Quo Vadit Chromium?
The Future Directions of Tanning*

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Abstract

From leather science, a deeper understanding of the theoretical basis of the tanning mechanism has unified the inorganic and organic chemistries of leather making processes. The 'link-lock' mechanism provides an explanation of present reactions and a tool for future developments.

The question now posed is: where does this new thinking take us, in terms of the future of tanning? The answer is: into a paradigm shift.

Chrome tanning will remain with us, but in the future it can be viewed very differently from its currently perceived technology. Options for transforming the process may now be proposed. Important in this exercise is to question closely the conventionally accepted features of the reaction.

Alternative technologies for tanning in the modern era can now be developed, to make high hydrothermal stability leathers. Here, the link-lock theory has demonstrated that such outcomes cannot be achieved by any single conventional reagent; at least two tanning components are needed. Moreover, tanning can be more accurately formulated to match the chemistry (or biochemistry) of the reaction to the performance and environmental impact requirements of the leather.

Resumen

De la ciencia del cuero, un entendimiento más profundo ha surgido acerca de la base teórica del mecanismo de curtición que ha unificado las químicas orgánicas e inorgánicas de los procesos de fabricación del cuero. El mecanismo de 'eslabón-cerrojo' provee una explicación de las reacciones hoy conocidas y una herramienta para futuros desarrollos.

La pregunta expuesta es: donde nos llevará este nuevo concepto en términos del futuro de la curtición? La respuesta es: a un desplazamiento paradigmático.

Curtición al cromo permanecerá con nosotros, pero en un futuro se visualizará muy diferentemente su tecnología por hoy percibida. Opciones para la transformación del proceso ya sí se pueden proponer. Es importante en este ejercicio cuestionar detalladamente los aspectos convencionalmente aceptados de esta reacción.

Tecnologías alternativas de curtición en la era moderna pueden ahora ser desarrolladas, para producir cueros altamente estables hidrotérmicamente. Aquí la teoría eslabón-cerrojo ha demostrado que tales resultados no son obtenibles con un solo reactivo, por lo menos dos componentes de curtido son requeridos. Más aun, la curtición podrá ser más acertadamente formulada para que encaje con la química (o bioquímica) de la reacción según su rendimiento y los requerimientos del impacto ambiental del cuero.

Introduction

In this paper, the principles of tanning science are applied to current tanning technologies, to assess the opportunities for positive change and the options for development. Hence the title:

> Where is chromium (or other tanning technologies, for that matter) going?

In the field of tanning science, the starting point is the recently developed theory of tanning: 'link-lock'.[1] Here, the outcome of any tanning reaction can be rationalised in terms of the number of components in the overall process and the nature of relationships between the components and the substrate, collagen.

The 'link' part of the reaction concerns the primary reactant, the main component that reacts directly with the collagen. All

tanning reactions exhibit this part of the mechanism, which may involve any or all types of reaction: hydrogen bonding, hydrophobic bonding, electrostatic interaction and covalent bonding. The effects are twofold.

o First, the structure of the supramolecular water[2] around the triple helices is modified, thereby changing the ability of the protein to spread into the interstices between the triple helices, when the helical structure begins to unravel as it denatures under hydrothermal conditions. All primary reactions produce the same outcome, with only a small variation: the observed shrinkage temperature of single component tannages is typically 75-85°C, although some may confer even less stability because of the nature of the chemical change. The actual value achieved depends on the effect of the reaction on the entropy of activation[3], which controls the rate of shrinking, reflected by the conventionally measured shrinkage temperature. Part of the modification is the nature of the primary interaction: the weaker the interaction, the lower the hydrothermal stability, but the upper limit to the hydrothermal stability is defined by the strongest interaction, covalent bonding. The degree of structure or additional bonding introduced by the tanning reaction has only a second order effect on the hydrothermal stability: regardless of the type of structure imposed by this reaction, the hydrothermal stability is limited.

o Second, the presence of the tanning agent modifies the shrinking reaction. The ease with which the triple helix can unravel into the region between triple helices depends on the resistance offered by the intervening chemical species. The mechanism of the shrinking reaction is independent of the chemistry of tanning[1], so the effect of the single tanning species is to hinder the outcome of unravelling. This view is consistent with the observation that any tanning reaction from a single component, which can only cause the linking effect, will confer the same moderate hydrothermal stability increase. Qualitatively, the effect of the primary reactant is to interfere with the unravelling process, as the collagen converts from the helical structure into the random coil structure. Hence the similarity of outcome. In addition, the interaction between the tanning species and the supramolecular water modifies the shrinking process, giving rise to the observed small variations in the moderate hydrothermal stability resulting from the single component reaction. The outcome of the linking step is independent of the ability of the tanning agent to crosslink. From the work of Das Gupta[4], mono-functional oxazolidine and bi-functional oxazolidine confer the same shrinkage temperature, about 80°C, see Fig. 1.

The 'lock' part of the mechanism refers to the action of a second component in the tannage. The second reaction can take several forms, as follows.

o The second tanning reaction may be independent of the first tanning reaction. For example, in chromium(III) retanning after vegetable tanning, regardless of the polyphenol type, hydrolysable or condensed, the chromium(III) fixation
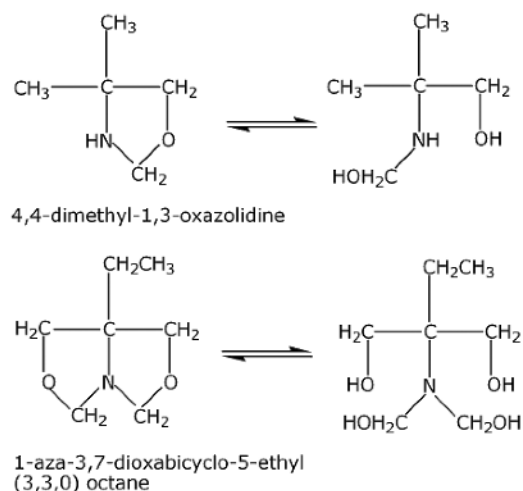
Figure 1: The tanning chemistry of oxazolidine: N-methyl derivatives.

TABLE I
Contributions to the hydrothermal stability of semi alum leather.[8]

Reaction	Ts (°C)	ΔTs (°C)
none	65	-
Al(III) tanning	75	10
Tara	80	15
Tara + Al(III)	115	50

reaction occurs with the carboxyl's of the collagen and not with the phenolic hydroxyls.[5] Therefore, the characteristics of the outcomes of the reactions are individual, rather than combined.

o The second reagent may interact with the first, but still have no effect on the outcome of the combined process. For example, in the combined tanning effect of metal, such as aluminium(III) and hydrolysable vegetable tannin, it is known that the semi metal reaction is dependent on the polyphenol being applied to the collagen first, followed by the aluminium salt, see below. However, if the polyphenol is applied after the metal salt, this will result in complexation of the metal by the polyphenol, but the outcome is characteristic of independent reactions.[6]

o The second reagent may react with the first reagent, creating a new tanning reaction; in other words the interaction is synergistic. This refers to the situation when the observed effect on the hydrothermal stability is greater than the sum of the contributions:

$$\Delta Ts_{obs} > \Delta Ts_1 + \Delta Ts_2$$

where ΔTs refers to the effect (rise) in shrinkage temperature conferred by the tannage. Note, if the sides of the equation are equal, the effects of the tanning reactions are independent and additive (to some extent), as described above. If the observed shrinkage temperature change is less than the sum of the contributions, the reactions are antagonistic ie one interferes with

the other, to decrease its effect. An example is the combination of hydrolysable vegetable tannin and aldehyde: the available sites on the gallic acid or ellagic acid moieties are unreactive to aldehydic attack and reaction, so the aldehydic reaction with collagen inhibits reaction between the polyphenol and the protein.[7]

Known cases of high hydrothermal stability exhibit positive interaction, which can be illustrated using the semi alum process, shown in Table I, in which the polyphenol is tara, a hydrolysable gallotannin.

The difference between the observed shrinkage temperature and the calculated sum of the contributions (here, 50 - (10 + 15) = 25) is indicative of the magnitude of the effect in creating a new tanning species and hence of the new reaction on the stability of the leather.

o The second reagent may additionally react both with the first reagent and the collagen; in this way it can link the matrix more firmly to the collagen. This happens in the combination reaction of condensed polyphenols and oxazolidine[9], when the dual reactions confer a positive effect to the tanning outcome. Referring back to Fig. 1, when the mono-functional oxazolidine is used to retan vegetable tanned leather, the shrinkage temperature is small, indicative of an independent addition, but the bi-functional oxazolidine causes a big increase in Ts, indicative of a synergistic crosslinking reaction with the polyphenolic vegetable tannin.[4]

If there is synergistic interaction between two components of the tanning reaction, the primary reactants are locked together by the second reagent, effectively changing the individual reactions into a concerted, single interaction. The consequence of forming a single chemical entity around the triple helices is to make it much more difficult for the collagen to collapse into the interstices. This is observed as high hydrothermal stability. It is critical that the reaction should take this form: merely filling the interstices with unlinked molecules, as happens in full vegetable tanning, cannot prevent molecular movement in the collagen as the triple helices unravel.

There are two observations in the shrinking transition that must be incorporated into the ideas of the mechanism of tanning.[10]

1. It has been demonstrated that the shrinking reaction is independent of the tanning reaction, because the energy is the same.

2. The shrinking transition does not involve the breaking of the artificial links between the tanning agent and the collagen.

It has therefore been postulated that the shrinking reaction involves the breaking of hydrogen bonds within the collagen structure. The new view of the structure of collagen, proposed here, which includes the presence of structural water in the supramolecular matrix, must play some part in the reaction. Indeed it has been shown that the water associated with the collagen structure is practically independent of the tanning chemistry: the amount is the same, about 23%, whether the collagen is stabilised with chromium(III), formaldehyde or
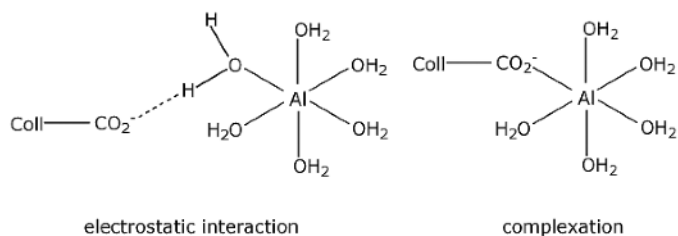

Figure 2: Interactions between collagen and aluminium.

high levels of vegetable tannin, hydrolysable or condensed.[11] It can be further postulated that there must be some of this structural water remaining in the matrix modified by the tanning chemistry. Therefore, shrinking involves the unravelling of the triple helix, aided by the breakdown of the residual structural water associated with the triple helix.

It has been demonstrated that the shrinkage temperature of collagen depends on its moisture content: this has been explained in terms of the close approach of the triple helices, as water is removed: the effect is to prevent the unravelling process, since there is decreased space for this to happen.[12] Of course, this is already known in leather technology, because it underpins the requirement for the shrinkage temperature to be conventionally measured under conditions of water saturation, when the state of the sample is simply defined and easily achieved in practice, so the shrinkage temperature is at its lowest. This can be understood in terms of the ease of displacement of the intervening molecular species during shrinking. Therefore, the idea that hydrothermal stability depends on the chemical situation within the collagen structure is consistent with the known role that water plays in the structure of collagen and hence also plays in modified collagen.

The important conclusions to be drawn from this analysis are as follows.

a. Single component tannages are restricted by the thermodynamics of the shrinking reaction to confer only moderate shrinkage temperature.

b. High shrinkage temperature can only be achieved by tanning with at least two conventional components.

c. High shrinkage temperature is achievable if there is strong primary chemical bonding between the tanning agent and the collagen and if the primary tanning agent is locked in place by a secondary tanning agent. The chemistry of the reactions is less important than conforming to the requirements. Therefore, high shrinkage temperature is achievable by many more routes than is currently known.

The arguments for the first and second conclusions have been presented above. The third conclusion can be rationalised by considering tannages that do conform and do not conform to this requirement. If the locked matrix is strongly bound to the triple helix, the ease with which the matrix can be displaced during unravelling is greatly affected, making it more difficult for the reaction to occur: this is observed as high hydrothermal stability, when more energy must be applied, to break down the

water-matrix structure. Alternatively, the formation of a matrix that is weakly bound to the triple helix or not bound at all infers a greater role for the structural water. For example, tanning with aluminium(III) salts can be compared with chromium(III) tanning: there are superficial similarities, but the outcome is quite different, because aluminium(III) salts alone are incapable of conferring high hydrothermal stability. However, it has been shown that the chemical environment of the aluminium(III) species is not changed by the shrinking reaction.[10] The possible interactions between aluminium(III) and collagen are modelled in Fig. 2.

The (basic) aqueous ion can interact electro-statically via a water ligand or a complex might be formed, which would be more electrovalent than covalent. Since it is known that aluminium(III) does not form stable complexes, it may be surmised that the former case is more likely. Therefore the bonding between the collagen and the matrix could break down hydrothermally, but the environment of the aluminium nucleus would not be substantially altered. Therefore, it can be concluded that the aluminium-based matrix involves water that can break down, to allow shrinking, ie the electrostatic interaction with collagen carboxyls is sufficiently distant to allow this to happen, but the aluminium(III) nucleus experiences no change in its magnetic field. Alternatively, covalent complexation between collagen carboxyls and chromium(III) is a direct interaction, which cannot break down under the conditions of shrinking.

By recognising these new principles of tanning science, the technology can be developed far beyond the current horizons of leather practice. Some of the options are explored below.

THE FUTURE OF CHROME TANNING

The environmental impact of chromium(III) is low: as a reagent, basic chromium salts are safe to use industrially and can be managed, to the extent that discharges can routinely be as low as a few parts per million. Therefore, it is clear that the industry should be able to meet all the future requirements of environmental impact. Consequently, we can reasonably assume that the future of tanning will include a major role for chrome. Nevertheless, the technology can be improved: efficiency of use can be improved, as can the outcome of the reaction, in terms of the performance of the leather (shrinkage temperature) and the effectiveness of the reaction (shrinkage temperature rise per unit bound chrome).[13]

It might be a cause for curiosity as to how this reaction, the best known high hydrothermal stability tannage, fits into the link-lock mechanism. It has been shown[14] that chrome tanning is not, in fact a solo tannage; it is a combination reaction, comprising the chromium(III) molecular ions and the counterion, where the counterion is not acting as a ligand in the chrome complex[15], illustrated in Fig. 3.

Chromium chloride or perchlorate confer only moderate hydrothermal stability to collagen, but when sulfate or any other locking ion is introduced, the familiar high shrinkage temperature
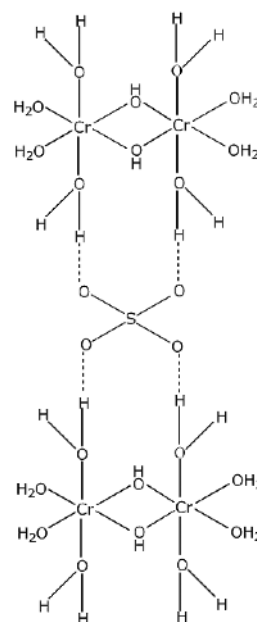
Figure 3: The possible interaction between chromium(III) species and sulfate, which may involve more water molecules between the aqua ligand and the sulfate ion.

is obtained.[16,17] Therefore, the process might be reconsidered in this light, that is, as a two stage/step reaction. Since there is an environmental problem with sulfate (as a solubilizer of concrete), the use of an alternative salt and another locking counterion would be advantageous.

It is useful to compare the conventional view of chrome tanning, the assumption of collagen side-chain crosslinking, and the new proposition, the matrix model. If the conventional view is correct, the tanning reaction should be independent of the nature of the counterion. However, that is clearly not the case, the reaction is highly dependent on the nature of the counterion: tanning is only moderately effective for chromium(III) chloride or perchlorate, it is effective in the presence of sulfate, but its effect is almost maximised in the presence of pyromellitate, 1,2,4,5-tetracarboxy benzene, if it acts as a counterion rather than a ligand.[18] Therefore, the matrix model explains the observations, but the traditional view does not.

The uniqueness of chrome tanning is not that it constitutes a single tanning agent, but that the linking and locking components of the mechanism may be applied at the same time.

The tanner's approach to chrome tanning can be enhanced and extended by including consideration of the role of the solvent and the nature of the chrome tanning complex. It has been argued[14] that the reaction between a solute and a heterogeneous substrate can be expressed in the form of stepwise reactions, as follows.

1. Transfer from the solvent into the substrate.

(solute)$_{solvated}$ + (substrate)$_{solvated}$ x (solute-substrate)$_{solvated}$
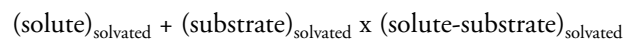
The equilibrium depends on the relative affinity of the solute for the solvent and the affinity of the solute for the substrate:
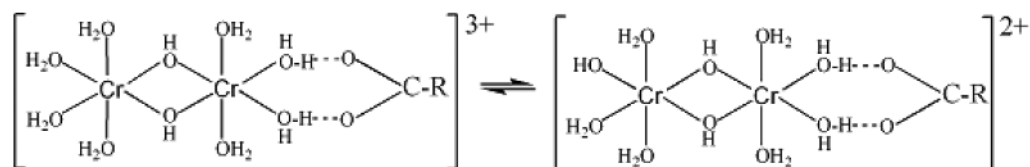
Figure 4: The rate determining step for carboxylate complexation of chromium(III).
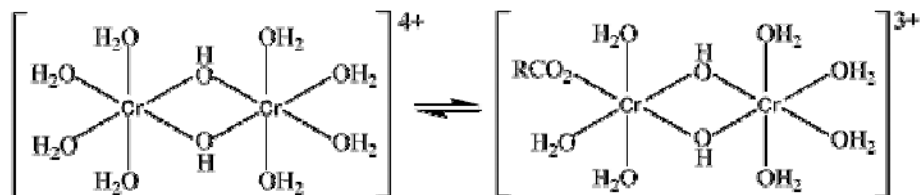

Figure 5: Introduction of a formate, as an example of a carboxylate species, into the ligand field of chromium(III).
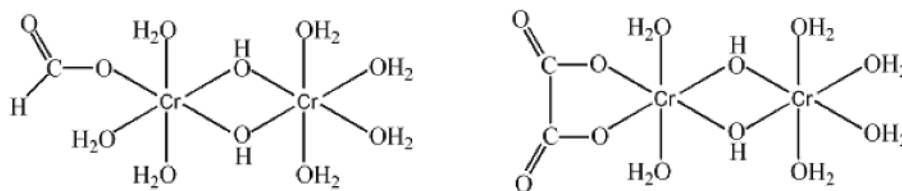

Figure 6: Masking with formate and oxalate.

TABLE II
The effects of masking agents on relative chrome uptake.[25]

Masking salt	Chelate ring size	Complex reaction	Relative chrome content	Masking effect
none	-	-	1.00	none
formate	-	-	1.06	hydrophobic
acetate	-	-	1.18	hydrophobic
oxalate	5	chelate	0.97	complexation
malonate	6	chelate	1.05	hydrophobic
maleate	7	chelate	1.40	hydrophobic
succinate	7	chelate	1.85	hydrophobic/
molecular size				
phthalate	7	chelate	1.93	hydrophobic
adipate	11	crosslinking	2.03	hydrophobic
				molecular size

the more hydrophobic the solute, the greater its relative affinity for the more hydrophobic environment of the substrate. Since this is a mixed phase step, its contribution to the reaction kinetics is to influence the partitioning of the solute between the phases, thereby facilitating the availability of the solute for the reaction within the substrate, but the kinetics of reaction are not affected, since the mechanism involves the chemical reactions of the bonding interaction[19,20], see below. Therefore, the effect of the transfer step is only an apparent change to the kinetics of reaction. Consequently, we can distinguish a differentiation between the rate of uptake of the solute and the rate of fixation. This can be understood more clearly by using the model of non aqueous solvent tanning of the type suggested by Wei.[21] Here, tanning of conventionally pickled wet pelt is conducted in paraffin as the tumbling and heating medium. Chrome tanning powder is added: the salt is insoluble in the paraffin, but is rapidly solubilized in the wet substrate. Although the uptake is highly efficient and effective, 100% uptake in a matter of minutes, the fixation is a different reaction, which proceeds much more slowly. Despite this example being more concerned with solubility than transfer, it can be regarded as an extreme example of the general case.

The role of the solvent in chrome tanning has already been exploited: Rohm and Haas marketed Chromesaver® A30, ethanolamine hydrochloride $HOCH_2CH_2NH_3 \cdot Cl^-$, as a pickling
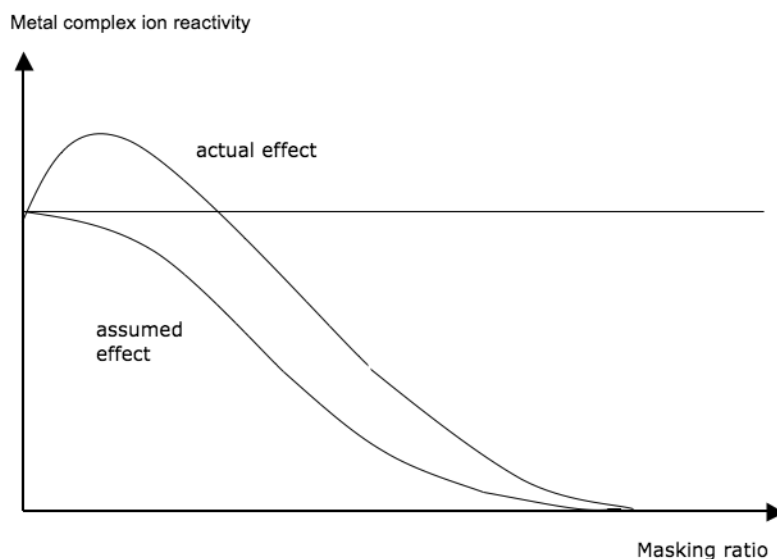
Figure 7: The effect of masking on metal ion reactivity to complexation with collagen.

auxiliary[22], which changes the dielectric properties of the solution, even at low concentrations. It is not immediately obvious that the solvent is changed by adding this solid product, but it becomes clearer if the action were to be reconstituted by mixing the organic liquid ethanolamine with the pickle solution and readjusting the pH to the required value. Strictly, in either case, the effect is to create a mixed aqueous organic solvent.

It is generally true that tanners usually do not use water in their processing (*Ed note: excluding wash water*). Consider the typical conditions in solution: often the process liquors are concentrated solutions of salts of different types, so the solvent properties are significantly different to water. In the thermodynamic sense, dilute solutions are defined as $<10^{-4}$ molal, above that concentration the solutes modify the water properties by creating an electric field. The higher the electrolyte concentration, the more the solvent functions as a charged medium, with charge-charge interactions between solvent and solute. An example of the effect is the technology of adding salt to the bath when using reactive dyes. Here, the charged nature of the brine means there is less affinity of the solvent for the dye, thereby driving the dye into the more hydrophobic environment of the substrate. In this way, the balance of the relative rates of hydrolysis and uptake are altered in the tanner's favour.

The effect of the species in solution should be considered when analysing any reaction and the same kind of analysis can be used to create improved or new outcomes.

2. Electrostatic interaction between the solute and the substrate.

All reactions of this type involve an initial electrostatic interaction, whether it is a simple charge-charge attraction between the reactants or a wider aspect of electrostatics, hydrophobic and hydrogen bonding. The contribution of this step extends into the initial step: the more highly the solute is charged, the greater the potential attraction into an oppositely charged substrate. Even

though charge on the solute will contribute towards the solvating effect of aqueous solvent and therefore affect the apparent rate of reaction, the overall reaction of complexation may not be dependent on a rate determining step of primary interaction by electrostatic attraction. An example of this step operating is given by vegetable tanning[23], when the transfer is facilitated by the hydrophobic nature of the polyphenols, giving rise to the conventional view that the initial interaction with the collagen is via hydrophobic bonding. The bonding then becomes converted to hydrogen bonding, as the ultimate electrostatic interaction.

In the case of carboxylate complexation with chromium(III) in solution, it has been shown that the rate of reaction is independent of the carboxylate compound, since the initial electrostatic interaction is fast, but the rate determining step is proton loss[19], shown in Fig. 4.

The charge on the complex will affect the interaction between the carboxylate and the charged complex, but this is a fast rate, not rate determining. Therefore, the charge on the complex is probably more important in determining the hydrophilic-hydrophobic properties and hence the initial attraction of the substrate for the solute. It is important to understand that all carboxylate complexation reactions run at the same rate, including chelation, so the rate of masking is the same as the rate of tanning.[24] This clearly has implications for the masked status of the chrome species at any time in the tanning process, depending on the chemical conditions before and during the reaction.[14] The role of masking is further discussed below.

3. Covalent reaction.

Initial charge based interaction may be followed by covalent reaction, if the chemistry allows, as it does in chromium(III) complexation or tanning with condensed polyphenols.

The solvent-solute interaction is sometimes characterised by the value of the hydrophilic-hydrophobic balance (HHB), alternatively designated hydrophilic-lipophilic balance (HLB),

and quantitatively measured by the chromatographic movement of the solute in a range of solvents with different dielectric properties. This is the parameter that controls the transfer reaction, probably most familiar to tanners with regard to dye properties. For example, the Sellaset® dyes have matched HHB properties, so their rates of reaction are the same and they appear to react as if the mixture was a single dye. In the case of chromium(III), the solvent interaction can be controlled by the ligand field, referred to in the jargon as masking. This is familiar technology: for example, the use of phthalate to make the chrome more reactive. Contrary to the popular belief that the dibasic phthalate ion makes the chrome more reactive by crosslinking molecular ions, it chelates a chromium atom and makes the molecular ion hydrophobic, due the presence of the benzene ring in the ligand field. Indeed, if the reaction is crosslinking, the effect on the reactivity of the chrome would be a second order effect[1]. Because the availability of reaction sites for complexation is at the ends of the chrome species, the trans sites (see Fig. 5), the reactivity would be practically unaffected by the masking reaction and the effect on the reactivity would be less dependent on the influence of the crosslinking agent on the HHB value of the complex.

The technology of masking must be reviewed, because there is much misunderstanding regarding its effects on chrome tanning. Introducing a ligand into the chrome complex can be considered to have two competing outcomes.

1. The reactivity of the chrome species to complexation with collagen is assumed to be reduced, because there is a statistical reduction in the number of available reaction sites, illustrated in Fig 5.

In the masking reaction, as in the tanning reaction, substitution occurs at the trans positions of the octahedral complex, the positions in the plane of the μ-dihydroxy bridges, shown in Fig. 5.[15]

2. The reactivity of the masked chrome species can be enhanced, because the complex becomes more hydrophobic by the introduction of the carboxylate into the ligand sphere and all carboxylates are more hydrophobic than an aquo ligand - at least those commonly used in the art.

The effects of masking with formate and other masking salts, which can react in different ways, are shown in Table II. Here the masking ratio is 1 mole per mole Cr_2O_3: the effect of the number of equivalents of carboxyl per mole should be taken into account. In each case, the effect of the masking on the reactivity of the chrome species is designated based on the known chemistry of the masking agent and the observation of the relative extent of reaction.

The designation of 'hydrophobic masking' indicates the influence of the masking agent on the properties of the complex and hence the element of the reaction mechanism that is affected: increasing the hydrophobicity of the complex encourages transfer from aqueous solution.

The designation of 'complexation masking' indicates that the net effect is to modify the ability of the complex to react further, i.e. this conforms more to the conventional view of
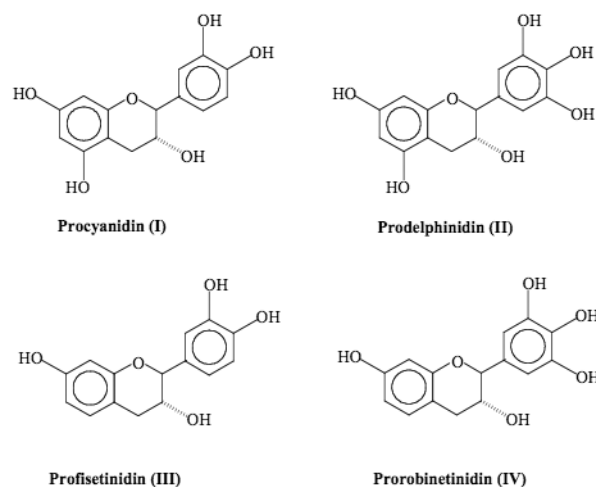

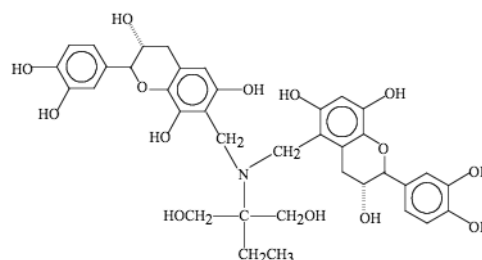Figure 8: The hydroxylation patterns in plant polyphenols for tanning.

Figure 9: Reaction between catechin and oxazolidine: reaction only occurs in the A-ring at the 6- and 8-positions.[34]
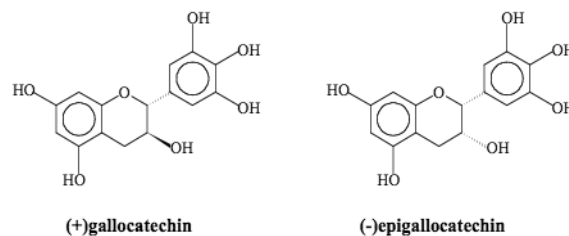

Figure 10: The stereochemical structures of gallocatechin and epigallocatechin.

TABLE III
Rates of reaction between flavonoid species and oxazolidine.[33]

Flavonoid	Rate ($M^{-1}s^{-1}$)
Catechin	0.18
Epicatechin	0.20
Epigallocatechin	0.22
Epigallocatechin gallate	0.24

masking. Comparing the effects of formate and oxalate masking in Fig. 6, the notional structures indicate that formate is likely to be less able to interact with water than an aqua ligand, thereby conferring a small degree of hydrophobicity. On the other hand, oxalate has the potential for effective hydrogen bonding, because it offers only carbonyl groups for interaction with the solvent, so the net effect is a reduction in the number of

TABLE IV
Rates of reaction between polyphenols and aldehydic crosslinkers.[33]

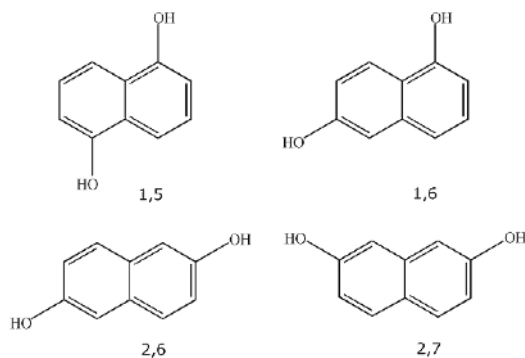| Polyphenol	Oxazolidine	Formaldehyde
Phloroglucinol - 1,3,5-trihydroxy benzene	0.433	0.234
Resorcinol - 1,3-dihydroxy benzene	0.024	0.008
Pyrogallol - 1,2,3-trihydroxy benzene	0.018	<0.001
Catechol - 1,2-dihydroxy benzene	<0.001	<0.001

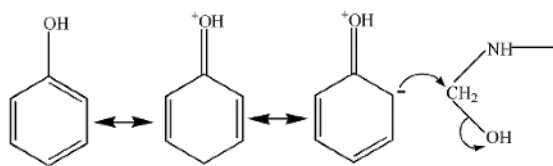Figure 11:   The structures of some naphthalene diols

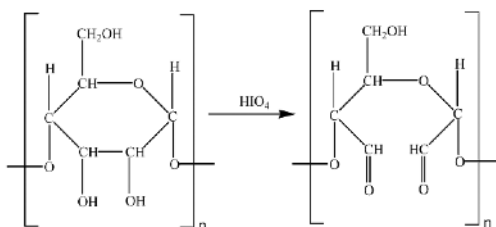Figure 12:   The reaction between the phenol and N-methylol moieties.

Figure 13:   Formation of starch dialdehyde

available reaction sites and hence reduced affinity for collagen carboxyl's, driven by the chelating mechanism.

The designation of 'molecular size' indicates the influence of crosslinking, to polymerise the molecular ions. This in itself will increase the rate of chrome fixation, since, even if the rate of complexation is unchanged, the rate of chrome uptake is increased.

The table illustrates the following important points.

a. If we assume that chrome content is a reflection of the overall reaction rate or reactivity, there is no indication that masking with formate at this level reduces the reactivity of the chrome salt; indeed, there is an increase in reactivity. This runs contrary to conventional thinking about the masking effect of formate. It must be recognised that the

relative effects of masking are dependent on the masking ratio. Those apparently contradictory effects are: the reduction in reactivity by using up reaction sites and the increase in reactivity by increasing the hydrophobicity. Taking the example of formate, as the simplest and commonest masking agent, at higher masking ratios, $[RCO_2]:[Cr_2O_3]>1$, the reactivity reducing effect will begin to dominate, typically resulting in a reduction in tanning efficiency.[26] At lower masking ratios, which is more typically related to industrial practice (the masking ratio of one mole of formate per mole of chrome oxide corresponds to a formic acid offer of 0.6% if the chrome offer is 2% Cr_2O_3), the outcome is an enhancement of chrome reactivity.

The effect of incorporating formate has the same hydrophobic effect as masking with malonate; the latter has a more predictable impact on the complex properties, because of the presence of the methylene group, but the outcome is similar for formate and malonate masking.

b. In recognising the role of masking ratio, the combination of the chemical outcome with the kinetics of the process must also be taken into account. Unless the chrome is masked by conducting the reaction separately, prior to starting the tanning process, the masking ratio will necessarily be low at the beginning of the chrome tanning reaction and then increase as the tanning reaction proceeds: the progress and change of masking ration will depend on the chrome fixation kinetics, controlled by the pH profile, and on the offers of chrome and masking agent.

The influence of masking ratio on chrome reactivity is modelled in Fig. 7. The assumed effect is to reduce the reactivity by eliminating reaction sites, but the actual effect is to include some enhancement of reactivity by changing the HHB value of the ion. In Fig. 7 the relative effects of those two contributing parameters will depend strongly on the chemistry of the masking agent. The role of masking in practical tanning depends on the tanner understanding the nature of the actual effect, even only qualitatively.

c. The extent of increasing the reactivity of the masked chrome is predictable, based on the evident chemical nature of the masking ligand ie the CH=CH π-bond of the maleate can interact with water more than the saturated linked methylene groups of succinate, which are in turn less hydrophobic than the large benzene ring of phthalate.

d. Crosslinking masking depends on the calculated chelate

TABLE V
Shrinkage temperatures of hide powder treated with dihydroxynaphthols and oxazolidine.[35]

Dihydroxyynaphthol	DHN alone	DHN + oxazolidine
None	57	75
1,5	56	85
1,6 (2,5)	64	90
2,6	62	110
2,7	62	79

ring size exceeding seven: for aliphatic dicarboxylates, it starts with glutarate and the effect of the four methylene groups in the chain of adipate is clear in the reactivity illustrated in Table I. Therefore, all crosslinking masking agents are likely to increase the reactivity of chrome: the effect is not concerned with the inherent reactivity towards complex formation, but is dependent on the enhancement of fixation rate by polymerisation.

The role of masking in chrome tanning is an important feature, which can be technologically exploited. The use of specific masking agents, which gradually increase the astringency of the chrome species, by increasing their tendency to transfer from solution to substrate, is an aspect of the reaction that has not received scientific attention. Here, the requirement is to match the rate of diminishing concentration of chrome in solution with the rate of masking complexation, to maintain or increase the rate of chrome uptake. This type of reaction is already technologically exploited by the use of disodium phthalate, although the degree of hydrophobicity conferred by even a very low masking ratio can cause undesirably fast surface reaction. Other hydrophobic masking agents could be developed, to give a more controllable increase in astringency.

It is already recognised that the chrome tanning reaction is controlled by the effect of pH on the reactivity of the collagen substrate: a second order effect is the increasing of the hydrophobicity of the chrome species by polymerisation. In addition, the rate of reaction is controlled by temperature. However, the efficiency of the process is limited by the role of the solvent, in retaining the reactant in solution by solvation: this is typically only countered by applying extreme conditions of pH, likely to create problems of surface fixation, causing staining and resistance to dyeing.[27]

The role of the counterion in chrome tanning offers potential for change. It has been shown[14,16,17] that the chrome tanning reaction is controlled by the particular counterion present. It was fortunate for the leather industry that chrome alum (potassium chromium(III) sulfate hydrate) was the most readily available salt for the original trials of tanning ability: sulfate ion is highly effective in creating a stable supramolecular matrix, because it is a structure maker in water[1,13] The effect is very different if other salts are used, e.g. chloride or perchlorate, when the outcome is only moderate hydrothermal stability. However, even if these salts are used, the high hydrothermal

stability can be acquired by treating the leather with another counterion. Since the effect is independent of a complexing reaction, the process of modifying the moderate tanning effect is fast. This opens up the chrome tanning reaction to modifications which exploit the separation of the link and lock reactions.

o The environmentally damaging sulfate ion might be replaced by other less damaging counterions, such as nitrate. Note, typical sulphur dioxide reduced chrome tanning powder contains about 50% sodium sulfate.

o The reactive counterions can then be applied; options include using the stoichiometric quantity of sulfate or organic anions.

o The counterion might be replaced with polymeric agents, including polyacrylates with the right steric properties.

OTHER MINERAL TANNING OPTIONS

It has been suggested[28] that the environmental impact of chromium can be alleviated by substituting all or part of the offer by other metal tanning salts, when the following options are the likeliest candidates:

Al(III), Ti(III)/(IV), Fe(II)/(III), Zr(IV), lanthanide(III)

The list of available options is limited to the few presented above by considerations of cost, availability, toxicity and reactivity towards carboxyl groups. All metals salts are mixable in all proportions in this context. However, the following general truism should be noted:

the damaging effect of any (alleged) pollutant is not eliminated and is barely significantly mitigated by reducing the degree to which it is used.

The benefits of introducing another metal salt can be summarized as follows.

o The efficiency of chrome uptake is improved by reducing the offer.[13]

o The rate of chrome uptake can be improved by the presence of another mineral tanning agent, applied as a pretreatment, demonstrated in the case of aluminium(III).[28]

The contra indications can be summarised as follows.

o In no case is the shrinkage temperature positively affected, the opposite applies. If it is required that the leather should be boil-fast, the chrome offer must be $\geq 0.75\%$ Cr_2O_3.

o The properties of the leather are modified, changed by the presence of another mineral tanning agent, maximized if the substitution is total.

o The change may be to the handle, in terms of collapsing (as with aluminium(III) salts) or filling (as with titanium(IV) or zirconium(IV) salts) the fiber structure.

o The leather will become more cationic and therefore more surface reactive towards anionic reagents.

o The color may be changed (as with iron salts). At all

proportions in a mixture with a colorless substitute, chrome tanned leather remains distinctly blue, even at very low chrome offers.

o The hydrothermal stability is adversely affected, in terms of the pH window within which the mineral-collagen bonding remains intact.

The stability of mineral tanned leather can be enhanced if the approach demonstrated by Holmes is adopted, in which he grafted multifunctional complexing sites onto collagen.[29] In this way, the linking part of the tanning mechanism is improved, fixing the matrix to the collagen more firmly. This is a chemical modification to the substrate that can be exploited further, but it clearly complicates the tanning operation. However, for some specialized applications, it could be appropriate.

ORGANIC TANNING OPTIONS

Polyphenol Chemistry

The best known example of plant polyphenol exploitation for high hydrothermal stability tanning is the semi metal reaction. Here, the requirement is for pyrogallol chemistry to create the covalent complex between the linking polyphenol and the locking metal ion[30]: in practice, this means using the hydrolysable tannins, but alternatively some condensed tannins can be used, shown in Fig. 8: the prodelphinidins (II) (eg *myrica esculenta*, pecan and green tea)[31] and prorobinetinidins (IV) (eg mimosa) each have the required structure in the B-ring. Many metal salts are capable of reacting in this way, even zinc[32], so there may be useful applications for the future. Note, semi chrome tanning has been shown not to be an example of a reaction between polyphenol and metal: in this case, the tanning agents react with collagen independently.[5]

The condensed tannins can confer high hydrothermal stability by acting as the linking agent, with aldehydic crosslinker acting as the locking agent, in the manner presented in Fig. 9. This applies to all flavonoid polyphenols, when reaction always occurs at the A-ring. In the case of the prodelphinidins and profisetinidins, additional reaction can take place at the B-ring.[33] The effect is to increase the ease of attaining high hydrothermal stability, as indicated in Table III.

The following conclusions may be drawn from the information in Table III.

o There is a clear indication that the stereochemistry of the polyphenol can influence the reactivity, at least as far as the locking aspect of tanning is concerned, see Fig. 10. This has not been investigated scientifically.

o In the only comparison possible from these results, the reactions for catechin and epicatechin, in which the locking reaction only takes place at the A-ring, the cis isomer favours the aldehydic crosslinking reaction.

o The presence of a pyrogallol B-ring increases the reactivity of the polyphenol to the aldehydic locking reaction; effectively it adds about 10% to the rate of reaction.

o The presence of a gallate group (esterified at the hydroxyl group of the C-ring) also increases the rate of reaction.

The reaction can take place even with the monomeric units of vegetable tannins, as is also the case with the polyphenolic components of the flavonoid ring system, as shown in Table IV.

From Table IV, the following conclusions can be drawn.

o Not all aldehydic locking agents react effectively.

o Phloroglucinol is a model for the A-rings of the procyanidins and prodelphinidins, which are more reactive than the corresponding sites on the profisetinidins and the prorobinetinidins.

o For oxazolidine locking reactions, the preferred B-ring structures are in the prodelphinidins and the prorobinetinidins.

The link-lock mechanism can be exploited in other ways, even using reagents that at first do not appear to be tanning agents: an example is naphthalene diols, as shown in Fig. 11 [35].

The behaviour of naphthalene diols in the tanning process is highly dependent on the structure of the isomer, as indicated in Table V. It is clear that the presence of a hydroxyl in the 2-position activates the naphthalene nucleus: the 1-position does not work, shown by comparing the 1,5 with the 1,6 diol.[2,5] When there are two groups in the 2,6-positions, they act together. When the hydroxyls are in the 2,7-positions they act against each other. The basis is the inductive effect of the hydroxyl on the aromatic ring, activating the ortho positions to electrophilic attack or allowing those positions to engage in nucleophilic attack at the methylene group of the N-methylol group of the oxazolidine, as demonstrated in Fig. 12.

The results in Table V also illustrate the principle that the linking agent may only exhibit a very weak effect in tanning terms, but successful locking of the linking species, combined with the ability to link the matrix to collagen in the locking reaction, can result in high hydrothermal stability.

Non-chemical polymerisation is less effective. Applying laccase (phenol oxidase enzyme) to hide powder treated with 2,6-dihydroxy naphthalene produced the highest rise in shrinkage temperature for the range of this type of linking agents tested, elevating the shrinkage temperature by 26ºC, to 85ºC.[35] It is clear that the locking reaction is more easily and effectively accomplished by applying a second reagent, rather than relying on direct reactions between linking molecules.

Polymer and Crosslinker

Perhaps surprisingly, it is less easy to create high stability tannage with polymers than it is using oligomers or monomers, depending on the polymeric compound. It has been shown that high hydrothermal stability can be achieved using melamine resin crosslinked with tetrakis hydroxymethyl phosphonium salt. Several conclusions were drawn from these studies[36]:
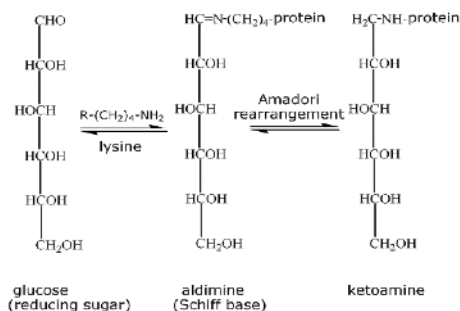
Figure 14: The Maillard reaction

Figure 16: Tollund man (source: Wikipedia)

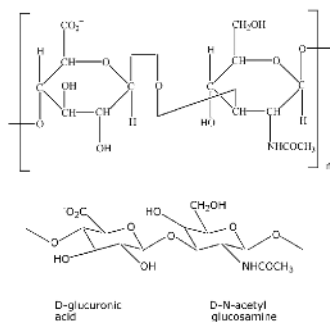
Figure 15: The structure of intact hyaluronic acid

o Not all melamine linking resins work. Therefore, the requirements for matrix formation are likely to be more important than possessing specific chemical reactivity. In this case, there appears to be an optimum particle size for the resin of about 80nm.

o Not all aldehydic locking agents work. The locking function does depend on creating stable bonding between the linking molecules and forming a rigid species capable of resisting the collapsing triple helices.

o The linking reaction is dependent on physical parameters; particle size may be critical. It is not sufficient to provide space filling.

o The ability to form the basis of a supramolecular matrix must depend on the stereochemistry of the linking agent. This requirement is more easily satisfied with lower molecular weight species.

This reaction provided an interesting aspect of the matrix theory of tanning, when an attempt was made to accumulate hydrothermal stability by adding a matrix to a matrix. Here, the sequence of reagent additions was as follows: melamine resin, phosphonium salt, condensed tannin (mimosa), oxazolidine. The observation was the achievement of high hydrothermal stability from the melamine resin and phosphonium salt, added to by the condensed tannin, reaching a shrinkage temperature of 129°C, thereby matching the maximum shrinkage temperature achieved by chromium(III) in the presence of pyromellitate.[18] The melamine and phosphonium salt create a matrix in which the melamine polymer reacts with the collagen via hydrogen bonds, the phosphonium salt

crosslinks the polymer, whilst probably linking the matrix to the collagen. The introduction of condensed polyphenol raises the shrinkage temperature by a small additive effect, since it is applied after the matrix formation, it has no affinity for the resin, but has limited affinity for the phosphonium salt. The subsequent addition of oxazolidine is capable of forming a synergistic matrix with the polyphenol, but the reaction causes the shrinkage temperature to drop significantly.[8] The clear inference is that the new reaction is antagonistic to the established matrix: by analogy with other antagonistic combination[7], there is competition with the mechanism that binds the first matrix to the collagen, effectively loosening the binding between the matrix and the collagen, allowing shrinking to occur, with the consequence that the hydrothermal stability is lowered. It is difficult to rationalise the observation by any mechanism other than the formation of matrices.

Natural Tanning Agents
Recently, new tanning chemistries have come to light: they have the characteristic of being biomimetic, using natural reactions in a new context. Such organic tanning reactions are of interest from three points of view. First, they offer new methods of making leather, to yield new products, which may contribute to lessening the environmental impact of tanning. Second, they offer new opportunities for high hydrothermal stability tanning, by acting as new linking agents, then allowing manipulation of the chemistry of the locking step. Third, they may involve the novel use of enzymes in tanning, operating as catalysing activating agents, so the rate of reaction is highly controllable.

Carbohydrates
Derivatives of carbohydrates are well known in the form of dialdehydes, obtained by the oxidative effects of periodic acid, illustrated in Fig. 13. Starch derivatives are well known in the industry, but dextrin is an alternative starting material; it is a chain of 11-12 glucose units, obtained by partial hydrolysis of starch, and the tanning effects are comparable with the best effects of starch dialdehyde.[3]

However, there can be direct reactions between carbohydrate and proteins, glycosylation-type reactions. Komanowsky effectively generalised these reactions in his studies of the reactions within collagen at low moisture contents (38). The basis of the
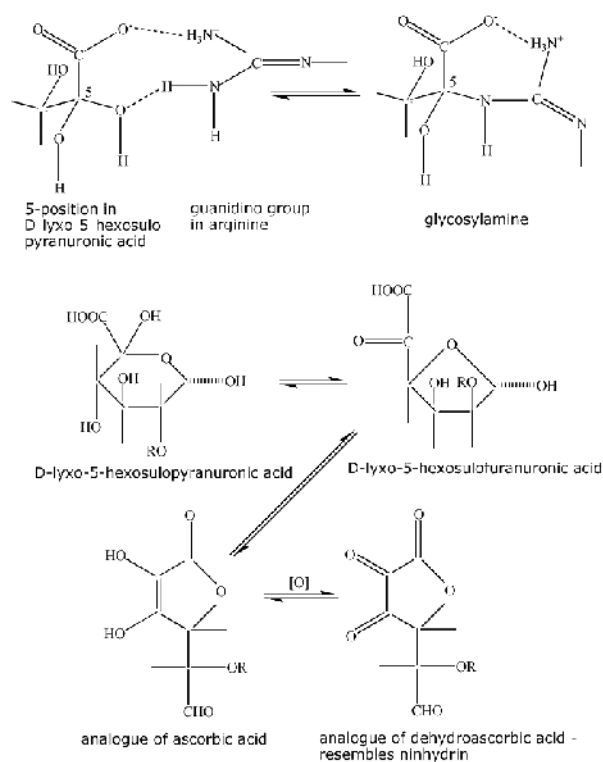
Figure 17: Reactions of decomposition products from sphagnum moss.

formation of permanent bonds is the Maillard reaction, responsible for many of the transformations during cooking of proteinaceous food. The reaction depends on reducing the moisture content, in order for the groups to approach close enough to react: it works better at higher temperature and lower pH, in contrast to the high pH requirements of most aldehydes, although not all aldehydic agents.[4,33]

The stabilising reaction is illustrated in Fig. 14: it is assumed that the ketoamine product can react further with collagen, to form a crosslink (of unknown structure), a reaction that becomes more feasible when the interacting chains are close, unlike the situation in wet collagen and leather.

The natural products which are responsible for the cooking reaction include: sugars and the glycosaminoglycans, hyaluronic acid, dermatan sulfate and chondroitin. These compounds or their derivatives might be applied as reagents as part of a two-step organic tannage. Hyaluronic acid and dermatan sulfate are by-products of the leather making process and offer the potential for useful new derivatives, indicated by the structure of hyaluronic acid in Fig. 15, with its analogy to the carbohydrate structure given in Fig. 13. In this case, the residual reactivity is enhanced by the greater variety of chemical moieties in the molecule.

A related stabilising process for protein that has not previously been reviewed in a leather context is the preservation of so called 'bog bodies'[39], illustrated by 'Tollund Man' in Fig. 16.

Perhaps surprisingly, the preservation mechanism is not an example of vegetable tanning. The environment in which the
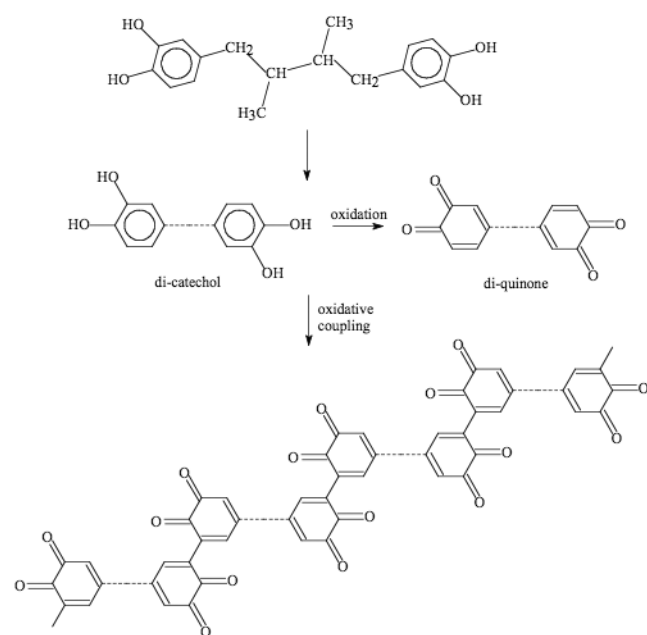

Figure 18: The reactions of NDGA, leading to the stabilisation of collagen

tissues of the body are preserved is typically a sphagnum peat bog: the effect is thought to be due to a Maillard reaction between free amino groups in the proteins and reactive carbonyl groups in a soluble glucuronoglycan, sphagnan, containing residues of D-lyxo-5-hexosulopyranuronic acid, shown in Fig. 17. It can form the furan derivative, which in turn can be converted into a species like ascorbic acid, which can be oxidised to form a species like dehydroascorbic acid, which resembles ninhydrin, the well known colour generating reactant for amino acid analysis.

Sphagnan is a pectin-like chemical, bound covalently to cellulosic and amyloid chains in sphagnum moss: it is liberated by hydrolysis as the moss turns into peat. As in periodic acid oxidised carbohydrate derivatives, the chain length of the sphagnam products may influence the tanning potential, but this has not been investigated. In nature the reaction is slow, due to the low concentration of the active species in solution, but this is not a limiting factor for the leather scientist.

Nor Dihydroguaiaretic Acid (NDGA)
NDGA is a naturally occurring polyphenol, isolated from the creosote bush; it has been proposed as a stabilising reagent for collagen, when it exhibits the unusual phenomenon of actually increasing the strength of the fibre[40], rather than the more common effect of lessening the weakening effect of processing. The mechanism of polymerisation of NDGA is presented in Fig. 18: the polymer is thought to align with the protein chains, constituting a supporting and strengthening structure. Clearly, the polymeric species offers opportunities for additional reactions.

Genepin
Genipin is an iridoid derivative, shown in Fig. 19, isolated from the fruits of *Gardenia jasminoides*. Its reaction with protein is characterised by the generation of deep blue colouration under the alkaline conditions required for fixing.
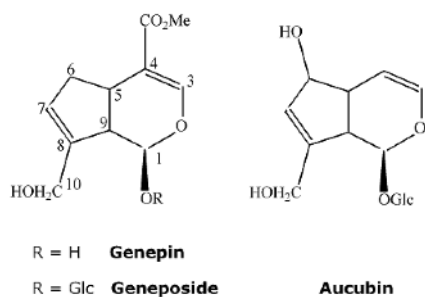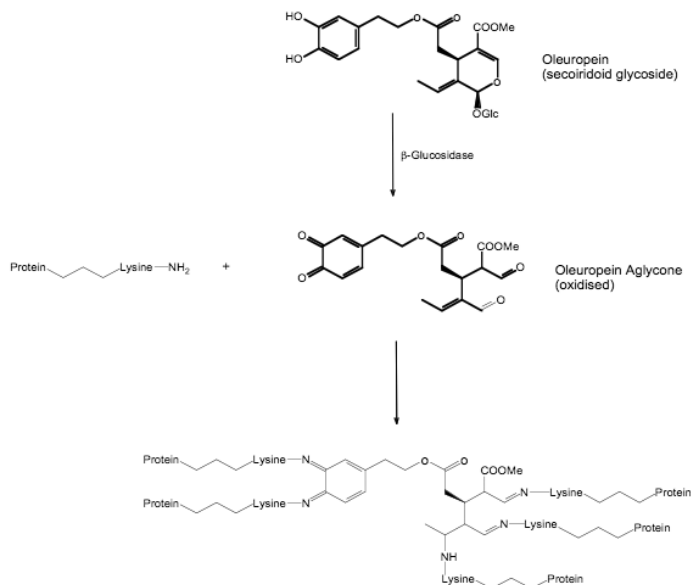
Figure 19: The structures of some iridoids.

Figure 20: Schematic representation of the oleuropein reaction with protein.[42]

TABLE VI
Stabilisation of collagen film.[43]

Stabilisation	Shrinkage temperature (°C)
Control	50
Oleuropein	67
Glutaraldehyde	68

The reaction mechanism by which protein is stabilised is not clearly understood, but is thought to derive from opening of the oxy heterocyclic ring, causing polymerisation, which is the source of the blue colour. It has been shown that the shrinkage temperature of hide powder can be raised to 85°C[41], characteristic of a single tanning reagent. That in itself is not important, but the incorporation of new reactive groups into collagen by a linking reaction using genipin may provide new sites for reaction in a locking step. Alternatively, genipin may provide another approach to the locking step in a combination tannage. There are many other iridoids, nearly 600 are known[42], characterised by the presence or absence of glucose moieties and the presence or absence of the cyclopentane ring.

Oleuropein

Oleuropein is a natural product, a secoiridoid glycoside, found in privet and olive vegetation, where its function is part of the self defence mechanism against infections and herbivores: it contains glucose, but not the cyclopentane ring in its structure. The mechanism of reaction with protein is presented in Fig. 20: it is thought to involve the activation of oleuropein to the aglycone form, which reacts with lysine residues on proteins.

From the work of Antunes et al., the stabilising effect can be compared with that of glutaraldehyde, as shown in Table VI, in which the collagen was recast as a film from solubilized collagen.

As with genepin, the chemistry of oleuropein offers the potential for acting as either a linking agent or a locking agent, using an appropriate complementary combination reagent.

These biomimetic approaches to tanning constitute a new, potentially powerful aspect to applications of biotechnology in leather making. However, it is equally clear that they do not offer the opportunity for a single step, high hydrothermal stability tannage. The advantages lie in the new, covalent binding reactions, which create the linking part of the supramolecular matrix, which is firmly bound to the triple helix, then is capable of undergoing a variety of locking reactions.

OTHER REAGENTS

There is a remaining class of reagents which might be classified as either linkers or lockers; the requirement for new components for tanning is that they should have the ability to react covalently under the typical conditions of tanning.[13] They are options already known in the leather industry in the form of reactive dye chemistries; it is merely a matter of widening the exploitation. Some of the reactive species are presented in Figs. 21 and 22.

The chemistries represented in Figs. 21 and 22 could be exploited in the form of multiple reactive groups in the same molecule. This notion has already been initiated by BASF in the form of their product (dye) Fixing Agent P, triacryoyl triazine, but there is clearly potential for developing the approach further.

COMPACT TANNING

The concept of 'compact processing' is the condensing or shortening of processing by combining two or more reactions into a single process step. In this way, time is saved and consistency is created in the interaction between the process steps involved, because only one reaction takes place, instead of two or more. This is a powerful contribution to innovation in the tannery. The idea of compact processing can be applied at any stage in processing, although it is more commonly applied in the later stages of wet processing. Therefore, thinking about this concept should not be limited in scope.

If it is accepted that high stability can only be achieved by a two stage tanning action, then there are opportunities to exploit such an approach to tanning in compact processing.
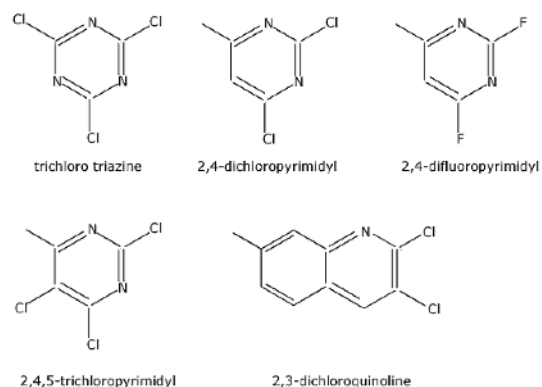
Figure 21: Heterocycles used in reactive dye chemistries.

The use of a non swelling acid incorporates the notion of pretanning. It may be possible to substitute pretanning for retanning. However, it should be recognised that the first tanning agent controls the character of the leather. In the case of prime tanning being conducted with vegetable tannins, the requirement for further tanning is uncommon. An exception would be organic tanning, which might be based on polyphenols, when there would be a requirement for applying the second component of a combination process for high hydrothermal stability. Such an approach is feasible for the combination of gallocatechin-type condensed tannins with oxazolidine, when the reaction is activated by elevated temperature.[7,9]

The case of chromium(III) tanning is less clear. No technologies have been offered to the industry, in which a retanning agent has been combined with conventional chrome tanning salt. The closest to that situation are products referred to as 'chrome syntans', well known to the industry. However, these are primarily offered as filling versions of chrome retanning, rather than a new approach to prime tanning. Note, chromium(III) has little affinity for phenolic hydroxide as a ligand[5], hence chrome syntans are either mixtures of syntan and chrome salt or the syntan may be capable of complexation with chrome, by having some carboxyl functionality in its structure. In the latter case, the function of retanning might be accomplished with tanning. Similarly, an extended application of masking, to confer additional features may be useful.

The conventional components of post tanning are: neutralise, retan, dye and fatliquor. In each case, an industrial process will use one or more agents for the purpose. The permutations and combinations are straightforward and some have found application already. Notable technologies include: neutralising syntans, vegetable tanning with bound dye (Forestal Quebracho) and retanning with fatliquoring and water resistance (Lubritan® by Rohm and Haas).

An alternative approach to colouring leather is to use the chemistry of melanin formation: using model reactant polyphenols and the aid of polyphenol oxidase, it is possible to achieve a tanning reaction and develop colour at the same time.[44] Here, the potential role of enzymes in tanning becomes apparent.
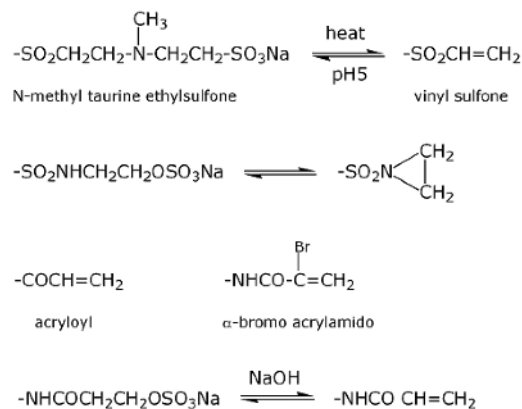

Figure 22: Other reactive dyes chemistries

Dyeing itself might be considered to be a retanning reaction. The type of dye determines the nature of the binding interaction with leather: chromium(III) 1:1 premetallized dyes fulfill this dual function. The use of reactive dyes would clearly constitute a form of retanning, because they bind via one or two covalent links to basic side-chains. The outcome will depend on the amount of reactive dye and the ability of the structure to interact with the aqueous supramolecular matrix.

It has been shown that it is feasible to create a mixture of reagents for retanning, dyeing and fatliquoring in a single post tanning processing step[45]: the development of a single reagent is clearly more difficult, but should not be chemically impossible.

The concept of compacting does raise the question of the role of the solvent.[46] If the tanner could use a more exotic solvent, simultaneously to solubilize a wider range of reagents than is possible in water, it might be feasible to apply all of the post tanning reagents at once, in a single step, with no residual effluent. According to the choice of solvent, there may be no need for neutralisation. Alternatively, neutralisation may have to be retained as an aqueous process, to achieve the charge required by the new mixed process.

ALTERNATIVE TECHNOLOGIES

It is conventionally assumed that tanning has to be conducted in aqueous solution. However, there are options available for the future. Wei demonstrated the possibility of processing water wet pelt in a tumbling medium of water-immiscible solvent.[21] The technology is feasible, but brings problems of its own, notably the requirement for diffusion across the pelt, unlike the conventional requirement for diffusion through the cross section. However, such difficulties are solvable, if the willingness is there.

The alternative is an essentially non aqueous process, as indicated in the context of compact processing: this approach to processing, including the use of liquid carbon dioxide, has been discussed for some steps[46], but industrial development has not yet followed. The advantage of such an approach to one step post tanning is that the substrate is dry (at least to the

touch), so the moisture in the leather would have a limited influence on the process. It is less clear that such an approach would be feasible for primary tanning, in whatever way that might be done chemically. If chrome tanning were to be developed in that direction, it is not difficult to imagine the HHB properties of the chrome complex being tailor-made for the solvent by appropriate masking.

It is useful to speculate on the roles that enzymes might play in tanning. It is clear that biotechnology has an increasingly important part to play in the beamhouse, but it is less clear if it can contribute to collagen stabilisation. From the matrix theory of tanning and collagen stabilisation, the inability of transglutaminaise to increase the hydrothermal stability is predictable and understandable, even though it is clearly capable of introducing crosslinking in the conventional sense.[47] Similar reactions, which can introduce crosslinks into collagen, are unlikely to function as useful tanning agents, beyond altering the texture of the protein.

At the other end of the processing procedures, the role of drying remains to be exploited to advantage by industry. Recent studies have linked the properties of leather, including area yield, to the programme of drying conditions[48]: softness does not depend on the rate of drying, only the moisture content. Using conventional plant, it is possible to modify the drying programme into two stages, to obtain advantage from the relationship between the viscoelastic properties of leather and its water content, so that area gain of intact leather does not have to be at the expense of softness.

In considering alternative technologies, it is useful to consider whether there is an alternative mechanism to link-lock i.e. whether or not there could be exceptions. If the mechanism of shrinking, as set out here, is right, then the impact of the tanning reaction on hydrothermal shrinking is right. Consequently, the use of conventional, penetrating reactants, in the way also outlined above, is also right. Therefore, the only exception to the link-lock mechanism would be a single step reaction which combines both features. The requirement would be the formation of the stabilising matrix from a single species polymerisation reaction, which would have to include reaction with the collagen. In this regard, polymerisation of cod oil is the closest reaction known in the art. However, in this case, despite the complexity of the chemistry of polymerisation by oxidation, there appears to be little direct interaction between the polymer and the collagen, despite the possibility of creating aldehyde groups.[49] Hence, the leather reaction does not elevate the s hrinkage temperature significantly. Nevertheless, it is not inconceivable that such a polymerising tannage might be developed, particularly if an extended range of practically useful solvents is made available to the industry

OVERVIEW

The range of chemistries available to the tanner is widening. By considering the molecular basis of the tanning mechanism, especially those requirements to confer high hydrothermal

stability, the options open to the tanner are widened. If high stability organic tannages are desired, they can be created just by observing the following rules.

1. Apply the first reagent, linking to the collagen with high stability bonding, preferably covalently. The reagent must offer the potential for a second reaction, by possessing usefully reactive groups, but need not have high molecular weight.

2. Apply the second reagent, to react with the first reagent by locking the molecules together; therefore the second reagent must be multi-functional. Contributing to linking the matrix to the collagen is useful.

The properties of the resulting leather can be controlled by the choices of reagents: this applies to both mineral and organic tanning options. In the absence of a polymerising tannage capable of meeting the stabilising matrix criteria, we are limited to the two step process. But the two step process does not have to extend processing times: this approach can contribute to compact processing, moreover it can offer specifically required properties and therefore offers the basis of the production of bio-vulnerable or so-called recyclable leathers. The latter category has not been adequately explored. The definition of tanning refers to the resistance to biodegradation of a previously putrescible protein material: here the resistance refers to proteolytic attack. Therefore, it is feasible to consider tanning processes which incorporate a degree of vulnerability. In this way, high hydrothermally stable leather could be chemically or biochemically destabilised, to allow denaturation of the collagen at moderate temperatures, so that proteolytic degradation can be achieved. Targeting specific groups in the matrix may be sufficient to degrade its effectiveness: options are hydrolyses, oxidizers, reducers etc., depending on the chemistry of the tannage.

CONCLUSIONS

The expression of the link-lock mechanism has made developments in tanning technology feasible. This new theory is a simpler and more powerful view of collagen stabilization than the older model of direct crosslinking between adjacent side-chains; it is a more elegant view. It is no longer worth pursuing the single reagent alternative to chrome tanning, because it does not exist. Indeed, why should we seek an alternative to chrome tanning? It works well, it can be made to work even better and, anyway, by all reasonable judgements it causes little environmental impact. However, organic options provide potential for new products from the leather industry.

The continuation of developing tanning and leather technology depends on constant reappraisal of all aspects of the subject. This is the role of leather science. Conventional, received wisdom should not be relied upon without critically reviewing exactly what it means, what it contributes to processing and products and what the wider implications are for the practical tanner. It is important to recognise that the scrutiny of current technology will often identify inconsistencies and misunderstanding of principles: the technology may work, but the science may not. However, this

is not always a bad thing, because it can lead to new thinking, new developments and more profitability in an environmentally sound, sustainable industry.

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