36th Congress of IULTCS, Addis Ababa, Ethiopia
November 2021

The Heidemann Lecture

What's the use of leather science?

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Paraphrasing Francis Crick:

…the problem of defining the structure of collagen is not as big as the human genome project, but it is more complicated

…therefore a subject worthy of what used to be called the Heidemann Collagen symposium originally held just before each IULTCS Congress

- I want to present a new way of thinking about leather making
- - in a scientific way
- This is an invitation to readdress your approach to processing for making leather
- This is a way to make real progress
- - in an efficient and effective way

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Current trends in leather science:
Journal of Leather Science and Engineering, 2:28, 2020.

- Preservation: use of indigenous plant material
- Unhairing: the role of sulfide ion
- Chromium: the question of Cr(VI)
- Vegetable tanning: thermodynamics
- Other tannages: triazine and isocyanate chemistries
- Dyeing: aryl carbonium, fungal
- Reagent delivery: bead medium, ionic liquids

The topics to be addressed today

- Sulfide unhairing
- Chromium(III) tanning
- General theory of tanning
- Reagent fixation
- Reagent delivery
- Prediction in processing
- End of life

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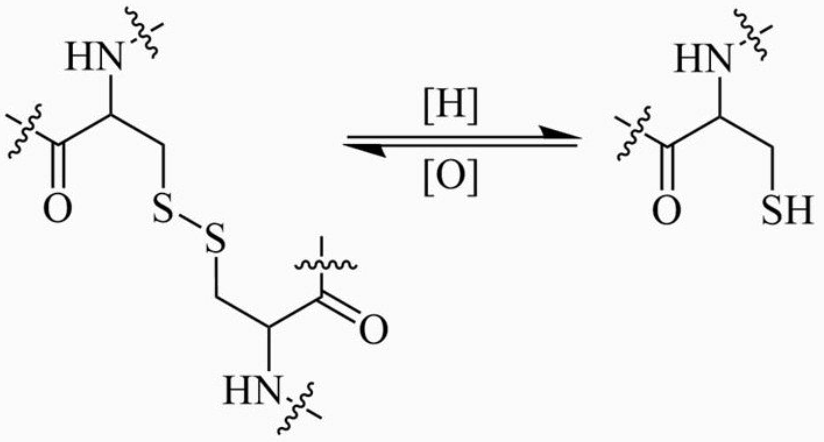
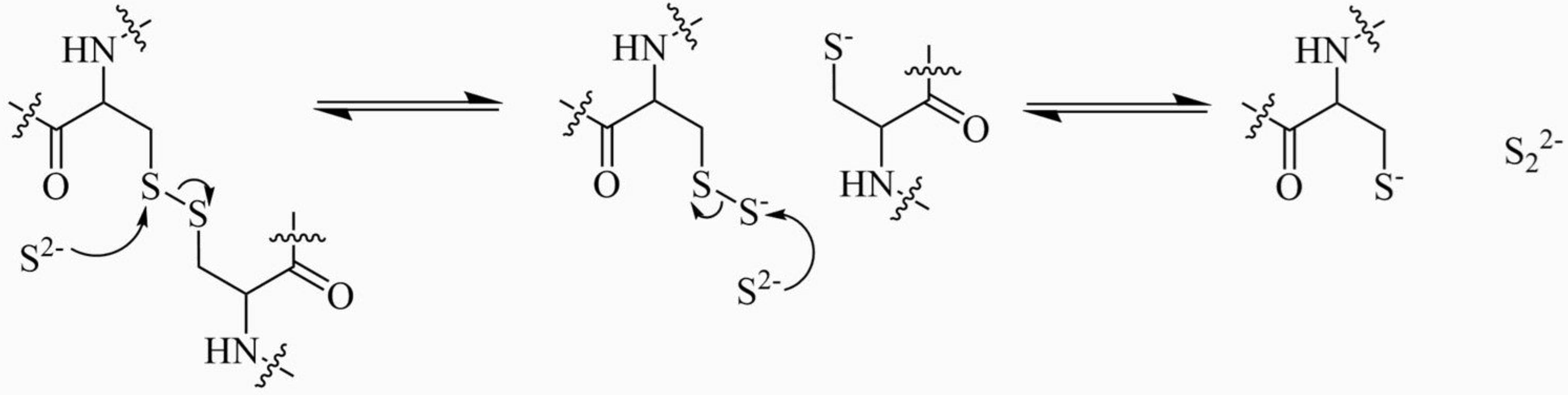
Sulfide unhairing



- **The previously accepted mechanisms of keratin degradation: oxidative and reductive routes are probably still right, but the sulfide reaction cannot be right.**

- **Sulfide, as S^{2-}, does not exist in water.**



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$$Rate(S^{2-}) = k_S[S^{2-}]^a$$

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

1. Is the mechanism primarily controlled by hydroxide?
2. Hydrosulfide functions as a ‘sharpening agent’?
3. Review and rethink the mechanism.
4. What are the implications for industry?

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A simplification of leather making

- **A two step process:**
  step no. 1 – taking stuff out
  step no. 2 – putting stuff in

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Beamhouse processing

- Soaking to pickling
- Two aspects:

  removal of unwanted skin components – but which ones?

  splitting the fibre structure – attacking what part of the collagen structure?

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Skin components and implications

- Hyaluronic acid – removed by electrolyte – may react with chromium(III)
- Albumens, globulins – filling ground substance
- Melanins – removed in conventional processing – otherwise perhaps not
- Type III collagen – influences grain structure and properties – typically ignored
- Elastin – affects area, softness, break

Skin components and implications

- Proteoglycans within the fibre structure
- Chondroitins A and C – minor components
- Proteoglycans attached to the fibre structure
- Dermatan sulfate – removed in liming – in vivo functions in hydration
- Decorin – as DS – allegedly influences physical properties, stretch

Beamhouse processing

- Currently, all hydrolytic reactions are controlled by time, pH and temperature – but not by targeted mechanisms
- Application of current biochemical agents does not add precision, merely acceleration of damage
- Better understanding of collagen and skin structure should allow better and more precise outcomes

Beamhouse processing

- Conventional liming causes swelling
  …(almost) independent of ionic strength
  …overdoing it is very bad for the leather!
- Allegedly controlled damage!
  Is swelling necessary for fibre splitting?
  Heidemann thought not!
  Alternatives? Lyotropy cf Rabinovich

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Pretanning, tanning, retanning – and anything else

- ‘Tanning’ terminology merely indicates chronology – nothing else
- All fixation reactions must be considered
- Understanding the stepwise mechanism of fixation allows prediction of outcome
- Understand the consequence of combinations

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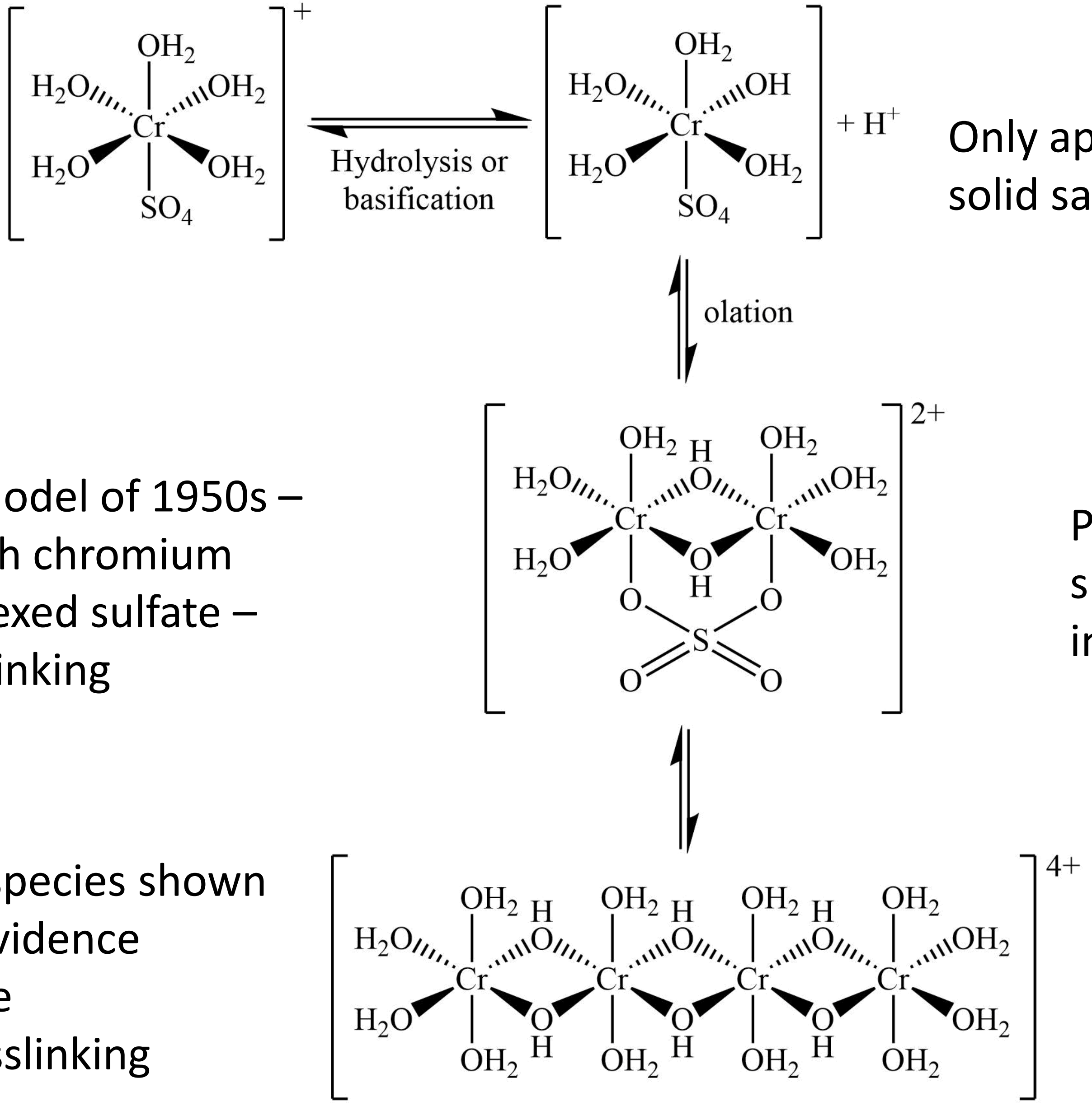

50% basic chromium(III)

Only applies to solid salt

Gustavson's model of 1950s – fixation at both chromium atoms, complexed sulfate – defined crosslinking

Putative bound species – wrong in all regards

Actual bound chrome species shown by synchrotron X-ray evidence
– no complexed sulfate
– no invocation of crosslinking

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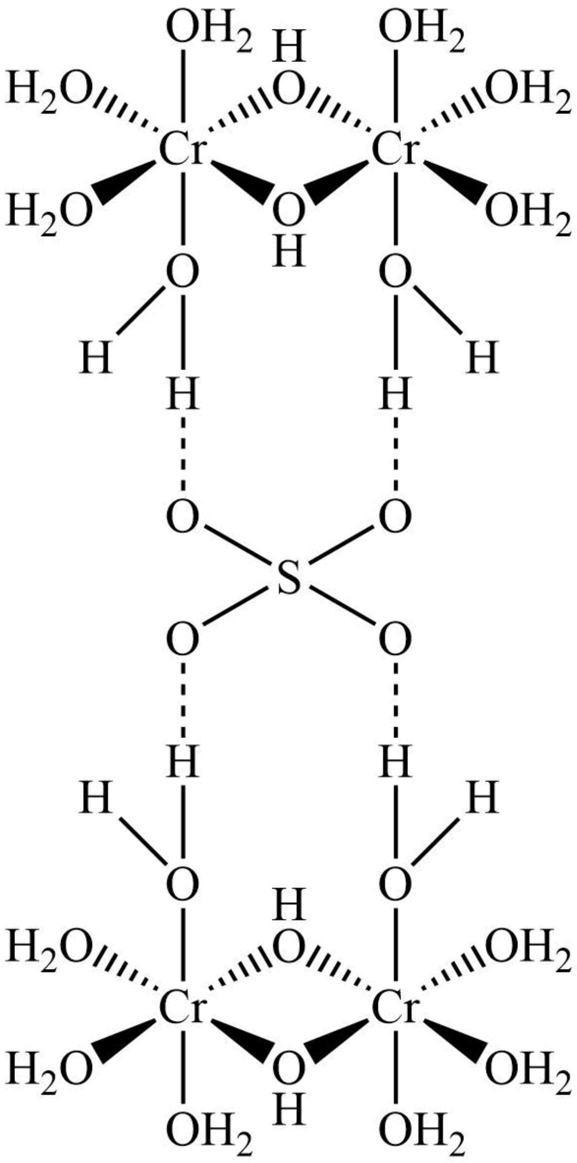

- Sulfur atom is too far from the chromiums to be 'seen' by EXAFS.

- The actual role of sulfate: not directly complexed to chromium – performs a bonding mechanism between chromium species.

Implications of the revised mechanism of chromium tanning.

- The reaction with the chromium(III) species is no more effective than other metal salts
- High hydrothermal stability depends on a second component of the reaction – usually sulfate ion
- This has been designated the link-lock mechanism
- From this, a general theory of tanning follows

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Components of heterogeneous fixation

reagent + solvent $\rightleftharpoons$ $[\text{reagent}]_{\text{solvated}}$ Part 1

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

Equilibrium depends on the affinity of the solvent for the reagent

$[\text{reagent}]_{\text{solvated}}$ + $[\text{substrate}]_{\text{solvated}}$ $\rightleftharpoons$ $[\text{substrate-reagent}]_{\text{solvated}}$ Part 2

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

Equilibrium depends on the affinity of the solvated reagent for the solvated substrate compared to the solvent

The general mechanism of fixation

1. **Transfer from solution to substrate**
   analogous to partitioning of a solute between two solvents
   cf solvent extraction

   depends on the relative similarity of chemical environments
   ie competition for the solute by solvent versus solid substrate
   in terms of hydrophilic/hydrophobic properties

Controls uptake rate but not fixation
– this is the delivery step

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Making Ionic Liquids :
courtesy of Prof. Andy Abbott, University of Leicester, UK

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The general mechanism of fixation

2. Electrostatic interaction

usually a charge-charge effect

commonly hydrogen bonding

includes hydrophobic interaction

influenced by type and magnitude of charge
and hydrophilic-hydrophobic balance

May be the final step in fixation

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Influence of charge

$$\mathrm{IEP} = \frac{\Sigma f_i[NH_2]_i}{\Sigma f_j[CO_2H]_j}$$

- Charge on substrate can be altered by bound species
- Charge more often defined by pH, controlled by isoelectric point ie the pH at which charge is zero

Influence of charge

- Isoelectric point can only be estimated
- IEP will change at every fixation step – the direction is known, but not the magnitude
- Profile of charge vs pH will change at each step
- Charge can affect kinetics of transfer
- Charge can influence speed of fixation reactions
- Therefore charge controls penetration versus surface fixation of charged reagents
- Cross section uniformity affects properties
- Surface uniformity affects aesthetics

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The general mechanism of fixation

3. **Covalent reaction**

   not all electrostatic interactions can convert to covalency

   - such as chromium(III) or condensed polyphenol

   chemical modification to substrate, reagent or electrostatic complex could result in covalency

The general mechanism of fixation

All fixation reactions are fundamentally the same.

It is only the chemistry of the reagents that varies affecting the affinity between elements of the ‘system’ and the number of steps.

The system: reagent + substrate + medium

Each component can be manipulated to the tanner’s advantage

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The cumulative effects of fixation

- ‘The properties of a leather are determined by the first tanning reaction’ – tanners’ rule of thumb
- Not always true
- Processing is an accumulation of combination reactions
- The outcome of combinations of reactions depends on the nature of the interactions on/in the substrate environment
- There are only three options for combinations

Independent reactions

- The reagents have no affinity for each other
- Different reaction sites, may cause some interference in fixation
- Combined effects may not be affected by the order of addition
- Relative offers influence relative effects
- Kinetics can affect relative effects
- Combinations are roughly additive

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Antagonistic reactions

- The reagents compete for reaction sites
- - reagents of the same chemical type – eg syntan and vegetable tannin
- Competitiveness depends on relative offers
- They might react with each other, but not synergistically
- Outcome is determined by the winner in the competition

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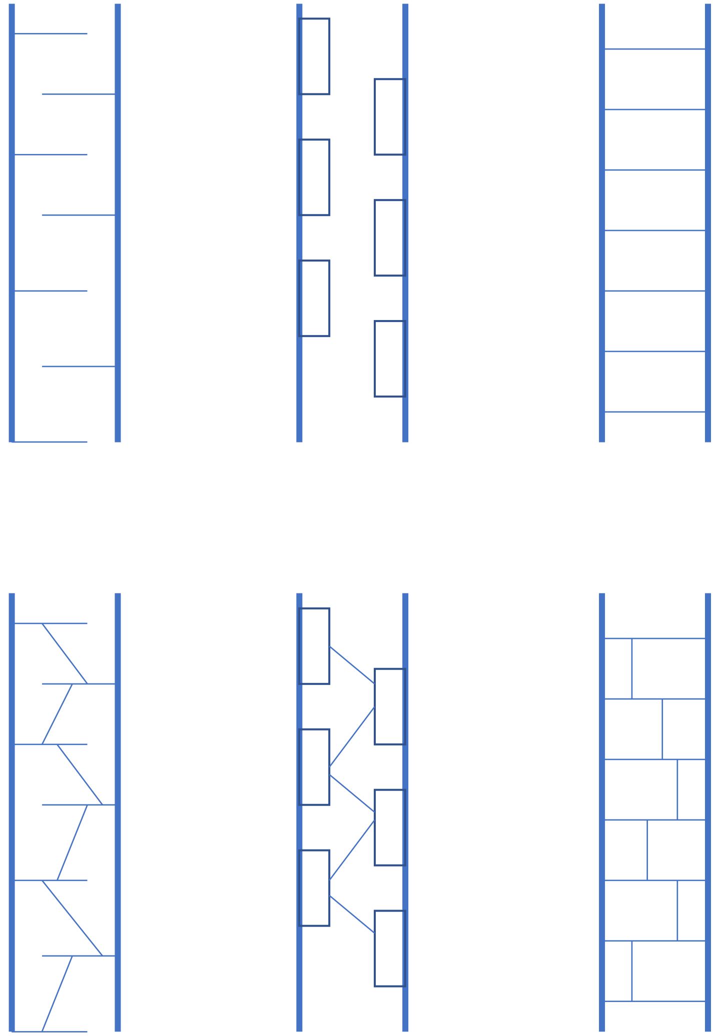
Synergistic reactions

- Synergy: 'the whole is greater than the sum of the parts'
- Link-lock mechanism of tanning
- The first reagent creates the 'link'
- The second reagent creates the 'lock'
- The order of addition is likely to be critical
- A new tanning species is formed, a matrix which reacts with the substrate in a concerted way
- A stable matrix makes shrinking more difficult, hence observed as high shrinkage temperature
- Combinations are somewhat additive in terms of conferred properties (not Ts)



Linking reactions confer only moderate hydrothermal stability

All tanning reactions conform to these three simple models

Locking reactions confer much higher hydrothermal stability

Combinations of linking reactions do not

Implications of the new mechanism of tanning.

- **Link-lock defines the conditions for moderate and high hydrothermal stability outcomes.**
  - **It explains the outcome of all tanning processes, known and unknown.**
  - **It leads to a general theory of fixation mechanism.**
  - **Understanding the principles of reagent fixation allows the prediction of process outcomes.**
  - **Understanding the effects of reactions allows the prediction of processes for product outcomes.**

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Dyeing, fatliquoring – and any other fixation reactions

- There are more fixing reactions to consider
- The stepwise mechanism is the same
- The range and types of chemical bonding are the same as for tanning agents
- But the offers may be smaller, particularly in molar terms

It is important to know the chemistry!

Predicting processing outcomes

- To predict the effect on leather properties, analyse change at every point in the process
- Understand the outcome of any change
- Know the impact of the chemistries of all reagents
- Know the technological effect of every reagent on properties and performance of the leather
- Understand the principle of accumulation of change

Reverse analysis: predicting processes

- What features/properties/performance characteristics are required?
- In what measure for each element?
- What is specifically not wanted?
- Modification of a current process?
- Completely new process?
- Conventional leather or extreme performance?
- Novel or new properties/performance?
- Conventional reagents? How much of each?
- New reagents/approaches required?

Reverse analysis: predicting processes

- Do the reagents fit into conventional processing steps order?
- Are they compatible with logical changes in pH, charge, isoelectric point?
- Is there a need to review and modify the relationships between conventional process steps?
- Current technology is only traditional and convenient

  …it is not written in stone!

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Reverse analysis: wider considerations

- What are the limits to performance of collagen-based biomaterials?
- Can the process be designed to be compact?
- Role of biochemistry for novel reactions
- Environmental impact?
- Cradle to cradle: end of life options

End of life options

- Recovery of leather and recycle/reconstitute
- Recover chromium, recover protein
- Chemical denaturation and degradation
- Biogas generation
- Redox mechanism of collagen degradation

So…what is the use of leather science?

- To make research and development logical
- To prevent research and development going down wrong tracks or reaching dead ends
- To eliminate assumptions based on incorrect premises
- To take quantum steps forward

So…what is the use of leather science?

- To effect a paradigm shift in thinking
- – we have all the theoretical tools for change
- To create new and novel leather technology
- But above all, to create a sustainable future for leather

'All science is right, until proved otherwise.'

Henri Saumier, 2018

'…assuming the science is feasible in the first place!'

A.D. Covington, 2021

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