Modern tanning chemistry

Anthony D. Covington

British School of Leather Technology, Nene College of Higher Education, Boughton Green Road, Moulton Park, Northampton, UK NN2 7AL

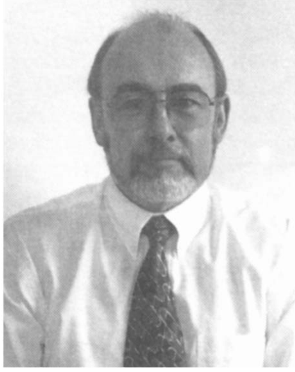
The range of chemistries used for tanning leather is reviewed; traditional methods of tanning are explained and the newer processes are described. The areas of tanning include: vegetable tanning with plant polyphenols, mineral tanning with metal salts, in particular chromium(III), oil and aldehyde tannages, synthetic tanning agents and organic tannages based on natural polyphenols or synthetic organic oligomers. The fundamental nature of the tanning reaction and the origin of hydrothermal stability are discussed.

1 Introduction

The conversion of animal hides and skins into useful artefacts may be man's oldest technology. Untreated skins have limited value, because when wet they are susceptible to bacterial attack and so they putrefy, but if they are dried they become inflexible and useless for purposes such as clothing. Those effects are eliminated by tanning: tanning is defined as a process by which putrescible biological material is converted into a stable material which is resistant to microbial attack and has enhanced resistance to wet and dry heat. Skin is vulnerable to heat, undergoing shrinking in water at *ca.* 60 °C or above, an effect observed in scalding with hot water. This transition is sometimes referred to as melting, when the fibrous structure becomes rubber-like; at higher temperature the skin becomes more amorphous, familiar as gelatine, and further heat degradation results in animal glue. Tanning raises the temperatures at which these changes in structure are initiated.

The main protein in skin is collagen. Other proteins are present in native skin, such as keratin, albumins and globulins, but these are removed during the early stages of the leather-making process, together with other non-collagenous components, such as glycosaminoglycans, especially hyaluronic acid, proteoglycans, especially dermatan sulfate, and triglyceride fats. Removal of these non-collagenous proteins is necessary to produce soft leather. Otherwise, the fibre structure may be cemented together during drying. Removal of glycosaminoglycans and particularly proteoglycans is necessary to allow the fibre structure to split apart; this 'opening up' effect allows penetration of tanning and lubricating agents, to produce the range of organoleptic properties or handle or feel required by the consumer.

Professor Tony Covington comes from a background of a PhD in physical organic chemistry with Professor R. P. Bell, then post-doctoral research in solute–solvent interactions with Professor A. K. Covington (no relation). In 1976, he went to work for the British Leather Manufacturers' Research Association, later BLC The Leather Technology Centre of Northampton, ultimately becoming Head of the Rawstock and Tanning Dept. In 1995, he joined the British School of Leather Technology at Nene College, Northampton; in 1996, he was awarded a Personal Chair in Leather Science. He is the current President of the International Union of Leather Technologists and Chemists Societies (IULTCS), the technical organisation of the world's leather industries, covering more than 30 national societies. IULTCS celebrates its centenary with a congress in London in September 1997—address E-mail enquiries to: tony.covington@nene.ac.uk



The fibrous structure of hide (from big animals) or skin (from small animals) is illustrated in Fig. 1(a) and (b); in the Figures, the hair has been removed by dissolving it in a solution of sodium sulfide buffered with calcium hydroxide and then the structure has been opened up by prolonging that treatment at pH 12.5, this was followed by the action of proteolytic enzymes (called bating) at pH 9 to break down albumins and globulins, then pickling to pH 3 with sulfuric acid in brine prepared the hide for tanning with chromium(III) salts.

The hierarchy of skin structure is well defined and is illustrated in Fig. 2(a) and (b): fibres are made of fibril bundles, the fibrils are the lowest level of structure that is visible in intact collagen and they are characterised by a repeating banding pattern which can be emphasised by staining with heavy metals. Disrupting the fibrillar structure by swelling it in acid reveals another level of structure, shown in Fig. 3, but its nature is not known.

To date, at least 12 collagens have been identified, each performing a different function in skin or other animal tissue.[1] Collagen is characterised by its glycine content, one glycine at every third residue (–gly–X–Y–), its uniquely high proline content, often next to glycine in the sequence (–gly–pro–Y–) and its unique hydroxyproline content, usually next to proline in the sequence: –gly–pro–hypro–gly–.[2]

The presence of proline in the sequence causes the chain to twist, forming a left-handed helix. The presence of glycine at every third residue allows three α helices to twist together in a right-handed triple helix, with the glycine methylene groups situated in the centre of the structure. The presence of the hydroxyproline provides a powerful stabilising effect by hydrogen bonding. The structure is illustrated in Fig. 4. In the case of type 1 collagen, the major collagen in skin, the triple helix consists of two $\alpha 1(1)$ and one $\alpha 2(1)$ chains, each 1052 residues long, distinguished only by minor differences in amino acid sequences.

Collagen is a polar protein; type 1 collagen contains 4.4% aspartic acid residues, $H_2N{\cdot}CH(CH_2)(COOH)COOH$, 7.2% glutamic residues $H_2N{\cdot}CH(CH_2CH_2COOH)COOH$ and 2.8% lysine residues $H_2N{\cdot}CH(CH_2NH_2COOH$. The pattern of charge distribution is repeated every 234 residues, although not necessarily with the same amino acid sequence; this is called the D period. The structure is further illustrated in Fig. 5(a) and (b), which are computer generated images of the model, based on the known sequences and water content, taken from the work of Brown and her coworkers at the US Department of Agriculture Eastern Regional Research Center, Pennsylvania.[3]

The triple helices are packed together longitudinally in a 'quarter stagger' arrangement, shown in Fig. 6. In this way, the

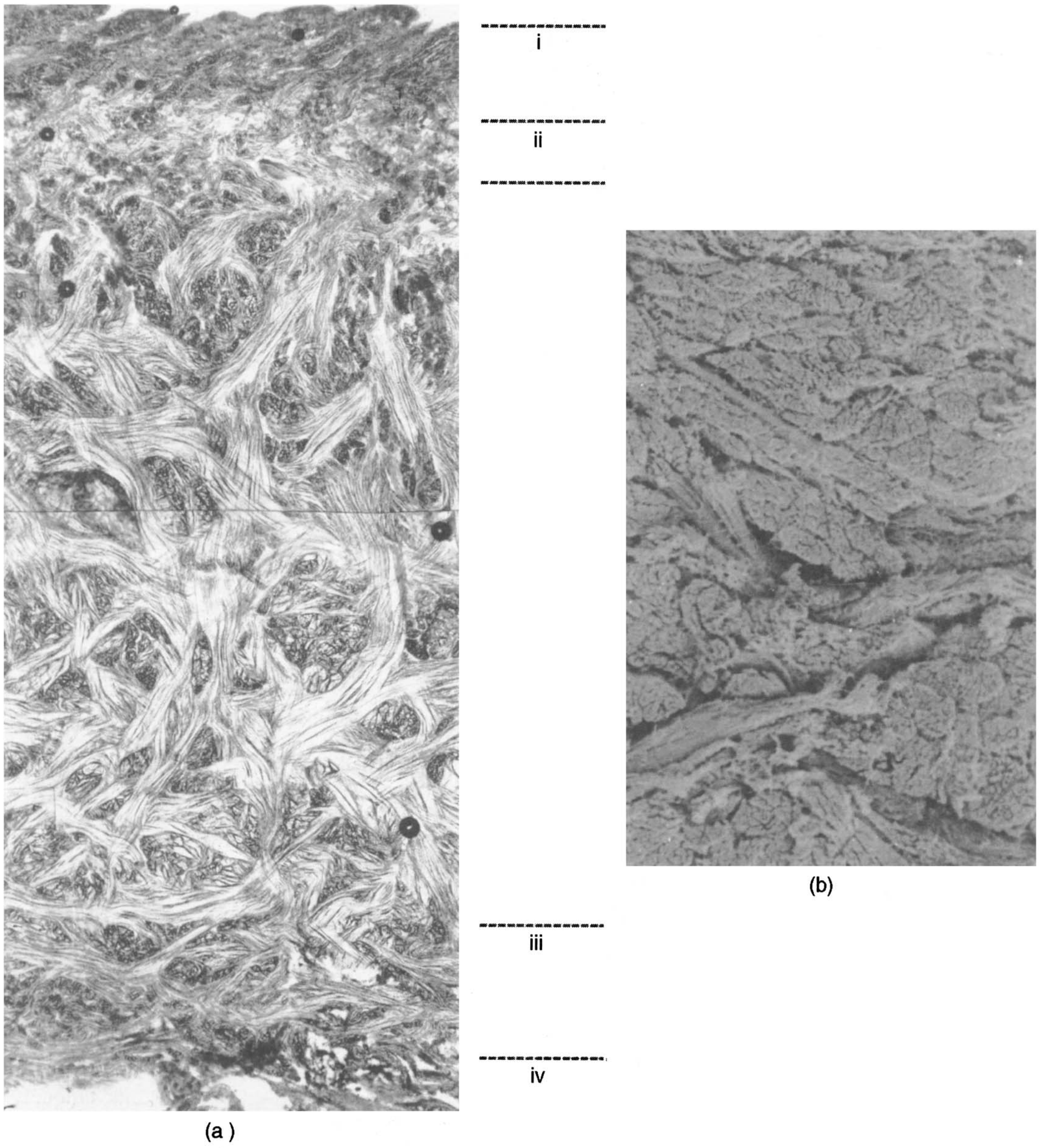


Fig. 1 Photomicrographs of tanned bovine hide (a) Light photomicrograph (× 40) of cross section i grain or corium major containing hair follicles ii grain–corium junction iii flesh layer iv residual muscle (meat) and subcutaneous fat (b) Scanning electron photomicrograph (×40) of corium

pattern of charge is matched and gives rise to the characteristic banding pattern of stained collagen Also shown in Fig 6 is that at each end of the helical region of the procollagen molecule, there is a non-helical or telopeptide region, the natural covalent crosslinks are situated between adjacent helical and telopeptide sites Whilst there is some evidence that packing in the third dimension involves subunits of five triple helices, the current view is that packing is continuous, a distorted hexagonal closest packing The structure of collagen has recently been rigorously reviewed by Kadler[4]

2 Tanning

The chemical nature of collagen allows it to react with a variety of agents, often resulting in its conversion to leather, of the changes in appearance and properties that are a consequence of tanning, one of the more important is the increase in hydrothermal stability This can be measured by observing the point at which a specimen shrinks, when it is held in water, heated at a rate of 2 °C per minute, this is the conventionally measured shrinkage temperature, T_s It is necessary to specify the conditions, because shrinking is a kinetic process and, as such, can be treated thermodynamically[5] This is illustrated in Table 1, which shows the relationship between shrinkage temperature and free energy of activation at 60 °C for the shrinking transition and the enthalpy of the endothermic reaction, the specimens represented in the Table are raw collagen in the form of kangaroo tail tendon or sheepskin flesh layer, tanned with either basic formato aluminium(III) sulfate or basic chromium(III) sulfate

The relationship between T_s and ΔH_{endo} indicates that breakdown of the tanning interaction is not the cause of shrinking, indeed, ^{27}Al NMR studies[6] demonstrate that even the weak, hydrolysable aluminium tannage is not reversed during shrinking The reaction which is manifested as heat shrinking is a breakdown of the hydrogen bonding in collagen or leather,

Table 1 The thermodynamics of collagen shrinking in wet heat at 60 °C

Tannage	T_s/°C	ΔG/kJ mol^{-1}	ΔH_{endo}/kJ mol^{-1}
Raw	60	103	104
Al^{III}	73	112	49
Cr^{III}	107	139	52

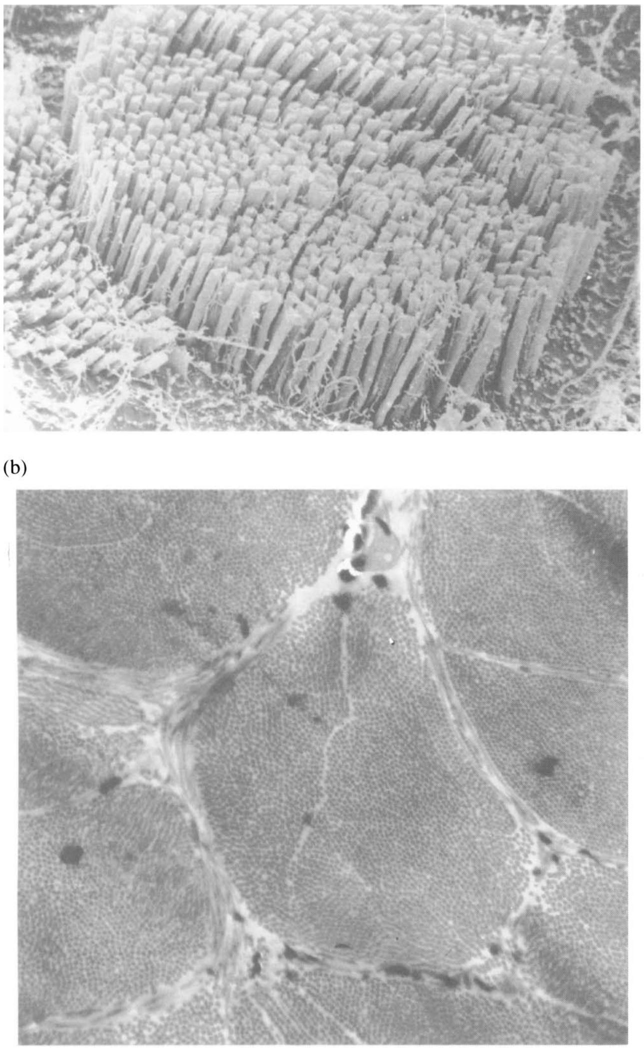


Fig 2 Elements of skin fibre structure (a) A fibre composed of fibril bundles emerging from the ice surface in a cryo SEM photomicrograph mag ×850 (b) Fibril bundles in cross section SEM photomicrograph mag ×10000

that is, regardless of the tanning process, the shrinking reaction is the same The hydrogen bonding is illustrated in Fig 7, taken from the work of Ramachandran,[7] it is this structure component that breaks down during shrinking

This begs the question where does hydrothermal stability come from? That is, if the tanning process only modifies the shrinkage temperature, without changing the shrinking mechanism, what causes the T_s to rise? The answer may have something to do with the size of the cooperating unit in the shrinking process the larger the unit, the slower are the kinetics, the higher is the shrinkage temperature[6] From measurements of rate of shrinking and entropy of activation, it was found that the size of the cooperating unit in raw collagen, with shrinkage temperature 60 °C, is 25 residues, but aluminium and chromium tanned collagens with shrinkage temperatures 73 and 107 °C have cooperating units containing 71 and 206 amino acid residues respectively

The nature of these crosslinks or cooperating units is not clear, a crosslink may function through the natural covalent crosslinks and additional hydrogen bonding structure elements in collagen, supplemented or modified by the tanning effects of hydrogen bonding or covalent crosslinking at polar groups on the amino acid sidechains or through multiple interactions at the peptide link itself

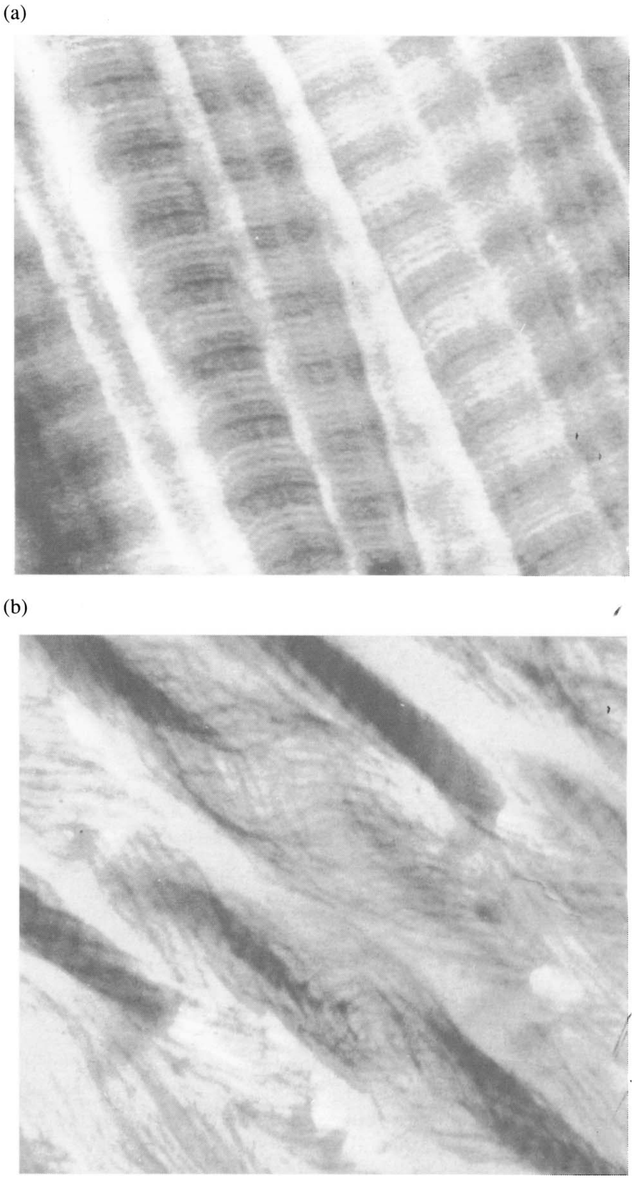


Fig 3 Skin fibril structure (a) Fibrils have a characteristic banding pattern when stained with heavy metals SEM photomicrograph mag ×100000 (b) Sub fibrillar structure is revealed by acid swelling

Thus, the tanning reaction may be highly complex on the molecular level, to the extent that there is no clear model of its effect on hydrothermal stability

(i) T_s appears to be related to the size of the artificial crosslink, which may be related to the size of the unit involved in the shrinking reaction,

(ii) The effect of the tannage may be related in part to the chemistry, that is to the particular reaction sites within the protein that are involved,

(iii) High T_s is achieved either by the precise effects of chromium(III) or by controlled multiple interaction between tanning species and collagen (see below)

Current tanning technology is dominated by chromium(III), it was introduced about 130 years ago and by the turn of the century had begun to replace the traditional tannages, which were based on plant polyphenols (so-called vegetable tannins) Today, *ca* 90% of the world's leather production is chrome tanned, the remainder is tanned with vegetable tannins, mostly for leathergoods or shoe soles Typically, chrome tanning alone is insufficient to provide the aesthetic requirements for the wide range of leather types produced by the industry, so the main or

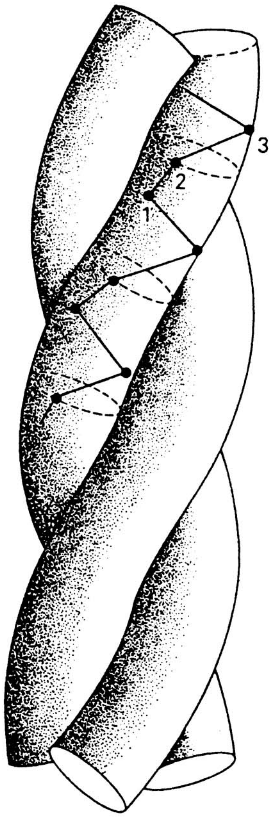


Fig. 4 The tropocollagen molecule. Three left-handed helices are twisted together, to form a right-handed triple helix

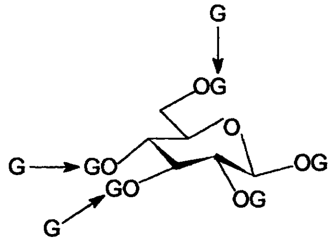
prime tannage is complemented with other tannages, which are applied after chrome. The full range of options available to the modern tanner will constitute the body of this review.

2.1 Vegetable tanning

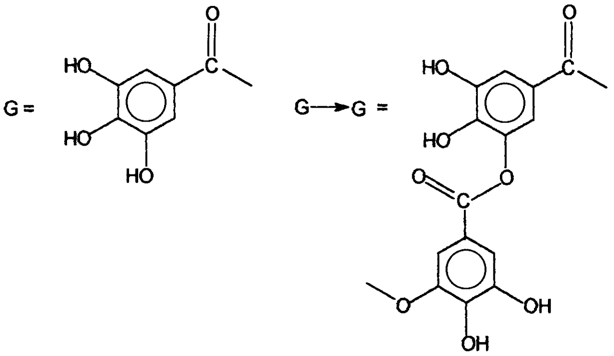
Many plant materials contain polyphenols which can be used in tanning. To be effective, the molecular mass must be 500–3000; lower molecular mass fractions in the tannin are referred to as non tans and higher molecular mass species are gums. Tanning products may be powdered plant parts or aqueous extracts of those parts; the properties they confer to the leather are as varied as the many sources from which they are obtained. Tannins are classified as follows: hydrolysable or pyrogallol tannins, subclassified as gallotannins (examples are Chinese gallotannin or tannic acid, sumac, tara) or ellagitannins (examples are myrobalan, chestnut, oak), and condensed or catechol tannins (examples are mimosa, quebracho, gambier).

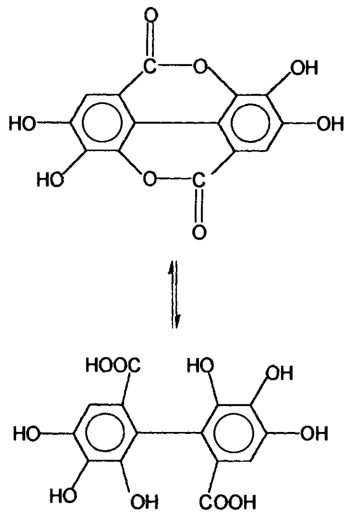
Hydrolysable tannins are sugar derivatives, based on glucose, but may be larger polysaccharides; plant extracts may contain tetrasaccharides as less useful gums. Gallotannins are characterised by glucose esterified by gallic acid; esterification may occur directly with the glucose ring or as depside esterification of bound gallic acid (**1**).[8] Ellagitannins have sugar cores, esterified not only with gallic acid, but also with ellagic acid (**2**) and chebulic acid (**3**). Examples of structures of hydrolysable tannins are chebulinic acid (**4**) from myrobalan, chebulagic acid (**5**) and vescalagin (**6**) and castalagin (**7**) of chestnut.

The traditional way to tan with vegetable tannins is in pits, where the slow penetration of large reactive molecules can take place over a prolonged period of time; when leather quality was overseen by the Guilds, hide had to stay in the pits for 'a year and a day', a form of quality assurance. Today, that tanning period has been reduced to a few weeks. A feature of pit tanning with hydrolysable tannins is that they deposit 'bloom'; natural fermentation breaks down the tannin into sugar acids and precipitates components such as ellagic acid. The bloom has a filling effect within the fibre structure, useful because sole leather is sold by weight, and the organic acid salts provide a buffer against the detanning effects of sulfur oxides and nitrogen oxides in the atmosphere. This latter reaction is known as 'red rot', familiar as the cracking and disintegration of bookbinding leathers, a phenomenon once investigated by Michael Faraday. Hydrolysable tannins typically raise the shrinkage temperature of collagen to 75–80 °C.

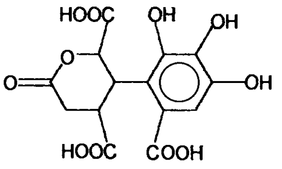


Chinese gallotannin (tannic acid) **1**



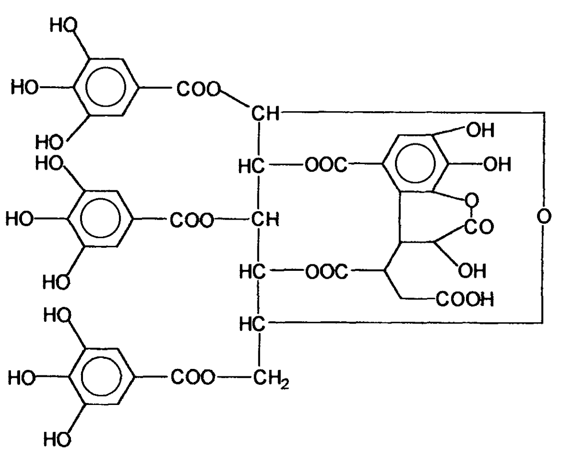


Ellagic acid **2**

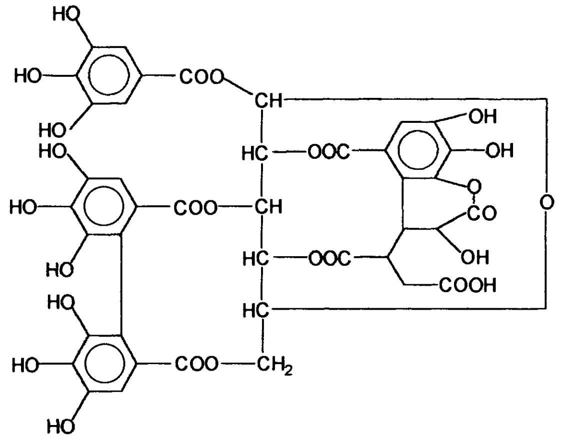


Chebulic acid **3**

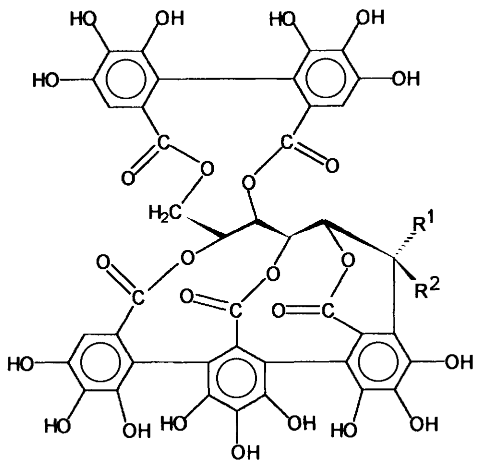
Condensed tannins are based on the flavonoid ring system, shown in Fig. 8. The A ring usually contains phenolic hydroxy groups and the presence of the C ring makes both rings reactive to forming carbon–carbon bonds; the B ring does not exhibit the same reactivity, it often contains the catechol group, hence the



Chebulinic acid **4** myrobalan tannin



Chebulagic acid **5**

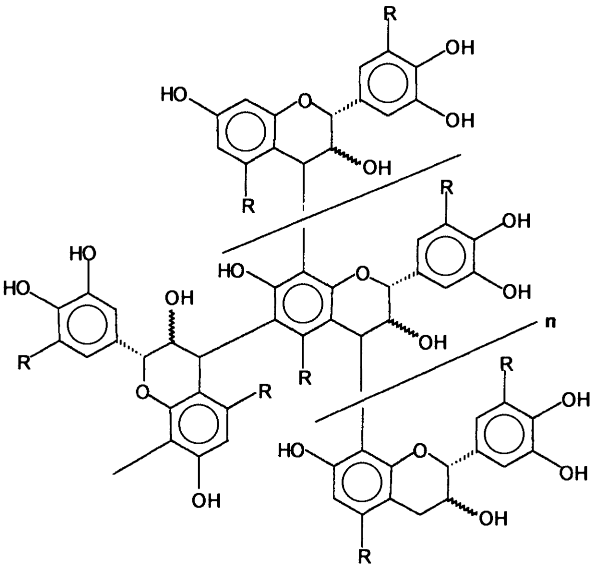


R^1 = OH, R^2 = H, vescalagin **6**

R^1 = H, R^2 = OH, castalagin **7**

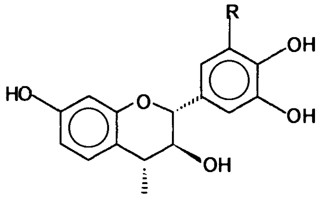
alternative name for this group of compounds. The condensed tannins are illustrated in the generalised structure (**8**)[9] and the monomeric units of mimosa (**9**) and quebracho (**10**) tannins.

The condensed tannins do not undergo hydrolysis, instead they may deposit a precipitate, an aggregate of polyphenol molecules, called 'reds' or phlobaphenes. Unlike the hydrolysable tannins, which are relatively lightfast, the condensed tannins redden markedly upon exposure to light; this is understandable in terms of their linked ring structure and ability to undergo oxidative crosslinking. Condensed tannins typically raise the shrinkage temperature of collagen to 80–85 °C.

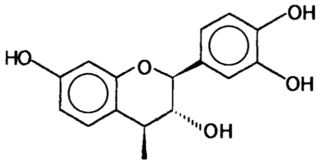


R = H, procyanidin
R = OH, prodelphinidin

Condensed tannins **8**



mimosa **9**



quebracho **10**

Vegetable tannins react with collagen primarily *via* hydrogen bonding, as indicated in the model presented in Fig. 9. This type of interaction is inferred from studies of reaction with polyamides. Also, it is known that polyphenols fix to amino sidechains by electrostatic salt links with carboxylate or hydrogen bonding with carboxylic acid groups (depending on pH). It is known that condensed tannins have an additional mechanism for reaction, because they are more resistant to removal by hydrogen bond breakers. For example, treating leather tanned with myrobalan (hydrolysable tannin) with 8 M urea removed 80% of the bound tannin, reducing the shrinkage temperature by 10–20 °C, but mimosa (condensed tannin) tanned leather treated under the same conditions lost only 50% tannin and the shrinkage temperature fell by 4–5 °C. It has been suggested that this additional interaction is covalent reaction between the protein and aromatic carbon in the tannin molecules *via* quinoid structures. Note that quinone itself can tan protein effectively, raising the shrinkage temperature to 90–95 °C; toxicity considerations rule the reaction out commercially.

Modern vegetable tanning, especially for sole leather, is still conducted in pits and the procedure retains some of the traditional elements. For example, the high affinity of polyphenols for protein means that the tannage must start in weak liquors and the hides are progressively moved through a series of pits containing increasing concentrations of the vegetable

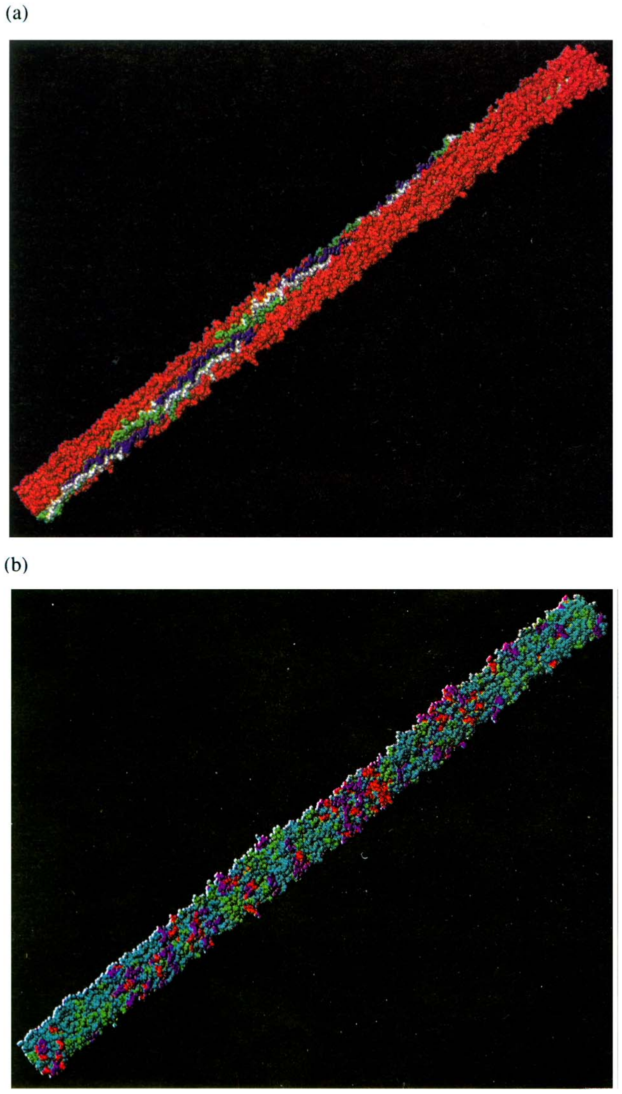


Fig. 5 Computer models of collagen. (Reproduced by kind permission of Dr Ellie Brown, USDA, Philadelphia). (a) A 40 nm segment of the microfibril (4 triple helices). Four of the five helices are coloured red; the fifth triple helix has its individual helices coloured green, blue and white. (b) The microfibril model shown with the residues coloured according to their sidechain properties: hydrophobic is green, polar is cyan, positively charged is purple, negatively charged is red. There are regions of higher and lower hydrophobicity and regions of higher and lower charge density.

tannins; depleted liquors are strengthened by topping up with stronger liquors and in this way the hides go one way through the system and the liquors go in the opposite direction, the countercurrent method of pit tanning. The use of extracts, rather than the plant material itself, allows highly concentrated solutions to be employed and by warming the pits, 'hot pitting', the whole process takes only a few weeks. Vegetable tanning can also be conducted in rotating drums, but there is a need to make the hide less reactive, to allow the tannins to penetrate into the thick hide; the oldest method is to pretan with synthetic analogues, syntans (see below), and one of the newer methods is to precondition the hide with polyphosphate, which has a weak tanning action. In this way, vegetable tanning can be shortened to a few days.

The study of plant polyphenols is an active field, not only because of application to tanning technology, but also (*inter alia*) because it is a fruitful area for a wide range of products, either isolated compounds or chemically modified polyphenols: that range includes adhesives, inhibitors to fungal, bacterial and viral growth and antitumour activity.[10,11]

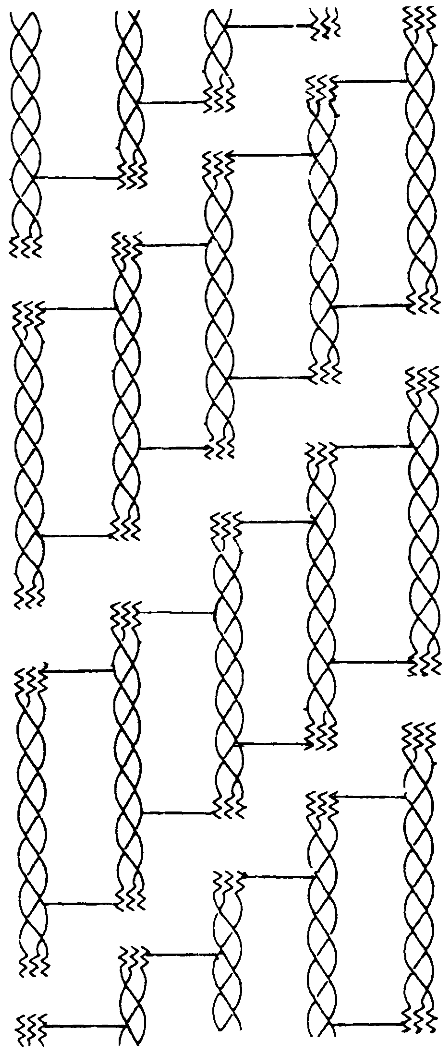


Fig. 6 Staggered packing of triple helices

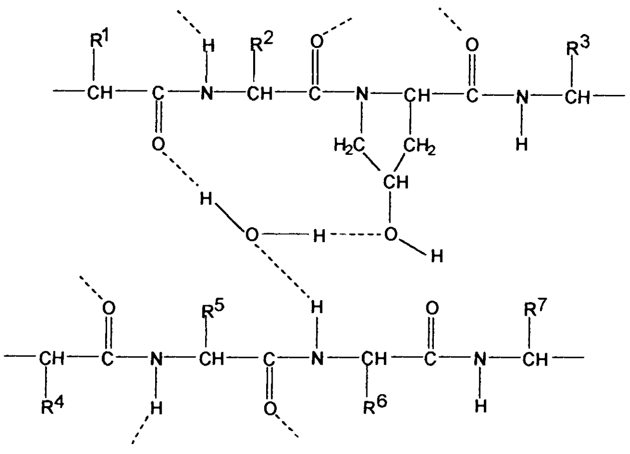


Fig. 7 Hydrogen bonding in collagen

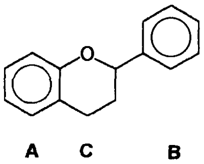


Fig. 8 The flavonoid ring system, on which condensed tannins are based

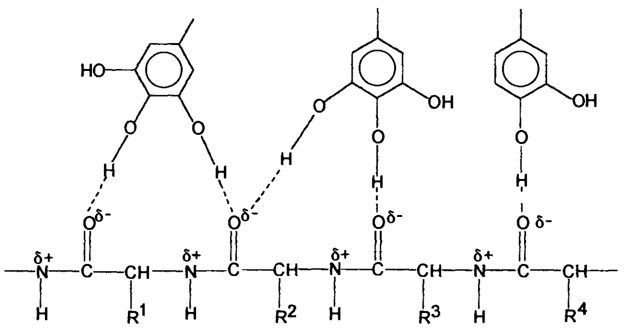


Fig. 9 Model of hydrogen bonding between plant polyphenols and collagen

2.2 Mineral tanning

A review across the Periodic Table of the tanning effects of simple inorganic compounds reveals that many elements are capable of being used to make leather[12]. But, if the practical criteria of effectiveness, availability, toxicity and cost are applied, the number of useful options is much reduced. In all cases, the benchmark for comparison is tannage with chromium(III): $T_s > 100$ °C is easily achieved, it is readily available, with large reserves in Southern Africa, it is relatively cheap and has minimum health hazards or environmental impact.

From the Periodic Table: Groups 1, 2, 6, 7, 8 do not tan. Groups 3, 4, 5: elements of the first period do not tan. The remainder have weak tanning powers, but only elements of the second period are of practical interest, of those, aluminium(III) has the best effect, silicates and polyphosphates have auxiliary functions in tanning. Transition elements: only titanium, zirconium, chromium and iron have practical possibilities. Lanthanides: individual elements or mixtures have moderate tanning properties.

So, in the whole Periodic Table there are only five elements plus the lanthanides that might find application in tanning, but only four of those play a significant role in the modern industry, summarised in Table 2.[13]

Table 2 Comparison of mineral tanning agents

Extent of complex formation (more stars = better reaction)	Cr^{III}	Al^{III}	Ti^{IV}	Zr^{IV}
Oxy complexes	**	****	***	*
Carboxy complexes	****	**	**	***
Amino complexes	**	*	**	**
Equivalent mass of oxide	38	25	40	61
Maximum T_s/°C	> 120	90	96	97

The chemistries of these tanning agents are presented below. Note, iron tannage was used in Germany when chromium was not available, but its effect is not unlike Al^{III}, to date, tannages employing mixtures of lanthanides have exhibited similar performance to Ti^{IV}.

2.2.1 Chromium(III) *salts*

There is a fortuitous coincidence of reactivities in chrome tanning. The reaction occurs at ionised carboxy groups, aspartic and glutamic acid sidechain carboxys have pK_a values 3.8 and 4.2 respectively, providing a reaction range at pH 2–6. Chromium(III) forms basic salts in the range pH 2–5, although in practice the useful range is pH 2.7–4.2, where the basicity ranges from 33 to 67%. Note, Schorlemmer basicity is defined by the number of hydroxy groups associated with the metal ion, relative to the maximum number allowed by the valency. In that useful range, the number of chromium atoms in the molecular ion increases from 2–3 to > 3 and the availability of ionised collagen carboxys increases from 6 to 47% of the total number.

Hide is prepared for tanning by pickling with sulfuric acid in a solution of sodium chloride, the neutral electrolyte is necessary to prevent osmotic swelling of the collagen. Chrome tanning is usually initiated at pH 2.5–3.0, using 33% basic chromium(III) sulfate in the form of spray dried powder, obtained from sulfur dioxide reduced chromic acid. During the course of the tanning process, the pH is raised to 3.5–4.0, causing the number of reaction sites on collagen to increase and the chrome species to increase in size. Starting the process under conditions of low reactivity of both collagen and chrome favours fast penetration of chrome into the substrate, but slow reaction, increasing the pH increases the reactivity of both components of the reaction, resulting in reduced penetration rate. To obtain a continuing balance between reaction rate and penetration rate is part of the tanner's art, this is not simple, especially if the skin is thick and it is not uncommon for heavier hides to be more than 1 cm thick in places.

The changes that occur in chrome species are set out in Fig. 10. The formation of olated species was first suggested by Bjerrum, to explain the hysteresis in delayed back titration of basified chromium(III) and the compound containing both hydroxy and sulfato bridges is well characterised.[14] Further change, into the oxolated (oxo bridged) species is postulated to happen during ageing after tanning.

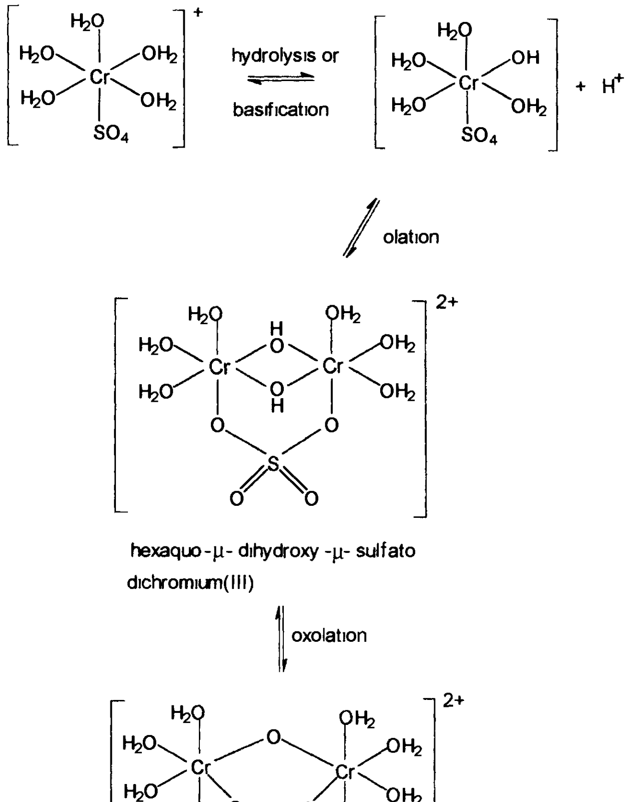
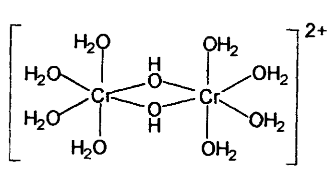


Fig. 10 Changes in chromium(III) species with pH

The presence of coordinated sulfate is necessary for the efficient reaction of chromium(III),[15] selective tannage with the isolated dichromium species (**11**) is 11 °C lower if sulfate is not present and 15 °C lower for tannage with the trimeric chromium species (**12**).

The coordination of ligands to chromium(III), to modify the properties of the salt, is routinely exploited as 'masking'. Monodentate ligands, especially formate, may be applied at different ligand to metal ratios, depending upon the degree of



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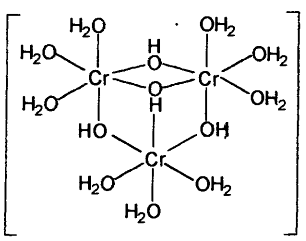


trimeric chromium (III) 12

effect desired. Reduction of cationic charge and statistical reduction in the number of reaction sites on the molecular ion make the species less reactive to collagen, hence enhancing penetration rate. In addition, such masking can increase the pH at which the salt precipitates; in these circumstances the final pH of the tannage may be elevated beyond that of unmasked tannage, thereby enhancing the reactivity of the collagen. In this way, the reaction rate can be accelerated, but without the same effect of increasing the size of the chrome species. Masking with bidentate ligands, which are capable of crosslinking chromium ions, causes a big increase in size, resulting in a statistically higher number of reaction sites per molecular ion; dicarboxylates containing two or more methylene groups perform this function [shorter chain molecules preferentially chelate chromium(III)], but phthalate is the salt of choice. Whichever masking salts are used, they are usually added to the tanning bath and the masking reaction proceeds at the same rate as the tanning reaction because the reactions are identical, the formation of carboxy complexes with chromium(III).[16]

The origin of the high hydrothermal stability of chromium(III) tanned leather is interesting because it is unique among solo tannages. By selectively deactivating collagen carboxy groups by esterification and amino groups by acylation, Sykes[17] showed that hydrothermal stability was controlled by reaction between chromium(III) and the carboxy groups, although the removal of these reaction sites did not result in zero chrome fixation. Hence, chrome fixation can occur in three ways:

(*i*) Covalent reaction between one chromium ion and one carboxy, this is unipoint fixation.
(*ii*) Covalent crosslinking between one chromium ion and at least two carboxys, this is multipoint fixation.
(*iii*) Hydrogen bonding between chromium species and the protein, especially along the polypeptide backbone.

It has always been assumed that the reaction which determines the high hydrothermal stability is multipoint fixation; unipoint fixation probably provides little hydrothermal stability (see Section 2.3 on oil tanning) because there are many examples of hydrogen bonding in tanning, including vegetable tanning, which confer only moderate hydrothermal stability. The effect of chromium(III) on crosslinking can be calculated as follows.

T_s > 100 °C is achieved with a chrome content of approx. 2.5% Cr on dry leather mass. Since complexes are binuclear or bigger, 2.5% Cr = 0.5 g atom kg^{-1} = 0.25 mol molecular ion kg^{-1}. 1 kg of dry collagen contains 1 mol of carboxy groups, therefore, only one quarter of the carboxys react with chrome. But, it has been estimated[18] that only 10% of the bound chrome is involved in crosslinking. Therefore, only 1/40 of the carboxy groups are involved in crosslinks with chrome. Collagen contains 11.6% acidic residues (asp + glu) and, since there are 1052 residues per chain, this is equivalent to 120 residues per chain = 360 residues per triple helix. Therefore, the number of residues reacted in crosslinks = 9. Or, the number of crosslinks per triple helix = 5. The size of the cooperating unit in chrome tanned leather is calculated to be 206 residues, so that suggests the effect of a chromium crosslink extends *ca.* 50 residues either side of each end of the crosslink, which is almost two complete twists of the triple helix.

The options for crosslinking are threefold, illustrated in Fig. 11:[19] they are intra single helix, intra triple helix and inter triple helix. From the known amino acid sequences of the $\alpha(1)1$ and $\alpha2(1)$ chains of type 1 collagen, the relative numbers of the crosslink types can be calculated; it is assumed that aspartic acid and glutamic acid sidechain carboxy groups are equally reactive and that a reaction can occur between two sidechains no more than three residues apart. The results are presented in Table 3; two sets of results are given, for native collagen and for completely deamidated collagen. Note, hydrolysis of amide groups on the sidechains of asparagine and glutamine does occur during the alkali treatment of hide, typically to the extent of *ca.* 50% converted to carboxy groups.

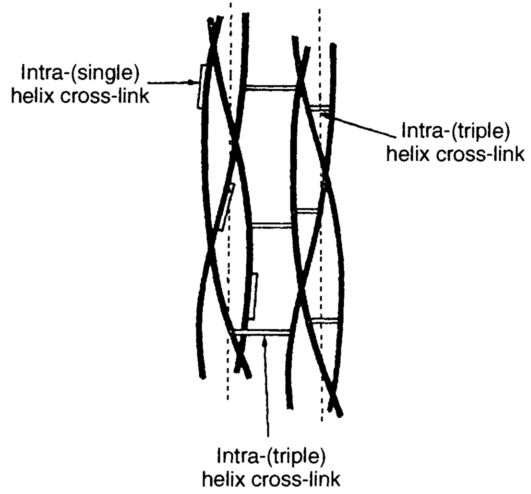


Fig. 11 Model of crosslink types in metal tanned collagen. (Reproduced by permission of *J. Soc Leather Technol. Chem.*).

Table 3 Calculated distribution of crosslinks possible in one triple helix of type 1 bovine collagen

	Intra single helix	Intra triple helix	Inter triple helix
Native collagen:			
asp–asp	5	15	6
asp–glu	15	7	15
glu–glu	13	34	18
Total, all crosslinks	33	56	39
Fraction	0.26	0.44	0.30
Deamidated collagen:			
asp–asp	22	24	7
asp–glu	38	10	26
glu–glu	34	52	33
Total, all crosslinks	94	86	66
Fraction	0.30	0.35	0.27

The assumption of equal reactivity may not be justified, since model studies indicate that poly glutamic acid is less reactive to Al^{III} than poly aspartic acid, presumably entropy controlled.[20]

It is interesting to speculate that, if the most likely stabilising crosslinks are between triple helices, then 50% deamidated collagen could form 52 crosslinks, but if only 10% of bound chrome is involved in crosslinking, perhaps only 10% of possible crosslinks are formed; this is in agreement with the calculation presented above. Experiments on native and variously deamidated collagens do indicate a difference in tanning effects, but it is not clear whether this is due to a difference in the availability of reaction sites or to a difference in the distribution of potential crosslinking sites.

Chrome fixation is accelerated by elevated temperature and pH; the higher the chrome content of the leather, the higher is the shrinkage temperature. But, the industrial requirement is to obtain high shrinkage from the minimum amount of chrome used. Studies have shown that temperature and pH do not have equivalent effects, demonstrated in Fig. 12, in which tanning effectiveness is measured by the rise in shrinkage temperature per unit of bound chrome.[21] It can be seen that under tanning condition of constant temperature and pH, rise in shrinkage temperature is controlled by pH. Furthermore, tanning effectiveness is better when low basicity chrome salts are basified during tanning, than if moderate or high basicity salts are employed at the beginning of tanning; this may reflect the crosslinking reactivity of species polymerising *in situ*, compared to starting the tanning reaction with large, olated complexes.

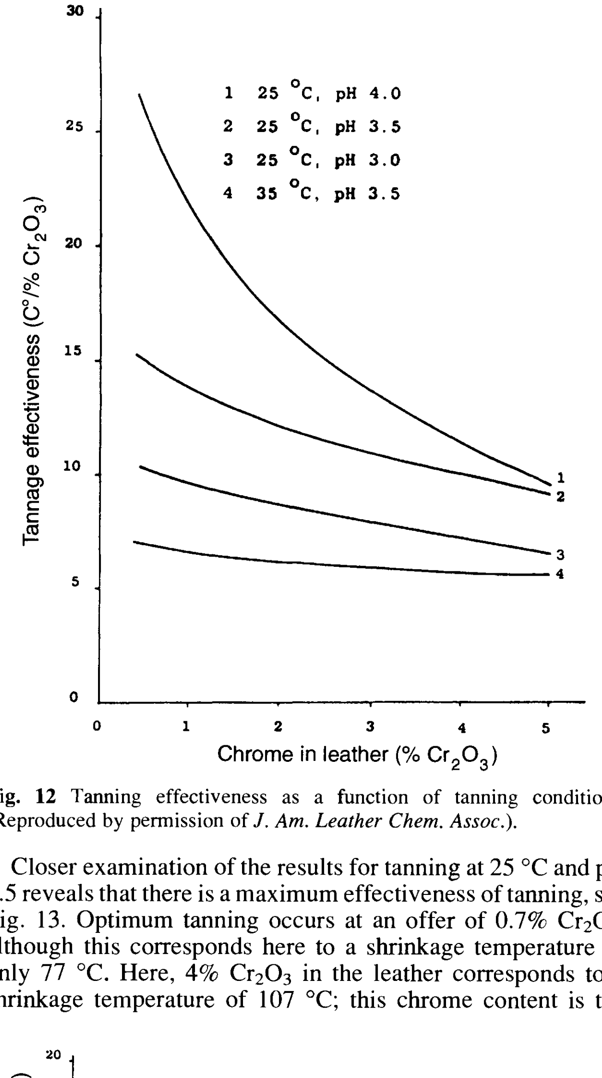


Fig. 12 Tanning effectiveness as a function of tanning conditions. (Reproduced by permission of *J. Am. Leather Chem. Assoc.*).

Closer examination of the results for tanning at 25 °C and pH 3.5 reveals that there is a maximum effectiveness of tanning, see Fig. 13. Optimum tanning occurs at an offer of 0.7% Cr_2O_3, although this corresponds here to a shrinkage temperature of only 77 °C. Here, 4% Cr_2O_3 in the leather corresponds to a shrinkage temperature of 107 °C; this chrome content is the industry standard to provide a degree of guarantee that the leather will withstand boiling water for at least 2 min.

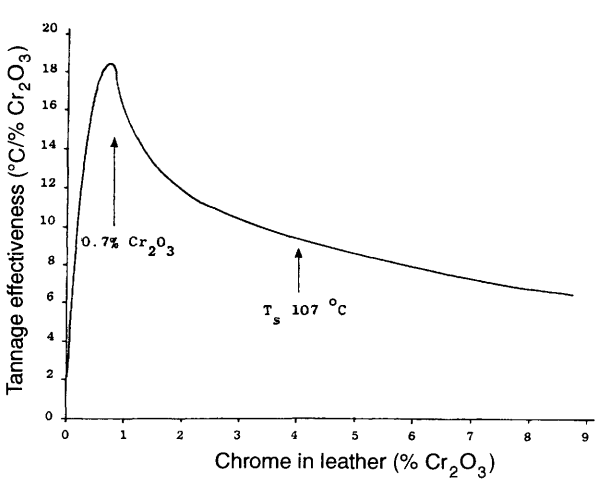


Fig. 13 Tanning effectiveness as a function of chrome fixation

Chrome tanned leather is highly versatile, largely due to the low level of tanning agent needed to achieve the desired stability. This means that the variety of retanning materials which might be applied to the part processed leather can produce a wide range of final products; indeed, from any one chrome tanned cattle hide, it is possible (at a pinch) to produce a sole leather or combat boot upper leather or softee shoe upper leather or upholstery leather or garment leather, all as full grain or suede leathers.

The part processed chrome tanned leather is called 'wet blue', because it is wet and it is blue. The colour comes from the protein carboxy complexes of chromium(III); the colour also depends on whatever masking salts are used, typically it is bright pale blue, but it can range from pale green to purple. This does introduce some difficulties regarding dyeing, but it has not restricted the colour range of fashion leathers to any great extent, with the possible exception of pure pastel shades.

2.2.2 *Aluminium*(III) *salts*

The use of potash alum in leathermaking is almost as old as leathermaking itself; it is known that the Egyptians used it 4000 years ago, because written recipes survive. Throughout tanning history, alum was often used in conjunction with vegetable tannins (see below); for example, in medieval times, Cordovan leather (from Cordoba in Spain, hence the name cordwainer, meaning shoemaker) was in widespread use in Europe, made by vegetable tanning then dyeing with cochineal.

Used by itself, alum (solution pH 2) interacts only weakly with collagen, scarcely raising the shrinkage temperature and having little leathering effect. However, in a mixture of water, salt, flour (to mask the aluminium ion and fill the fibre structure) and egg yolk (the lecithin content is an effective lubricant), skin can be turned into a soft, white, leathery product, traditionally used in the past for gloving. But, even in this case, the shrinkage temperature is not raised (hence, it is possible to discriminate between leathering and tanning) and the aluminium salt can be washed out of the leather if it gets wet; for these reasons, this process is called 'tawing', to distinguish it from tanning.

The reaction sites for aluminium(III) are the collagen carboxys, but unlike chromium(III) to which it bears a superficial resemblance in a tanning context, Al^{III} does not form defined basic species nor does it form stable covalent complexes with carboxy groups; that interaction is predominantly electrovalent, accounting for the ease of hydrolysis. The reaction can be optimised for tanning by modifying aluminium sulfate with masking salts, such as formate or citrate, and basifying the tannage to pH 4, close to the precipitation point. (There is a rule of thumb in tanning technology, that any metal salt has its greatest tanning effect just before it precipitates). In this way, reversibility of tannage is minimised and shrinkage temperatures as high as 90 °C can be achieved. Basic Al^{III} chlorides are also well known in leathermaking and several commercial tanning formulations are available. As solo tanning agents, they are slightly superior to salts based on the sulfate. However, the leathering effect of aluminium(III) is inadequate, producing firm leather, which may dry translucent due to the fibre structure resticking. Therefore, as tanning agents, aluminium(III) salts have limited value.

Where aluminium salts are useful is their ability to accelerate chrome tanning; this is demonstrated in Fig. 14.[22]. Following a pretreatment with aluminium(III), the incoming chrome displaces it, shown in Fig. 15. It is known that the rate of exchange of solvate ligands is 10^6 times faster at Al^{III} than at Cr^{III}, so it is possible to postulate that Al^{III} can react quickly with other ligands, including collagen carboxys, in a loose association that is entropy favoured or not disfavoured. This allows orientation of the carboxy bearing sidechains, from lowest energy conformation to conformation for reaction with metal salts, including crosslinking. When chromium(III) enters the system,

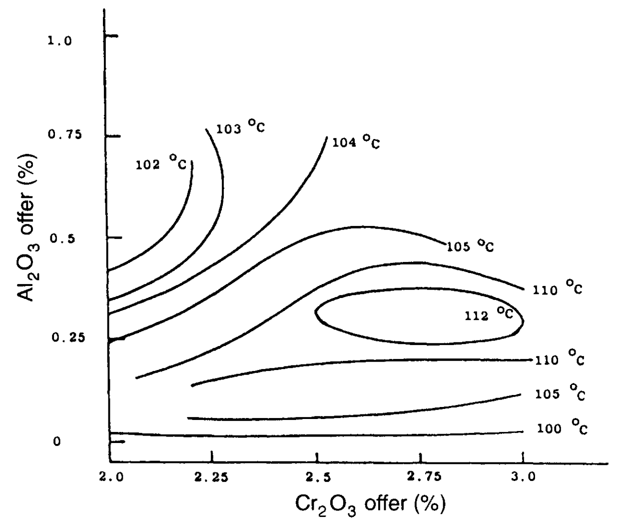


Fig. 14 The influence of aluminium(III) and chromium(III) offers on the shrinkage temperature of rinsed bovine wet blue. (Reproduced by permission of *J. Soc. Leather Technol. Chem.*).

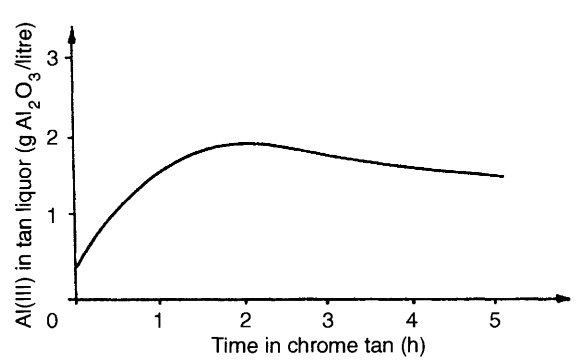
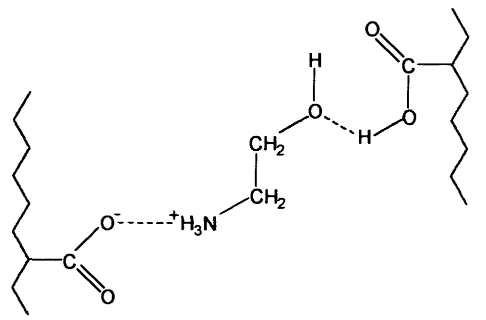


Fig. 15 The displacement of bound Al^{III} from hide by Cr^{III} at pH 3.8–4.0; mineral offers were 0.25% Al_2O_3 then 2.0% Cr_2O_3. (Reproduced by permission of *J. Soc. Leather Technol. Chem.*).

the activation barrier is lower, because the reactants are effectively shifted along the reaction coordinate, so the reaction is accelerated. Since aluminium(III) is present only at low concentration and plays a facilitating role, this process appears to be catalytic.

A similar effect has been observed for pretreatment of collagen with ethanolamine.[23] The mechanism is more speculative, but paper chemistry interactions between ethanolamine and the collagen carboxys can be proposed (**13**), operating in an analogous way to that argued for aluminium(III).



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Aluminium salts are not much used in the tanning industry because of regulatory pressure and the perception of toxicity; the latter influence is fuelled by the (continuing, but misinformed) association with Alzheimer's disease and accidental poisoning, such as the recent experience at Camelford, UK.

2.2.3 Titanium(IV) *salts*

In tanning terms, the chemistry of titanium(IV) salts lies somewhere between Al^{III} and Cr^{III}. Empirically, the chemistry is dominated by the titanyl ion TiO^{2+}, but the species are chains of titanium ions bridged by hydroxy and sulfato ligands,[24] like Cr^{III}. However, the coordinating power is weak with respect to carboxy complexation, so the interaction is more electrostatic than covalent.

The traditional use for titanium(IV) in tanning was in the form of potassium titanyl oxalate, to retan vegetable tanned leather for hatbanding, a product for which demand has reduced in the latter half of the 20th century.

Titanium solo tanning is only moderately effective, because large quantities are required to achieve the highest shrinkage temperatures, > 95 °C, but this causes the leather to be overfilled, although remaining soft. In addition, high hydrothermal stability is only achieved when the collagen is pretreated with phthalate, possibly resulting in interaction of the following type:

$$\text{Collagen–}NH_3^{+}\text{---}{}^{-}O_2C{\cdot}C_6H_5{\cdot}CO_2H\text{---}{}^{-}SO_4[Ti(OH)_2]_nSO_4^{-}$$

Also, Russian work has shown that the tannage is best basified with a mixture of hexamethylenetetramine and sodium sulfite; the mechanism is not understood.

An advantage of tanning with titanium(IV) is that it is a colourless tannage and therefore makes white leather. Hence, it has found application in tanning sheepskins with the wool on; this is a problem area, firstly because the use of chromium(III) produces a discolouration by reaction with the partially degraded keratin at the weathered wool tips and secondly because the reaction must be conducted using high solution to skin ratios, to avoid tangling (felting) the wool. However, one of the problems of using Ti^{IV} salts is their tendency to hydrolyse and precipitate in dilute solution. A comparison between the properties of Al^{III} and Ti^{IV} is in Table 4.

Table 4

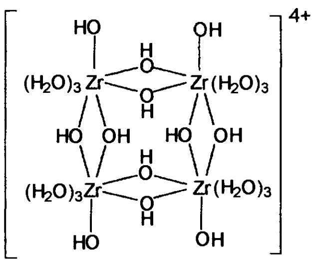
	Al^{III}	Ti^{IV}
Tanning effect	Weak	Weak
Stability to hydrolysis	Good	Poor
Filling effect	Poor	Good
Optimum tanning pH	4	4

It was argued that a mixture of salts might produce a tanning complex of better value than the individual salts. It was found that mixtures of the metal sulfates could be stabilised against hydrolysis at pH 4 by complexing (masking) with gluconate [$HOCH_2(CHOH)_4CO_2^{-}$] and in this way the mixed salt could be used to tan white sheepskin rugs; in more concentrated tanning solutions, shrinkage temperatures as high as 95 °C can be achieved. It is known that Al^{III} and Ti^{IV} salts can form mixed complexes in which the ions are bridged by hydroxy and sulfato ligands, but they still interact with collagen in a primarily electrostatic manner, just like the individual ions.

2.2.4 Zirconium(IV) *salts*

The development of zirconium tannage is relatively recent,[25] but it soon gained industrial acceptance. From its position in the Periodic Table, Zr^{IV} might be expected to display similar tanning properties to Ti^{IV}. A comparison of those properties is set out in Table 2. It can be seen that the tanning power exceeds that of Al^{III}, but in no way matches Cr^{III}. Whilst the tanning effects of Zr^{IV} and Ti^{IV} are similar, the chemistries of their salts are different. Zirconium(IV) salts are characterised by eight-coordination and high affinity for oxygen, resulting in a tetrameric core structure; the basic unit of structure is four Zr ions at the corners of a square, linked by diol bridges, above and below the plane of the square, (**14**).

By hydrolysis or basification, the tetrameric units can polymerise, by forming more diol or sulfato bridges. In this



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way, zirconium species may be cationic, neutral or anionic and large ions can form. So, tanning may involve all the polar sidechains of collagen, those bearing carboxy, amino or hydroxy groups. Hydrogen bonding *via* the hydroxy groups in the Zr^{IV} species is an important feature of the tanning reaction; together with the filling effect by the big molecules, the overall tanning effect is somewhat similar to tanning with plant polyphenols, hence zirconium tanning has been referred to as the inorganic equivalent of vegetable tanning.

Zirconium(IV) is not often used as a solo tannage, partly because of its indifferent effectiveness at raising the shrinkage temperature and partly because the acidity of the salts and the vulnerability to hydrolysis mean they must be applied at high concentration and at $pH < 1$, therefore running the risk of osmotic swelling in the hide; its main use is for retanning, to fill and firm (tighten) the grain or to make better suede.

2.3 Oil tanning

The familiar wash leather (chamois or 'chammy') is tanned with unsaturated oil;[26] the preferred agent is cod liver oil. Useful oils contain fatty acids, either free or as glycerides, which are polyunsaturated; the degree of unsaturation is critical, because if there is too little unsaturation the oil will not oxidise readily and therefore function only as a lubricant, if there is too much unsaturation the oil will crosslink itself and harden with oxidation, like linseed oil.

In this tannage, sheepskins are processed in the normal way to the pickled state, when they are then swollen by the osmotic effect in water, so they can be split more easily. Usually the skins used for chamois have inferior or damaged grain surfaces and this portion of the skin is discarded. The flesh splits are then treated with the cod oil; a traditional method of forcing the oil into the wet pelt was to use 'fulling stocks' or 'kickers', in which the oil was literally hammered into the skin by wooden mallets, nowadays rotating drums are sufficient. Blowing warm air into the vessel serves two functions: the skins are dried a little, to aid oil penetration and autoxidation of the oil is initiated, which is the basis of the process.

The actual nature of the tannage is not known, except for the following observations:

(*i*) The unsaturation decreases.
(*ii*) Peroxy derivatives are formed.
(*iii*) Hydroxy function appears.
(*iv*) Acrolein, $CH_2{=}CH{\cdot}CHO$, is produced.

It is thought that the tannage may be due in part to an aldehyde reaction (see below) and to polymerisation of the oil; the presence of the latter effect could account for the difference between the characteristics of oil and aldehyde tanned leathers. The situation is further complicated by the observation that oil tanning hardly raises the shrinkage temperature of collagen; so this is a leathering process rather than a tanning process, based on the accepted criteria of tanning.

Oil tanned leather exhibits the interesting Ewald effect: if the leather is heat shrunk in water at 70 °C, but immediately placed in cold water, it rapidly relaxes to regain *ca.* 90% of its original area and this is repeatable. (Normally, heat shrinking is an irreversible phenomenon). Furthermore, if the wet leather is held under tension whilst it is being heat shrunk, the dried leather remains soft and flexible, unlike other leathers which may come hard and brittle. This process, known as 'tucking', is used to mould leather to a desired shape, but keeping its feel.

Note, heat moulding can be applied to vegetable tanned leather, when it is known as *cuir bouille*; here, the collagen is partially gelatinised, causing the fibre structure to be glued together when it is dried and thereby producing a hard, inflexible, non-porous material, which can be used for a variety of purposes, including drinking vessels.

The most remarkable feature of oil tanned leather is its hydrophilicity, surprising considering its tanning process. A well tanned chamois leather is expected to take up at least 600% water on its dry mass and to be hand wrung to 180%. Also, this must be repeatable after drying. In use, no grease must be exuded to cause smearing.

A synthetic version of oil tanning is to use a sulfonyl chloride, which reacts predominantly with the amino groups on collagen:

$$\text{Collagen–NH}_2 + C_{16}H_{33}SO_2Cl \longrightarrow \text{Collagen–NH–SO}_2{\cdot}C_{16}H_{33} + HCl$$

Clearly this is not a crosslinking reaction, so it is not surprising that the shrinkage temperature is not raised by this tannage; but there is a powerful leathering effect and the product exhibits similar properties to oil tanned leather.

It was pointed out that acrolein is produced during the oil tanning reaction; indeed, acrolein itself can be used to make a leather similar to oil tanned. But, although it is not used itself for this purpose (for toxicity reasons), it is used indirectly, as a component of wood smoke. The traditional method of preserving hides and skins used by the plains dwellers, such as the North American Indians and the Mongols, is to use brains tanning. In this process, the animal brain is partly cooked in water, so it can be mashed into a paste, which can be worked into the pelt. The leathering effect turns the skin into a soft, open structured leather, buckskin, largely due to the lubricating power of the phospholipids of the brain. The Sioux Indians have a saying: 'every animal has enough brains to tan its own hide'. The leathering effect is serviceable, as long as the pelt is not rewetted, because then it will harden on drying due to the fibres resticking. To make the leather resistant to wetting, the solution is to smoke it over a wood fire; the multiplicity of free radical and other reactions do not adversely affect the handling qualities and they are made permanent.

2.4 Aldehyde tanning

2.4.1 Formaldehyde tanning

The archetypal aldehyde tannage is with formaldehyde, probably most familiar in preserving biological specimens or in embalming. Reaction occurs primarily at amino groups:

$$\text{Collagen–NH}_2 + HCHO \longrightarrow \text{Collagen–NH–CH}_2\text{OH}$$

The *N*-hydroxymethyl group is highly reactive and crosslinking can occur at a second amino group:

$$\text{Collagen–NH–CH}_2\text{OH} + H_2N\text{–Collagen} \longrightarrow \text{Collagen–NH–CH}_2\text{–HN–Collagen}$$

In this way, the shrinkage temperature can typically be raised to 80–85 °C. However, the crosslinking is relatively inefficient, probably because the formaldehyde species are not monomeric. Amongst the species formed in solution is paraformaldehyde, $HOCH_2(CHOH)_nCHO$. The presence of polyhydroxy species and their reaction with skin produces a white, spongy, hydrophilic leather, although the absorptive property of oil tanned leather is not matched.

The health and safety implications associated with formaldehyde mean that its use as a tanning agent is effectively banned. The only remaining common functions are for fixing casein, which is fused to the grain surface in glazing operations, or to impose permanent straightening to the wool of rugskins or sheepskin clothing leathers, by reacting with the keratin under conditions of wet heat and tension.

2.4.2 Glutaraldehyde tanning

Of the many mono- and multi-functional aldehydes which might be used for tanning (and all can be made to work), only glutaraldehyde and its derivatives have found commercial acceptance, with the possible exception of the more expensive starch dialdehyde. The reactions of glutaraldehyde are set out in Fig. 16. The crosslinking options are wider than for simple aldehydes, but the result is the same, a shrinkage temperature of 85 °C maximum. In the same way that formaldehyde is not a simple species in solution, glutaraldehyde is polymerised, shown in Fig. 17. The terminal hydroxy groups of the polymer are active and capable of reacting with amino groups. The polymer itself can interact with the collagen peptide links by hydrogen bonding *via* the alicyclic oxygens and so the leather is given its spongy, hydrophilic character.

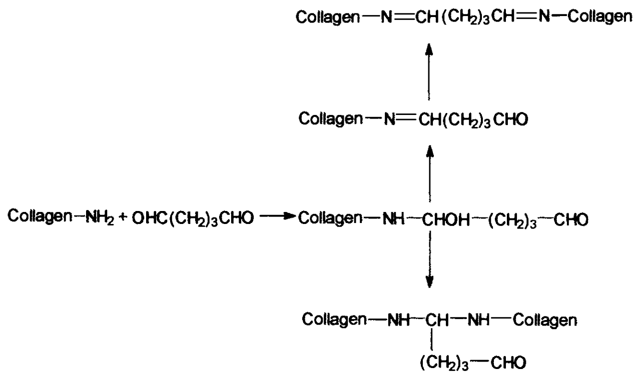


Fig. 16 The tanning reactions of glutaraldehyde

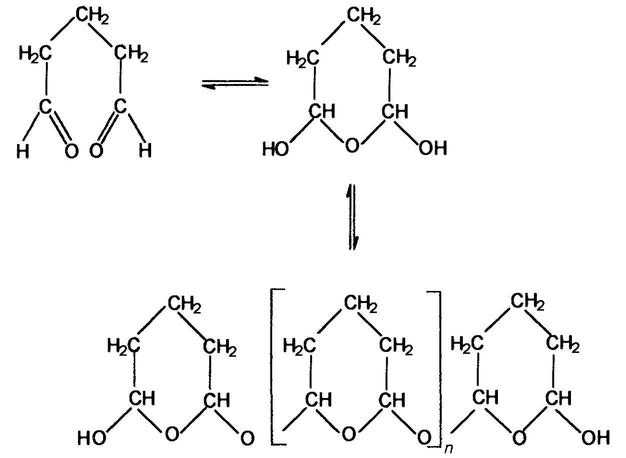
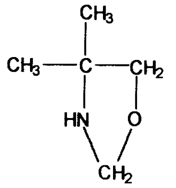


Fig. 17 The reactivity of glutaraldehyde

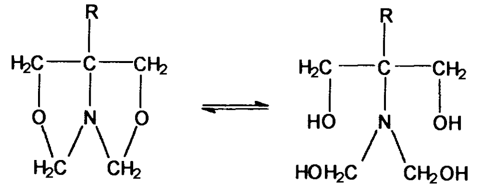
Tanning with glutaraldehyde itself confers a yellow–orange colour to the leather, which is undesirable. Several attempts have been made to modify the chemistry, to prevent colour development, including making the monobisulfite addition compound or hemiacetals, but none has been totally successful. Glutaraldehyde is coming under scrutiny with regard to health and safety implications, so it too may have to be phased out of the tanners' options.

2.4.3 Oxazolidine tanning

An alternative to aldehyde tanning, but which retains the essential reactions, is to use oxazolidines, developed less than 20 years ago.[27] These compounds are alicyclic derivatives of an amino alcohol and formaldehyde (**15**), (**16**); under hydrolytic conditions, the rings can open, to form an *N*-hydroxymethyl compound (**17**), which can react with one or more amino sites, in an effective though acridly odiferous tannage.



4,4-dimethyl-1,3-oxazolidine **15**



5-(ethyl or hydroxyethyl)-1-aza -3,7-dioxabicyclo[3.3.0] octane **16**

1,3-dihydroxy-2-(ethyl or hydroxyethyl)-2-*N,N* bis (hydroxymethyl) propane **17**

An important effect of these agents is their influence on the chrome tanning reaction, promoting the fixation; it is not known whether this is a function of the chemistry analogous to ethanolamine (see above).

2.4.4 Active hydroxy compounds

The reactivity of the carbon in *N*-hydroxymethyl compounds is not the only example of an active hydroxy. Similar reactivity has been observed in the following compounds:

$[P(CH_2OH)_4]^+$ (SO_4^{2-} or Cl^-)	$(HOCH_2)_3CNO_2$
tetrakis-hydroxymethyl	tris-hydroxymethyl
phosphonium sulfate or chloride	nitromethane

The phosphonium salts are available as bactericides (because they tan the bacteria), but they are not available in sufficient quantities to be industrial tanning agents (see below). So far, the nitromethane derivative is only a chemical curiosity.

2.5 Syntans

The term syntan means synthetic tanning agent. This class of tanning agents was introduced early this century, with the purpose of aiding vegetable tanning, although the range of reactivities currently available means that they may serve several different functions. They are classified into three types, according to their primary properties.

2.5.1 Auxiliary syntans

These compounds are frequently based on naphthalene and are synthesised by the 'Nerodol' method, *i.e.* the base material is sulfonated to a high degree and then may be polymerised by formaldehyde, illustrated in Fig. 18; the products are usually relatively simple chemical compounds. The presence of the sulfonate groups means that these compounds can interact strongly with the amino sidechains of collagen at pH < 6:

$$\text{Collagen–}NH_3^+ \text{---} {}^-O_3S\text{–Syntan}$$

In this way, reaction sites for vegetable tannins can be blocked (see Section 2.1), promoting penetration through the hide cross section. At the same time, they serve to solubilise the aggregated phlobaphenes of condensed tannins, thereby reducing reaction with the hide surfaces. Similarly, they can disperse acid dyes (most commonly used in leathermaking) and reduce the reactivity of the leather to dyeing, producing more level colouring.

A further function of these simple reagents is to act as non-swelling acids for pickling to low pH, to avoid osmotic

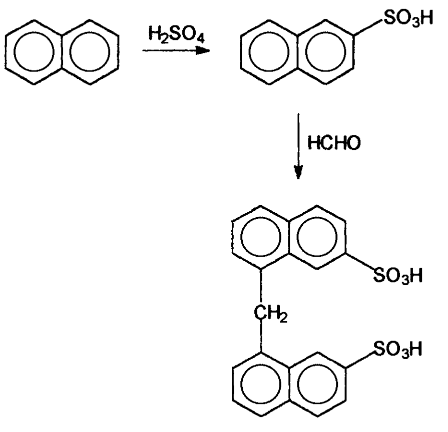


Fig. 18 The Nerodol synthesis of syntans

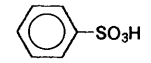
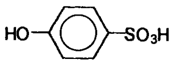
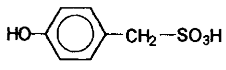
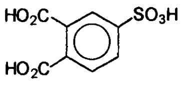
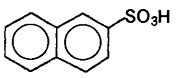
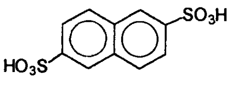
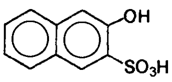
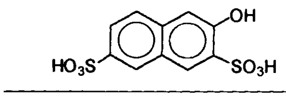
swelling. The auxiliary syntans are characterised by their low tanning power. Some may have tanning properties, by virtue of their phenolic hydroxy content, from the base material. The tanning power is a function of the number of phenolic hydroxy groups in the molecule, and the degree of swelling they produce in pickling is inversely proportional to the rise in shrinkage temperature conferred by the 'non-swelling acid', demonstrated in Table 5.

From Table 5, there is no clear dividing line between non swelling acids and auxiliary syntans or the next class of syntans, combination syntans.

2.5.2 Combination or retanning syntan

These syntans are usually based on simple phenolic compounds, they are synthesised by the 'Novolac' method, *i.e.* the base material is polymerised with formaldehyde and then the product may be partially sulfonated, as illustrated in Fig. 19.

Table 5 Examples of non-swelling acids/auxiliary syntans (T_s = shrinkage temperature)

Acid	pH	T_s/°C	Swelling (%)
None	6.3	66	100
H_2SO_4	1.2	43	235
	1.8	49	198
	1.8	58	193
	2.1	65	62
	1.7	62	112
	2.3	61	101
	1.8	60	114
	2.1	68	63
	1.7	63	87

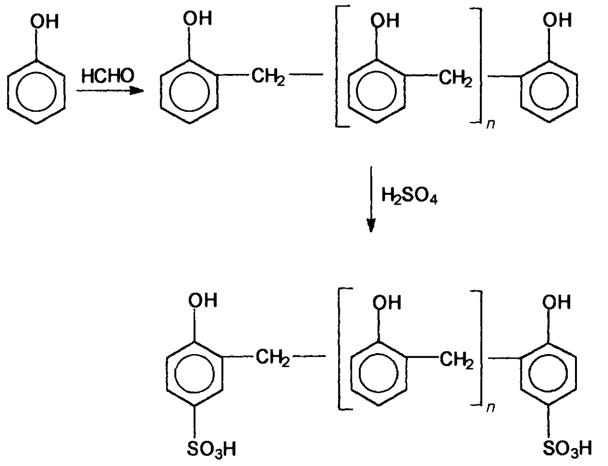


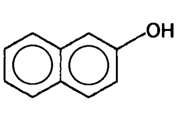
Fig. 19 The Novolac synthesis of syntans

The products are more complex than the auxiliary syntans, having higher molecular masses, and may be crosslinked in two dimensions. Their enhanced tanning functionality means that they can confer hydrothermal stability and their larger molecular size means that they can have a filling effect. (Note, the fibre structure of a hide or skin varies over its area, being markedly looser in the belly region; part of the tanner's art is to make the non-uniform raw material into a uniform leather and this is accomplished in part by filling up the interstices of the fibre weave).

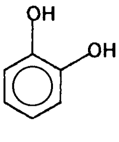
Because they are relatively small polymers, with consequently weak tanning power, these syntans work best as retanning agents; they are applied after main chrome tannage, to modify the handling properties of the leather.

2.5.3 Replacement syntans

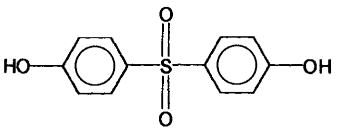
By increasing the tanning power of syntans, the agents may be classified as replacement syntans, by which it is meant that they could replace vegetable tannins. These syntans can be used for solo tanning, because their properties of tanning are comparable with plant polyphenols. Again, there is no clear distinction between the retanning syntans and the replacement syntans, the difference lies in the degree of the effects. Base materials for syntans can range from the simple to the relatively complicated (**18**)–(**20**). In addition, the bridging groups may be more diverse, including dimethyl methylene, ether, urea. They rely less on sulfonate groups for their reactivity, but synthesis by the Novolac method may incorporate some sulfonic acid functionality.



2-naphthol
18



resorcinol
19



bis (4-hydroxyphenyl) sulfone
20

The replacement syntans vary in their effects on leather, but can produce properties similar to vegetable tannins, including raising the shrinkage temperature to 80–85 °C. They are still used to prepare hide to receive vegetable tannins, though they can be used in their own right, to make leather that is more lightfast than vegetable tanned leather; a common use is for making white leather.

2.6 Organic tanning

In the modern leather industry, the preferred method of tanning is to use chromium(III) salts, because they are versatile, effective, easy to apply and have low environmental impact. Despite the evidence to the contrary, the latter aspect of chromium(III) is not wholly accepted by regulatory authorities (with the exception of the USA) and consent limits for discharge of chromium are increasingly stringent; discharge limits of <5ppm Cr ($<10^{-4}$ M) are typical. Consequently, although there is a commitment to continuing to use chrome, the industry is constantly searching for a viable alternative.

The ideal tannage to rival chrome tanning should incorporate the following features:

(*i*) High hydrothermal stability, $T_s > 105$ °C.
(*ii*) No metal salts.
(*iii*) White or pale coloured leather.
(*iv*) Lightfast.
(*v*) Low environmental impact.
(*vi*) Comparable cost.

The most difficult criterion to achieve is that specifying shrinkage temperature, which has hitherto been impossible to achieve with organic compounds alone. However, recent developments have indicated that the target is achievable.

2.6.1 Semi metal tanning

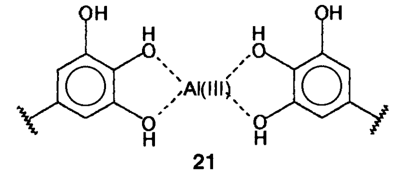
The only established organic tannage capable of producing leather with high hydrothermal stability is that in which the collagen is first tanned with vegetable tannin, then retanned with a metal salt, preferably aluminium(III); semi alum leathers made with condensed tannins typically have shrinkage temperatures *ca.* 90 °C (mimosa is exceptionally higher, possessing pyrogallol groups), whilst semi alum leathers made with hydrolysable tannins have shrinkage temperatures of 115–120 °C.

There is a correlation between shrinkage temperature and the presence of the pyrogallol group. This effect can be seen even by treating collagen with catechol or pyrogallol themselves, then retanning with aluminium(III); resulting shrinkage temperatures are 71 and 98 °C respectively and the same pattern is obtained for more complex polyphenols.

The synergistic interaction between the polyphenol and the aluminium(III) may arise from one of the following options:

Collagen–Al–veg–Al–Collagen
Collagen–veg–Al–veg–Collagen
Collagen–veg–Al–Collagen

It is known that applying the aluminium salt before the vegetable tannin produces only moderate shrinkage temperature, characteristic of aluminium alone. Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminium(III) to crosslink the vegetable tannin.[28] In effect, the crosslinking polyphenol on collagen is itself crosslinked, to form a matrix within the collagen matrix, to stabilise the collagen by a multiplicity of connected hydrogen bonds in the new macromolecule (**21**).



21

Because of the importance of the presence of pyrogallol groups, semi metal tannages are confined to the hydrolysable tannins and the condensed tannin mimosa. Many metals can perform this function, depending on the affinity for phenolic hydroxy, but aluminium(III) is the best. It is probable that this tannage is thousands of years old, because of the availability of native potash alum, which must have been used together with vegetable tannins, if only for the purposes of mordanting for dyeing.

2.6.2 High stability tannages based on natural polyphenols

The alternative to reaction at the phenolic hydroxy groups is to exploit the reactivity of the A and C rings of the condensed tannins; this is illustrated in Fig. 20. Aldehydes other than formaldehyde can perform this crosslinking function, although at much slower rates; some of those reactions are important for making for example wood glues. This type of chemistry has been used in tanning, but the perceived benefit was to reduce the leachability of vegetable tannins from leather.

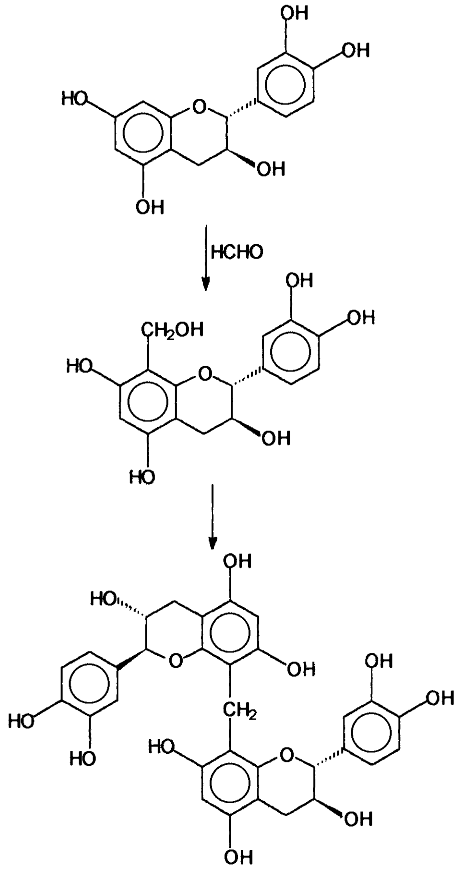


Fig. 20

Recently,[29] it has been shown that specific reactions are potentially commercially useful, demonstrated in Table 6, in which crosslinkers are applied to vegetable tanned leather (East Indian buffalo calf, tanned with an unknown mixture of locally available plant extracts).

Table 6 Shrinkage temperatures of EI buffalo calf retanned with 10% crosslinker on dry weight

	Shrinkage temperature/°C		
Reaction temperature/°C	20	40	50
Control, no crosslinker		84	
Phosphonium salt[a]	94	93	93
Gluaraldhyde derivative	90	91	92
Oxazolidine[b]	100	105	110

[a] See Section 2.4.4. [b] See Section 2.4.3.

The reason for using elevated temperature is because the usual control parameter of pH is not allowed; aldehyde or other active hydroxy tannage is accelerated by pH > 7, but vegetable tannins are stripped from collagen at pH > 6, alternatively, vegetable tannins are firmly fixed at pH < 4, but aldehyde tannage is very slow at pH < 6. Hence, the reaction can only be driven by heat. The most effective and most temperature dependent reaction is crosslinking with oxazolidine. This reaction has been further studied,[30] to determine the magnitude of the synergistic effect, shown in Fig. 21(a–c).

This is the first time it has been demonstrated that it is possible to achieve a commercially exploitable organic tannage, conferring high hydrothermal stability to the leather, which can then withstand the rigorous requirements of modern shoemaking. The major shortcoming of this leather is its hydrophilicity, due to the presence of the vegetable tannin. However, by applying fluorochemicals, it has been shown that adequate water and soil resistance for shoes can be obtained.

2.6.4 Synthetic organic tanning

The advantage of tannages based on plant polyphenols is that the reagents are obtained from a renewable resource, but the primary disadvantage is the presence of the natural components of the extract that do not contribute to the chemistry of the process, which means that the reaction is not precisely controlled. Clearly, one option would be to isolate the preferred species and that is a possibility for the future, but at an additional cost. A better option might be to target more precisely the required properties of the organic system and to synthesise the reagents.

Recently, a major breakthrough was claimed;[27] it is based on the use of melamine–formaldehyde polymers, shown in Fig. 22. It was found that oligomers could be further reacted *in situ* on collagen with additional crosslinker, to raise the shrinkage temperature to previously unachievable high values. The chemistry is analogous to the crosslinking of vegetable tannins, insofar as the pH requirements for the components are mutually exclusive and the reaction must be driven by elevated temperature. Not all crosslinkers will work equally well in this reaction; for example collagen tanned with 10% melamine resin (Granofin MH ex Hoechst) then reacted overnight at 50 °C with glyoxal or oxazolidine had a shrinkage temperature of 106 °C, but crosslinking with the organic phosphonium salt produced 112 °C.

Not all melamine resins work, indeed most of the available commercial products yield only moderate shrinkage temperatures, even in the presence of the preferred crosslinker; this is a tanning option that is well known. However, this new tannage depends on a property of melamine resins to aggregate; relatively small oligomers clump together to form larger particles and it is in this form that they usually react with collagen. The hitherto unobserved effect of high temperature processing is to break those aggregates, so that the polymer will react in the form of the oligomers. This is demonstrated in Fig. 23, in which the effect of reaction temperature on polymer particle size and consequent shrinkage temperature clearly exhibits a preferred particle size range of 50–60 nm.

Furthermore, the particle size effect outweighs even the melamine : formaldehyde ratio, since the relationship between shrinkage temperature and particle size is the same for melamine to formaldehyde ratios of 5 or 7, typically used in commercial products.

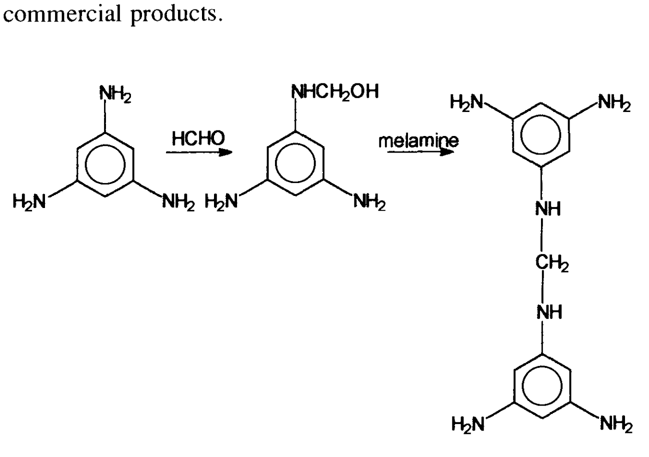


Fig. 22 Melamine–formaldehyde polymers

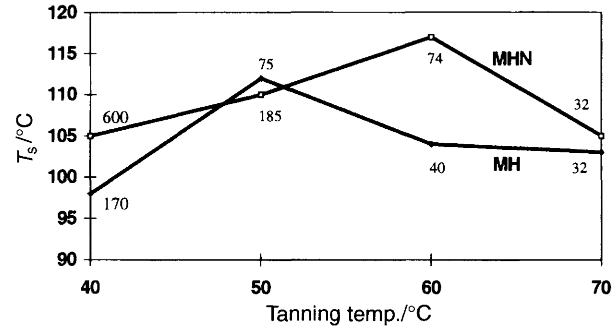


Fig. 23 The effects of reaction temperature and particle size (nm) on shrinkage temperature

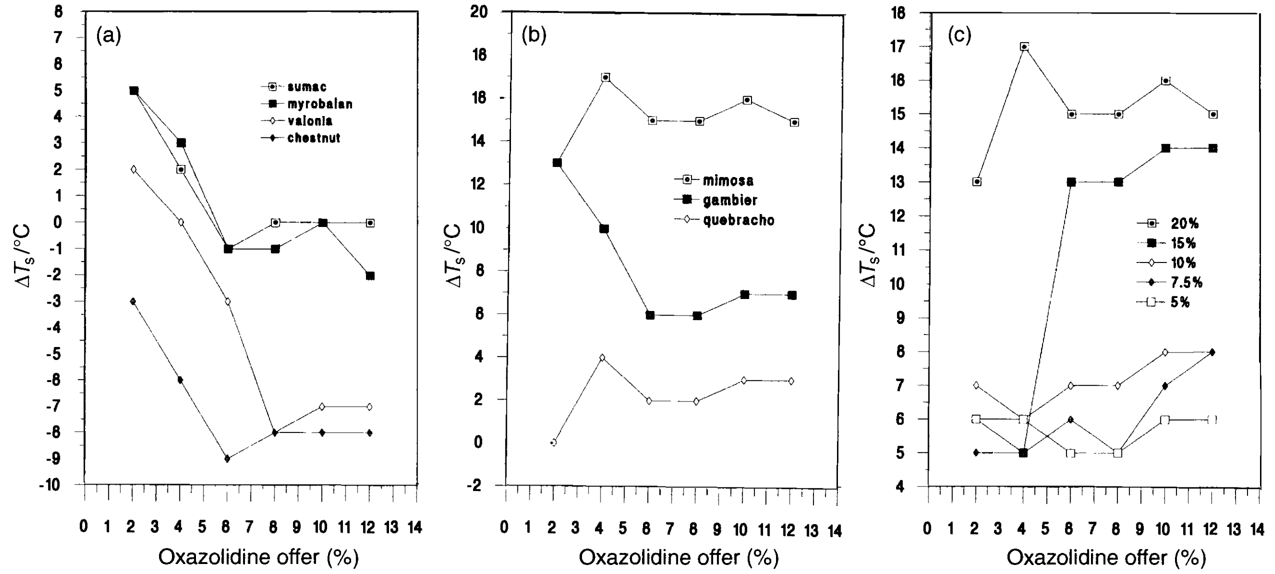


Fig. 21 (a), (b) Change in shrinkage temperature showing the interaction between tannage and retannage above the additive effect: hydrolysable tannin tannage (20% offer), then oxazolidine retannage. (c) Change in shrinkage temperature showing the interaction between mimosa tannage and oxazolidine retannage above the additive effect.

These new tannages satisfy the criteria of hydrothermal stability, metal free, white and lightfast. An additional benefit is the speed of the reaction, shown in Fig. 24; maximum shrinkage temperature is reached in 3 h, compared with the 15 h typically required for chrome tanning. The only problem in leather terms is that the leather is weaker than a chrome tanned counterpart. This is due primarily to the filling effect of the resin and the loss of strength is proportional to the amount of resin used. It is probable that the tannage has not been optimised with regard to applying a single or major resin species, so by targeting the reaction more precisely, by minimising the quantity of resin required to obtain the desired shrinkage temperature, the strength of the leather will be maximised.

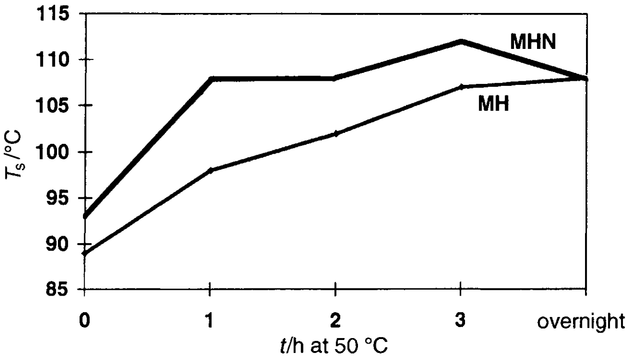


Fig. 24 The rate of tanning with THPS and melamine–formaldehyde resins

This could be the basis of the tanning chemistry of the 21st century. The remaining questions are: what is the level of the environmental impact of the change in tanning methods and what is the cost in comparison to chrome tanning? The first question cannot be answered until a full environmental impact study is undertaken, but it is known that melamine–formaldehyde polymers are non-toxic and the crosslinkers are safe if handled properly. Cost will depend on the scale of adoption; the basic cost is going to be higher than for chromium(III) salts, but savings may be made through reduced quantities of dyestuffs and lubricants needed for the new leathers.

3 Discussion

Contrary to popular perception, the tanning industry is ecologically sound. It has a reputation for producing noxious waste and smells, but it should be remembered that the raw material for leather is a byproduct of the meat industry; if the tanners did not turn the hides and skins into leather, the abattoirs would be faced with a disposal problem that would far outweigh the alleged pollution by tanneries. In recent years, tanners in many countries have cleaned up their act, to the extent that they can operate successfully in modern city centres, unlike their historical predecessors, who were frequently compelled to work away from habitation. It is perhaps an indication that tanning is becoming more environmentally acceptable, that tanners worldwide no longer automatically occupy the lowest level of the social totem pole.

Tanners have a good record of improving the quality of their waste products. The traditional method of tanning in closed drums means that processes were developed which would progress satisfactorily without constant monitoring or needing frequent changes in the chemical conditions. The consequence is that these traditional processes tend to be less environmentally acceptable. They are gradually being phased out, replaced by cleaner technologies, incorporating more precise process control, more recycling of chemicals and greater reliance on biochemical rather than chemical agents.

It might be thought anachronistic, not only to continue to make leather but also to develop the chemistry of leathermaking, when so many synthetic materials are available, with such a range of excellent properties. Reconsider that thought in the light of these questions.

What is the material of choice for your shoes or handbags?

How many shoe upper materials allow wet air to pass freely from one side, whilst completely preventing liquid water passing through from the other side?

How many fabrics will abrade, as you skid along the ground having fallen off your motorcycle, without fusing with your soft tissues?

How many materials can resist the effects of splashing with molten metals (*e.g.* sodium, steel), without melting or transmitting the heat to the wearer of protective clothing?

How many materials are used both for fire resistant upholstery and as fire blankets?

How many materials retain their integrity and performance in the temperature range −100 to +100 °C?

Many materials can exhibit some of those properties, but only leather has them all!

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Received, 3rd June 1996
Accepted, 29th November 1996