



Prediction in leather processing: a dark art or a clear possibility?

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1. Introduction

At the heart of the requirements for scientific understanding of leather technology lies a firm theoretical view of the mechanisms by which reagents are bound to collagen and the consequences of the reactions, in terms of the chemical and physical modifications they confer to the leather(1), leading to specific properties and performance. In order to be able to predict the outcomes of process steps, it is important to address the following features of processing.

- (i) What are the principles of the mechanism that control the fixation of reagents?
- (ii) What controls the overall accumulative effect of multiple reagent processing?
- (iii) How do multiple fixation reactions control the accumulated properties of the leather?

2. Tanning

In an analysis of the consequences of reactions involving fixation to collagen or leather, it is not necessary to distinguish between tanning and retanning in post tanning or indeed pretanning (which are terms merely indicating the relative timing of the process step), because the outcome is the accumulation of effects from start to finish of wet processing.

It has been proposed (1) that the mechanism of fixation has three main elements. In this way, the mechanism can be considered to be general ie it is the same for all fixation reactions, regardless of chemistry, although the chemistry will determine the details of the reaction, such as the type of bonding in the final product. The mechanism proceeds by the following steps.

- (i) Transfer from solution to substrate.

The mechanism initially depends on the fact that the reaction is invariably heterogeneous: there are two phases, the solution and the solid substrate. Transfer is a process analogous to partitioning a solute between two solvents in the procedure of solvent extraction or the preferential solvation of an ion in a mixed solvent. The affinity of the reagent for the substrate will depend on the solvating power of the solvent: in industry this is typically water, modified as a solution (often) of neutral electrolyte. The relative preference of the reagent for the solvent or the substrate depends on the hydrophilic-hydrophobic balance (HHB) of the two components, ie the degree to which the properties of the components can be characterised as hydrophilic or hydrophobic or somewhere between the two extremes. The less powerfully the solvent solvates the reagent, the more likely the reagent will favour transfer into the environment of the substrate. That is, the more soluble the reagent is in the solution, the less favourable the transfer process will be: this is analogous to the free energy of transfer of a solute from one solvent to another. The closer the HHB properties of the substrate and reagent are, the more the transfer process is favoured, observed as a fast rate of the loss of the solute into/onto the substrate.



The tanner has control over the reactivity of all three components of the process. The HHB of the reagent and the substrate can be altered by the charge each carries or the chemical composition, the choice of reagent chemistry. For example, chromium(III) tanning salts can be made hydrophobic to varying degrees by masking (1,2). The charge on the substrate is controlled by pH, dependent on the value of the isoelectric point (see below), and it can be treated with hydrophobic materials such as fatliquors. The solvent properties can be modified with charged ions or organic agents such as ethanolamine etc.: the former make the solvent more hydrophilic, the latter make the solvent more hydrophobic (1).

(ii) Electrostatic interaction between substrate and reagent.

All reactions between the substrate and a reagent involve a primary electrostatic interaction, which may be a conventional charge-charge effect or hydrogen bonding, but can include hydrophobic interaction, such as the preliminary mechanistic step of vegetable tanning fixation, because such interactions involve induced charges. The reaction can be influenced by modifying the charges on either or both the components, for example by altering the pH, the charge on collagen or modified collagen is changed.

In many cases, this is as far as the reaction can go.

(iii) Covalent reaction

Not all electrostatic interactions can turn into covalent reactions: this is entirely dependent on the chemistry of the reagent and the reaction sites on the substrate. If covalent reaction is required from a reagent which ordinarily reacts electrostatically, then the chemical properties must be altered accordingly, either by synthetic modification or the use of an additional reagent in the process.

The impact of reactions in which the substrate is modified by reagents depends on two main factors.

(a) The nature of the reaction between the reagent and the substrate: the chemistry of the bonding and the availability of reaction sites within the substrate.

(b) The residual chemistry of the reagent: the potential for further reaction with other reagents.

The combination of these factors determines the reversibility of the fixation reaction and the likely interactions between consecutive reagents and the consequences for leather properties.

The cumulative effect of fixation reactions depends on the following three possible interactions between the reagents, which should all be predictable from knowledge of the chemistry and reactivity of the reagents. Also, it is useful to recall the tanner's 'rule of thumb', which states: *the properties of a leather are controlled by the first tanning reaction*. This essentially means that the first tanning reagent has the advantage of interacting with reaction sites first or interfering with subsequent reactions.

(i) Independent reaction

Here, the reactions between the reagents and collagen are sufficiently different to be regarded as independent, because the reagents have affinity for different sites on collagen and no affinity for each other. In this way, they function as separate tanning outcomes: examples of this are semi chrome tanning, in which vegetable tanning is followed by chrome tanning, or the other way around, chrome retan (1). The outcomes of independent reactions are determined by the following factors.

(a) The order of addition

Apparently independent reactions may not be entirely independent. The reaction between a reagent and the substrate can be modified by the presence of another reagent, even though they do not interact,



because the first reagent can act as a simple barrier between the protein or leather and the subsequent reagent. The usual effect is to slow the rate of fixation of the subsequent reaction, observed in chrome retanning of vegetable tanned leather.

An additional effect is for the first reagent to modify the nature of the substrate, by altering the charge and/or the hydrophilic/hydrophobic balance. These factors will probably not change the nature of the interaction between the substrate and the incoming reagent, but can alter the kinetics and affinity of the new reaction, which affect the uniformity of the reaction.

(b) The relative offers.

The greater the difference between the offers, in molar terms, the more likely the reagent at the higher offer is to react as though applied alone and dominate the properties of the leather.

(c) The rate of reaction.

If the reactions are conducted simultaneously or consecutively in the same float, then the substrate properties are controlled by the fixation mechanisms set out above. The effect may be to define the extent to which one reagent is a barrier to the other.

Alternatively, one reagent may react faster than the other, due either to astringency/reactivity difference or the ability to penetrate faster by virtue of lower molecular weight. Independent reactions have an additive effect on the physical/handle properties of leather which become predictable. The exception to additivity is hydrothermal stability: if the reactions are independent, then each can only have the effect of interfering with the denaturation process, so the shrinkage temperature is only ever moderate.

(ii) Antagonistic reaction.

Here the reagents are incompatible for the following reasons.

(a) They compete for the same reaction sites on collagen.

The reaction sites on collagen are limited to the following: carboxylates for cationic reagents eg metal salts, amino groups for aldehydic reaction and hydrogen bonding, peptide amide links for hydrogen bonding, polar groups such as serine and hydroxyproline for hydrogen bonding, non polar groups such as alanine for hydrophobic bonding.

(b) They react with each other, but in a way that cannot be construed as synergistic, see below.

An example is tanning with a metal salt such as aluminium(III) and retanning with a hydrolysable vegetable tannin: the polyphenol reacts preferentially with the metal rather than the collagen, but the complexation does not contribute to the hydrothermal stability of the leather.

The outcome of antagonistic reactions is largely defined by the winner in the competition: the mere presence of a reagent within the fibre structure cannot influence the properties of the leather in a primary way, it must be chemically bound in order to influence the leather properties significantly.

(iii) Synergistic reaction

This is the situation when the first reagent reacts powerfully with the collagen and the second reagent reacts with the first reagent. Synergy is defined as *'the whole being greater than the sum of the parts'*: here this means that the combination of two or more reagents is more than additive, a new tanning reaction is created. The second reagent can react in the following ways.



- (a) It reacts with the collagen in an independent manner.
- (b) It reacts only with the first reagent.
- (c) It reacts with the first reagent to link it to collagen.
- (d) It reacts with the first reagent, crosslinking it.

It is possible that all four reactions occur at the same time, in which case the first reaction has only an additive effect, as described above, and the second reaction will modify the effects of the first reaction and the impact should be predictable from the chemistries of the reagents. It is the latter two that are of interest with respect to synergy. If the first reagent is crosslinked, then the new matrix interacts with collagen in a concerted way, referred to in the Link-Lock view of tanning reactions (3). The bound molecules of the first reagent become locked together like a macromolecule, so the polymeric nature of the matrix within the fibre structure makes the unfolding reaction of denaturation more difficult, observed as a higher transition temperature. The effect is heightened if the crosslinking reaction serves also to link the matrix to the collagen more firmly eg covalently (1,4).

The mechanisms of binding/crosslinking and their outcomes are illustrated diagrammatically in Fig. 1. Situations **a** and **d** refer to a monofunctional reaction between the first reagent and a crosslinking effect from the second reagent. In **b** and **e**, the first reagent is capable of multifunctional reaction within a triple helix. In **c** and **f**, the first reagent can crosslink between triple helices. The simple representations make it clear that **a**, **b** and **c** do not constitute major barriers to the unravelling effect of denaturation: **d**, **e** and **f** make unravelling more difficult.

The extent to which the synergistic effect extends to more than two reagents has not been tested comprehensively. However, it is likely that the rules regarding combinations of reagent will apply equally to three or more reagents and this becomes more important when extending the analysis beyond conventional tanning into post tanning, see below. Limited experience indicates that the role of antagonism comes more into play as the number of reagents considered increases (1,5).

Whilst it is possible to predict whether or not reactions are synergistic and hence to predict the effect on the hydrothermal stability, other properties are more uncertain. However, predictions can be made from the generalised properties they confer to the leather, as set out in Table I. Tanners can construct their own matrix, based on knowledge of specific reagents which they use.

Having set out the generalised properties of tanning agents, attention can be turned to the likelihood of them interacting with each other. Table II generalises the relationships between common reagents, characterised as independent, antagonistic or synergistic. As for Table I, tanners can substitute more accurate judgements for the specific reagents which they use. The generalisations as set out in Table II can be substituted in practice by more precisely known attributes of individual reagents: this is especially important for those reagent classes, such as the syntans, which can confer a range of properties dependent on structural characteristics (1). In combination processing, the outcome depends on the substrate properties, which it acquires depending on the accumulated fixation reactions it undergoes.



Fig. 1. Variations in modes of fixation of reagents to collagen triple helices:
a is unipoint fixation of a single reagent, **b** is intramolecular crosslinking, **c** is intermolecular crosslinking, **d-f** are the corresponding models of crosslinking with a second reagent.

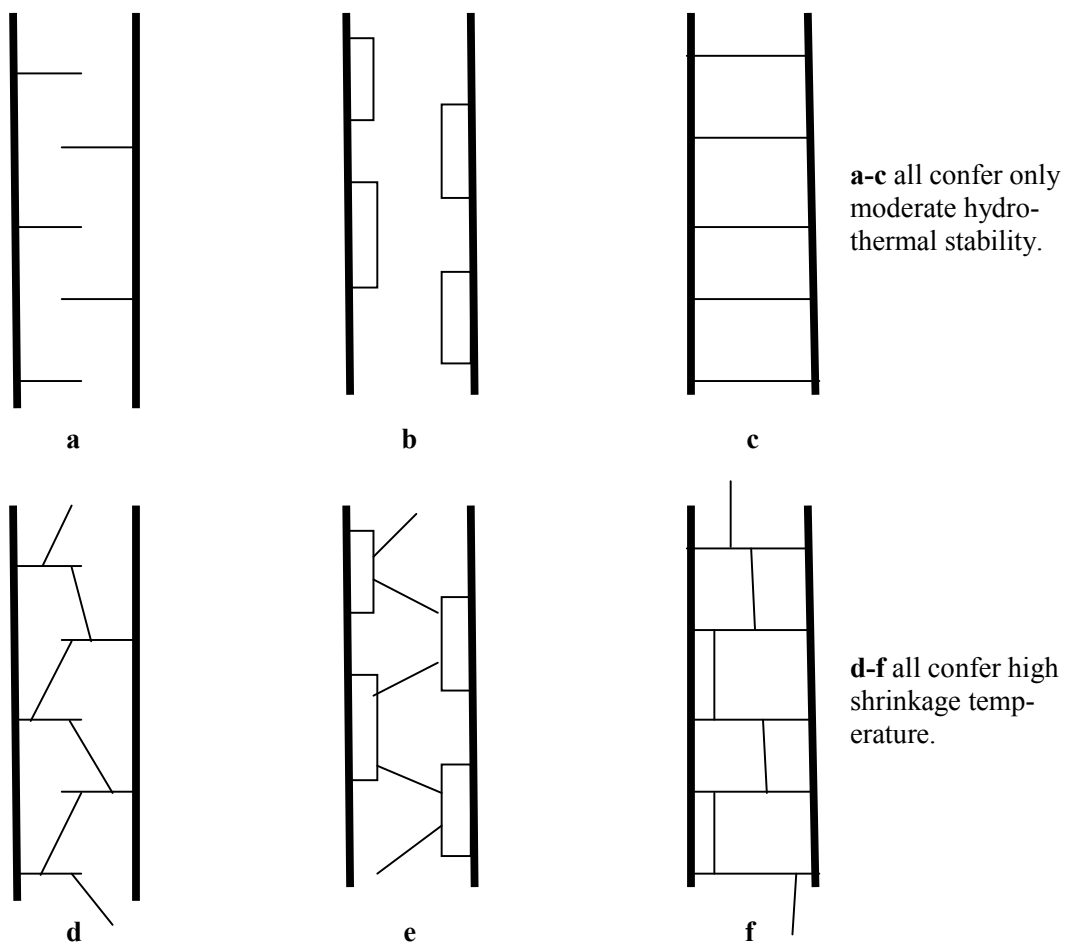




Table II. Generalised properties conferred to leather by common tanning agents.

	Stable tannage	Ts ^a	Filling ^b	Soft- ening ^{c,d}	Hydro- philic ^{d,e}	Weaker leather ^{d,f}
Metal salts, oxyanions	no	low	no	no	nk	yes
Chromium(III)	yes	high	no	no	yes	yes
Aldehydes, aldehydic	yes	low	yes	yes	yes	yes
Hydrolysable polyphenols	no	med	yes	yes	yes	yes
Condensed polyphenols	yes	med	yes	yes	yes	nk
Retanning syntans	no	med	no	nk	yes	nk
Replacement syntans	no	med	yes	yes	yes	yes
Resins/ polymers	no	low	yes	yes	nk	no
Oil, sulfonyl chloride	yes	low	yes	yes	yes	no
Epoxide, isocyanate	yes	low	no	nk	nk	yes

^a low means < 75°C, med means 75-85°C, high means > 100°C

^b 'no' does not necessarily mean that the structure becomes collapsed, which only applies to some metal tannages eg Al(III). The degree of the filling effect depends on chemical structure, molecular weight and offer.

^c The degree of softening effect depends primarily on the nature of the chemical reaction and molecular weight.

^d nk indicates not known, an uncertain outcome, depending on the chemical structure.

^e Hydrophilicity depends on chemical structure and the chemical nature of the reaction.

^f With a few exceptions, all reactions cause the leather to be weaker, dependent on the chemistry and the offer.



Table II. Generalised interactions between common tanning agents, where I means independent, A means antagonistic, S means synergistic.

First tannage	Second tannage									
	Metal salts	Cr	Alde-hydric	Hydrol. veg.	Cond. veg.	Retan syntan	Repl. syntan	Resin	Oil	Epox., Isocy.
Metal salts	A	A/S	I	I/A	I	I	I	I	I	I
Cr(III)	A	I	I	I	I	I	I	I	I	I
Alde-hydric	I	I	A	I	A	I	I	I	I	A
Hydrol. veg.	S	I	I	A	A	A	A	I	I	I
Cond. veg.	I/S	I	A/S	A	A	A	A	I	I	I
Retan Syntan	I	I	I	A	A	A	A	I	I	I
Repl. Syntan	I	I	I	A	A	A	A	I	I	I
Resin	I	I	I/S	I	I	I	I	I	I	I
Oil	I	I	I	I	I	I	I	I	I	I
Epoxide, Isocyan.	I	I	A	I/A	A	I	I	I	I	I

The ways in which properties are generated from multiple reactions can be summarised as follows.

(i) Tannage stability

The stability or reversibility of the tanning effect depends on the chemistry of the interactions between the reagents and the collagen. Thus is subject to the effects of antagonism and competition between reagents which rely on electrostatic bonding (charge-charge, hydrogen or hydrophobic bonding). Covalent reaction can be considered permanent in conventional leather processing.

(ii) Shrinkage temperature

Hydrothermal stability is defined by either the individual chemistries of the reagents or by their synergistic interaction. This is a property which is additive only to a limited degree; hence low shrinkage temperature can only be elevated to moderate by multiple reactions of individual tanning agents, but moderate shrinkage temperature can only be elevated to high shrinkage temperature by a synergistic interaction between two reagents.

(iii) Filling

Filling is a cumulative property: the expansion of the fibre structure by reagents can only increase, it is unlikely to be reversed by subsequent flattening reactions, even powerful reactions such as tanning with the strongly cationic aluminium(III).

(iv) Softening

The softening effect is analogous to filling, insofar as it depends on the effect of the chemistry of the reagent in keeping the fibre structure open and capable of easy distortion. However, the effect can be



reversed by reagents which have a marked collapsing or filling effect. This property is dominated by fatliquoring, so tanning has only a second order effect on softness (6).

(v) Hydrophilicity

The hydrophilic/hydrophobic characteristic of the substrate depends on the nature of the reagents, which can make the leather increasingly hydrophilic or increasingly hydrophobic by the cumulative effect of appropriate reagents. Similarly, reagents can have an antagonistic effect on either property.

(vi) Weakness

The more the natural structure of collagen is modified, the weaker it becomes, which is a cumulative effect, dependent on the extent to which the natural structure is disrupted by the bound reagents. Since this is not always an effect of high magnitude, useful leather can still be made, even though it may contain a significant fraction of bound chemicals. Nevertheless, it is useful to note the consequences of tannages on leather strength: in general they have a weakening effect, but some reactions are known which contribute to leather strength, notably synergistic or polymerisation tannages. In this way, there may be a previously unrecognised relationship between hydrothermal and physical stability (1).

3. Post tanning

3.1. Dyeing

It is frequently not recognised that dyes function in the same way as conventional tanning agents, because of the ways in which they interact and bind chemically to collagen/leather, summarised in Table III. Although the tanning effects of dyes are rarely if ever measured or assessed and their effects are typically not apparent. Dyes can affect the isoelectric point (see below) and hence change the charge at any given pH; they can affect the hydrophilic-hydrophobic balance, depending on their own HHB characteristics, and they can influence the reactions of subsequent reagents by the nature of their chemistries and reactivity towards the substrate

Table III. Dye fixation mechanisms: ✓✓ primary mechanism, ✓secondary mechanism.

Dye type	Electrostatic	Covalent	H-bonded	Hydrophobic
Acid	✓✓		✓	
Basic	✓		✓	✓
Mordant	✓	✓		
Direct	✓		✓✓	✓
1:1 premetallised	✓	✓✓		
1:2 premetallised	✓		✓	✓
Reactive	✓	✓✓	✓	
Sulfur				✓✓

Dyes affect the properties of the leather through their fixation reactions, but they can also influence properties by their residual reactivity via their auxochromes which modify the colour, the structural components bound to the central chromophores which define the base colour. This is the basis of sandwich dyeing and colour enhancing processes (1) and of mordanting reactions which can be used as additional fixation, in the same way as ‘capping’ with metal salts such as chromium(III) is used to enhance the water resistance effects of fatliquors and other specific water resistance treatments (1).

The more penetrating the dye is (from aqueous solution), the more hydrophilic it is, conferring hydrophilicity to the leather; the more surface reactive the dye is, the more likely it is to confer some



degree of hydrophobicity. Dyeing may be conducted in more than one step and it is typically followed by fatliquoring, but there is no hard and fast rule that processing must follow the conventional pattern of tan then retan the dye then fatliquor. It is always useful to consider all options of process step sequences.

3.2. Fatliquoring

The structure of the sulfo fraction, the carrier for the lubricating neutral oil, is invariable simple, whether the oil is sulfated, sulfited or cationic, so it functions like an auxiliary syntan. The tanning action is effectively zero, but the impact on the substrate may be marked because of the interaction with charged sites on the substrate. Nor can the effect of the neutral oil be completely ignored: it will alter the HHB characteristic of the substrate, depending on its own properties, because it will coat the fibre structure at the level corresponding to the mode of delivery (6) and may be regarded as a hydrophobic reagent. Most conventional fatliquors make the leather hydrophilic, because of the effect of the sulfo fraction, when the magnitude of the effect depends on the degree of sulfation or sulfonation. Some fatliquors, designated water resistant, can confer a degree of hydrophobicity: although the effect is typically referred to as 'shower resistance', they can be much more effective if all other processing is conducted to minimise hydrophilicity, especially if the water resistance treatment includes 'capping' with chromium(III) salt, when the residual anionic nature of the reagent is neutralised by cations (1,5).

4. The influence of charge

The numerical value of IEP depends on the ratio of the total numbers of amino and carboxyl groups on the protein sidechains and those numbers can be altered by removal or addition in processing. However, the effect of reagents on the availability of the groups to participate in the ratio is less clear: there is no mathematical model to allow calculation of IEP as a function of process steps. This is unfortunate, because it is critical to the success of any reaction to know the IEP, the point on the pH scale at which the charge is zero: at pH values below the IEP, the charge is increasingly positive the further the pH is below the IEP; at pH values above the IEP the charge is increasingly negative the further the pH is above the IEP. The sign and magnitude of the charge will determine the ability of a reagent to penetrate or react at the substrate surfaces. Guideline effects of reagents can be assumed, as indicated in Table IV (1), although it is recognised that the true values of the changes depend on both the nature of the individual chemical species and the offer.

Some reagents can add charge to the substrate, so that the effect of isoelectric point can be overridden. This was implied above, in terms of the impact of anionic reagents, particularly in conventional post tanning, when the reagents are dominated by anionic charge, usually from sulfonate groups.

A more powerful effect can be achieved through cationic species, often metal ion complexes, but also for example quaternary ammonium compounds. It is known that chromium(III) usually carries a positive charge, but its influence is weakened by covalent reaction with collagen, by basification with hydroxyl ion and by distribution of the charge over the large complex of metal nuclei and ligands. This is not the case for other metal ions, notably aluminium(III). Such metal ions react electrostatically, consequently there is considerable residual positive charge and this can dominate the reactivity of the substrate, to the extent that all anionic species tend to react on the surface and fatliquor emulsions can crack. The charge can only be effectively dissipated by complexation eg by polyphosphate or polyphenol (5).



Table IV. Known and estimated changes in the isoelectric point of Type I collagen due to leather making processing.

Process	Reaction	Estimated effect on IEP
None, native collagen		Physiological pH 7.4
Liming	Amide hydrolysis	5.0 to 6.0
Chrome tanning	Reaction with carboxylate	6.5 to 7.5
Retanning reactions: aldehyde vegetable tannin syntan resin	Covalent bonding Electrostatic bonding Electrostatic bonding No effect	Estimate Δ IEP = -1.0 Estimate Δ IEP = -0.5 Estimate Δ IEP = -0.5 Estimate Δ IEP = 0
Dye reactions: Acid dye 1:1 premetallised dye Reactive dye	Electrostatic bonding with NH_3^+ Metal complexation at carboxyl, sulfonate reaction at amino Covalent reaction with NH_2 Electrostatic reaction with NH_3^+	Estimate Δ IEP = -0.5 Estimate Δ IEP = +0.5 Estimate Δ IEP = -1.0
Fatliquor, sulfo reaction at amino	Electrostatic bonding	Estimate Δ IEP = -0.5

5. Reverse analysis

If it is understood how reagents interact in a tanning context and it is known what properties they are capable of conferring, it is possible to reverse the analysis of outcome in processing. What this means is that a leather with a suite of properties and performance can be imagined and then a process to obtain those features in the leather can be devised. The logical steps can be summarised as follows in a guideline question sequence.

(i) What features are desired eg flatness, fullness, strength, softness, stability of tannage, physical and chemical or hydrothermal stability; in what measure for each property? What is specifically not required?

(ii) Is the desired outcome the creation of a conventional leather or is extreme performance required?
Is the process likely to be constructed from conventional reagents applied in conventional technology or are new approaches indicated?

(iii) Which reagents are potentially capable of conferring those properties, in the relative importance and prominence desired and defined?

How much of each reagent will confer the required features? What are the relative offers?

Here there is need for leather technology input, based on known effects from reagents.

(iv) What interactions are required between the reagents, to refine the options? How do the properties of the reagents influence the effectiveness of other reagents?

Are the choices consistent with what is both wanted and not wanted?

(v) How do the reagents fit into a conventional, practical process eg are they compatible with a logical programme of pH change and IEP/charge variation?



Any new process must make technological sense, so that the damaging effects of swinging between pH extremes are avoided. Is there a need to review the relationships between process steps?

(vi) Can the desired product be made with conventional, available chemicals/biochemicals?
What reactions might be facilitated by the use of enzymes, particularly those new to the leather industry?
Will it be necessary to source or even design new reagents?

(vii) Can the processing be designed to be compact ie combine steps by rethinking the processes?

(viii) In imagining new leathers with new properties, what are the limits to performance of collagen-based biomaterials and how might those limits be achieved if necessary?

Leathers can be made to be effectively waterproof, the shrinkage temperature is probably limited to about 155°C (7). But what are the upper limits for strength, fire resistance etc.?

The thinking can be extended to include all collagenic biomaterials, such as the requirements for 'smart' materials which react to conditions to change those conditions in a predicted way. The latter have clear application for sectors such as wound management: it has been demonstrated that active agents, such as antibiotics, can be chemically bound to reconstituted collagen and remain active (8). It is not inconceivable that, with a suitable choice of substrate and linking chemistry, practically any chemically or biologically active agent may be bound to collagen in all its natural or reconstituted forms.

6. Conclusions

Predicting the outcome of any technological change in complex systems of leather processing is not an exact science. Nevertheless, by adopting the kind of approach set out here, drawing on both scientific and technological principles, it is possible to go a long way towards accurate and useful prediction of the effects of concurrent and consecutive process steps. This can make developmental programmes much more efficient.

Perhaps more importantly, the ideas proposed here will allow prediction of not only the processes designed to make leathers with desired properties, but also the constitution of reagents to achieve the end. This constitutes a paradigm shift in thinking and hence in creating strategies for advancing leather development and for defining and making new collagenic biomaterials.

7. Acknowledgement

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