

## The Heidemann Lecture

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### What's the use of Leather Science?

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#### Abstract

Over the last ten years, the leather science content of the literature has diminished compared to the technology content, but the published reports have still yielded useful pointers to the future of leather technology. The use of indigenous plant material for rawstock preservation, unusual sources of colorants and new methods of reagent delivery are amongst the more important developments.

Three areas of new leather science are addressed here. First is the process of sulfide unhairing: the mechanism accepted for the last century must be reappraised, since it has recently been shown the  $S^{2-}$  species does not exist in aqueous solution. Whilst this does not immediately affect the technology of unhairing, there may be implications for future developments.

Second is the fundamental mechanism of tanning. It has long been a mystery why different chemistries have the same moderate effect on the hydrothermal stability of the leathers they create. Also, why do just a few reactions produce

high hydrothermal stability? An explanation is given by the two step link-lock mechanism, which also has far-reaching implications for developments in leather technology.

Third is the mechanism of reagent reaction in the heterogeneous conditions of leather making, including the role of the delivery method. Consideration of the proposed principles allows prediction of multiple reagent impact on leather properties: reversing the analytical methodology, allows prediction of processes to meet the needs for creating leathers with required properties.

This presentation emphasises the importance of treating the mechanisms and outcomes of leather making as a function of the system: the medium for the heterogeneous reaction, the changing substrate and the reagent at any point in the overall process. In this way, leather science provides the mechanisms for efficient and effective change in leather technology.

**Keywords:** mechanisms, theory, tanning, fixation, paradigm

## 1. Introduction

In a review of published leather science over the last decade, the following topics or themes were identified.

- The use of indigenous plant material for rawstock preservation.
- The role of sulfide in unhairing.
- The analysis of chromium(VI) in the presence of chromium(III).
- The thermodynamics of vegetable tanning.
- Other tannage chemistries: triazine, isocyanate.
- Dyeing with aryl carbonium or fungal species.
- Reagent delivery by plastic beads or ionic liquids.

In this brief updating presentation, we will examine some of those topics: the mechanisms of unhairing and general reactions in leather making and the implications of that new understanding from leather science feeding into the future requirements of leather technology.

## 2. Sulfide unhairing

If the familiar mechanism of sulfide attack on keratin at the cysteine moiety in Fig. 1 applies, then the kinetics can be expressed in the following way:

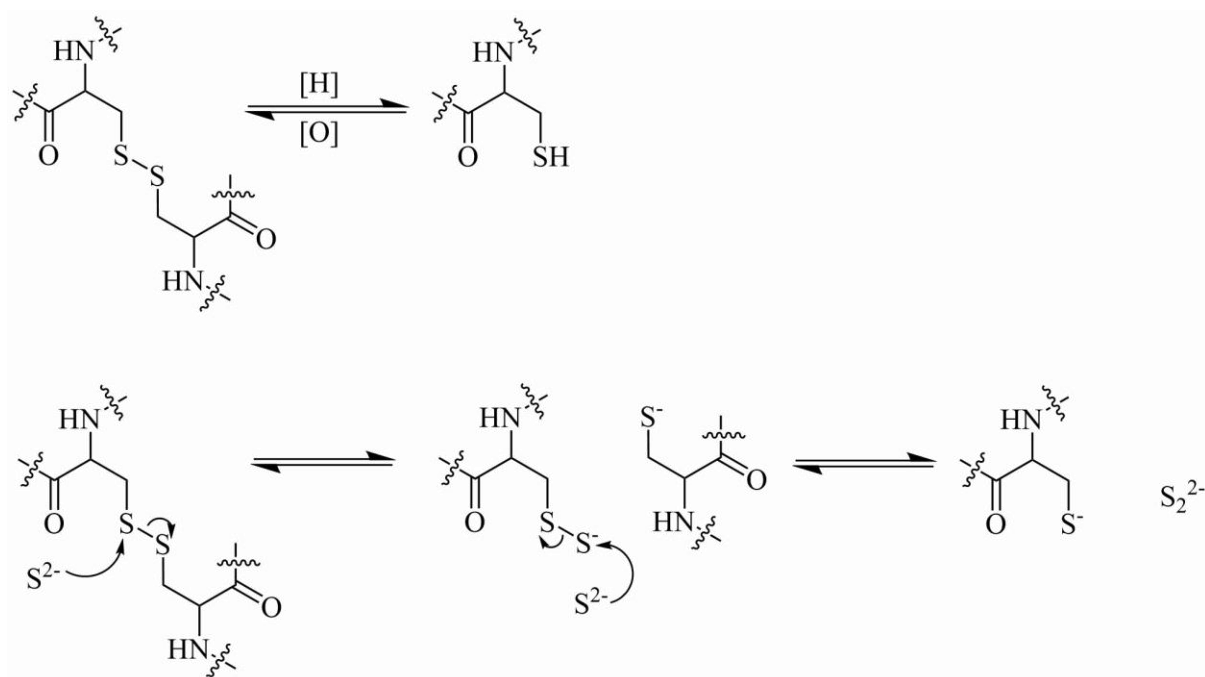
$$\text{Rate (S}^{2-}) = k_s[\text{S}^{2-}]^a$$

But we now know that it cannot be right, because  $\text{S}^{2-}$  does not exist in aqueous solution. If the new information is taken into account, the kinetics must be modified as follows:

$$\text{Rate (HS}^-) = k_{\text{HS}}[\text{HS}^-]^b[\text{OH}^-]^c$$

Whilst the current technology still applies, this raises the question as to whether the primary agent is hydroxyl ion with the hydrosulfide species only acting as a traditional 'sharpening agent'.

Fig.1. The traditional and currently accepted mechanisms of the breakdown of keratin, by reduction, oxidation or sulfide ion.



### 3. Simplifying leather processing. Part 1. Taking stuff out.

In the beamhouse steps, we rely on the hydrolytic reactions of hydroxide ion and proteolytic enzymes to open up the skin structure and collagen itself. The reaction is non-specific and impacts on the components of skin as set out in Table I.

The hydrolytic reaction is controlled by time, pH and temperature, but is not at all targeted, except at protein, including the collagen itself. Addition of current biochemical agents does not add precision, merely acceleration of rate and damage. This is where better understanding of skin structure may allow better targeting and more precise reactions for improved quality and properties of leather.

Table 1. Opening up targets.

<b>Species in skin</b>	<b>Function in skin</b>
Hyaluronic acid	Resiliency, filling
Albumens, globulins	Filling (ground substance)
Melanins	Colouring – no structural effect
Type III collagen	Influences grain structure
Elastin	Area, softness, break
Chondroitins A and C	Minor, non structural
Dermatan sulfate	Hydration
Decorin	Stretch

Inherent in the hydrolytic approach to opening up is the role of swelling. It has long been assumed that controlled swelling is a good thing, assisting the splitting of the fibre structure of collagen. But is it necessary? Heidemann thought not, but having seen his leathers, his argument is not compelling. It is worth considering an alternative approach – the lyotropic mechanism and considerations of the Hofmeister series as discussed by Rabinovich could be novel and useful in this regard.

#### **4. Simplifying leather processing. Part 2. Putting stuff in.**

The second part of leather making is the fixation of reagents to modify the properties and performance of collagen as leather. There is no specificity in the terms pretanning, tanning and retanning – this merely indicates chronology in processing steps. All fixation reactions must be considered to contribute to the stabilisation of collagen and to conferring new properties. It is necessary to

understand the mechanism of fixation to be able to predict the outcome, especially the consequences of multiple combinations of reagents.

A rethinking of the mechanism of chrome tanning has provided the basis for a general theory of tanning and leads to an understanding all fixation reactions.

The first equilibrium in Fig. 2 applies only to solid basic chromium(III) sulfate. The second reaction, olation and dimerisation, was the accepted mechanism for over half a century. However, synchrotron X-ray studies by my group at Northampton showed that the structure of the bound sulfato complex is wrong in every regard. The actual bound species at the end of tanning is the linear tetrameric 50% basic species. Reaction by this compound alone only confers moderate hydrothermal stability to collagen, as evidenced by tanning with chromium(III) chloride or perchlorate.

Fig. 2. The chemistry of chrome tanning.

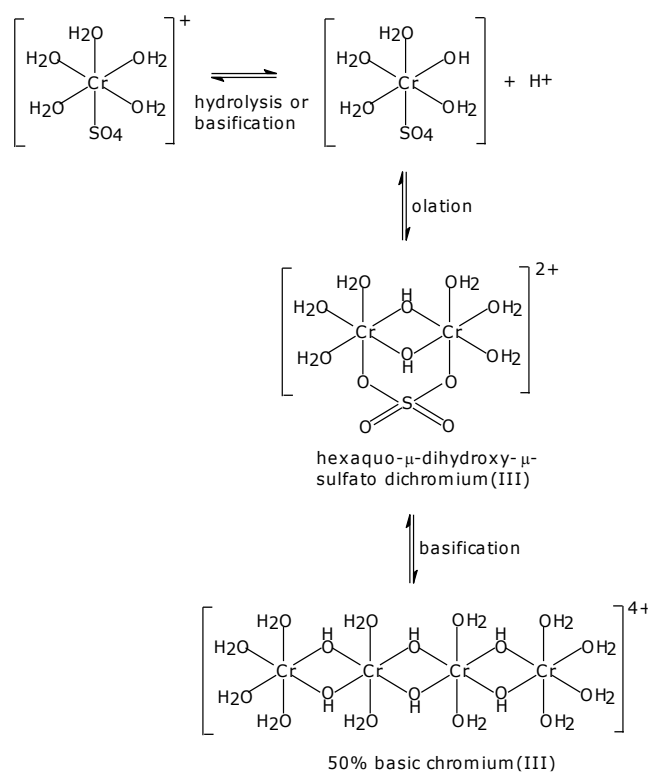
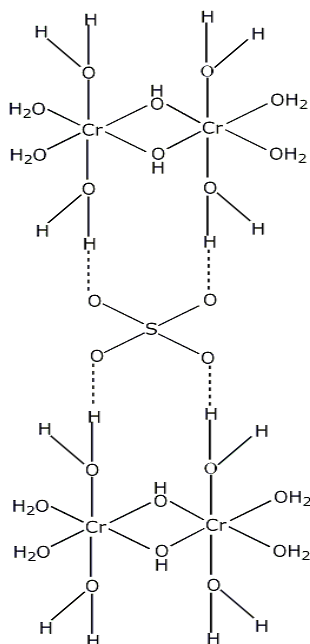


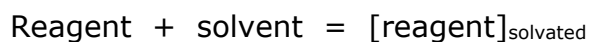
Fig. 3. The relationship between the chromium complex and sulfate counterion.



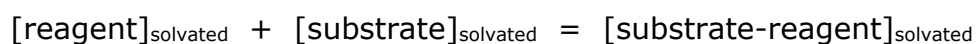
The sulfate counterion does not function as a complexing ligand – it locks two chromium species together by electrostatic bonding at the aquo ligands. It is this secondary reaction that creates the synergistic effect and raises the hydrothermal stability to high values. This is the link-lock mechanism of tanning. The principle can be generalised to apply to the effect of any single tanning agent and then to the impact of a second reagent, which might cause a synergistic effect on hydrothermal stability depending on the chemistries of the two reagents.

### 5. Stepwise mechanism of fixation.

All leather making reactions are heterogeneous in nature because they involve a liquid medium and a solid substrate. Therefore, any reagent must pass from the liquid environment into the solid environment: this involves a competition to partition the reagent between the two other parts of the 'system'.



$$K_1 = \frac{[\text{reagent}]_{\text{solvated}}}{[\text{reagent}][\text{solvent}]}$$



$$K_2 = \frac{[\text{substrate-reagent}]_{\text{solv}}}{[\text{reagent}]_{\text{solv}}[\text{substrate}]_{\text{solv}}}$$

The first equilibrium constant refers to the affinity of the reagent for the solvent or the solubility: the greater the affinity, the lower the tendency of the reagent to transfer to the substrate. The second equilibrium constant refers to the competition between the affinities of the solvent and the substrate for transfer and interaction with reagent. This delivery step controls the uptake rate, but not the fixation: this is where variation in the delivery mechanism can affect the overall fixation. Current processes are conducted in an aqueous medium, but the properties of the water can be manipulated by other solutes, salts or organic chemicals. New options are to substitute part of the float with plastic beads or change the medium completely to an ionic liquid.

The fast transfer reaction depends on electrostatic interaction between the reagent and the substrate: interactions may be charge-charge, hydrogen bonding or hydrophobic bonding. Here, the impact of isoelectric point is important: this is the point on the pH scale at which the net charge on the substrate is zero.

$$\text{IEP} = \frac{\sum f_i [\text{NH}_2]_i}{\sum f_j [\text{CO}_2\text{H}]_j}$$



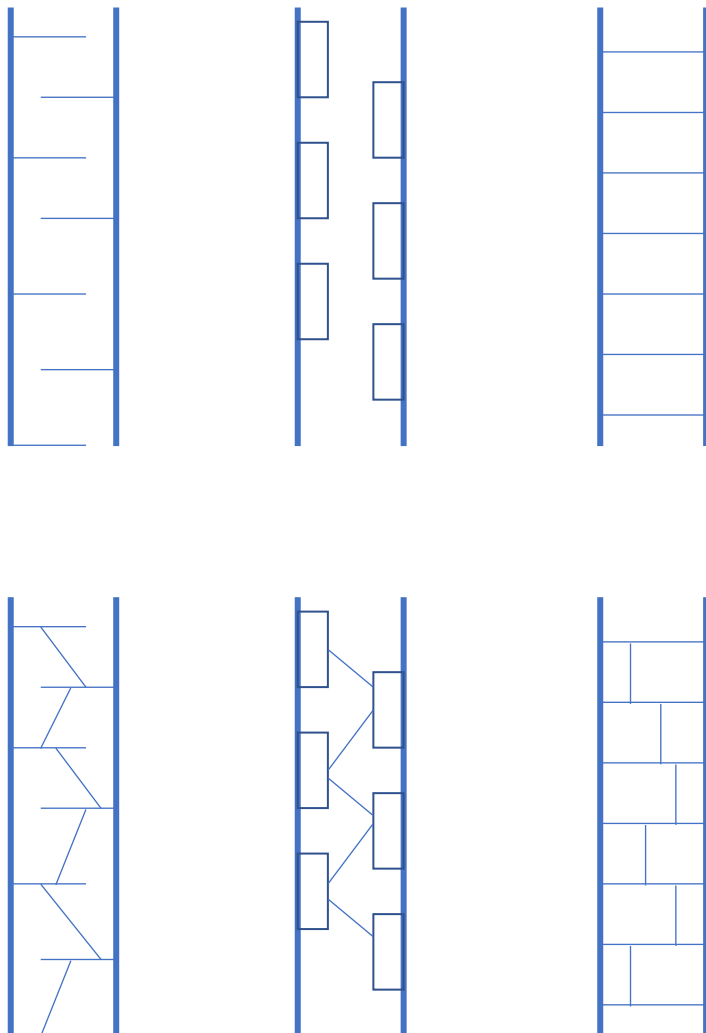
The higher the pH is above the IEP, the greater the negative charge on the substrate: conversely, the lower the pH is below the IEP, the greater the positive charge on the substrate. The relative charges on the reagent and the substrate will determine the rate of interaction and consequently, the degree of penetration into the substrate or the uniformity of reaction over the surface: reaction through the cross section will define the properties of the material, surface reaction determines the aesthetics. The electrostatic interaction may be followed by covalent reaction, depending on the chemistry, such as with chromium(III) or condensed vegetable tannins.

Since there are always multiple fixation reactions in any leather making process, the impact of accumulated reactions must be analysed and the outcomes predicted. There are only three types of consecutive reaction. The first is 'independent', when the reactions have no affinity for each other and they are likely to have different reaction sites on the substrate. The order of addition may be unimportant, but the order might be, and the effects on the subsequent properties can be roughly additive. The second is 'antagonistic', when the reagents are in competition: order is important in determining the winner, the reagents may react with each other but not in any important way. The third is 'synergistic', when the link-lock effect is to create a new matrix around the collagen and the result is high hydrothermal stability: the impact on properties is a blend of the two contributions.

In Fig. 4, the top row of notional structures describes the possibilities for all reactions. Each of which can only confer moderate hydrothermal stability, since there is only moderate resistance to shrinking – notably including what might be considered to be classical crosslinking. In the second row, the locking reactions markedly raise the resistance to shrinking, observed as high shrinkage

temperature – this is synergy. It is important to recognise that all fixation reactions should be included in analytical thinking, dyes, fatliquors and any other specialised treatments.

Fig. 4. Types of combined reaction.



## 6. Implications of understanding the mechanism of tanning.

The theory outlined above covers all known and unknown fixation reactions and their effects on the properties and performance of the product. It allows the tanner to predict the outcome of processing, even complex combinations of reagents. By analysing the effect of change at every point in the process,

understanding the outcome of individual reagent fixation and the accumulated impacts, the overall properties and performance of the resulting leather can be estimated with accuracy.

By reversing the process, it is possible to predict the process needed to make a leather with required properties. The methodology is to ask critical questions: what are the required characteristics, what is the relative importance of those characteristics, can it be achieved with a current process or must it be a new process, is the envisaged leather conventional or extreme performance, can it be made with conventional chemicals or must the reagents be designed? Furthermore, does the new process conform to conventional processing technology or must the relationships between process steps be reviewed and modified? It is important to bear in mind that current processing technology is traditional and convenient, not written in stone.

If processing is to be changed radically, wider considerations should come into play: what are the limits to performance of a collagen-based biomaterial, can the new process be made compact, is there a role for biochemistry, what is the overall environmental impact and what are the options for end of life?

## **7. So...what is the use of leather science?**

As with all branches of science, the purpose of studying it is to make thinking and consequently research and development logical. This is necessary to prevent R&D going down wrong tracks or reaching dead ends, by eliminating assumptions based on incorrect premises. In our case, the purpose is to effect a paradigm shift in thinking: we have most of the theoretical tools for predictable, effective change.

In the end, the answer to the question is:

***to create new, novel and better leather technology for a sustainable future.***

## **References**

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