thus by reference to the figures in Table 4(d), XXIII it will be seen that the retanned normal collagen showed only a small fall in shrinkage temperature; both the deaminated and acetylated collagens, especially the latter, were responsible for very large losses in hydrothermal stability. On the other hand the retanned carboxylated pelt showed a consistent increase in shrinkage temperature.

Table 4(d) XXIII
Fall in Shrinkage Temperature on Ageing, ΔTs °C

	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
Original Ts	112.3	116.3	107.6	84.8	105.3
Δ Ts accel. age	1.3	- 4.0	4.7	9.1	2.8
Δ Ts nat. age	2.5	- 0.5	2.4	4.0	2.1

Thus on natural ageing the fall in shrinkage temperature of the

Table 4(d), XXV

Increase in Acidity on Ageing, $\Delta[H^+] \times 10^5$

Accelerated Ageing

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	1.25	0.00	1.00	1.50	0.94
4% tans	3.25	0.00	1.75	2.50	1.87
8% tans	4.25	0.25	3.00	2.75	2.56
16% tans	8.00	0.50	3.50	4.00	4.00
Mean	4.19	0.19	2.31	2.69	2.34

Natural Ageing

Level of Retannage***	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
nil	0.70	0.25	0.40	0.70	0.51
4% tans	1.85	0.07	0.95	1.05	0.98
8% tans	2.00	0.37	1.47	1.65	1.37
16% tans	3.70	1.75	2.35	2.45	2.56
Mean	2.06	0.61	1.29	1.46	1.36

tanned normal collagen was greater than on accelerated ageing, but both the deaminated and the acetylated collagens were more susceptible to a decline in shrinkage temperature at elevated temperature and humidity. This is probably the result of disruption of the protein during modification so that it was more susceptible to hydrolytic degradation on accelerated ageing. The carboxylated pelt was stabilised by the additional formaldehyde tannage.

Leathers tanned with the 50% basic chromium compounds showed less hydrothermal stability on ageing than the 33% basic chromium tanned leathers. This effect is shown in Table 4(d), XXIV for each of the two ageing treatments. The lower stability of the 50% basic chromium tanned leathers on ageing is probably related to the increased tannin fixation as mentioned in a previous section (see p. 103).

Table 4(d), XXIV
Fall in Shrinkage Temperature on Ageing, ΔTs ^{o}C

	Basicity of Chromium*		
	33% basic	50% basic	Mean
Original Ts	106.4	104.2	105.3
ΔTs accel. age	1.1	4.6	2.8
ΔTs nat. age	0.6	3.6	2.1

(iii) Increase in hydrogen ion concentration on ageing was greater in leathers made from tanned normal collagen than in leathers based on modified collagen substrates, very small increases in acidity being shown by the carboxylated collagen leathers even at the highest level of retannage. In Table 4(d), XXV are presented the values for the increase in hydrogen ion concentration of the four collagen substrates from which the enhanced effect of increasing the level of vegetable retannage can also be observed.

The greater increase in acidity due to the high level of chromium tannage compared with the low level did not reach statistical significance at the 5% level, but the effect of masking was very important. Thus from Table 4(d), XXVI it will be seen that, probably as the result of the buffering action of the formate, the increase in acidity of the leathers tanned with the masked chromium compounds was less than if the leathers had

been tanned with unmasked chromium salts.

Table 4(d), XXVI
Increase in Acidity on Ageing, $\Delta [H^+] \times 10^5$

	Masking of Chromium***		Mean
	not masked	formate masked	
Original $[H^+]$	2.82	1.41	2.00
$\Delta [H^+]$ accel. age	3.28	1.40	2.34
$\Delta [H^+]$ nat. age	1.83	0.88	1.36

Compared with the mimosa retannage, myrobalans caused more acid to be developed on ageing, particularly under conditions of elevated temperature and humidity, as shown in Table 4(d), XXVII. This is probably due to the higher content of active groups in myrobalans.

Table 4(d), XXVII
Increase in Acidity on Ageing, $\Delta [H^+] \times 10^5$

	Retanning Material***		Mean
	mimosa	myrobalans	
Original $[H^+]$	1.59	2.51	2.00
$\Delta [H^+]$ accel. age	1.75	2.93	2.34
$\Delta [H^+]$ nat. age	1.14	1.57	1.35

(iv) Increase in free sulphate differed in amount depending on the substrate, although this effect was considerably greater when the leathers had been stored under warm, humid conditions than if they had been stored in a more temperate atmosphere. The results of these treatments are shown in Table 4(d), XXVIII. The extremely low value of the naturally aged acetylated collagen is worthy of note, although the reason is not immediately apparent.

Table 4(d), XXVIII
Increase in Free Sulphate on Ageing
10^2 m. moles SO_4/g. collagen

	Collagen Substrate***				Mean
	normal	carboxylated	deaminated	acetylated	
Original free SO_4	10.65	8.71	6.98	9.22	8.89
Increase on accel. age	1.91	0.90	1.03	0.98	1.21
Increase on nat. age	1.01	0.44	0.33	0.07	0.46

Table 4(d), XXIX

Increase in Free Sulphate on Ageing

10^2 m. moles SO_4/g. collagen

Accelerated Ageing

Retanning Material*	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
mimosa	0.03	0.76	1.01	2.40	1.05
myrobalans	0.07	1.15	1.37	2.85	1.36
Mean	0.05	0.95	1.19	2.62	1.21

Natural Ageing

Retanning Material*	Level of Retannage***				Mean
	nil	4% tans	8% tans	16% tans	
mimosa	- 0.10	0.07	0.40	0.84	0.30
myrobalans	- 0.22	0.17	0.49	2.07	0.63
Mean	- 0.16	0.12	0.44	1.45	0.46

In Table 4(d), XXIX are given the values for increase in amount of free sulphate depending on the type and amount of retanning material offered. The increased displacement of sulphate by myrobalans relative to mimosa extract was barely significant, but the increase in free sulphate with increasing level of retannage was an important effect.

Probably as the result of increased stability or replacement of sulphate by formate, the tannage of pelt with masked chromium compounds resulted in the development of less free sulphate on ageing compared with the unmasked chromium tanned leathers, the effect being less marked on natural ageing than on accelerated ageing, as shown in Table 4(d), XXX.

Table 4 (d), XXX
Increase in Free Sulphate on Ageing
10^2 m. moles SO_4/g. collagen

	Masking of Chromium**		Mean
	not masked	formate masked	
Original free SO_4	10.15	7.63	8.89
Increase on accel. age	1.44	0.97	1.21
Increase on nat. age	0.65	0.28	0.46

The amount and basicity of the chromium salt used in tanning had an important influence on the displacement of sulphate only on accelerated ageing. On natural ageing the effect was not significant at the 5% level. The results of these two factors are shown in Tables 4 (d), XXXI and 4(d), XXXII.

Table 4(d), XXXI
Increase in Free Sulphate on Ageing
10^2 m. moles SO_4/g. collagen

	Quantity of Chromium Offered**		Mean
	4% Cr_2O_3	7% Cr_2O_3	
Original free SO_4	7.99	9.78	8.89
Increase on accel. age	1.01	1.41	1.21
Increase on nat. age	0.33	0.59	0.46

Table 4(d), XXXII

Increase in Free Sulphate on Ageing

10^2 m. moles SO_4/g. collagen

	Basicity of Chromium*		
	33% basic	50% basic	Mean
Original free SO_4	9.17	8.61	8.89
Increase on accel. age	1.36	1.06	1.21
Increase on nat. age	0.49	0.43	0.46

As expected, the increased sulphate content of the leathers tanned with the high level of chromium resulted in more sulphate displacement on ageing, warm, moist storage being more effective than the temperate storage conditions. On the other hand, the higher basicity of the chromium compound resulted in less sulphate being available for displacement.

Discussion

Modification of the collagen has affected all of the properties measured, the most important of which were the chromium content of the leather, the displacement of chromium during retannage, the amount of vegetable tannin irreversibly fixed and the quantity of sulphate liberated during retannage and on drying. The results of these assessments are summarised in the table below.

Collagen Substrate	(1) Chromium content	(2) Chromium displaced	(3) Tannin fixed	(4) SO_4 displaced	
				during retannage	on drying
Normal	0.58	0.49	3.4	1.59	10.65
Carbox.	0.59	0.21	2.5	1.83	8.71
Deam.	0.39	0.35	2.5	3.09	6.98
Acetyl.	0.43	0.47	2.3	2.52	9.22

NOTE: 1. Chromium content - mg. atoms Cr/g. collagen

2. Chromium displaced - % of chromium in the leather displaced during retannage.

3. Tannin fixed - g. tannin/100 g. collagen unextractable with aqueous dioxan.

4. SO_4 displaced - 10^2 m. moles SO_4/g. collagen.

Carboxylation resulted in a small increase in the amount of chromium in the leather probably because of the increased number of sites for co-ordination, but this effect was probably restricted because of the limited amount of chromium offered. Of greater importance was the fact that less of the chromium attached to the carboxylated pelt was displaced during retannage, indicating that a greater amount of weakly held chromium was present in the normal collagen. Both deamination and acetylation resulted in lower chromium fixation, but the resistance to displacement was no better than that in normal collagen. Thus carboxylated collagen contained more chromium more firmly held than any of the other collagen substrates.

Of considerable importance was the discovery that although the carboxylated collagen contained more chromium than normal collagen, the amount of tannin irreversibly fixed was lower, indicating that reaction with the chromium may not be the only cause of tannin fixation. Moreover, it is significant that the three modifications of the collagen which have each been responsible for the reduction in the number of basic groups have resulted in the same low level of tannin fixation regardless of the chromium content, and it therefore seems possible that these groups are important auxiliary binding sites accounting for part of the tannin fixation. These sites cannot, of themselves, be responsible for irreversible tannin fixation, because recent work has shown that vegetable tannage of collagen is completely reversible[8]. Furthermore, removal of these reactive groups by deamination has only reduced the tannin fixation, the amount fixed still being high relative to normal collagen.

That complex formation occurs between vegetable tannins and chromium compounds has been amply demonstrated[39-41,62], and evidence from the work reported earlier in this thesis and in this section has shown that retannage has resulted in displacement of sulphate from the chromium-collagen compound confirming complex formation. The rapid displacement of sulphate which occurred during retannage was probably mainly that ionically bound by basic groups, but the greatest effect occurred on drying when sulphate was displaced from the chromium complex with an attendant increase in acidity.

It is possible that the importance of the basic groups in the

fixation of tannin by chromium tanned collagen has been over-emphasised[138], since examination of the above figures for sulphate displacement indicate that tannin fixation is directly related to the amount of free sulphate. Reduced co-ordination of vegetable tannins by the chromium complex in the carboxylated collagen may be the result of reduced accessibility due to the more highly cross-linked structure of this modified protein. The lower tannin fixation by the other modified collagen substrates may be a reflection of the lower chromium content of these proteins and unrelated to the reduction in the number of basic groups.

Confirmation of the importance of complex formation and the minor role of reactive sites on the protein on the fixation of tannin is given by the figures for the two types of vegetable tannin as shown below.

Retanning Material	(1) Chromium content	(2) Chromium displaced	(3) Tannin fixed	(4) SO_4 displaced	
				during retannage	on drying
Mimosa	0.50	0.34	2.6	0.75	8.84
Myrob.	0.50	0.40	2.7	3.74	8.95

NOTE: 1. Chromium content = mg. atoms Cr/g. collagen

2. Chromium displaced = % of chromium in the leather displaced during retannage.

3. Tannin fixed = g. tannin /100 g. collagen unextractable with aqueous dioxan.

4. SO_4 displaced = 10^2 m. moles SO_4/g. collagen.

Chromium displacement was slightly higher when the chromium tanned pelt was retanned with myrobalans, but of much greater importance are the figures for sulphate displacement. It will be seen that the myrobalans extract with its higher content of ionising groups has caused considerable immediate displacement of sulphate during retanning and whilst this is regarded as mainly ionically bound sulphate, some complex formation could have taken place. On drying when complex formation is thought to occur, the amounts of sulphate displaced by mimosa and myrobalans were not significantly different, and the amounts of irreversibly fixed tannin were also not significantly different. Thus it would appear that sulphate displacement, and therefore reaction with the chromium

complex, is related to tannin fixation. Moreover, reference to the relative amounts of mimosa and myrobalans tannin fixed by chromium tanned modified collagen (see Tables 4(d), VII and 4(d), VIII) shows that more myrobalans than mimosa tannin was fixed by the substrates in which the basic groups had been reduced, and this is the opposite of what would be expected if basic groups were important sites for the irreversible fixation of tannin by chromium tanned pelt.

Thus, whilst basic groups may assist in promoting tannin fixation by rapid reaction with charged tannin particles, it is considered that irreversible fixation of tannin is the result of complex formation between the chromium compounds and vegetable tannins with the displacement of sulphate and to a very small extent the displacement of protein carboxyl groups. This is in general agreement with Vivian's observations[139] that tannin fixed by moist cationic chromium tanned hide powder is due to the formation of chromium-tannin complexes rather than the activation of amino groups[60].

However, contrary to Vivian's findings[139], the present work has shown that further reaction of the vegetable tannin with the chromium-collagen complex occurred on ageing. Vivian claimed that the amount of tannin resisting elution with aqueous acetone did not increase, whereas the results reported above, and in the preceding sections of this chapter have shown an increase in fixed tannin on ageing. It is considered that this reaction which involves the displacement of sulphate groups, thus increasing the acidity of the leather, is responsible for promoting the deterioration of the leather.

The factors controlling the chromium tannage are also important in determining the extent of the reaction. Thus increased level of chromium tannage increased the reactivity of the system, whereas formate masking reduced the reactivity except at high temperature and humidity. These observations generally confirm the findings of the previous sections with regard to these factors, and are to be discussed more fully in the final chapter.

CHAPTER 5

OBSERVATIONS ON THE PRACTICAL APPLICATION OF MIMOSA EXTRACT FOR RETANNING

5(a) Factors Influencing the Strength of Chromium Tanned Leather Retanned with Mimosa Extract [134]

The retannage of chromium tanned upper leather with vegetable tanning extracts and synthetic tannins has certain advantages in that, if correctly carried out, some of the variability inherent in low-grade hides is levelled out. In the retannage the flanks are filled and possibly tightened, grain defects are minimised, deep buffing is possible and a uniform basis is laid for the finishing processes particularly if the leather has been paste-dried. In fact developments in retanning and the adoption of paste drying have gone hand-in-hand. Chrome-retan leather in general does not handle as well as full-chrome leather, hence mechanical treatments should be reduced to a minimum. Softness should therefore be obtained by changes in the chemical processing, rather than by mechanical action. Staking should be at a minimum, and, by correct control of fatliquor and moisture content when the leather is removed from the drying plates, it is possible to eliminate this operation completely, since the buffing action will impart adequate softness.

Analyses of commercially produced chrome-retan leathers indicate that much heavier retannage is common in the U.S.A. than in Europe. Although this leather has good cutting value and is therefore liked by footwear manufacturers, its physical strength frequently leaves much to be desired. Zacharais and co-workers [31] found that chromium tanned leather retanned with vegetable tanning extracts was inferior in tearing strength to full-chrome leather, but that certain tannage factors tended to enhance the strength of chrome-retan leather. Thus, lower chromium content, lower level of retannage and the use of glucose-reduced chromium tanning salts all tended to enhance the strength of chrome-retan leather. Even so, the reduction in strength brought about by retannage was more than could be attributed to the plumping action of the retannage. In addition there is considerable evidence to show that

vegetable retanned chrome leather tends to lose strength during storage[32-34,36,87].

This section is primarily concerned with the results obtained from a series of experiments on retannage which have been published in the form of Research Bulletins[140-144] which are given in detail in Vol. 2, p. 68-109 and 128-139; together with some of the more important recent work[145-149] see Vol. 2, p. 55-67; 110-127, and 140-162, although the ageing characteristics will be dealt with later.

Information Obtained from the Testing of Commercial Leathers

A number of retan side leathers was obtained from South African footwear factories during 1954, and were representative of medium weight men's shoe upper leathers in use at that time. The leathers originated from North and South America and Europe in addition to those produced in South Africa. These leathers were subjected to detailed physical and chemical analysis[37]. From the chemical tests the amount of retannage was estimated, and the leathers were divided into three groups, viz., light retannage (5-13.3%), medium retannage (13.4-20.0%), and heavy retannage greater than 20%.

Table 5(a), I
Relationship between Amount of Retannage and the Properties of Commercially Produced Retan Leathers

Property	Retan Content (leather at 14% moisture)		
	5.0-13.3%	13.3-20.0%	Greater than 20.0%
Range of Atkin-Thompson Figure	2.4-4.7	2.5-4.0	2.1-2.5
Mean Atkin-Thompson Fig.	3.3	2.8	2.3
Range of stitch-tear strength	664-1429 lb./in.	520-1298 lb./in.	523-1037 lb./in.
Mean stitch-tear strength	1130 lb./in.	937 lb./in.	775 lb./in.
Range of slit-tear strength	232-688 lb./in.	123-678 lb./in.	158-243 lb./in.
Mean slit-tear strength	380 lb./in.	318 lb./in.	207 lb./in.
Range of Loads at grain crack	514-2790 lb./in.	850-2480 lb./in.	380-1550 lb./in.
Mean Load at grain crack	1630 lb./in.	1690 lb./in.	1000 lb./in.
Range of Hide substance content	54.4-72.1%	56.8-63.6%	50.3-55.4%
Mean Hide substance content	65.0%	59.5%	53.2%

N.B. All samples cut parallel to backbone line from A.L.C.A. official Upper Leather sampling position.

In Table 5(a), I, the range of values obtained from certain physical and chemical tests are given for each group of leathers, together with the mean values applicable to each group. Two general trends are immediately obvious from inspection of this table. Firstly that on average the heavily retanned leathers were more acid, tore more easily, and contained less hide substance than did those which were lightly retanned. Secondly within each group there is a wide range of values which indicates that other factors such as hide origin, and tannage variables other than amount of retannage must play a big part in determining strength. It must also be noted that these leathers may have had a more satisfactory strength when manufactured but some deterioration due to ageing may have taken place before they were tested. However, the information obtained was of considerable value as a foundation for the work to be described.

The Reactivity of Chrome Stock towards Retanning Materials

Normal chrome stock tends to be very reactive towards vegetable tannins[27,28,138], and it is this factor which in practice is important in determining the depth of retannage. Reducing immediate surface reaction will therefore induce deeper penetration of the tanning material into the chrome stock[53,150] and so increase grain strength, although this might be more than counterbalanced by impairment of the over-all tearing strength due to retannage of the centre layer of the leather. It has already been mentioned that a dominant reason for retanning is to fill the chrome leather, and there is probably no reason why any inert filler should not be satisfactory, provided that the filler does not detract from the desired properties of the leather. A number of so-called resin retannages are commercially available which in effect fill the loose areas within the fibre matrix of the leather. Two of these materials were therefore compared with mimosa extract as retanning materials. Pieces of shaved chrome stock were neutralised and retanned with either mimosa extract, Bedafil CF (I.C.I.) or Retingan R6 (Bayer); other pieces were finished as full-chrome leather for the control. The data presented in Table 5(a), II shows that all three "retannages" had the

same degree of filling action on the leather as measured by increase in thickness. All reduced the load at grain crack/unit thickness to some extent, but when allowance was made for the plumping action of the retannage (3rd line of results) only the chemically active mimosa extract had reduced the grain strength significantly.

Table 5(a), II
Properties of Chrome Leather Retanned with Various Materials**

Property	Nature of Retannage			
	Nil	12% mimosa extract solids	11% Retingan R6 | 1.5% Retingan ZN	24% Bedafil CF
Thickness as % shaved thickness	101	127	127	126
Lastometer load at grain crack	2790 lb./in.	1725 lb./in.	2005 lb./in.	2130 lb./in.
Relative grain strength based on equal thickness of shaved stock prior to retannage	2810 lb./in.	2190 lb./in.	2550 lb./in.	2680 lb./in.

** All results are means of six results, treatments allocated to leather pieces by random numbers.

On economic grounds the lower price of vegetable tanning extracts, compared with the resins just mentioned, is a big incentive for their use, provided the problems of adequate initial strength and satisfactory durability are solved. In the light of the results quoted in Table 5(a), II it appears that the problem of producing durable high strength retan leather resolves itself into one of reducing the reactivity of the chromed hide/vegetable tannin system. Two approaches to this are:

(a) Inactivating the vegetable extract; for instance, acetylation of mimosa extract would block the reactive ortho-hydroxy groups, and minimise reaction with the chromed hide. The problem here would be to find a suitable dispersing agent to act as a carrier for the water-insoluble acetylated tannin.

(b) Reduce the reactivity of the chrome leather. Much of the work to be described in this section has been on this approach, and it is

Table 5(a), III

Significance of Tannage Factors on the Strength and Durability of Chrome Retan Leather

Factor Varied	Direction of Change	Significance Level
4-day paddle liming v. 1 day drum liming ... 4 days in white lime v. 2 days in white lime subsequent to depilation by pulping	Paddle liming improved tear and grain strength	++
	Longer liming improved tear strength	+
No bating v. 1% Bate for ½ hr.	Bating improved grain strength	++
Depilation by sulphide paste (1 hr.), followed by 24 hr. lime at 20 C and ½ hr. bating or 24 hr. lime at 35 C and no bating	Warm lime without bate gives higher tear and grain strength ...	++
1.25 or 2.0% Cr_2O_3 offered	* Low chrome improves tear strength*	+
Basicity of chrome offered, 33% or 50% ...	Higher basicity resulted in lower tear and grain strength (mean chrome content 3.4% in each case)	++
Method of reducing chromate for 1-bath chrome tanning salt, SO_2 v. glucose	* Glucose reduced C.T.S. gave higher tearing strength*	++
Use of masking agents during chrome tannage	* Effect is an interaction between type and concentration of organic anion. Optimum amount of formate, phthalate and sulphophthalate all improve grain strength*	+
Addition of complexing ion to neutralising liquor subsequent to unmasked tannage	* Tear and particularly grain strength improved, approximate order of efficiency as follows :	
	Sodium Bicarbonate only 100	
	Addition of :	
	High molecular weight phosphate ... 106	not significant
	Calcium formate 109	
	Medium molecular weight phosphate. . 114	
	Sodium citrate 115	+
	Sodium sulphophthalate 116	
	Low molecular weight phosphate ... 116	
	Syntan A 116	++
	Syntan B 117	
	Sodium oxalate 118	
Temperature of retannage, 20°C v. 40°C ...	Higher temperature gives plumper leather but lower grain strength ...	+++
Period of retannage, 1 hr. v. 6 hrs.	Higher grain and tearing strength after 1 hr. retannage	++
Degree of retannage 5% v. 15%	* Low retannage improves tearing strength*	+++
Adjusting pH of retanning liquor to 3.5 or 5.0	* Does not affect tearing strength, but grain strength higher after retannage at pH 5.0*	+
Method of adding retanning material, in one lot, or 25% initially followed after 15 mins, by remainder	* Split feed gives rise to better grain strength when syntan used in blend	++
Replacement of ¼ of wattle extract by synthetic tannin	* Suitable syntans with wattle all give 20-25% improvement in tear strength, only improve grain strength when retannage is at pH 3.5* ...	+++ ++
Application of ½ the fatliquor prior to retannage, or all subsequent to retannage	Application of some oil prior to retannage improves grain strength ...	+

NOTES

1.—Unless otherwise stated results refer to retannage of chrome stock with 16.7% wattle extract at natural pH for 4 hrs. in 125% float at 21-25°C.

2.—Tearing Strength refers to buckle tear strength/unit thickness.

3.—Grain Strength refers to lastometer load at grain crack/unit thickness.

4.—All results have been abstracted from factorial experiments, statistical tests have been applied to determine whether the change observed is real or not.

\+ 95-99% chance that observed effect is due to process change.
++ 99-99.9% chance that observed effect is due to process change.
+++ Greater than 99.9% chance that observed effect is due to process change.

*These factors also give improved durability on storage.

interesting to note that Otto[53] has reached essentially similar conclusions, using an entirely different approach. He allowed vegetable tannins to react with freshly precipitated chromium hydroxide under controlled conditions, and determined the absorption of the former.

Conditions of Tannage which Influence the Strength of Chrome Retan Leather

At an early stage in this work it was found that almost every process of leather manufacture exerted some influence on the properties of the finished retan leather. Use was therefore made of statistically planned factorial experiments, similar to those recommended by Mitton[69], in studying this problem. Details of the statistical plans, and an outline of the experimental methods are given in Chapter 2.

Assessment of the Leathers

Attention has been confined to the physical properties of the leathers. Two tests were used, namely, the buckle tear strength and the load and extension at grain crack as measured by the lastometer. These two tests were chosen as measures of widely different leather characteristics: the lastometer yields information on the strength and extensibility of the grain, whilst the buckle tear gave some indication of the over-all strength of the leather fibre. Detailed tabulation of the actual results from each experiment is not warranted, but in Table 5(a), III a summary is given of those factors which were found to be of importance in determining the strength of chrome leather retanned with mimosa extract. The number of crosses in the right-hand column of Table 5(a), III indicates the significance of the change in leather characteristics introduced by the process variable recorded on the same line in the left-hand column.

Influence of the Degree of Retannage

In addition to the factors summarised in Table 5(a), III the amount of vegetable tanning extract offered during retannage must have a very pronounced effect on the physical characteristics of the leather. Data obtained from an experiment in which the amount of mimosa extract offered was increased from 3.3% to 26.7% on the blue weight of leather is given in Table 5(a), IV.

Table 5(a), IV

Effect of Increasing the Degree of Retannage on the Tearing Strength and Acidity of Leather

Amount of Mimosa Extract Offered on Shaved Blue Weight	Buckle Tear Strength lb./in.	pH of 5% Aqueous Extract
3.3%	559++	4.2++
6.7%	517	4.2
9.9%	515	4.1
13.4%	452	3.9
16.7%	446	3.8
20.0%	403	3.8
23.3%	410	3.8
26.7%	410	3.8

++ Mean figure from 8 replicates

It appears that with increasing level of retannage the strength tended to fall, until a limiting value was reached when 20% of extract had been offered. Although there was an expected increase in acidity of the leather which had been more heavily retanned, the relatively high average pH indicated that the fall in strength was unlikely to be influenced to a great extent by this particular increase in acidity. It is suggested that a more likely cause of the decrease in strength was the increased over-all degree of tannage, and may not be specific to the chromium/mimosa tannin system.

Additive Effect on Some Process Changes

Whilst the factors influencing the strength of chrome-retan leathers are not necessarily additive, the experiment to be described indicated the very large differences in leather strength which can be brought about by relatively simple process changes.

A number of calf-skins were split in half down the backbone after soaking, and alternate lefts and rights were taken for process A or B. Except where stated, all processing was identical.

Variable	Tannage A	Tannage B
Liming	4 day paddle lime	1 day drum lime
Chrome Tannage	1.78% Cr_2O_3 offered as 33% basic salt	1.78% Cr_2O_3 offered as 50% basic salt
Retannage	15% mimosa extract offered, drum run 1 h.	15% mimosa extract offered, drum run 6 h.
Mean Buckle Tear Strength	865 lb./in.	574 lb./in.

Thus even though the amounts of tanning materials offered were identical, relatively slight changes in the method of application and in the liming can bring about very big differences in the strength of the retan leather.

Discussion

The work that has been summarised above indicates that the choice of processing conditions can affect the tearing and grain strength of chrome-retan leather very considerably. The following conditions tend to produce higher quality leather.

1. Mellow liming with a minimum of mechanical action.
2. Chrome tannage with about 1.25% 33% basic Cr_2O_3.
3. Introduction of a chrome complexing agent into the leather during neutralisation; sulphophthalate and certain neutralised syntans appear to be promising.
4. Apply part of the fatliquor immediately after neutralising.
5. Retan in as short a time as possible, but preferably add in two lots, especially if syntan forms part of the retanning blend.
6. Adjust drying conditions and fatliquor composition so that staking can be minimised or eliminated.

5(b) Factors which Influence the Storage Stability of Chromium Tanned Leather Retanned with Vegetable Tanning Extracts and Syntans[132]

The retannage of chrome leather, which is complementary to the paste drying process, introduced new problems to the leather industry. Some years ago reports were received from South African tanners that vegetable retanned leathers which had a reasonable strength when control tested after manufacture, were being returned as unsatisfactory by shoe manufacturers after a few months' storage. At about the same time, 1954, various reports[32-34,36] from the U.S.A. indicated that this was by no means a purely local problem, and that vegetable retanned chrome leather was prone to deterioration particularly under tropical storage conditions, humidity being an important factor. Accelerated test methods based on warm, humid storage have been investigated to determine their usefulness for predicting the stability of chrome retan leather under normal storage conditions. Dudley[151] reported changes in tensile strength and the chemical composition of retan leathers stored in saturated atmosphere at various temperatures. Sykes & Williams-Wynn[87] published a brief note on some limitations of these tests. This paper also indicated that retan leathers which were relatively acid tended to deteriorate more rapidly than those which had a higher pH. Lollar[58] has stated that leathers having a pH of aqueous extract (1 : 20) of less than 3.0 must be considered as unstable, and in a survey of commercial retan leathers it was found that low strength tended to be associated with high acidity[134].

Experiments carried out over a number of years have been directed towards elucidating some of the factors which affect the strength and stability of chrome retan leathers, particularly the chromium/mimosa tannin system. In the previous section some process variables which influenced the strength of mimosa retanned chrome leather soon after manufacture were discussed. The present report is primarily concerned with the stability of chromium-vegetable retan leather stored under temperate conditions, viz. at 21°C and 65% r.h.

The investigations have been based on the hypothesis that a major factor influencing the deterioration is the instability of the chromium leather/vegetable tannin system. Evidence for this comes from the

tendency of retan leather to become more acid during storage[87], and the fact that leather retanned with inactive resin fillers or certain syntans does not lose strength to anything like the same extent as vegetable retanned leather[34,134].

Although it was initially thought that mimosa retannage was peculiar in bringing about a reduction in strength of chrome leather, this was soon discounted when the American reports were received, since quebracho was almost certainly used in the U.S.A. as the retanning agent.

Comparison of Retanning Materials

A preliminary experiment was set up to compare the effect of various retanning materials. Six goatskins were painted with sulphide paste to remove the hair, then limed for 5 days, prior to deliming and bating. The skins were tanned with 2.25% Cr_2O_3, offered from a 33% basic solution; bicarbonate was used to basify the tannage to a final pH of 3.5. Each skin was treated as a block and from it six samples were taken. One sample from each skin was taken for retannage with a particular material. After neutralisation with 1½% sodium bicarbonate, the skins were retanned for 45 min. in a 150% float at 30°C using the quantities of material given in Table 5(b),I which reduce to approximately 10% tannins.

Table 5(b),I

Changes in the Buckle Tear Strength of Chrome Retan Leather During Storage

Retanning Material	Amount offered on shaved wt. of leather	Original Buckle tear strength	Buckle tear strength after 9 mths. at 21°C and 65% r.h.	Aged Buckle Tear Strength as % of original
Nil	0	802 lb./in.	780 lb./in.	97%
Mimosa extract	16.7%	464 "	375 "	81%
Bisulphited mimosa	equivalent to 16.7% natural extract	458 "	355 "	77%
Soluble Quebracho (bisulphited)	15.4%	413 "	340 "	82%
Sumac leaves	42%	460 "	394 "	85%
Orotan TV (Rohm & Haas)	32.3%	454 "	419 "	92%

A number of factors are immediately apparent from this table. Irrespective of the nature of the retanning material there was a very large reduction in the strength of the leather. In fact, the difference in strength found in this experiment is more than usual. Secondly, the deterioration of the vegetable retanned leathers is virtually independent of the type of extract. The syntan, "Orotan TV" was chosen because American reports had shown it to yield a very stable leather[34]. Their findings have been confirmed.

Although this experiment showed that the deterioration of chrome-retan leather was not peculiar to the use of mimosa extract, the later investigations reported here have been confined to this material.

The Reaction Between Chromium Salts and Phenolic Materials

On ageing the acidity of an aqueous extract of chrome-retan leather increases initially but subsequently falls[87] (see Vol. 2, p.47), and this may account for some conflicting reports in the literature that the pH of a retan leather is virtually unaltered during deterioration. Many years ago Burton[152] suggested that the fall in the pH of chrome leather during retannage was due to displacement of sulphate groups from the chromium complex by the vegetable tannins and the formation of strong acid. Amos, Thompson & Tolliday[29] consider that during a long period of retannage or ageing, vegetable tannins penetrate the chromium complex and liberate H^+ ions. Dudley[151] investigated the reaction of phenolics with chromium salts and found that a fall in pH took place.

It is well known that carboxylic acids form more stable co-ordination complexes with chromium than do sulphate ions, and that if a solution of chromium sulphate is boiled with acetic acid there is a fall in the pH of the solution, as sulphate is displaced and strong acid formed. It was considered probable that this reaction also took place to a limited extent when polyphenolics reacted with chromium sulphate in leather. If, however, the sulphate had been displaced by a strongly co-ordinating organic acid ligand, then subsequent reaction with the tannin should be reduced. Spectrophotometric evidence has been used to show that pyrogallol and catechol had virtually no reaction with chromium sulphate which had been masked with a large amount of citrate[54].

The following experiment was therefore undertaken to investigate this point further. A 50% basic solution of chromium sulphate was prepared by SO_2 reduction of potassium dichromate, and neutralised with sodium hydroxide. The strength of the solution was adjusted to 10% Cr_2O_3 w/v. 50 cc. aliquots of this solution were refluxed for 1 h. with partially neutralised formic, acetic and citric acids so that the final pH values of the solutions were approximately 3.2. Amounts of acid equivalent to 0.5 or 2.5 moles/g. atom Cr were used, and after cooling the volume was made up to 100 cc. 25 cc. aliquots of this solution were mixed with an equal volume of a solution containing 10% w/v. of catechol, pyrogallol or soluble mimosa polyphenols*. The pH was determined immediately after mixing and after standing at 21°C for ½ h., 8 h. and 720 h. These times were chosen to represent the changes which might take place (a) during the course of retannage, ½ h.; (b) between retanning and completion of drying, 8 h.; and (c) during storage. The results converted to changes in hydrogen ion concentration are reported in Table 5(b), II.

Table 5(b), II

Increase in Acidity of Masked 50% Basic Chromium Sulphate Addition of Phenolics ($\Delta[H^+] . 10^4$)

Masking Agent	Phenolic Material: Catechol			Pyrogallol			Purified Mimosa Extract		
	Hours after original mixing of solutions								
	0.5	8.0	720	0.5	8.0	720	0.5	8.0	720
None	2.0	4.9	9.0	2.1	8.7	21.2	1.7	9.0	18.7
0.5 mole Formate/mole Cr	0.7	3.9	6.8	1.4	7.1	17.8	0.7	7.0	12.9**
2.5 mole Formate/mole Cr	nil	2.9	2.7	0.1	5.9	9.9	nil	4.6	6.6**
0.5 mole Acetate/mole Cr	1.6	5.6	8.1	2.9	9.3	19.0	2.8	8.3	13.1
2.5 mole Acetate/mole Cr	nil	nil	1.0	2.1	6.1	7.6	3.2	7.2	11.7
0.5 mole Citrate/mole Cr	1.3	8.3	8.3	1.5	12.2	17.6	nil	5.7	11.2
2.5 mole Citrate/mole Cr	nil	2.6	3.7	nil	nil	3.9	nil	nil	3.0

** Indicates gel formation.

It appears that the purified mimosa extract was more similar to pyrogallol than to catechol. All three organic acids under consideration

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* Mr. E.A. Maihs of this Institute prepared a soluble fraction of wattle polyphenolics by extracting fresh bark with ethyl acetate, the sample used contained 92% polyphenolics on a dry basis as estimated by U.V. Spectrophotometric analysis.

limited the increase in acidity which followed the addition of polyphenolics to the chromium solutions. Further, the presence of a larger amount of organic acid was more effective than a small amount. It seems therefore, that the indications given by spectrophotometric studies[54] have been confirmed and that the introduction of complexing agents at some stage during the chrome retan process would tend to reduce the liberation of strong acid with consequent improvement in the durability of the leather. Another important factor is likely to be the amount of chromium present in the leather; the greater the amount of chromium the larger the amount of displaceable sulphate. Similarly, the degree of retannage might be expected to accelerate the rate of deterioration. These and other variables in the retanning process will now be considered in relation to their effect on the stability of mimosa retanned chrome leather.

Information Obtained from the Prolonged Storage of Experimental Retan Leathers

All the data discussed in this section were obtained from leathers tested two to three weeks and nine to ten months after manufacture. The results have been taken from a number of statistically planned factorial experiments, and details of the tannage methods have been published[134]. Some of the factors which have shown to be statistically significant will now be considered. In all cases storage was at 21°C and 65% r.h. with free air circulation.

1. On the Level of Chrome Tannage

In the previous section it was shown that reducing the amount of chromium offered brought about an increase in the buckle tear strength of the leather, and it was concluded that this was related to the smaller load carried by the leather fibres. This effect was obtained in two experiments. However, when these same leathers were stored for nine months it was found that the leathers containing the larger amount of chromium were more stable. Table 5(b), III shows the average results from the two experiments. Each figure is a mean of 32 determinations.

Table 5(b), III

Effect of Chromium Content on the Stability of Retan Leathers

Experiment A				Experiment B			
	Buckle Tear Strength lb./in.				Buckle Tear Strength lb./in.		
% Cr_2O_3 offered on limed wt.	Original	After 9 months	% of original	% Cr_2O_3 in leather	Original	After 9 months	% of original
1.25	489	422	86	3.09	471	422	89
2.0	440	399	90	3.78	383	369	96

These differences were significant at the 1% level and are real. They indicate that initial strength is not necessarily related to storage stability.

2. On the Degree of Retannage

The amount of mimosa extract offered was found to exert a considerable influence on the initial strength of chrome retan leather. It was also found that the degree of retannage had a highly significant effect on the stability of the leather. Increasing the level of retannage reduced the stability in simple chromium/mimosa tannin systems. Table 5(b), IV demonstrates this for a series of leathers; the results are means of 32 determinations.

Table 5(b), IV

Changes in Strength in Relation to Degree of Retannage

Test	Amount of extract offered	Original leather	Leather after 9 months storage	% of original
Stitch Tear	2% on blue weight	962 lb./in.	881 lb./in.	91
	15% on blue weight	802 lb./in.	665 lb./in.	83
Load at Grain Crack	2% on blue weight	1157 lb./in.	917 lb./in.	80
	15% on blue weight	1059 lb./in.	801 lb./in.	76

3. On the Use of Masking Agents

The work reported earlier in this section on the reduced reactivity of masked chromium salts to phenolics led naturally to an investigation of the protection which might be afforded to leather by masked chrome tannages. Lotz[33], commenting on a paper by Roddy & Jansing, stated that experience had shown formate masked tannages to have better ageing characteristics than straight chrome tanned leather when retanned with vegetable extracts. Preliminary experiments confirmed that mimosa retannage of masked chromium tannages gave leathers which deteriorated less than those which had had a straight chromium tannage,[87] (see Vol. 2, p.47). It was considered desirable to confirm this finding and also to determine whether the amount of masking agent used was of importance. Four calfskins were used in this trial, each being cut into 16 pieces and grouped at random prior to tannage with chromium masked with 0.5 or 2.5 moles of either formate, phthalate or sulphophthalate as masking agent. The leathers were retanned with 16.7% mimosa extract on shaved weight. The grain strength of the leathers was significantly improved by the presence of masking agent, although the ratio of masking agent to chromium did not prove significant. Similarly, after 8 months storage, only the type of masking salt and not the amount used influenced the loss in grain strength. The relative results are given in Table 5(b), V.

Table 5(b), V

Influence of Masking Agents on the Load at Grain Crack of Chrome-Retan Leather

Masking Acid	Original Load at Grain Crack	Load at Grain Crack after 9 months ageing	Aged Load as % of Original
none	1797 lb./in.	1255 lb./in.	70%
Formic	2048 "	1688 "	82%
Phthalic	2066 "	1824 "	88%
Sulphophthalic	1975 "	1621 "	82%

Thus it will be seen that a reasonable level of protection is imparted to the leather by using a masking agent in the chrome tannage. Although the amount of masking agent did not significantly affect the grain strength, it did have an effect on the tearing strength initially, and after 9 months' ageing. This is recorded in Table 5(b), VI.

Table 5(b), VI
Influence of Masking Agents on the Buckle Tear Strengths of Retan Leather

Masking Acid	Amount used moles/mole Cr	Original Buckle Tear	Buckle Tear after 9 mth. ageing	Aged Load as % of original
Formic	0.5	450 lb./in.	408 lb./in.	91
Formic	2.5	405 "	424 "	104
Phthalic	0.5	456 "	365 "	80
Phthalic	2.5	407 "	402 "	99
Sulphophthalic	0.5	380 "	366 "	96
Sulphophthalic	2.5	459 "	390 "	85

It will be seen that there is a definite interaction between the amount of masking agent used and the nature of the masking acid. It seems likely therefore that for any particular organic acid there is an optimum quantity which should be used to obtain good initial strength in conjunction with adequate resistance to deterioration. The results quoted above indicate that high initial strength is not necessarily associated with high resistance to deterioration.

4. On the Use of Blends of Vegetable Extract and Syntan

Mann[34] reported that chrome leather retanned with a syntan "Orotan" showed much less reduction in Ball Burst strength than vegetable retanned leather. The superiority of this syntan over vegetable extracts has already been noted, and it was therefore considered useful to determine whether a blend of syntan and mimosa extract would produce a more stable leather than vegetable extract alone. To determine this, a factorial experiment was set up to compare four retanning blends, applied at two pH levels, 3.5 and 5.0, and two temperatures, 20°C and 40°C. A commercial side suitable for retanning was obtained in the blue and shaved to give about 2 mm. final substance. The retanning blends used were 100% mimosa and 75% mimosa with 25% of either Irgatan AGI (Geigy), Orotan TV (Rohm & Haas) or Tanigan Extra Special P.1 (Bayer). (Percentages based on actual tan content as given by manufacturer, not on total weight). The load at grain crack in the lastometer was used to determine the initial and final strengths of the leathers. Table 5(b), VII shows the interaction between pH of retannage and the composition of the blend; each result is the mean of 16 replicates.

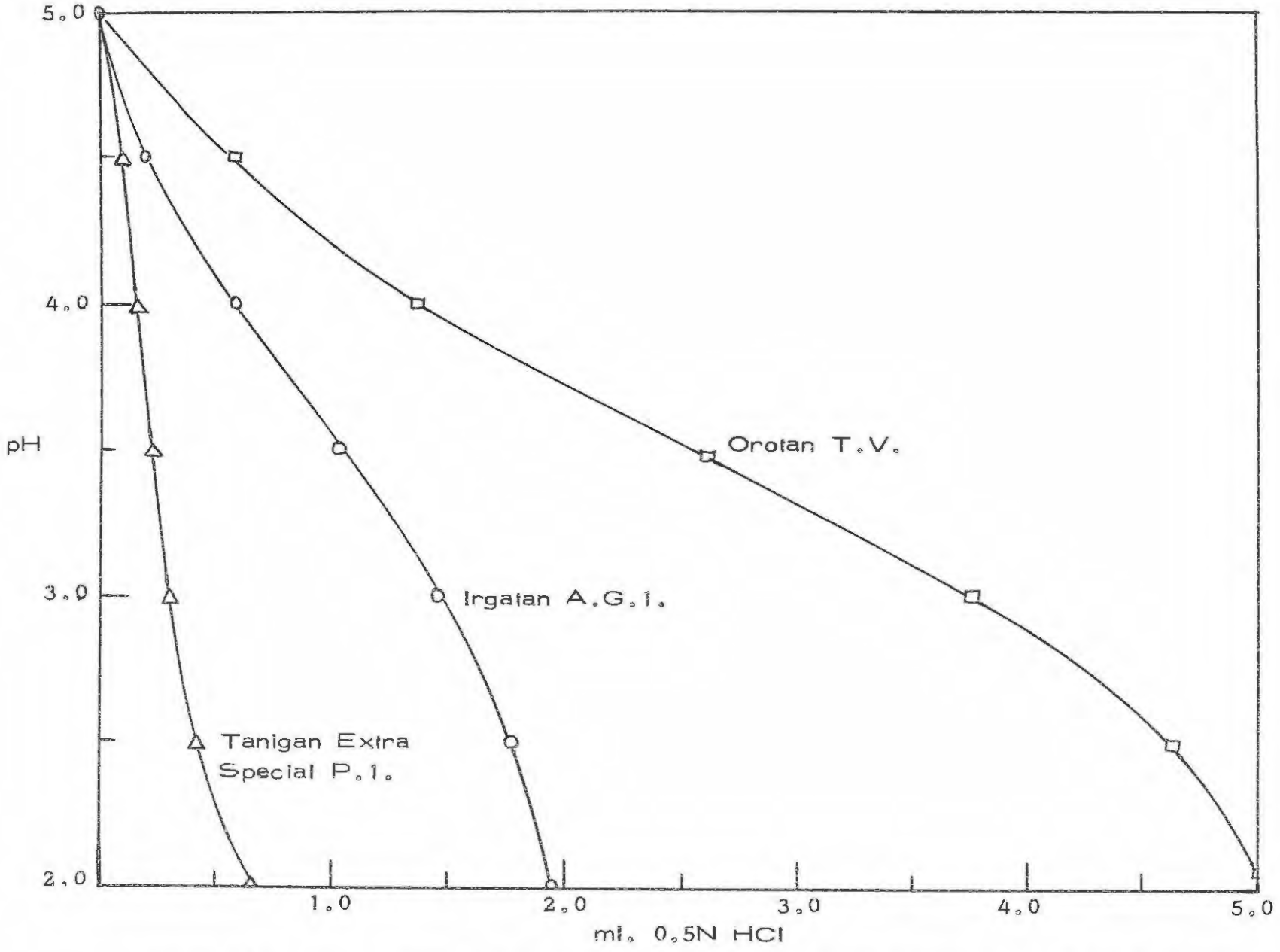

Figure 5(b), 1. Titration curves of 50 ml. aliquots of syntan solution each made up to contain 25% tannins and initially adjusted to pH 5.0 with NaOH.

Table 5(b), VII

The Strength and Stability of Chrome Leather Retanned With Blends of Mimosa Extract and Syntans

(Load at grain crack in lb./in. and changes as %)

Retanning Blend adjusted to		Composition of Retanning Blend (12% as tans offered)			
		100% Mimosa	25% Irgatan AGI 75% Mimosa	25% Orotan TV 75% Mimosa	25% Tanigan E.S.P.1 75% Mimosa
Original Leather	(pH 3.5	829	1001	1039	1013
	(pH 5.0	963	941	961	1014
Leather after 9 months storage	(pH 3.5	517	739	814	669
	(pH 5.0	669	735	830	764
Final strength as % of Original	(pH 3.5	62.5	74.0	78.5	66.0
	(pH 5.0	69.5	78.0	86.5	75.0

None of these leathers showed particularly good ageing characteristics, but it is useful to note that increasing the pH of the retanning blend in every case brought about a reduction in the extent of deterioration. Initially, the use of syntan brought about a significant (1% level) increase in the strength of the leathers retanned at pH 3.5 but hardly affected those retanned at pH 5.0. The use of 25% syntan in the retanning blend reduced the rate of deterioration compared with the mimosa control at the same pH. Of the three syntans compared, Orotan TV appeared to be the most useful under the conditions of the present experiment. In this connection it is interesting to note that Orotan TV is much more highly buffered than the other two syntans. Fig. 1 gives the titration curves of these materials based on equivalent "tannin" concentration, but not at the same total solids concentration. On inspection of the titration curves it appears that Orotan TV contains a considerable quantity of formic acid (pk 3.7). This same experiment also showed that increased temperature of retannage adversely affected initial strength and storage stability.

Table 5(b), VIII
Strength and Stability of Chrome Leather Retanned at High and Low Temperatures

Temperature of Retannage	Original load at grain crack	Load at grain crack after 9 mth. storage	Aged grain strength as % of original
20°C	1021 lb./in.	791 lb./in.	77.5
40°C	919 lb./in.	645 lb./in.	70.0

Each result is mean of 64 samples.

It is suggested that these results indicate an increased reaction between retanning material and chrome leather at higher temperature, possibly leading to a greater displacement of acid. Some confirmation of this comes from the pH of the spent retan liquors which are given in the two-way table below.

Table 5(b), IX
pH of Spent Retan Liquors after Retannage at High and Low Temperatures

Initial pH of Retanning Liquor	Temperature of Retannage	
	20°C	40°C
3.5	3.4	3.3
5.0	4.5	4.2

The higher temperature of retannage appeared to liberate more acid from the chrome stock, indicating a more complete chemical reaction. The presence of syntan in the blend also limited the formation of acid during retannage, but the changes here are not related to the buffering capacity of the syntans.

Table 5(b), X
pH of Spent Retan Liquors after Retannage with Blends of Mimosa Extract and Syntans

Initial pH of Retanning Liquor	100% Mimosa	25% Irgatan AGI 75% Mimosa	25% Orotan TV 75% Mimosa	25% Tanigan E.S.P.1 75% Mimosa
3.5	3.15	3.4	3.4	3.45
5.0	4.1	4.5	4.4	4.4

(Composition of Retanning Blend 12% of tans offered)

Discussion

The above results give information on the storage stability of some of the chrome-retan leathers which have been discussed in the previous section; the storage conditions, 21°C and 65% r.h., being laid down in the Society of Leather Trades Chemists' specification for the standard atmosphere for physical testing of leather[86].

In a preliminary experiment it was found that wattle extract is not unique in causing vegetable retanned chrome leather to deteriorate on prolonged storage. Quebracho, widely used in the U.S.A., and Sumac, a common mordanting agent, both brought about a considerable decrease in strength of the leather after 9 months storage. It seems certain that the retannage conditions and the nature of the chrome stock must be to a large extent responsible for this deterioration. Although Zacharais and co-workers[31] have reported on some tannage factors which affect the strength of heavily oiled leathers, they did not relate initial strength to storage stability.

The present work has shown that increasing the level of retannage in general leads not only to a decline in initial strength, but also to a more rapid rate of deterioration. The addition of masking agents has been shown to limit the reaction between phenolic materials and solutions of chromium tanning salts, findings which have been confirmed by the increased initial strength of the leather[53,134], and also by the reduced rate of deterioration under standard conditions. However, the results presented in this report indicate that for any particular masking agent there is an optimum quantity which will give the best balance between initial strength and stability. The amounts of masking agent which give maximum initial strength do not necessarily give the greatest resistance to deterioration on prolonged storage, and further detailed work on the use of masked chrome tannages is required.

Blending synthetic tannins with vegetable extracts brings about an improvement in the initial strength which is pH dependent and at a given pH does improve the storage stability. There appear to be significant differences between the syntans under review, although all of

them are recommended by their respective manufacturers for use in the retanning of chrome leather.

In the introduction to this section it was suggested that many of the observed facts regarding the deterioration of chrome-retan leather were consistent with slow changes which might arise from liberation of strong acid from the chromium-collagen complex, as vegetable tannins entered the complex and displaced sulphate. The work reported here does not contradict this concept, and the results of the experiments detailed in Chapter 4 have shown that the above is the most likely explanation.

5(c) The Storage Stability of Chrome-Retan Leather under Warm Humid Conditions[88]

The chrome-retan leather uppers of footwear that had been stored in tropical areas showed serious deterioration and there seems to be no doubt that the deterioration observed in chrome-retan leather generally is accentuated by a combination of high temperature and high humidity. The rapid deterioration seems to be peculiar to the chromium-vegetable combination tannage, since neither chrome leather nor vegetable tanned leather deteriorates to the same extent. It has also been found that the rate of deterioration is pH dependent, the lower the pH the greater the deterioration, and loss of strength is associated with an increase in the acidity of the leather[87,132,153].

From the results so far available it seems that strong acid is liberated from the chromium complex in the leather by the retanning materials employed; the more vegetable tanning material used the greater the amount of acid liberated and the greater the rate of deterioration. Since this is undoubtedly a chemical process, the effect of temperature and humidity can be readily understood. If, as is suspected, the deterioration is caused by hydrolysis under the acid conditions prevailing in the leather, the breakdown of the leather will be increased by an increase in the temperature. This view is supported by evidence that has been obtained from ageing tests in which leathers have been found to contain protein degradation products[32,87]. These decomposition products were detected at an earlier stage in leathers stored at high temperatures.

Further experiments were directed towards elucidating the means whereby the deterioration can be reduced or eliminated. Unfortunately the rate of deterioration is fairly slow and an ageing experiment carried out under conditions of normal temperature and humidity requires from nine months to a year to complete. Accelerated test methods based on warm humid storage have been investigated to try to reduce the time required to complete the experiment.

Experimental

Two series of leathers were produced from the same chromed stock; one was retanned with 5% of mimosa extract and the other with 15%. The finishing procedures in each case were identical. Thus the only variable was the degree of retannage. Eight pairs of samples, one for buckle tear and one for lastometer test were cut from the two types of leather and stored under each of the following conditions of temperature and humidity.

1. 20°C, 65% r.h., normal conditions for testing
2. 20°C, 85% r.h., satd. NaK tartrate
3. 20°C, 100% r.h., water
4. 45°C, 65% r.h., satd. NH_4Cl + KNO_3
5. 45°C, 85% r.h., satd. NaK tartrate
6. 45°C, 100% r.h., water
7. 55°C, 65% r.h., satd. $NaNO_3$
8. 55°C, 85% r.h., satd. KNO_3
9. 55°C, 100% r.h., water

The leathers were tested initially and after 1, 2, 3, 5, 9, 18 and 32 weeks' storage. The results obtained have shown that the lastometer load at grain crack was the most sensitive of the tests performed and this correlated strongly ($r = 0.545$, d.f. = 36) with the loss in strength as determined by the buckle tear test. The pH of a 5% aqueous extract of the leathers was also measured after each time interval. It was observed that on prolonged storage the pH of the retan leather which originally had fallen, began to rise, and at the same time decomposition of the leather was taking place as shown by the presence of protein decomposition products, which can be detected with ninhydrin[154].

The amount of mimosa extract offered has been shown to exert a very considerable influence on the initial strength of chrome retan leather[134], as well as on the stability of the leather under normal storage conditions[132]. Thus increasing the level of retannage reduced the stability in simple chromium/mimosa tannin/pelt systems. This was also found to be the case under conditions of high temperature and humidity, and when the leathers were stored for 3 weeks at 45°C and 95+%r.h. the amount of deterioration almost exactly equalled the deterioration after 32 weeks natural ageing, see Table 5(c), 1.

Table 5(c), I

Effect of Degree of Retannage on the Deterioration of Leather

Degree of Retannage	Original load at grain crack lb./in.	Fall in load at grain crack			
		Accelerated Ageing		Natural Ageing	
		lb./in.	% of orig.	lb./in.	% of orig.
5% wattle extract	1236	272	22%	259	21%
15% wattle extract	1154	265	23%	265	23%

An interesting sidelight on this experiment was the observation that leathers stored under normal conditions increased in strength for the first few weeks immediately after manufacture. A number of tanneries have also reported similar observations and it is therefore necessary to allow leathers to age for about 3 weeks before subjecting them to various tests. In normal tannery practice the post-tanning operations occupy quite a long time and this problem would not arise, but when experimental packs are rushed through it would be as well to bear this in mind.

The main observation as mentioned above was the fact that storage in a saturated atmosphere at 45°C for 3 to 4 weeks was approximately equivalent to 6 to 8 months storage under normal conditions i.e. 65% r.h. and 21°C, and this was adopted in the accelerated ageing test. The higher temperature (55°C) was excessive, resulting in darkening and cracking which are not normally associated with natural ageing.

When the accelerated ageing test was applied to leathers containing appreciable quantities of organic buffer salts it was found that the leathers that contained these organic acids deteriorated more rapidly than leathers which contained no buffer salts. Moreover the reverse was the case when the leathers were tested after 9 months storage at 65% r.h. and 21°C. These leathers contained appreciable quantities of salts of organic acids and a possible reason for the rapid deterioration at high temperature and humidity is that the weak acids have a peptising effect on the leather fibre with consequent loss in strength similar to that found when sole-leather is hot-pitted indiscriminately (155).

Since large quantities of uncombined organic acid anions were thought to be harmful when the leathers were subjected to conditions of

high temperature and humidity, leathers were prepared using masked chrome tanning salts or by neutralising the chrome leather with alkaline solutions containing strongly complexing materials and all the free material was removed by thorough washing before retanning. These leathers were aged both artificially and naturally and it has again been shown that when organic salts were present, 3 weeks storage at 45°C and 95+% r.h. did not give a true reflection of the deterioration to be expected after prolonged storage under normal condition. In Table 5(c), II below, results are given for the fall in load at grain crack for leathers containing three masking agents and a control, when these had been aged naturally for 9 months, and under the conditions of the accelerated ageing tests. It will be seen that, although the masking agents to some extent improved the resistance to deterioration under conditions of high temperature and humidity, they were not as effective as they were in preventing deterioration under normal storage conditions.

Table 5(c), II

Effect of Masking Agents on the Deterioration of Leather +

Masking Agents	Original load at grain crack lb./in.	Fall in load at grain crack			
		Accelerated Ageing		Natural Ageing	
		lb./in.	% of orig.	lb./in.	% of orig.
None	1797	690	38%	640	36%
Formate	2048	590	29%	360	18%
Phthalate	2066	450	22%	240	12%
Sulphophthalate	1975	420	21%	350	18%

+ The results quoted in this table are means of 8 samples.

Innumerable organic acids could be investigated in the hope that one or more would be effective in preventing deterioration under warm humid conditions, but since the masking salts that have been tried are the types commonly offered for masking, and since other complexing agents such as phosphate, citrate and oxalate have not imparted increased stability under accelerated ageing conditions[142,143], (see Vol. 2, p. 82 and 90) more complex materials, namely syntans, have been investigated (see Vol. 2, p. 98 and 110).

Chrome leather retanned with syntans is claimed to be more

resistant to deterioration than leather produced by vegetable retannage[34]; this has been confirmed as far as storage stability under normal conditions is concerned[132]. Leathers were prepared using as retanning agents 100% mimosa and 75% mimosa with 25% of either Irgatan AG1 (Geigy), Orotan TV (Rohm & Haas) or Tanigan Extra Special P.1. (Bayer). The load at grain crack was used to determine the initial strength and the fall in strength on accelerated and natural ageing. Table 5(c), III shows the fall in strength obtained on ageing together with the initial strength of the leathers. Each result is the mean of 16 replicates.

Table 5(c), III

Effect on Syntans on the Deterioration of Leather +

Retanning Material	Original load at grain crack lb./in.	Fall in load at grain crack			
		Accelerated ageing		Natural ageing	
		lb./in.	% of orig.	lb./in.	% of orig.
Mimosa	896	431	48%	403	45%
25% Irgatan AGI 75% Mimosa	971	313	32%	234	24%
25% Orotan TV 75% Mimosa	1001	225	22%	178	18%
25% Tanigan ESP1 75% Mimosa	1013	353	35%	297	29%

+ The results quoted in this table are the means of 16 samples.

None of these leathers had good ageing characteristics. In fact the leathers retanned with only mimosa lost nearly half their strength after 9 months natural ageing or 3 weeks accelerated ageing. This is due to the fact that the leathers were prepared under conditions which we know lead to less durable leather[132], in order to magnify the effects of the syntans. The incorporation of a syntan in the blend resulted in an increase in the initial strength of the leather and reduced the extent of deterioration under both conditions of ageing. But as was the case with the masking agents, the presence of syntans resulted in a greater deterioration relative to the 100% mimosa tannage when the leathers were stored under warm humid conditions compared with that obtained on natural ageing.

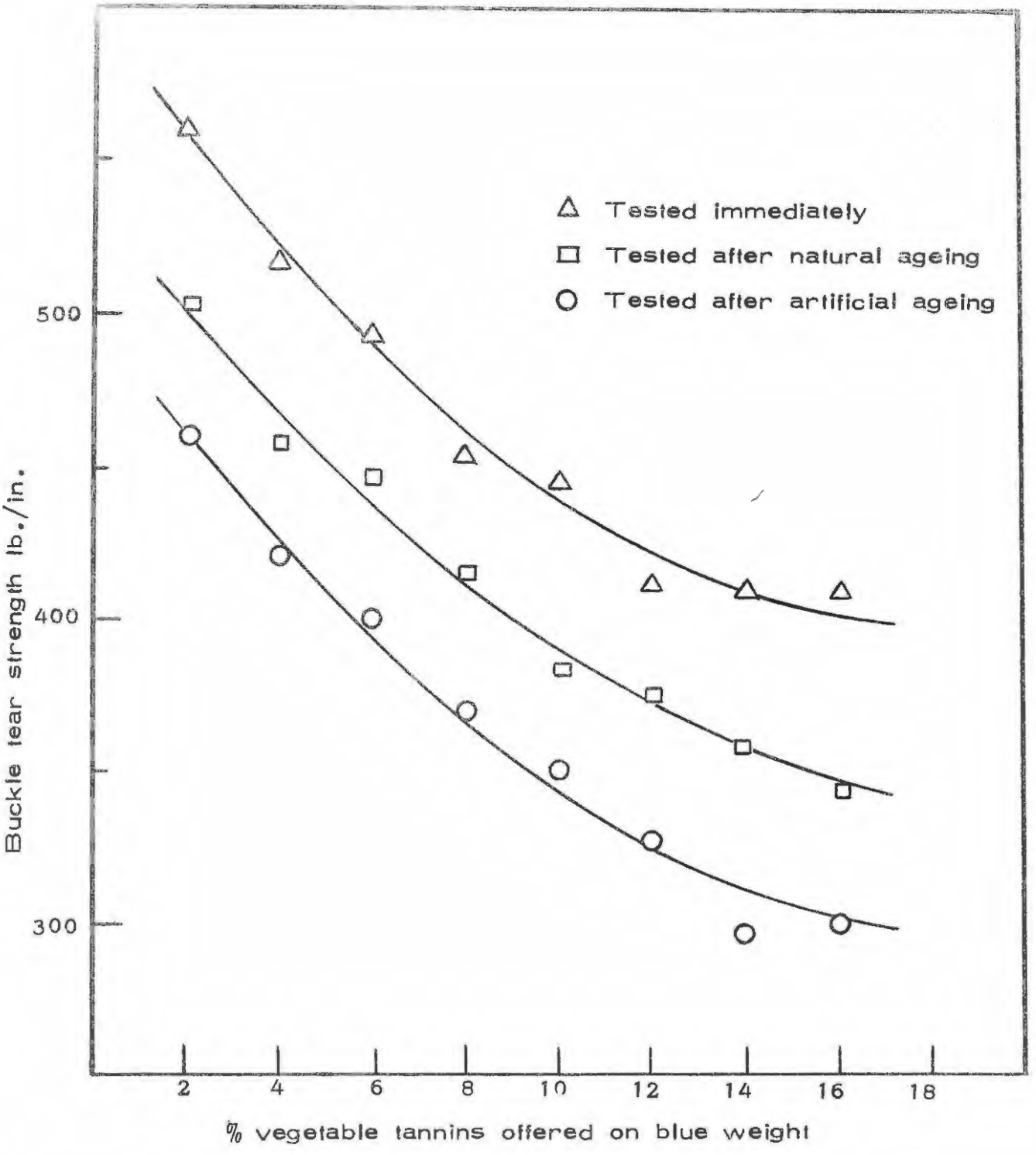

Figure 5(c),1. Variation in strength of chrome-retan leather with degree of retannage

Since it is thought that the fundamental form of almost all leather deterioration is an hydrolysis of the protein-tannin complex[58], moisture must be considered to play an important rôle. To determine this, a factorial experiment was undertaken to study the effect that the exclusion of moisture would have when leathers are stored under warm humid conditions[156]. In this experiment leathers were sealed in polythene containers before being stored for 3 weeks at 45°C and 95+% r.h., and the deterioration was compared with that obtained from samples of the same leather stored unsealed under the same conditions. The results are presented in Table 5(c), IV and give conclusive evidence of the importance of moisture in the degradation process. They also show the effect of the degree of retannage on the extent of deterioration.

Table 5(c), IV
Effect of Moisture on the Deterioration of Leather

Degree of Retannage	Original load at grain crack lb./in.	Fall in load at grain crack			
		Aged at 45°C, 95+% r.h.		Aged at 45°C moisture excluded	
		lb./in.	% of orig.	lb./in.	% of orig.
2% Mimosa	1084	257	24%	78	7%
5% Mimosa	883	256	29%	38	4%
10% Mimosa	840	290	34%	107	13%
15% Mimosa	827	288	35%	125	15%

It is evident that when moisture is excluded from leather deterioration is considerably reduced, in some cases to as little as one-fifth of that obtained in a saturated atmosphere.

This table also brings out another important aspect of retannage: that of the degree of retannage. It will be seen that increasing the degree of retannage reduced the initial strength of retan leather. The diagram, Fig. 1, reproduced from the publication referred to in reference 141, (see Vol. 2, p. 128), shows the influence on strength of the amount of mimosa tannin offered. With more than 10% of tans the initial strength decreased no further, and this is confirmed by the figures in Table 5(c), IV. It is also apparent that the rate of deterioration was influenced by the degree of retannage, but again once 10% of tans has been offered, little increase in the rate of deterioration occurred.

Discussion

In simple chromed pelt/vegetable tannin systems, deterioration as determined by loss of strength and increase in acidity occurred in much the same way, but more rapidly, under conditions of high temperature and high humidity as it did under normal storage conditions. Various factors unconnected with the composition of the retanning mixture or the chromium complex had an important bearing both on the strength and on the durability of chrome-retan leather. For example, the present work shows that increasing the level of retannage led not only to a reduction in the initial strength of the leather, but also to a more rapid rate of deterioration.

The addition of masking agents reduced the rate of deterioration of leather under standard conditions of storage but was not effective in preventing deterioration under warm, humid conditions. Syntans behave similarly when used in blends with mimosa.

The importance of moisture in the deterioration process has been strikingly demonstrated. Where moisture had been excluded, the extent of deterioration ~~had been~~ was drastically reduced and it is possible that, had the leathers been thoroughly dried before sealing, the deterioration would have been still further reduced. Whilst is seems certain that deterioration of chrome-retan leather under normal conditions occurs as a result of slow changes which are the result of the liberation of acid from the chromium-collagen complex by the penetration of vegetable tannins into the complex, the deterioration under warm, humid conditions is more involved, and storage under these conditions does not give a true reflection of the durability of chrome-retan leather regardless of method of manufacture. A probable explanation is that at normal temperatures the sulphuric acid liberated from the chromium sulphate complex by the vegetable tannin is capable of hydrolysing the protein, whereas the weak acids liberated from masked chromium complexes do not have this power of hydrolysis. At elevated temperature not only are the weak acids more readily displaced from the chromium complexes resulting in a greater concentration than is obtained at normal temperatures, but also at high temperatures the solubility of proteins is increased particularly in the presence of acid/salt systems[157].

5(d) The Manufacture of Strong, Durable Chrome-Retan Leather [158,159,160]

In the preceding sections of this thesis, a detailed report has been given of the study of the reactions which take place when vegetable tanning extracts react with the chromium-collagen complex, both during retannage and on ageing, and this has been of considerable assistance in determining the optimum conditions for the manufacture of chrome-retan leather. Not only is more vegetable tannin fixed by chromium tanned pelt than by raw hide, but also the tannins, and particularly the non-tannins enter the chromium-collagen complex displacing sulphate and liberating strong acid which tends to produce unstable leather. The replacement of sulphate groups from the chromium complex in chromium tanned leather by masking or by the addition of complexing agents during neutralising is particularly effective in reducing the avidity of chromed stock for vegetable tannins, and, by the judicious choice of materials and procedures, strong, durable leather can be made.

Combinations of the two tanning procedures result in products with widely different characteristics depending on the degree of retannage of the leather and to a lesser extent on the quantity of chromium present[159]. Thus lightly retanned leathers retain most of the properties of full-chrome leather, and heavily retanned leathers approach more nearly the character of vegetable tanned leather. Furthermore, chrome leather retanned with vegetable extract possesses intrinsic properties which make it superior in many ways to full-chrome leather[161]. Greater stability for some manufacturing processes, excellent dimensional stability on wetting and drying, improved flexibility, and greater comfort to the wearer are acknowledged properties of chrome-retan shoe upper leather.

Since the main purpose of retanning chrome leather is to obtain more fullness, and hence to improve the loose areas of the leather, the plumping action of the retanning material is of considerable importance. Mimosa extract is particularly suitable for the retannage of chrome leather and the plumping action is illustrated in the diagram Fig.1 which shows the percentage increase in substance obtained by retanning (a) lightly chromed leather and (b) full-chrome leather with 5% or 15% of mimosa extract.

It will be seen from the diagram that retannage with mimosa produces large increments in the substance of the leather, particularly on lightly chromed stock. It will also be noted that increasing the quantity of mimosa extract offered from 5% to 15% has a great effect on the substance of the leather, even on a full-chrome leather. It is quite clear, therefore, that the fullness of the retanned leather can be regulated by the quantity of mimosa extract offered and that maximum effects are obtained on stock with a low chromium content[162].

A wide variety of vegetable tanning extracts is used for retanning, but mimosa extract is one of the more successful of the vegetable tanning materials for improving substance, and in a comparative study mimosa compared favourably giving the best overall rating of properties as shown in the accompanying table[148], (see Vol. 2, p.140).

Relative Effects of Various Extracts on Leather Properties

	Plumpness	Lastometer Load	Lastometer Extension	Tearing Strength	Shrinkage Temp.
Mimosa	1	2	1	3	2
Chestnut	3	4	5	4	4
Myrobalans	5	1	2	2	5
Myrtan	4	3	2	1	3
Quebracho (sulphited)	1	5	4	5	1

The leathers were retanned by offering the equivalent of 5% tannin on the blue weight, all other treatments being similar. The greatest degree of plumpness was given by mimosa and quebracho, the best lastometer values were obtained using mimosa and myrobalans, and the highest tearing strengths were given by myrtan. Thus it is obvious that no one extract is superior in every respect, but the leathers retanned with mimosa are full and plump yet maintain satisfactory physical characteristics.

Whilst the manufacture of chrome-retan leather requires a different approach from that for the production of full-chrome leather, there is nothing inherently difficult in the processing of this type of leather, provided certain precautions are taken. Hence, if correctly carried out,

this type of tannage will produce good quality, strong, durable leather, which can be easily finished and embossed and has excellent perspiration resistance and comfort properties.

It is virtually impossible to produce good quality chrome-retan leather from chromed stock originally intended for full-chrome leather. In the first place the beamhouse conditions for making chrome-retan leather are different in many respects from those needed for producing full-chrome leather, and secondly, the chrome content is usually much higher than is advisable for chrome-retan leather. For these reasons it is necessary to commence the tannage in the lime yard, and factors that are important in the manufacture of chrome-retan leather are discussed below.

Beamhouse Operations

Since retannage tightens and firms the grain, beamhouse processes should be such that greater flexibility is imparted to the leather than is normal for full-chrome leather. Soaking should be thorough to ensure complete rehydration of the fibres and to remove the curing salt and other soluble interfibrillary matter. The use of mildly alkaline soaking aids would be beneficial, but if soaking is performed in a drum, mechanical action should be kept to a minimum.

Paddle or suspension liming with a minimum of sulphide to effect hair loosening and operated at a uniform temperature of between 20 and 25^{o}C for four days gives leathers with excellent tear and grain strength, and the mild mechanical action ensures that the grain is not excessively loosened. Under these conditions the hair can be saved, but if drum liming is desired the sulphide concentration should be adequate to pulp the hair although mechanical action should be kept to a minimum. At this stage the hide should be passed through an unhairing machine which sets out the hide and removes a moderate amount of scud, but excessive scud removal may result in loss of grain tightness[163]. Transferring the unhaired hide to a white lime for a further period improves the condition of the pelt prior to splitting and results in leather of higher tearing strength. If the second liming is performed at elevated temperature then bating can be omitted.

If the goods are split in lime the subsequent processes are more uniform and the splits can be treated separately. On the other hand splitting in the blue is more accurate and the flanks will be better since there is less change of substance after splitting.

The usual deliming materials are probably all satisfactory, although the use of ammonium sulphate should be examined critically since there is the danger that calcium sulphate may result in grain embrittlement. Probably the most reliable and safest deliming agent is boric acid.

Bating is not an essential prerequisite in the production of corrected grain upper leather, especially if the grain is heavily buffed. Nevertheless grain texture and strength are improved by bating, and if the leather is to be heavily retanned bating will probably be beneficial.

Pickling and Chrome Tanning

The pretanning processes are most important. It has been found that an aldehyde pretannage results in tighter grain[164], improved resistance to deterioration under moist heat[62,165,166], and better ageing characteristics[165,166], although the increased plumpness normally associated with retanning may be partially offset by this pretreatment.

In the conventional pickling process, use is sometimes made of buffer systems (formic acid or its salts being the most favoured additions) to give a milder action to the salt/sulphuric acid system. The addition of organic acids at this stage is less effective than when they are used for masking the chrome liquors for tanning[116,167]. It is essential that excessive amounts of chromium should not become fixed in the grain, since the increased reactivity of the heavily chrome-tanned fibres may lead to case hardening. Thus it is necessary that the chromium distribution be as even as possible, and this is achieved by pickling with small amounts of acid followed by acid chrome liquors, the proportions being adjusted to ensure a suitable final pH without the addition of basifying alkali.

The composition of the chrome tanning liquor has a very important bearing on the quality of the leather. Experience has shown that organic reduced chrome liquors are superior to sulphur dioxide

reduced liquors for prechroming hide to be retanned. The mild masking action of the oxidation products must be responsible for this, and incorporation of additional masking agents into the chrome liquors increases the effectiveness of these liquors. The tearing and grain strengths of the leather are substantially increased, and the ageing characteristics of the leather improved, if the optimum amounts of organic anions are used. Thus for formate and phthalate masking the optimum amount of acid is about 0.5 mole/mole Cr_2O_3, and for sulphophthalate about 1.0 mole/mole Cr_2O_3. Since the acidity developed during manufacture and storage is thought to account for at least part of the lower strength of chrome-retan leather as compared with full-chrome leather[40,60], small amounts of mimosa have been used in admixture with the chromium liquor (i.e. wattle masking) so that the acid developed can be neutralised before the end of the tannage. Interesting results have been obtained and this approach warrants further investigation[39,168-170].

As mentioned above, acid chrome liquors should be used. Thus 33% basic chrome liquors give more even penetration and superior leather quality than is obtained if more basic liquors are used. This is confirmed in recommendations from various sources where 33% basic chrome tanning salts are suggested in preference to 42, 45 or 50% basic materials[134,167].

The effect of the quantity of chromium is so well known as to require very little comment. Except for vulcanisable upper leather where a high chrome content is necessary and the degree of retannage automatically must be kept at a low level, the chrome content should be low. The effect of this factor on the avidity of chromed stock for vegetable tannins and the resultant possibility of case-hardening has been demonstrated[26,28,38,60,134,139]. In addition the higher chrome contents give more acid on storage and hence greater deterioration, and, therefore, increasing the level of chrome tannage is likely to result in less durable leather.

Neutralisation

Neutralisation is of the utmost importance. Two difficulties face the tanner retanning chrome tanned pelt with vegetable extracts. Firstly, there is the tendency to drawn grain, and secondly, there is the possibility of case hardening. Both of these difficulties are related to the avidity with which vegetable tannins react with chrome tanned collagen, the greater the acidity the more reactive the system. Thus, neutralisation of the chrome leather prior to retannage reduces the reactivity and allows the tannin to penetrate, overcoming the tendency to excessive fixation in the grain and the resultant embrittlement of the leather. Nevertheless, neutralisation with the usual mild alkalis is seldom sufficient to reduce the acidity of the chromed pelt to an acceptable level, since there is a limit to the amount of alkali which can be used to increase the pH if undesirable side reactions are to be avoided. Additives incorporated during or immediately after the neutralising process have been found to be most beneficial from the point of view of improving both the initial properties of the leather and the ageing characteristics[134,158].

Since the increased reactivity of chrome tanned pelt with vegetable tannins is due to the release of internally neutralised basic groups as well as to complex formation with the chromium/collagen compound, substances which will block the reactive sites will reduce the avidity of the chromed pelt even if the pH is unaffected. The addition of complexing anions such as sulphophthalate, EDTA, or the low molecular weight polyphosphates, is very effective, but neutralised or slightly alkaline syntans are the most effective[31], and these additives also lead to better storage stability[132]. If the latter are used, the conventional neutralising procedures can be omitted, and the quantity of the retanning material proportionally reduced.

Retannage

The degree of retannage is the most important single factor determining the strength and durability of chrome-retan leather[134,171]. Increasing the degree of retannage reduces the tearing strength and the grain strength of the leather, and also results in more rapid deterioration on storage[88,132,172]. Nevertheless, the increased plumping and

improved cutting value often makes a heavy retannage very desirable. Fortunately the strength of full-chrome leather is invariably considerably greater than is necessary and the loss of strength on retannage can normally be tolerated. Very considerable differences in strength can be achieved by variations in technique, although the same quantities of reacting materials are used in each case[134]. Hence the conditions under which the retannages are effected must be carefully regulated.

The retanning material should be drummed into the hide in as short a time as possible. It has been found that extending the time beyond that necessary to ensure adequate uptake of the vegetable tannin results in weaker leather without a compensating increase in plumpness or tightness of grain.

Retannage should be conducted at as low a temperature as possible. Thus if fresh floats are used for retanning, cold water should be employed. Some tanners retan after fatliquoring (see below) and under these conditions it is normal for the goods to be warm when the retanning agent is added. If this is the practice, the fatliquor should be no warmer than is absolutely necessary and cold fatliquoring might be considered at this stage of the process.

The retanning material should be added in as concentrated a form as possible. This assists in driving the vegetable tannin into the hide, and enables the retanning time to be reduced to the minimum. For this purpose the spray-dried powdered extracts are most suitable since, if they are added to drained goods in the drum, they dissolve instantly in the moisture in the pelt making a concentrated tan liquor which is rapidly taken up.

When blends of syntan and vegetable tanning material are used for retanning, it is advantageous to add the syntan in advance of the vegetable extract, since syntans invariably have less affinity than the extract for chromed collagen and result in a milder but less plump tannage. If an adequate quantity of a suitable syntan is used in the neutralising process, no further syntan should be necessary, and the mixture is in fact less effective in plumping and filling than an all mimosa retannage.

Fatliquoring

It is generally necessary to add more oil to chrome-retan leather than is usual for full-chrome leather, and a total of up to 6% may be required. Because of the dry nature of the tannage, mineral oils can be used in admixture with the normal fatliquoring oils, and may be as much as 25% of the oils present. However, it is necessary to keep in mind the end use of the leather since mineral oil may impair the adhesion of vulcanised soles and adhesive joints generally.

The addition of some of the fatliquor before the retannage is advantageous and serves two purposes. Firstly, the presence of oil serves to lubricate the leather, and the mechanical action in the drum is less vigorous, whilst increase in temperature during the subsequent dry retannage is minimised. The second and probably more important factor is the improvement of the strength of the grain, since the presence of fat in the grain tends to reduce the uptake of vegetable tannin in that layer of the skin.

Whilst the conventional sulphated oil emulsions are suitable for the pre-retan fatliquor, the chrome-stable reactive oils are not. Nevertheless their use in the chrome tannage does lead to softer leather, but there has been no evidence that their use improves the strength or durability of chrome-retan leather[173].

The degree of sulphation of the oil is of less importance in chrome-retan leather than it is in full-chrome leather[174,175]. It is usually better to apply an emulsion consisting of a greater proportion of medium to low sulphated oil and a small quantity of raw oil, than to use lower quantities of highly sulphated oil and larger amounts of raw oil. The addition of surface active agents is not to be recommended.

Cationic fatliquors are also extensively used to top leathers fatliquored with the conventional sulphated oil emulsions in order to facilitate removal of the leather from the paste drying plates after drying, but they must be used with caution since the surface fatting may lead to finishing difficulties. Nonionic surface active agents may cause the topping to penetrate more deeply than is desirable and uneven penetration due to differences in the structure of the hide may be accentuated on grain correction.

Recommended Process

The effects quoted above have all been confirmed in tannery trials, and the following suggested procedure should provide a basis from which tanners can work.

Soaking should be gentle but thorough to ensure that the collagen fibres are adequately rehydrated. Soak in water to remove as much as possible of the adhering dirt and curing salt and then in a fairly long float containing about 0.1% of sodium hydrosulphide. Rehydration is probably most effective in a drum which should be turned only once or twice every hour. Agitate thoroughly for a few minutes at the end of the soaking process and green flesh.

Liming is best effected in a paddle or in a suspension pit. Transfer the soaked hides to an old lime for one day and then into a fresh lime liquor for two days, the composition of the lime liquor before entering the hides being:

400% water
3% slaked lime
2% sodium sulphide

In a drum process the float should be shorter and the drum turned infrequently and used only as a stirring device. The following has been found to be suitable:

250% water
2% slaked lime
1% calcium chloride
2% sodium sulphide

The goods remain in this liquor for two days and then are unhaired by machine, fleshed and split.

Deliming can be effectively performed in a drum and the subsequent processes of bating, pickling and chrome tanning can be carried out in the same drum without handling. Float the goods in about 200% of water at 35°C and add 1% of boric acid. Run the drum for 30 minutes, then add 1% of pancreatic enzyme preparation and bate for 30 minutes. Drain the liquor, rinse with cold water to stop the bating action.

Pickle by adding water and salt to the drum and run in the diluted sulphuric acid through the hollow axle while the drum is turning.

The following has been found to be a suitable formulation:

50% water
3% salt
0.5% sulphuric acid

Run the drum for one hour, then add the chrome tannin, liquid or powder.

Chrome tan by adding to the pickle liquor in the drum 1.5% to 2% Cr_2O_3 as a solution of the 33% basic chrome tanning salt in 30% of water or as the dry chrome tanning salt. The float at this stage is about 80%. Drum for several hours and leave in the liquor overnight. Drum for a further two hours and drain. The liquor pH should be about 3.7 and the leather will normally stand the boil. The amount of pickle acid should be adjusted so that the final pH is reached without the addition of neutralising alkali. Pile the leather for at least one day before continuing with the retanning process.

After sammying, setting out, splitting (if this is necessary), and shaving, the goods are rinsed once for a few minutes in a revolving drum, drained, and then floated in 100% of water. 0.5% of a suitable complexing agent (e.g. sodium sulphophthalate, tetrasodium EDTA, or polyphosphate) is added, followed by 1% of sodium bicarbonate to neutralise the goods. Alternatively neutralising can be effected by treating the pelt with 2 to 5% of a suitable slightly alkaline syntan.

Wash in warm water and reduce the float to about 50% and add 2% of a medium sulphated sperm or neatsfoot oil. When this has been taken up, drain ready for retanning.

Retannage should be effected in as short a float as possible to ensure rapid uptake of the retanning agent. Thus it is convenient to add dry powdered extract or concentrated tan liquor to the drained goods in the drum. If extra syntan is required this should be added first and given 15 minutes to be distributed and to fix, before adding the mimosa extract. The degree of retannage varied widely between 5% and 20% of mimosa extract and drumming should not be prolonged beyond the time necessary to take up the retanning material, and in any case should be no longer than one hour.

Wash with warm water to remove surface uncombined tannins and refatliquor with about 2 to 3% medium sulphated oil and 1 to 1.5% raw oil. After about 40 minutes top with 0.25 to 0.5% cationic fatliquor and drain.

Horse over-night, set out and paste dry. Since buffing exerts a mild staking action, the leathers should not be excessively staked. Softening should be achieved during the tannage (e.g. during liming or in fatliquoring) and mechanical treatments should be kept to a minimum. Leathers from this process are flat, and easily buffed and finished using modern techniques.

CHAPTER 6

DISCUSSION AND CONCLUSIONS

6(a) Consideration of the Vegetable Tannin/Chromium-Collagen System

Although chromium salts are the most commonly used of all the tanning materials generally available, particularly in the manufacture of upper leather, combination tannages are usually employed for the reasons discussed in Chapter 1. Chromium tanned pelt can be regarded as the basic material in dual tannages and several classes of compound have been recommended or suggested as suitable for retanning and filling side leather. Of these the vegetable tannins have been the most common, although resin tannins have tended to become of increasing importance because of the difficulties that may be encountered when vegetable tannins are used. The problems with which the tanner is faced when using combination tannages of chromium and vegetable tannins include the considerably increased reactivity of chromium-tanned pelt for vegetable tannins, with the consequent possibility of overloading the grain, and the lack of storage stability of the leathers especially when exposed to moist heat.

In this thesis, a study has been made of factors in the manufacture of chrome-retan leather which it was thought might influence the strength and stability of the leather. These investigations revealed that weak leathers which deteriorated relatively rapidly resulted from (a) a high chromium content especially if the chromium tannage had been effected with highly basic liquors, (b) a high degree of retannage especially if the period of retannage was prolonged, and (c) a high temperature retannage. On the other hand, the application of masking agents during the chromium tannage, or of complexing agents in the neutralising, resulted in improved physical properties and greater resistance to deterioration.

These results suggest that the lower initial strength is probably due to the greater avidity of chromium tanned pelt for vegetable tannin, resulting in the first place from the liberation of internally neutralised reactive sites which are not normally available in straight vegetable tannage, and secondly, co-ordination of vegetable tannin to the chromium complex by the displacement of sulphate radicals or water. These reactions would

result in increased tannin uptake in limited regions of the skin, and this in turn would cause overloading of the fibre and an increased number of cross-links, both of which would tend to give weak leather.

By reducing the degree of chromium tannage, or by introducing complexing agents or other anionic substances such as syntans before retannage, the number of reactive sites would be reduced. This occurs because the lower chromium content would liberate fewer reactive sites on the protein and less tannin would be complexed by the chromium, while the anionic groups would tend to block the sites both on the protein and in the chromium compound normally reactive to tannin. Masking or complexing would react in two ways: firstly, by creating more stable chromium complexes which would be less reactive to tannin, and secondly, the chromium complexes, by becoming more negatively charged, would tend to reform the internal links with the basic groups so that the vegetable tannin would be less readily fixed. Thus vegetable tannin distribution would be more uniform and the tendency to case-hardening would be reduced.

On storage and ageing, the pH of an aqueous extract of the chrome-retan leathers fell initially and then began to rise and at this stage protein degradation products could be detected. This suggests that deterioration with loss of strength on ageing is primarily a hydrolytic degradation of the protein which is catalysed by acid, those factors which favour the formation of acid causing greater and more rapid deterioration.

The results of the technological work have been confirmed in tannery trials, and factors which are important in the production of chrome-retan leather are given in detail in Chapter 5.

The conclusions drawn from the above results are indicative of the reactions which take place during retannage and on ageing, but the importance of each of the various factors can be gauged only by a quantitative and fundamental study of the vegetable tannin/chromium-collagen complex system. Thus measurements were made of the extent of chromium displacement, sulphate liberation, increase in acidity, and fixation of tannins when chromium tanned pelt was retanned with a variety of vegetable tanning materials, and when the resulting product was aged.

These are fully discussed in Chapter 4. Moreover, the results of these measurements furnish evidence from which the mechanism of the reactions which take place on vegetable retanning and ageing of the leather can be deduced, and provide confirmation of the effective measures which have been recommended to minimise undesirable effects.

The factors that have been studied, all of which have proved to be highly significant in the properties measured, can be divided into two groups, namely, the factors that control the chromium tannage and the factors that control the vegetable retannage. In addition, a study was made of the modification of the collagen substrate, and each of these factors will be discussed.

(i) Quantity of chromium offered. As expected, increase in the amount of chromium offered increased the chromium content of the leathers, but this also resulted in considerably more chromium being stripped when the pelt was subsequently retanned. In addition, more sulphate was displaced from leather which had been more highly chromium tanned, and this corresponded with increased acidity of the spent retan liquors.

Leathers with higher chromium contents had higher shrinkage emperatures, absorbed more tanning material and fixed more vegetable annin as determined by resistance to extraction by aqueous organic olvent. They were slightly more acid and contained considerably larger mounts of free sulphate than the leathers pretreated with the lower level f chromium.

On ageing, the increase in the amount of irreversibly fixed annin was greater for the leathers with the lower chromium contents, but is can be attributed to the greater quantity of solvent-soluble tannin in the aged leathers. In some cases, particularly with the highly chromium nned pelt, shrinkage temperature fell on ageing, but this was dependent the type of vegetable tanning material used in the retannage. It is gnificant that the hydrolysable tannins were particularly active in causing decline in hydrothermal stability. The increase in acidity and also of e free sulphate content of the leathers with the high chromium contents as greater than that of the leathers with the lower chromium contents. ese observations are indicative of the increased reactivity of vegetable nins with collagen when it is pretreated with chromium.

(ii) Basicity of chromium salt. Probably as a result of increased stability due to olation, increase in the basicity of the chromium compounds used in the chromium tannage reduced the tendency of chromium to be displaced from the pelt during retannage, but basicity had no influence on the amount of sulphate displaced, although the spent retan liquors were less acid than those from less basic tannages.

The basic tannage resulted in higher chromium fixation, caused more vegetable tanning material to be absorbed, and an increase in fixed tannin, but had no influence on the shrinkage temperature. Slightly less free sulphate was found in the leathers tanned with the 50% basic chromium compounds than with the 33% basic compounds, but there was no effect on pH.

The higher basicity chromium tannage showed a trend towards increased tannin fixation on ageing although this was not accompanied by an increase in free sulphate, but there was a decrease in shrinkage temperature which indicated a tendency towards detannage.

(iii) Masking of chromium salt. Less sulphate was displaced from the masked chromium complex than from the unmasked and the acidity of the spent retan liquors was lower. In addition, the masked chromium complex was more resistant to stripping during retanning. Thus the masked complexes were more stable and resistant to the action of vegetable tannins.

Further evidence for the resistant nature of the masked chromium-collagen complexes is shown by the fact that these leathers absorbed less vegetable tanning material, although this may partly be due to the lower chromium content of the leathers which had had the masked tannage. Moreover, the acidity was lower and less free sulphate was found in the leathers which had been tanned with masked chromium compounds, and on ageing, whether in a temperate atmosphere or if exposed to moist heat, these leathers developed less acidity although the increase in tannin fixation was not affected. Thus, apparently, tannin altered the masked chromium complex, liberating the comparatively weak formic acid, which accounts also for the smaller increase in free sulphate of these leathers on ageing.

(iv) Type of retanning material. Marked differences can be attributed to the use of various types of vegetable tanning materials in retanning, and these are generally the result of the high content of ionising groups in the hydrolysable tannins compared with the condensed tannins. Thus, during retanning, the former group of vegetable tanning materials, especially myrobalans, was particularly effective in stripping chromium from the pelt, as well as causing extensive displacement of sulphate from the chromium-collagen complex. This also resulted in relatively lower pH values in the spent retan liquors.

Absorption of tanning material was greatest from quebracho retannages, which also resulted in the highest total fixed tannin unextractable by aqueous organic solvent, whereas the greatest amount of free sulphate was found in the myrobalans retanned leather. This indicates that complex formation had taken place with charged groupings in the vegetable extracts; in the case of the quebracho, sulphonated large particle size tannins reacted, but in the case of the myrobalans extract ionised tannins and low molecular weight non-tannins took part in the reaction, which accounts for the lower uptake of the latter tannin. Mimosa extract reacted more slowly, which confirms that charge effects are important in initial reaction, but there was indisputable evidence that the reaction of vegetable tannin with the chromium-collagen complex continues on ageing, and it is the liberation of sulphate and the consequent increase in acidity which, it is thought, promotes the deterioration of chrome-retan leather, especially under warm, humid conditions[40,60]. Thus tannins which readily form co-ordination complexes with chromium are unlikely to produce stable chrome-retan leathers. Confirmation of this is given by the fact that myrobalans is not recommended for retanning chromium tanned leather because of its detanning effect[41,43], and in the present work myrobalans retanned leather has been shown to lose hydrothermal stability on ageing. Stability can be increased by introducing competing complex forming compounds either as masking agents[116,167], or during neutralising[132,134,158], and this approach is particularly effective in mimosa retannages.

(v) Non-tannins in vegetable tanning extracts. Several workers attribute the reactions that take place when chromium tanned pelt is retanned with vegetable tanning materials to the action of the non-tannins on the chromium-collagen complex[29,30,38], and there is no doubt that vegetable extracts rich in non-tannins are very reactive. The present work has shown that purified mimosa tannin is also capable of the reactions which take place on retanning, and it is concluded that both the tannins and the non-tannins are involved in the reactions. However, it is evident that mimosa non-tannins are responsible for most of the chromium stripped and sulphate displaced during retanning, but on drying and on ageing of the leathers, little difference could be detected between those tanned with the purified tannin or the whole extract. Thus it appears that the non-tannins which contain ionising groups probably in the form of the amino- and imino-acids which have been shown to be present[52], react rapidly, and subsequent reactions of the tannin with the chromium-collagen complex are slow.

(vi) Quantity of tannins offered. All of the observed effects increased with increasing quantity of vegetable tannin offered, although even the lowest level of retannage (4% tannin) showed marked effects compared with no retannage. In particular, sulphate displacement, acidity and shrinkage temperature increased immediately, with a further progressive increase as the amount of tannin applied increased. However, only at high levels of retannage was the displacement of chromium markedly increased. Most of the tannin in the lightly retanned leathers was irreversibly fixed, but as the amount offered increased so the proportional amount of tannin fixed decreased, although there was an increase in the absolute amount fixed. Shrinkage temperature increased as the level of retannage increased, and on ageing little loss of hydrothermal stability was noted except in myrobalans, and to a lesser extent chestnut retanned leathers, and then mainly if stored in a warm, humid atmosphere. In these two cases there was also a marked increase in acidity.

(vii) Temperature of retannage. Considering the important effects of the temperature of retanning on the physical properties of chrome-retan leather, see Table 5.(a), III, it is surprising that this factor had no significant influence on any of the analytical values reported in Chapter 4.

(viii) pH of retannage. Retannage at low pH values tended to strip chromium from chromium-tanned pelt more readily than at higher pH values, but although with increasing pH of retannage less chromium was displaced, progressively more sulphate was found in the spent retan liquors. Thus it is apparent that increasing the pH of retannage increased the tendency of vegetable tannins to co-ordinate with the chromium, since the high pH of retannage resulted in high levels of irreversibly fixed tannin and considerable increase in the free sulphate in the leather. This seems to indicate that acidity, rather than complex formation of tannin with chromium, is responsible for chromium displacement and detannage. However, there is strong evidence that co-ordination of myrobalans with chromium leads to detannage, while the detanning effect of mimosa or quebracho must be negligible.

On ageing, the leathers retanned at low pH values showed a considerable increase in acidity, with a corresponding increase in free sulphate. Thus it is obvious that stability of the leather will be increased if the retannage is conducted at relatively high pH. It has been recommended that leathers be neutralised during or after the retannage to neutralise the acid liberated during manufacture[177], or sparingly soluble basic compounds can be incorporated in the retanning blend which will ensure a high pH even under adverse conditions of storage[178].

(ix) Type of collagen substrate. In the study of the retannage of chromium tanned modified collagen in which the substrates used were normal collagen, carboxylated collagen, deaminated collagen and acetylated collagen, there is evidence to show that basic groups probably play an important part in the rapid, but reversible absorption of vegetable tannin by reaction with charged groups in the tannin. This displaces ionically bound sulphate from basic groups and results in a small increase in the acidity of the system. However, it is considered that irreversible fixation of tannin by chromed pelt is the result of complex formation between the chromium compound and vegetable tannins with the displacement of sulphate, and to some extent the displacement of protein carboxyl groups. While the presence of chromium in the spent retan liquors is indicative that detannage had occurred, it is evident that stable cross-links had not been disrupted,

because shrinkage temperature was not reduced. Thus chromium must have been displaced from sites which contribute little to the tannage, confirmation for which is given by the increased resistance to chromium stripping of the chromium tanned carboxylated collagen, in which the proportion of chromium held by residual valencies must be lower.

The importance of the basic groups in the fixation of tannin by chromium tanned collagen may have been over-emphasized[138], since it has been shown[6-9] that no reaction of vegetable tannins with reactive sites on the protein under normal conditions of tannage imparts resistance to extraction with aqueous dioxan. The above observations are in general agreement with Vivian's conclusions[139] that tannin fixed by moist cationic chromium tanned hide is due to the formation of chromium-tannin complexes, rather than to the activation of amino groups.

(x) Ageing. Deterioration of the physical properties of chrome-retan leather on ageing indicates that the chromium-collagen/vegetable tannin system is unstable, and measurements have shown that changes which were noted after storage are consistent with the hypothesis that further reaction of the vegetable tannin with the chromium-collagen complex had occurred. Thus tannin fixation increased with time, and this was accompanied by an increase in the amount of free sulphate and acidity of the leather. At elevated temperature and in the presence of moisture these reactions were accelerated, but measures, such as masking or the application of competing complexing agents, which normally inhibit the further reaction of vegetable tannins with the chromium, were ineffective under these conditions. Thus, although there was a reduction in the development of strong acid which is generally regarded as promoting the hydrolysis of the protein with consequent loss of strength, at elevated temperature the liberation of weak acids from the chromium complex occurred, and these are known to have an adverse effect on the collagen fibre[155]. Complexing agents with stronger co-ordinating affinity for chromium than those that have been studied may resist displacement by tannin under conditions of moist heat, but it seems probable that these will cause detannage by successfully competing with the protein carboxyl groups.

In conventional chrome-retan leather, detannage does not appear to be a contributory cause of deterioration since in most cases,

and certainly with the condensed tannins, shrinkage temperature of the leathers was well maintained even under the most adverse conditions of storage. In the case of retannage with the hydrolysable tannins with a high content of dissociating groups, detannage, as evidenced by a small loss in hydrothermal stability, is a possible additional cause of deterioration.

(xi) Conclusions. It is concluded that chromium pretannage of collagen increases its reactivity with vegetable tannins by initially making available additional reactive sites not normally accessible in vegetable tannage; the charged aminogroups are probably involved by reaction with charged groups in the vegetable tannin. Simultaneously, a co-ordination reaction of both tannins and non-tannins with the chromium compound occurs, displacing both sulphate groups and, to a much smaller extent, protein carboxyl groups, the latter being dependent on the type of vegetable tanning material, the hydrolysable tannins being much more active in this respect.

On drying, further reaction of the vegetable tannins and the non-tannins with the chromium-collagen complex takes place with the fixation of tannin, the liberation of sulphate groups and an increase in acidity. This reaction is greater than that which takes place during the retanning process, as shown by considerable increase in free sulphate and in acidity, with the result that neutralisation procedures which are performed before drying have a limited effect. On ageing, still more vegetable tannin enters the complex, with the result that the free acid in the leather is increased, and the chemical changes which occur are consistent with the hypothesis that the loss of strength is the result of hydrolytic degradation of the protein which is catalysed by acid. Those factors which favour the formation of acid cause greater and more rapid deterioration. Modification of the chromium-collagen complex by the incorporation of complexing agents of various kinds, reduces the tendency for components of the vegetable tanning extracts to enter the complex, with the result that less strong acid is developed during manufacture or on storage.

As a result of the better understanding of the reactions which take place (a) when chromium tanned pelt is retanned with vegetable tanning extracts and (b) on storage, it has been possible to recommend satisfactory procedures for the manufacture of strong, durable chrome-retan leather.

6(b) Consideration of the Zirconium/Chromium-Collagen System

The use of basic zirconium sulphate for retanning chromium tanned leather is increasing[179], and the rapidly increasing popularity of zirconium tanning agents for this purpose may be attributed to a number of decisive advantages, namely, reduction of stretch of the leather, low swelling of the grain, retention of the mineral characteristics, distinct improvement in the tightness of the grain, very good light-fastness and excellent dyeing properties[177]. However, although zirconium is regarded as a mineral tanning agent, its special chemical characteristics have to be taken into account in its application to chromium tanned leather. Zirconium salts hydrolyse even at low pH values, and it has been shown that chromium tanned leather has to be acidified to a pH of about 3.0, preferably with the addition of citric acid, to ensure adequate penetration and distribution of the zirconium tanning salt. The results of practical importance have been summarised in Chapter 3, but details are given in Vol. 2, p. 1 to 46.

Important observations of theoretical interest have been made from a study of the reaction of zirconium compounds with the chromium-collagen complex, but because of an imperfect knowledge of the reaction of zirconium with collagen it has not previously been possible to propose a reaction mechanism. The work reported in this thesis has shown that tannage with zirconium sulphate cannot be considered to have a similar mechanism to chromium tannage. Although zirconyl chloride appears to react with carboxyl groups, its affinity for collagen is low and there is no marked rise in hydrothermal stability. Yet basic zirconium sulphate, which from practical experience is known to be the more successful of the two zirconium compounds studied, appears to have no affinity for carboxyl groups and seems to be dependent more on the amino groups for fixation and increase in shrinkage temperature. However, zirconium tannage cannot be limited to the amino groups alone since acetylated collagen fixes appreciable amounts of zirconium from sulphate solution with a corresponding increase in hydrothermal stability. It therefore seems likely that zirconium tannage depends on multipoint attachment of the tanning material by secondary valency forces to peptide and amino groups in the protein.

If the above postulation is correct then pretreatment of

collagen with chromium should not have a very great effect on the fixation of zirconyl sulphate, although zirconyl chloride fixation should be inhibited. In general this is what has been found to be the case, although zirconium fixation from zirconyl sulphate solution was substantially lower on chromium tanned collagen than on normal collagen, the reduction being greater than anticipated. As expected, fixation of zirconium from zirconyl chloride solution by chromium tanned pelt was reduced to negligible proportions. This confirms that zirconyl chloride is dependent on reaction with carboxyl groups for fixation by collagen, whereas only part of the fixation of zirconium from zirconyl sulphate was at sites occupied by chromium. In addition, it was noted that fixation of zirconium was further reduced if the chromium tanned collagen had been pretreated with aldehyde, an indication that basic groups may be auxiliary binding sites for zirconyl sulphate.

It had been observed that the shrinkage temperature of some commercial chromium tanned leathers was slightly reduced when they were retanned with basic zirconium sulphate. In this work when zirconyl chloride was used in retanning the effect on shrinkage temperature was very marked but when zirconyl sulphate was used, the hydrothermal stability of the leather was relatively unaffected despite a significant reduction in the chromium content. Thus zirconyl sulphate and chromium appear to compete for auxiliary binding sites on the protein, while the chromium co-ordinately bound by carboxyl groups was unaffected, and effective cross-linking was not disrupted. On the other hand, zirconyl chloride caused no displacement of chromium, yet the shrinkage temperature was much reduced, indicating that this zirconium salt competes with chromium for reaction with carboxyl groups with disruption of the cross-linking and consequent loss of hydrothermal stability.

It appears that under the acid conditions of the zirconium retannage, the protein carboxyl groups temporarily released from combination with the chromium are able to compete successfully with the monodentate chloride for reaction with zirconium, but are unable to displace bidentate sulphate groups. Therefore the more stable zirconyl sulphate forms no co-ordination compound with the protein under these conditions. Zirconyl chloride tends to be predominantly cationic [12], and

therefore unlikely to have affinity for amino groups, whereas significant amounts of zirconyl sulphate compounds are anionic [17,108,110] especially if masked with citric acid, which may account for the affinity of this zirconium compound for basic groups.

As previously mentioned, basic zirconium sulphates are of greater practical commercial interest, and the use of these tanning salts in preference to zirconyl chloride for retanning can be justified on theoretical grounds. Although in practice a small reduction, $\Delta Ts = 2^{\circ}C$, in shrinkage temperature of the chromium leather was found when retanned with zirconyl sulphate, the decline in shrinkage temperature was insignificant when compared with the effect of zirconyl chloride retannage, $\Delta Ts = 14^{\circ}C$. Furthermore, the affinity of zirconyl sulphate for chromium tanned collagen was greater, yet the physical properties of the chromium tanned leathers were not seriously affected by retannage with zirconyl sulphate, nor was there evidence of deterioration on storage. Consequently, although the small loss of shrinkage temperature on retanning suggests an interaction of zirconium with the chromium-collagen complex (and this may be largely a pH effect), this reaction must be completed during retannage because there was no evidence of further interaction on storage. Thus the major portion of zirconium fixation occurs at sites not important for chromium tannage, in confirmation of the assertion [64] that chromium and zirconium tannages are independent of each other.

6(c) General Conclusions

Three aspects of this work are of special importance, namely, (a) the reasons for and methods of minimising the weakness of chrome-retan leathers and their deterioration on ageing, (b) evidence from which the mechanism of zirconium tannage can be deduced, and (c) evidence for the existence of weakly bound chromium which does not contribute to the hydrothermal stability of chromium tanned leather.

Leathers containing zirconium compounds or vegetable tannins show superficial similarities in physical characteristics even when examined under the electron microscope, and it is probable that the main reaction of each with collagen is due to the formation of multipoint cross-linking bonds by means of secondary valency forces. However, in combination tannages involving chromium tanned leather and either zirconium compounds or vegetable tannins, these two classes of tanning materials behave quite differently with the chromium-collagen complex.

Chromium pretannage of the collagen increases its reactivity towards vegetable tannins by liberating charged amino groups and other sites not normally available, with the result that vegetable tannins are rapidly absorbed in the surface layers of the skin and this in turn causes overloading of the fibre and increased cross-linking, both of which tend to give weak leather. In addition, it has been shown that vegetable tannins and non-tannins form co-ordination compounds with the chromium in the leather, displacing sulphate with a consequent increase in acidity, and the possibility exists, especially in retanning with hydrolysable tannins, that protein carboxyl groups may be displaced from the chromium-collagen complex with the result that a degree of detannage occurs. Moreover, on ageing, the reaction of the vegetable tannins with the chromium-collagen complex continues, with the displacement of additional sulphate groups and a further increase in acidity which is thought to promote the hydrolytic degradation of the protein and results in the deterioration of this type of leather. The strength of the leather can be improved by reducing the avidity of the chromium tanned pelt so that a more uniform distribution of the vegetable tannin is obtained, and durability is increased by the inclusion of compounds which react preferentially with the chromium-collagen complex and inhibit the entry of vegetable tannins so that the acidity of the leather

is maintained at a satisfactorily low level. Choice of the type of vegetable tanning extract is also of importance; members of the hydrolysable group of tannins should be avoided because of their greater reactivity with chromium compared with the condensed tannins.

The reaction of zirconium with chromium tanned collagen depends on the nature of the zirconium salt used. Thus zirconyl chloride forms co-ordination compounds with the carboxyl groups on the protein at the expense of the chromium already fixed at these sites, and although dechroming does not seem to occur, disruption of effective cross-linking takes place as shown by a loss of hydrothermal stability. By contrast, basic zirconium sulphate is more stable and under the acid conditions necessary for tannage, the protein carboxyl groups are unable to form co-ordination bonds with this zirconium compound which, it is thought, forms bonds with collagen by less specific residual charges. In chromium tanned leathers retanned with zirconium compounds there is no evidence that zirconium reacts with the chromium complex since no acid is developed and the leathers are stable on storage.

Thus the essential differences between the reactions of zirconium compounds and vegetable tannins with the chromium-collagen complex are: (a) zirconium sulphate competes with that portion of the chromium attached by secondary valency forces, but does not release acid from the chromium complex during ageing; (b) vegetable tannins also compete with the non-complex bound chromium, but there is a further reaction during ageing which involves penetration into the chromium complex and release of acid. The vegetable tannins which contain carboxyl groups also displace complex bound chromium from the protein, resulting in loss of hydrothermal stability.

An interesting side issue is the conclusive evidence for the existence of chromium loosely bound by secondary valency forces in chromium tanned leather. Inactivation of the basic groups of the collagen substrate reduced the fixation of chromium without affecting the rise in shrinkage temperature associated with chromium tannage. Moreover, confirmation of the presence of chromium attached at sites other than

carboxyl groups is given by the displacement of chromium by zirconyl sulphate which is fixed by secondary valency forces to peptide and amino groups, without affecting the shrinkage temperature of the leather. Thus it must be accepted that chromium fixation occurs by both co-ordination with carboxyl groups and by secondary valency forces, although only the co-ordination reaction gives the high hydrothermal stability associated with chromium tannage.

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The following are to be published in the J. Soc. Leather Trades' Chemists:

1. The Effect of Chromium Pretreatment on the Fixation of Zirconium by Collagen.
   By D.A. Williams-Wynn
2. The Reaction of a Selection of Vegetable Tanning Extracts with Chromium Tanned Collagen.
   By D.A. Williams-Wynn
3. The Reaction of Vegetable Tannins with Chromium Tanned Modified Collagen.
   By D.A. Williams-Wynn.

APPENDIX

I. Computer Programme for 128 Sample Factorial Design

II. Typical Data Sheet Print-out for Factorial Experiments

III. Computer Programme for Back Calculations

IV. Typical Tabular Print-out for Back Calculations.

I. Computer Programme for 128 Sample Factorial Design

```
010  CHAPTER1
020  X%192
021  Y%0
031  READ£X1¤
032  JUMP5@X1£99999999
033  JUMP6
034  5¤ACROSS5/7
040  6¤1£2£1¤128
050  READ£X1¤
060  REPEAT
080  107£1¤X1@128
100  PRESERVE
110  L£1£1¤7
120  1£1£1¤128
130  Y£0PARITY£1¤
140  JUMP1@Y%0
150  JUMP2
160  1¤J£0INTPT£.5!¤
170  XJ£X1&X£1-1¤
180  2¤REPEAT
190  106£1¤X65@128
200  K£1
210  1£65£1¤192
220  Y£0PARITY£1¤
230  JUMP3@Y%0
240  JUMP4
250  3¤J£1-K
260  XJ£X1-X£1-1¤
270  K£K&1
280  4¤REPEAT
     1£129£1¤196
300  X1£0
310  REPEAT
330  107£1¤X1@128
350  REPEAT
360  107£129¤X1@128
370  RESTORE
380  107£260¤X1@128
381  CLOSE
382  CHAPTER2
383  VARIABLES1
400  PRINT$                                                    EXPERIMENT$
401  SPACE2
420  NEWLINE
430  SPACE51
440  PRINT$------------------------------$
450  NEWLINE4
460  SPACE20
470  PRINT$PROPERTY    $
490  SPACE57
500  PRINT$UNIT$
510  NEWLINE
520  SPACE19
530  PRINT$-----------------------------------------------$
540  SPACE20
550  PRINT$---------------$
560  NEWLINE2
570  PRINT$   ORIGINAL          FINAL              ORIGINAL          $
580  PRINT$FINAL               ORIGINAL        FINAL$
590  NEWLINE
600  PRINT$   RESULTS          TOTALS             RESULTS           $
610  PRINT$TOTALS              RESULTS         TOTALS$
620  NEWLINE3
630  CLOSE
```

```
640  CHAPTER3
650  VARIABLES1
660  L@0
670  JUMP2@20SET
680  JUMP3@21SET
690  JUMP4@22SET
700  2MP@4
710  Q@0
720  R@6
730  S@0
731  J@11
732  K@12
733  M@8
735  O@10
736  T@11
737  ACROSS1/4
740  3MP@3
750  Q@3
760  R@5
770  S@2
771  J@7
772  K@11
773  M@4
775  O@6
776  T@10
777  ACROSS1/4
780  4MP@0
790  Q@4
800  R@0
810  S@7
811  J@1
812  K@6
813  M@0
815  O@0
816  T@6
820  ACROSS1/4
821  CLOSE
822  CHAPTER4
823  VARIABLES3
830  1M1@1Z1X42
1690 106Z260&LMX1@1
1700 106Z303&LMX3@1
1710 106Z346&LMX5@1
1720 106Z129&LMX2@1
1730 106Z172&LMX4@1
1740 106Z215&LMX6@1
900  NM@4M
910  JUMP5
920  5MPRINT$I $
930  PRINTZX1MP@Q
940  SPACEJ
950  PRINTZX2MR@S
960  SPACEK
970  PRINT$I $
980  PRINTZX3MP@Q
990  SPACEM
1000 PRINTZX4MR@S
1010 SPACEK
1020 PRINT$I $
1030 JUMPZNM
1040 4MPRINTZX5MP@Q
1050 SPACEO
1060 PRINTZX6MR@S
1070 SPACET
1080 PRINT$I$
1091 L@L&1
1090 NEWLINE
1100 REPEAT
1000 106Z302MX1@1
1010 106Z345MX3@1
1020 106Z171MX2@1
1030 106Z214MX4@1
1150 NM@6M
1160 JUMP5
1170 6MNEWLINE3
1180 CLOSE
1190 CHAPTER5
1200 X%127
1210 106Z22MX1@3
1220 106Z26MX4@3
1230 106Z30MX7@1
1240 106Z32MX8@1
1250 106Z38MX9@2
1260 106Z42MX11@3
1270 106Z46MX14@3
1280 106Z50MX17@7
1290 106Z57MX24@1
1300 106Z59MX25@5
1310 106Z70MX30@3
1320 106Z74MX33@2
1330 106Z78MX35@3
1340 106Z82MX38@4
1350 106Z87MX42@9
1360 106Z98MX51@11
1370 106Z110MX62@2
1380 106Z113MX64@2
1390 106Z117MX66@3
1400 106Z121MX69@3
1410 CLOSE
```

```
1420  CHAPTER6
1430  VARIABLES5
1440  C%0
1450  D%0
1460  E%0
1470  F%0
1480  G%0
1481  U%0
1482  V%0
1483  W%0
1490  C@0
1500  D@0
1501  U@0
1502  V@0
1503  W@0
1510  E@0
1520  F@0
1530  G@0
1540  I@1@1M71
1550  C@XIXI
1560  D@D&C
1570  E@E&1
1580  REPEAT
1590  F@D/E
1600  G@=SQRT@FM
1630  U@2G
1640  V@2.66G
1650  W@3.46G
1660  JUMP1=20SET
1670  JUMP2=21SET
1680  JUMP3=22SET
1690  1MM@11
1700  N@0
1710  P@9
1720  Q@0
1730  R@6
1740  S@0
1750  ACROSS4/7
1760  2MM@9
1770  N@4
1780  P@7
1790  Q@4
1800  R@5
1810  S@2
1820  ACROSS4/7
1830  3MM@0
1840  N@8
1850  P@0
1860  Q@8
1870  R@0
1880  S@8
1890  ACROSS4/7
1891  CLOSE
```

```
1892  CHAPTER7
1893  VARIABLES6
1900  4MSPACE4
1910  PRINT$ERROR S.S.$
1920  PRINT@DMM=N
1930  PRINT$   FOR$
1940  PRINT@EM3=0
1950  PRINT$  D.F.$
1960  NEWLINE
1970  SPACE4
1980  PRINT$ERROR VARIANCE.   $
1990  PRINT@FMP=Q
2000  NEWLINE
2010  SPACE4
2020  PRINT$TOTALS ARE SIGNIFICANT IF  $
2040  PRINT@GMR=S
2050  NEWLINE
2060  SPACE23
2070  PRINT$2.00    $
2071  PRINT@UMR=S
2080  NEWLINE
2090  SPACE23
2100  PRINT$2.66    $
2110  PRINT@VMR=S
2120  NEWLINE
2130  SPACE23
2140  PRINT$3.46    $
2150  PRINT@WMR=S
2160  NEWLINE4
2180  STOP1155
2190  ACROSS1/0
2200  5MEND
2210  CLOSE
```

```
      CHAPTER0
      1MA@A
2230  CLOSE
```

II. Typical Data Sheet Print-out for Factorial Experiments

EXPERIMENT RESTAN (AGED)

PROPERTY LASTOMETER LOAD — UNIT lbf in.

ORIGINAL RESULTS	FINAL TOTALS			ORIGINAL RESULTS	FINAL TOTALS			ORIGINAL RESULTS	FINAL TOTALS			
1423	189293		SUM	767	- 1367		ABDF	1557	129		BCEG	
2770	- 16217	***	A	1828	3065		CDF	2100	- 4037		ABCEG	
1240	- 12013	**	B	1151	- 3077		ACDF	1489	- 855		DEG	
1439	7381		AB	1559	4175		BCDF	790	451		ADEG	
1670	- 8183		C	1196	1817		ABCDF	2120	8519		BDEG	
1108	- 1933		AC	1250	- 4393		EF	2120	7009		ABDEG	
1860	- 2185		BC	1247	801		AEF	1862	7917		CDEG	
678	2609		ABC	1504	- 2751		BEF	1630	- 5873		ACDEG	
1095	- 10229	*	D	1240	- 5429		ABEF	1250	- 4053		BCDEG	
1026	4685		AD	1530	- 3805		CEF	1463	5557		ABCDEG	FH
1118	9973	*	BD	623	- 11067		ACEF	1596	- 3923		FG	
1205	- 7177		ABD	1625	- 203		BCEF	985	2599		AFG	
885	1343		CD	1380	- 481		ABCEF	1670	- 4037		BFG	
1040	- 2055		ACD	1370	- 575		DEF	1370	2085		ABFG	
1924	- 7007		BCD	1728	5419	B	ADEF	1801	- 615		CFG	
1210	- 3725		ABCD	1545	3375		BDEF	1072	- 7077		ACFG	
2120	4073		E	1442	1377		ABDEF	1377	2647		BCFG	
1712	4923		AE	1183	- 651		CDEF	2240	- 1567		ABCFG	
1500	- 809		BE	1954	4287		ACDEF	1840	- 2985		DFG	
1420	5857		ABE	1458	507		BCDEF	1175	1929		ADFG	
1996	2473		CE	1310	- 3339		ABCDEF	GN 1195	873		BDFG	
1572	715		ACE	2080	539		G	959	5779		ABDFG	
1230	- 8561		BCE	2030	- 2683		AG	979	3275	B	CDFG	
1283	- 2415		ABCE	1335	1725		BG	898	- 4867		ACDFG	
1480	11815	*	DE	1235	10975	*	ABG	1350	2861		BCDFG	
1750	7273		ADE	3060	507		CG	1116	63		ABCDFG	EH
1420	- 4103		BDE	1576	5317		ACG	3230	8041		EFG	
1412	2811		ABDE	1207	- 5853		BCG	1383	- 7613		AEFG	
2260	- 945		CDE	1302	- 393		ABCG	1605	- 17593	B	BEFG	
1880	- 8503		ACDE	1573	- 2535		DG	1037	4817		ABEFG	CDH
1200	- 7751	B	BCDE	1203	- 181		ADG	2200	- 7679		CEFG	
1084	4491		ABCDE	2230	4815		BDG	1547	- 781		ACEFG	
2990	- 3209		F	1272	- 975	B	ABDG	834	- 7041		BCEFG	
1821	- 3607		AF	1092	- 11263	*	CDG	678	2649		ABCEFG	DH
2020	481		BF	1178	- 6197		ACDG	1198	- 3893		DEFG	
1522	5251		ABF	1304	- 1993		BCDG	1552	2469		ADEFG	
1793	- 4305		CF	641	- 839		ABCDG	1117	8189		BDEFG	
1293	3705		ACF	1880	1935		EG	2500	- 1921		ABDEFG	CH
1105	3601		BCF	965	- 2075		AEG	2290	3659		CDEFG	ABH
1148	659	B	ABCF	1316	- 139		BEG	822	- 7435		ACDEFG	BH
1681	1449		DF	1327	3015		ABEG	1044	13		BCDEFG	AH
1394	5667		ADF	1502	- 3929		CEG	1018	5511		ABCDEFG	H
1710	- 5481		BDF	1552	- 1903	B	ACEG					

ERROR S.S. 1607028200 FOR 71 D.F. ABCD CDG

ERROR VARIANCE. 22634200

TOTALS ARE SIGNIFICANT IF 4758 CDE

2.00 9515 5%

2.66 12655 1% ABG

3.46 16461 0.1%

EXPERIMENT CHOTAN

PROPERTY SLIT TEAR - ORIGINAL

UNIT LB/IN

ORIGINAL RESULTS	FINAL TOTALS			ORIGINAL RESULTS	FINAL TOTALS			ORIGINAL RESULTS	FINAL TOTALS		
173	27799		SUM	231	201		ABDF	184	559		BCEG
442	1791	*	A	256	- 861		CDF	433	483		ABCEG
422	- 905		B	195	263		ACDF	176	721		DEG
262	1591	*	AB	209	- 485		BCDF	453	-1015		ADEG
188	- 363		C	180	- 249		ABCDF	245	-1155		BDEG
179	- 971		AC	199	389		EF	271	- 131		ABDEG
129	- 735		BC	191	- 427		AEF	229	1651		CDEG
220	489		ABC	219	- 403		BEF	191	- 933		ACDEG
189	- 633		D	211	-1195		ABEF	183	- 53		BCDEG
189	459		AD	297	143		CEF	144	- 357		ABCDEG FH
175	- 185		BD	258	- 81		ACEF	126	315		FG
197	- 21		ABD	312	- 301		BCEF	209	- 49		AFG
279	- 179		CD	158	1131		ABCEF	86	- 689		BFG
174	- 15		ACD	121	- 79		DEF	328	3		ABFG
253	537		BCD	301	3173	B	ADEF	232	113		CFG
486	845		ABCD	201	961		BDEF	171	741		ACFG
267	703		E	389	1157		ABDEF	112	- 207		BCFG
295	351		AE	202	1059		CDEF	242	1301		ABCFG
127	-1221		BE	182	947		ACDEF	225	43		DFG
244	- 789		ABE	110	143		BCDEF	237	-1277		ADFG
291	- 347		CE	179	107		ABCDEF	221	1639		BDFG
340	- 219		ACE	195	- 507		G	220	343		ABDFG
176	-1147		BCE	155	921		AG	222	2353	B	CDFG
209	-1083		ABCE	169	- 579		BG	124	785		ACDFG
177	- 617		DE	202	377		ABG	158	- 183		BCDFG
128	91		ADE	353	- 161		CG	296	- 335		ABCDFG EH
179	171		BDE	187	35		ACG	350	-1333		EFG
208	-1817		ABDE	301	315		BCG	193	-1833		AEFG
254	-1491		CDE	97	7		ABCG	172	-2245	B	BEFG
204	-1591		ACDE	167	689		DG	175	- 113		ABEFG CDH
199	-1899	B	BCDE	293	665		ADG	277	1121		CEFG
95	1113		ABCDE	87	- 751		BDG	236	661		ACEFG
165	- 859		F	188	-2359	B	ABDG	140	- 539		BCEFG
144	- 835		AF	131	-1053		CDG	143	-1551	*	ABCEFG DH
229	- 343		BF	217	179		ACDG	171	- 389		DEFG
228	625		ABF	101	7		BCDG	256	707		ADEFG
190	- 17		CF	266	1639		ABCDG	239	219		BDEFG
196	287		ACF	259	1317		EG	189	- 29		ABDEFG CH
185	- 793		BCF	145	177		AEG	274	- 71		CDEFG ABH
241	- 569	B	ABCF	133	417		BEG	355	609		ACDEFG BH
374	1113		DF	419	109		ABEG	110	- 371		BCDEFG AH
118	365		ADF	117	- 535		CEG	198	- 699		ABCDEFG H
112	- 51		BDF	268	1547	B	ACEG				

ERROR S.S. 45307911 FOR 71 D.F.

ERROR VARIANCE. 638139.590000

TOTALS ARE SIGNIFICANT IF 798.836400

2.00 1598 5%

2.66 2077 1%

3.46 2716 0.1%

AB

CDH

III. Computer Programme for Back Calculations

IV. Typical Tabular Print-out for Back Calculations

BACK CALCULATIONS.

COLTAN IV INCREASE IN H& ON NATURAL AGEING

	Chestnut	Mimosa	Myrobalans	Quebracho	means***
nil	0.0000000 / 00	0.0000000 / 00	0.0000000 / 00	0.0000000 / 00	
	0.00	0.00	0.00	0.00	0.00
4% tans	0.2500000 / 00	0.2500000 / 00	0.7500000 / 00	0.2500000 / 00	
	0.25	0.25	0.75	0.25	0.37
8% tans	0.1250000 / 01	0.7500000 / 00	0.1500000 / 01	0.5000000 / 00	
	1.25	0.75	1.50	0.50	1.00
16% tans	0.3750000 / 01	0.1500000 / 01	0.4000000 / 01	0.5000000 / 00	
	3.75	1.50	4.00	0.50	2.44
means***	1.31	0.62	1.56	0.31	0.95

BACK CALCULATIONS.

COLTAN IV INCREASE IN FREE SO4 NATURAL AGEING

	Chestnut	Mimosa	Myrobalans	Quebracho	means***
nil	0.2000000 / 01	-0.2250000 / 01	0.2000000 / 01	-0.1750000 / 01	
	0.20	-0.22	0.20	-0.17	0.00
4% tans	0.2750000 / 01	0.4750000 / 01	0.6000000 / 01	0.4000000 / 01	
	0.27	0.47	0.60	0.40	0.43
8% tans	0.1200000 / 02	0.5500000 / 01	0.1025000 / 02	0.1425000 / 02	
	1.20	0.55	1.02	1.42	1.05
16% tans	0.1775000 / 02	0.1700000 / 02	0.1400000 / 02	0.2050000 / 02	
	1.77	1.70	1.40	2.05	1.73
means	0.86	0.62	0.81	0.92	0.80