

## **An Overview of Leather Processing**

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### **Abstract**

A current watchword in the leather industry is sustainability, which may be defined in terms of the ecological impact, incorporating efficient and effective use of reagents and materials, and the present and future effective and efficient development of new collagenic biomaterials in an increasingly economically competitive global sector.

Correct mechanisms in leather science and their understanding for application in leather technology are critical: current thinking developed over the last quarter of a century constitutes a shift in approach to leather science, yielding a new paradigm in leather technology. The result is a new way of ensuring that development strategies are likely to be predictably successful, unlike the inevitable outcome of the alternative, ‘trial and error’.

Key words: mechanisms, paradigm, development

### **1. Introduction**

This brief review of leather processing provides a ‘snapshot’ of the current state of leather science and the consequent leather technology which creates the processes. Any overview of the global leather industry with regard to its methodology of processing must consider the following elements: the current understanding of the science underpinning the technology, the drivers for change and the shortcomings in the required science. (Covington and Wise, 2020, 2020a) Around the world, a general principle dominating the industry is sustainability, defined by the United Nations Brundtland Commission as ‘meeting the needs of the present without compromising the ability of future generations to meet their own needs’. This goes further than the previous preoccupation of the industry, the ecological impact of operations. In other words, the imperative for modern leather making is that it should be environmentally sound, both in general production and in the creation of new, innovative collagen-based biomaterials: implicit in this view is the elimination of errors in the thinking upon which processing is founded.

The key to achieving these aspirations is an understanding of the scientific principles underpinning the technology of leather making. Not taking advantage of the latest leather science only leaves a ‘trial and error’ approach to development, based on the false premise that experience is enough: getting the science wrong leads to the same outcome. Either way, progress is either static or inefficient and costly. Recent developments in thinking (Covington and Wise, 2020) have effectively created a paradigm shift, allowing a quantum step forward in

the potential for modifying processing and prediction of the outcome of fixation reactions on collagen. This is a new logical mindset rather than a set of rules and recipes.

Sustainability should not be considered in terms of setting out a list of preferred technologies, BATNEEC (best available technology not entailing excessive cost) is not absolute, much as 'clean' technologies have been in the recent past, when the favoured processes depended on the fashion of the time, rather than clear thinking about principles. The key to sustainable development and a successful future is sound leather science.

One of the features of leather science in recent decades has been the correcting of misapprehensions and errors in the technology of leather making. Some of these are addressed in this brief overview of the present status of leather processing: the importance here is to avoid taking research and development down non-productive 'blind alleys'.

## 2. Beamhouse

### 2.1. Collagen structure

An understanding of the fundamental nature of the substrate at the heart of leather making is critical to formulating strategies for consolidating and improving processing. Unfortunately, there are significant gaps in that knowledge. Whilst the hierarchy of collagen structure is broadly defined – amino acid sequences in the alpha chains, the triple helix unit and quarter stagger formation, leading to fibril formation and thence to fibre structure – some elements of structure remain unclear. Examples are presented in Figs. 1 and 2, illustrating that fibrils, which appear solid under the transmission electron microscope, exhibit different appearances when acid swollen or extracted from bone. (Covington and Wise, 2020a)

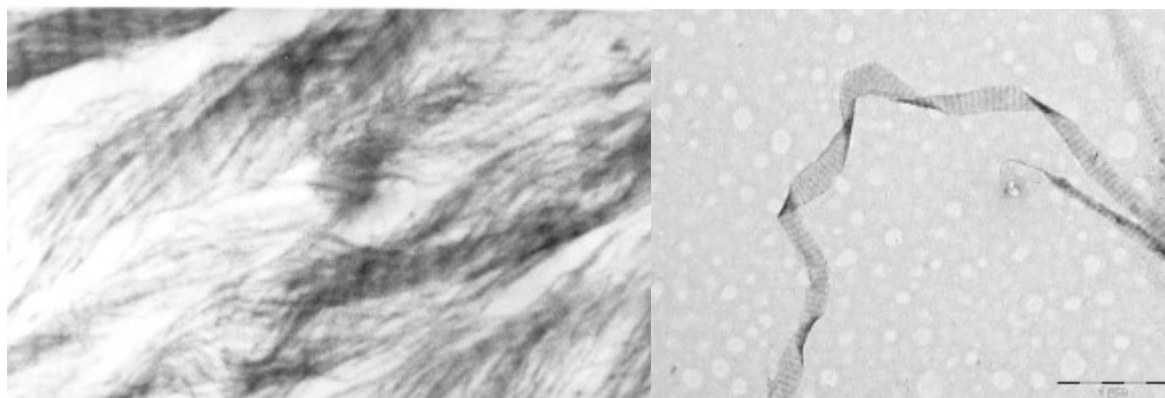


Fig. 1. Acid swollen fibrils

Fig. 2. Fibril extracted from bone  
(courtesy HEC Koon).

If the fibrils are not hollow in its native state (as might be assumed), the nature of the chemical species acting as the filler within fibrils is unknown: it is therefore not accounted for in any stage of processing and hence might or might not contribute to the desirable properties and performance of the resulting leather. In addition, the full and complete role of the water bound to collagen is not well understood and, as a consequence, it is not known if the *in silico* modelling of collagen in a range of situations is accurate. The issue of collagen hydration is exemplified by interrogating the Protein Data Bank, where multiple conflicting results are encountered.

## 2.2. Skin structure

Skin is not an homogeneous, uniform material, although until the 20<sup>th</sup> century it was effectively treated as such by tanners. Now tanners can have a clearer view of the components of skin, structural and non structural, major and minor, with knowledge of the roles they play in the properties and performance of skin and the potential roles they might play in leather, both wanted and unwanted. One example is elastin, which influences softness, stretch and area, depending on the impact of processing on it. (Addy and Covington, 2003) Other minor components such as proteoglycans and glycosaminoglycans are currently not addressed for their effects on leather handle and hydration: typically they are labelled as part of the ‘ground substance’ and consequently removed to some degree in traditional opening up at high pH.

### *Curing/preservation*

Holding rawstock in good condition is a problem facing the industry in all parts of the world, both developed and developing economies. It is recognised that the current greatest associated ecological problem is the discharge of neutral electrolyte, of which the biggest contributor is sodium chloride used for pelt preservation. Here, we can distinguish between long term preservation and short term preservation. The industry standard is salting with sodium chloride: it has the advantage that curing carries a low risk, because the technology is simple and effective when done properly, viable for many months. But the associated waste stream from subsequent processing is highly damaging to the environment, not least to plant growth.

Alternative long term preservation technologies are limited to alternative electrolytes, drying to low moisture content, freezing or extremes of pH, which all have processing implications which have to be considered. (Covington and Wise, 2020a)

#### (a) Other osmolytes

Inorganic salts as alternative candidates are limited: potassium chloride has been shown to be practical, albeit with some associated problems, including lower solubility. (Bailey, 1995) Sugar-based reagents can control bacteria, as in the use of honey as a traditional wound dressing; the cost, availability and tendency to allow fungal growth are problematic. (Covington and Wise, 2020b)

#### (b) Drying

Reducing the moisture content limits the ability of bacteria to thrive; this is one of the features of the salting effect. Drying is familiar in the traditional shade drying technology of areas such as East Africa. The apparent simplicity of the technique is deceptive: the temperature cannot be too high and the air movement about the pelts must be free, otherwise bacterial growth is faster than the water removal. Alternative dehydrating methods are available, such as superabsorbent polymers used in diapers, but cost and limitation to short term preservation are shortcomings. (Covington and Wise, 2020a)

#### (c) Reduced temperature

Bacterial growth is dependent upon the environmental temperature, since the damaging organisms grow optimally at around 35°C: chilling pelts will preserve them, but only in the short term. This is practical and well known, but only in the developed economies. Cooling

below freezing point will extend the period, as is well known in the domestic experience. Handling and defrosting are major operational difficulties, not to mention the damaging effect of ice crystal growth, causing disruption and loosening of the fibre structure.

(d) pH

Bacteria are sensitive to the pH of their environment, growing best at physiological conditions, around pH 8: growth is increasingly reduced the further away they are from that condition. High pH is not feasible because of the rate of damaging the pelt. Storage pickling is well known for sheepskins and is effective and practical: the modern version relies more on saturated brine than on the acid, which brings us back to the electrolyte problem and might make this technology counterproductive for all rawstocks.

All other modes of preservation can be described as short or medium term, depending on the degree of treatment, such as the amount of salt applied or the extent of drying. Since not all applications of preservation require continuing effectiveness for a year or more, a few weeks or months might suffice, less extreme treatment can be perfectly acceptable; this opens up a wider range of approaches.

(a) Reduced quantity of salt, with or without additives.

Preservation period and effectiveness is proportional to the salt offer on pelt weight. Substitution of all or some of the usual salt offer by the use of inorganic or organic additives is already well known in the trade, but limits the effect, whilst having a minor improvement in the ecological impact, considering also the added impact of those additives. Also, it is a general truism that the reduction in use of a pollutant is not a solution to the problems posed by the pollutant. This is a blind alley of development.

(b) Other preservatives

Whilst there are practical preservation options available to the developed economies, they do not necessarily apply to the developing economies. One approach which seems to offer potential is the use of powdered locally indigenous plant material: this could be in the form of salt-accumulating plants grown in brackish waters or land based. The presence of salt may be regarded as a disadvantage, but the effect of other plant components, such as terpenes, can be useful in creating short term preservation by a biologically degradable reagent. (Covington and Wise, 2020b) Availability in sufficient quantity for local industry might be a limiting factor.

It may be that preservation solutions, particularly local options, will be constituted by combinations of elements of the approaches set out above: practical technologies can only be created by understanding the principles and outcomes from interacting conditions.

*Opening up*

‘Opening up’ is an umbrella term defining the removal of (assumed) unwanted components of the skin, including splitting of the fibre structure, although it does not carry an indication of which components should be targeted or to what extent the changes should be made. Treatment of the pelt with alkali – often calcium hydroxide – is a violent and indiscriminate chemical process, catalysing multiple and non specific hydrolytic reactions, including weakening the pelt, but there can still be a consistent outcome in terms of the overall softening outcome. The process step depends on consistency in all parameters: pH, float to goods ratio,

chemical offer, temperature, degree of mechanical action, time, in no particular order of precedence.

A priority for leather science is to codify the targets for opening up, with limits for component removal: this would allow prediction of appropriate enzymes for specific elements of the total desired outcome.

### *Sulfide unhairing*

The common technology of keratin degradation by lime+sulfide, ‘hair burning’ unhairing, has been in place for over a century, with an associated mechanism available in the literature and accepted for over half a century. However, the mechanism is in error, simply because the previously accepted value for  $pK_{a2}$  the second dissociation constant of sulfide was in error, underestimated up to the beginning of the 21<sup>st</sup> century: the consequence is that sulfide ion,  $S^{2-}$ , actually does not exist in aqueous solution. This means that the kinetics have to be revised in the following way. (Covington and Wise, 2020b)

Rate ( $S^{2-}$ ) =  $k_s[S^{2-}]^a$  would be the form of the rate equation for the aqueous sulfide reaction.

Rate ( $HS^-$ ) =  $k_{HS}[HS^-]^a[OH^-]^b$  is the form of a modified rate equation.

The inevitable conclusion is that the revised mechanism of hair burning must be a function of the hydrosulfide ion,  $HS^-$ , with the involvement of hydroxyl ion, an extra level of complexity. Whilst this revelation may not immediately impact on the technology of unhairing, it begs the question as to how the mechanism and its implications should be reassessed, including other hair burning chemistries and even some hair saving techniques.

### *Hair saving*

Conventional hair burning unhairing processes have high ecological impact and cannot be sustained, so they are gradually being replaced by hair saving techniques. These chemistries (with some biochemical assistance) are well known in the art, but because they are necessarily more complicated, they do carry additional risks with regard to the efficacy of hair removal and possible adverse effects on the pelt itself. They too should be reviewed in the light of the role of the sulfide species, if that is part of the technology.

### *Liming*

The principles of the other beamhouse process steps, involving the removal of skin components, are generally assumed to be understood: the opening up of the collagenic fibre structure, the coarse or fine splitting of the units of structure – the nature of the fibrils notwithstanding – is well known from microscopic observations. However, (the importance of) the role of swelling is also assumed from observation but not from a chemical mechanism: Heidemann postulated that swelling is not necessarily a *sine qua non* of ideal opening up. It is well known that osmotic liming is a high risk process step, but less risky options have rarely been investigated, for example Rabinovich’s ideas of lyotropic interactions to modify collagen properties, which might be more targeted and therefore safer. (Rabinovich, 2011)

### *Bating*

The role of bating seems straightforward: proteolytic enzymes (from a variety of sources) are applied to pelt under the appropriate conditions, ideally around pH 9 and 35°C, so that the non structural proteins can be degraded, thereby eliminating to some degree the adhesions between

elements of the collagen structure. However, it has always been recognised as a risky step, because enzymes are highly efficient and hence unwanted side effects can occur with unwanted rapidity. Consequently, it is common to observe tanners applying bating enzymes to bovine hide under conditions that are markedly far from optimum in order to mitigate the risks.

For rawstocks that do not strictly require bating through the cross section, the desired bating reaction is actually confined to a cleaning effect on the grain. It would be less risky to the quality of the product to address the actual requirements of the step ie just to remove residual epidermis and hair debris: one solution would be use a keratinase product (ensuring the reagent is free of protease) so the rest of the hide structure is unaffected, especially the valuable grain enamel. (Covington, 2021)

### *Pickling and swelling*

Pickling is an apparently necessary step in preparation for chrome tanning: it is a process step that conventionally needs a high offer of neutral electrolyte to avoid the damaging effect of swelling under acid conditions. There are approaches to mitigate the impact, such as chaser pickle or the use of non swelling acids or pretanning, all of which are associated with consequences which might be counterproductive: chaser pickle tanning has a risk of uneven chrome fixation, non swelling acids are a form of low reactivity tanning reagent, causing pretanning, which alters the properties of the leather. (Heidemann, 1993) Equally, all of these approaches can be useful and successful in processing, but only as long as the underlying principles and technological outcomes are clearly understood by the tanner.

## 3. Tanning

### *Definition*

Table 1. Variations in tanning outcome measured by hydrothermal stability.

<b>Tanning reagent(s)</b>	<b>Indicative denaturation temperature (°C)</b>
None	65
Metal salts: eg Al(III), Ti(IV), Zr(IV) etc.	70-85
Plant polyphenol: gallotannin or ellagitannin	75-80
Plant polyphenol: flavonoid	80-85
Synthetic tanning agent: polymerised, derivatised phenols	75-85
Aldehyde: formaldehyde or glutaraldehyde	80-85
Aldehydic: phosphonium salt or oxazolidine	80-85
Basic chromium(III) sulfate	105-115
Semi metal: hydrolysable polyphenol then eg Al(III)	110-120
Vegetable retan: metal eg Al(III) then hydrolysable polyphenol	80-85
Synthetic polymer then aldehydic reagent eg melamine-formaldehyde then oxazolidine	105-115
Aldehydic reagent then synthetic polymer eg oxazolidine then melamine-formaldehyde	80-85

The process of tanning results in changes to the pelt, some chemical and some physical, but perhaps most notable is the rise in hydrothermal stability. However, this outcome is highly

variable, as indicated in Table 1, so it does not define the process step. The definition of tanning must take into account those processes known as ‘leathering’, in which collagen is modified into a leather-like product but the shrinkage temperature remains unchanged, for example in oil tanning or alum tawing. (Covington, 2018)

Shrinkage temperature, a measure of the hydrothermal stability of the modified collagen, is a useful parameter in process control. Tanning causes a range of changes to collagen, all of which exhibit variations depending on the chemistry of the process step, so they cannot define the process. Tanning is strictly defined as the conversion of a putrescible material into one which can resist biochemical attack, being rendered imputrescible: this is a consistent outcome independent of tanning chemistry.

Any theoretical understanding of the mechanism of collagen stabilisation must be overarching, with no exceptions. A major feature of discussions on tanning principles to date has been the assumption of ‘crosslinking’ as the underpinning rationale. This way of thinking assumes there is a general mechanism whereby there is direct chemical linking between triple helices, in a manner analogous to sewing or scaffolding. This is a critical aspect of leather science which is addressed in detail below.

### *Chromium(III) tanning*

The industry global standard is chromium(III) tanning; it took over the leather industry around the turn of the 19<sup>th</sup> century because of the advantages over vegetable tanning, notably the speed of processing and the versatility of properties it offered. In the latter half of the 20<sup>th</sup> century it was shown that the reaction centred on reaction between the chromium(III) molecular ions and the carboxylate groups on collagen (Sykes, 1956), but the nature of the molecular ion was not addressed.

The technology of ‘masking’ has been widespread, the creation of modified tanning properties by complexing the chromium(III) species with organic ligands: the underlying assumption was that the complexing reaction, often using formate, could control the tanning reaction by reducing the reactivity of the chromium species. It was not until late in the 20<sup>th</sup> century that it was shown that under typical industrial masking conditions, tanners were actually counterproductively making the chromium complex more reactive. (Covington, 2010) In addition to the affinity of the chromium species for collagen carboxyls, it is necessary to understand the relative relationships between the chrome with the solvent and the chrome with the substrate – the bigger picture. Understanding the wider implications of chromium complexation leads to a rationale of the technologies involving other added ligands and opens up the potential for accurately controlling the changing chrome tanning reactivity during the process.

It was not until the turn of the 20<sup>th</sup> century that advanced X-ray analysis showed that the tanning species at the end of the process is unipoint fixed linear tetrachromium molecular ions and consequently precisely how the mechanism of conferring high hydrothermal stability works, based on the additional chemistry of the counterion. (Covington *et al.*, 2001) Note the term ‘unipoint fixed’ – not fixed at both ends of the complex – therefore not crosslinking in the typically understood sense of the word.

Chromium tanning as an industrial process is fairly ‘foolproof’ and capable of being applied successfully in relatively non technical factories. It is constantly under attack as an alleged

polluting technology because it is based on transition metal chemistry. A detailed knowledge of the mechanism of the tanning process is critical to sustainability, by both maximising fixation efficiency and minimising the impact of discharges to the environment.

### *Link-lock*

If the data presented in Table 1 constitute a reasonable summary of tanning outcomes, it is apparent that they can be grouped into two populations: one at about 85°C and the other at about 110°C ie moderate and high hydrothermal stability. The lower shrinkage temperature group may be characterised as processes involving a single reagent. The higher shrinkage temperature group is less easy to generalise: two components appear to be necessary, but then the order of addition is critical and chromium tanning appears to be anomalous.

Chrome tanning with the chloride or perchlorate salts results in leather with a shrinkage temperature about 85°C, addition of sodium sulfate raises the shrinkage temperature to 110°C or higher, the same as tanning with (basic) chromium(III) sulfate. Other counterions can do the same thing, notably the effect of treating wet blue with pyromellitate (1,2,4,5-tetra carboxy benzene) which can raise the shrinkage temperature to about 130°C in a reaction that is so fast it can only be electrostatic in nature and not covalent complexation. Therefore, chromium tanning is actually a two component system and its stabilising effect is dependent on the chemistry of the counterion. Furthermore, high shrinkage temperature is confirmed to be only achievable by a two component tanning reaction. (Covington, 2010)

The high hydrothermal stability tannages can be described in the following terms: the first component links to the collagen either covalently or via multiple electrostatic interaction such as hydrogen bonding, then the second component reacts with the first, resulting in the locking of the molecules into a matrix around the triple helices. The effect is to make it difficult for the helical structure to collapse when the hydrogen bonding is broken hydrothermally: this is observed as high shrinkage temperature by the link-lock mechanism. Alternatively, the effect of any single tanning agent is merely to hinder such a collapse, so all such reactions result in similar moderate shrinkage temperature increase, practically independent of the chemistry.

If the components of a high shrinkage temperature process are offered in a different order the outcome may be different: the new first component reacts with the collagen, but the second component only reacts with the first component on collagen, no matrix is formed and the net effect is tanning by the first component alone, giving only moderate hydrothermal stability. The focus on high hydrothermal stability is important for many commercial applications of leather, where heat is a necessary part of the manufacturing process, such as heat lasting of shoe uppers or steam pressing of leather garments.

One consequence of the link-lock mechanism is how the notion of ‘crosslinking’ is viewed: this has been a commonly used term, which refers to the direct linking of triple helices, as envisaged by Gustavson. (Gustavson, 1953) That representation of collagen stabilisation has been discredited, if only because of the entropic penalty of such a defined and specific interaction. Link-lock replaces his mechanism with a more general and simpler model of reagent function. (Covington *et al.*, 2008) The concept of crosslinking is not helpful in explaining tanning outcome, indeed it is misleading and counterproductive, so the use of the term should be discontinued.

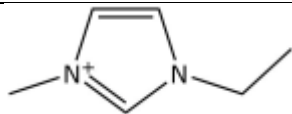
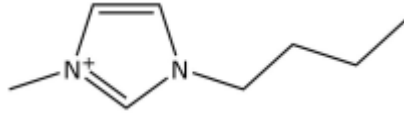
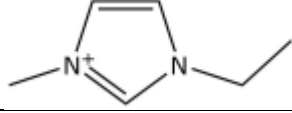
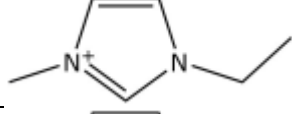
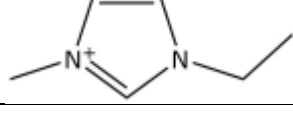
### Post tanning or multi-component processing

It is common in the industry to refer to pretanning, tanning and retanning or post tanning as separate and specific process steps: this is not useful, the terms merely indicate the order of application of whatever reagents. It is more constructive to consider these stabilising reactions as a multicomponent system in which the substrate (raw collagen or chemically modified collagen) and the solvent are two additional components at any stage of the overall process.

The substrate has a role in the chemistry and the outcome of change, because reactions may occur on the collagen in isolation or at reagents already fixed on the collagen creating a changing substrate. These reactions and interactions can be characterised in the following ways: independent, in which case the reagents react with different sites on the collagen nor do they interact with each other; antagonistic, when the reagents compete for reaction sites on the collagen and factors such as order of addition offer and reactivity determine the winner; synergistic, when there is strong interaction between reagents that is more important than their reactions on collagen, when the requirements for the link-lock mechanism are fulfilled.

The aqueous solvent is typically overlooked as a component in the tanning reaction mechanism, indeed it is a powerful driving force leading to the kinetics of reactions and fixation outcome. Some conventional processes already rely on manipulating the solvent properties to achieve the desired outcome, well known in the art, as the following two examples demonstrate. Reactive dyeing depends on a high concentration of neutral electrolyte to provide charges in solution to repel the hydrophobic dye molecules onto the substrate; pickling with ethanolamine hydrochloride ( $\text{HOCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ ), a commercially available option, creates a hydrophobic aqueous medium which drives hydrophilic chromium(III) species onto the charged collagen environment.

Table 2. Melting points of some ionic salts.

Cation	Anion	m.pt. (°C)
$\text{Na}^+$	$\text{Cl}^-$	801
$\text{K}^+$	$\text{Cl}^-$	772
	$\text{Cl}^-$	87
	$\text{Cl}^-$	65
	$\text{NO}_3^-$	38
	$\text{AlCl}_4^-$	7
	$\text{CF}_3\text{CO}_2^-$	-14

The advent of low temperature eutectic liquids and ionic liquids constitute alternative solvents to water (or organic compounds): the latter is exemplified by the data on the effect of crystal lattice energy on the melting point of some ionic salts presented in Table 2, offering the potential to revolutionise tanning processes by matching the properties of the solvent and solute, allowing the use of the chemistries of reagents which currently cannot be used in water or modified aqueous media. (Wise *et al.*, 2015)

It must also be recalled that any fixation reaction on collagen is a contributor to the multicomponent system, since they all rely on exactly the same range of reaction mechanisms that define tanning agents: electrostatic, ionic, covalent, hydrogen bonding and hydrophobic interactions. Hence dyeing, fatliquoring and other specialised processes, such as water and fire resistance treatments should be included in the analytical thinking.

#### (a) Retanning

Retanning can be defined as the conventional tanning process step which follows the primary tanning step, often this is chromium(III) but includes vegetable tannage and increasingly also applies to processes referred to as ‘wet white’, differentiating them from the ‘wet blue’ product of chrome tanning. Wet white tanning typically comprises two components, a syntan and an aldehydic reagent, but usually they are not separated in the jargon to tan and retan; since the processing breaks at this point, the part processed wet white product is then retanned in the conventional sense. Note, the components of the wet white process typically act independently because they are not chosen for their affinity for each other, hence they do not fulfil the criteria for a link-lock reaction and the shrinkage temperature is limited to moderate values.

In terms of the chemistry, there is no difference between retanning and the conventional tanning step: retanning is conducted with a wider range of reagents than main tanning, but that is merely the requirements of the technology involved in making the required leather with its associated properties and performance. The only difference between tanning and retanning, apart from the timing, is the nature of the substrate and the necessity of recognising that the reaction kinetics and outcome are likely to need some modification to the reaction conditions, as indicated above.

Retanning includes specialist steps, conferring such properties as water and fire resistance, which have in the past proved to be difficult to achieve consistently. That is less problematic in the current industry, but the interest in exploiting more exotic, effective and hydrophobic water-sensitive reagents points the way to technologies employing nonaqueous solvents.

#### (b) Dyeing

Colouring chemistry witnessed an explosion of new reagents following the advent of the synthetic dye mauveine towards the end of the 19<sup>th</sup> century. In the modern industry, tanners are familiar with mordant, acid, basic, direct, premetallised, reactive and sulfur dyes and their chemistries. However, there is a mounting problem concerning the environmental impact of some of these reagents, particularly with regard to aromatic amines in the dyes or in their decomposition products. Consequently, alternative colourants are being sought. Notably, aryl carbonium based dyes are contenders: interestingly, the original synthetic dye, mauveine, falls into this class of chemicals, as does Malachite Green shown in Fig.3. Fungal sources of colourants offer novel chemistries, but have yet to be shown to be commercial options. (Covington and Wise 2020b)

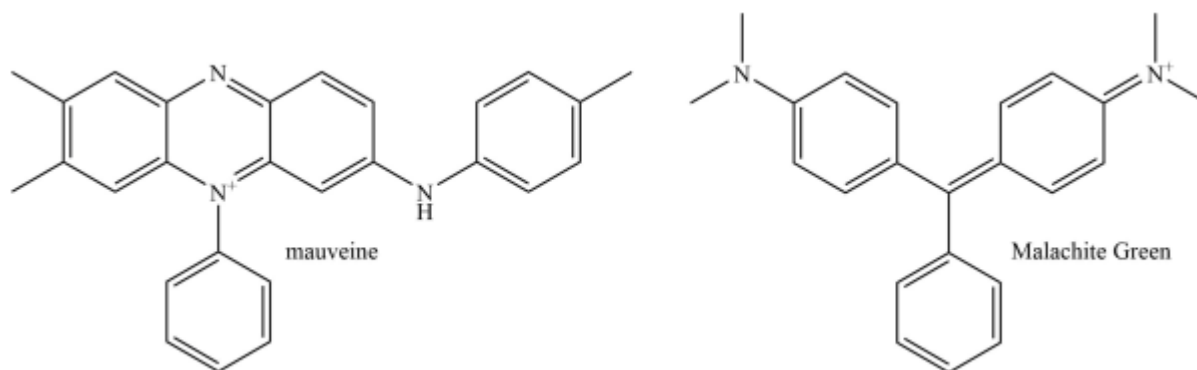


Fig.3. Structures of Mauveine and Malachite Green

### (c) Lubricating

The conventional fatliquoring step, usually the last in post tanning, has not changed much over the decades. Its primary purpose is to prevent fibre sticking during drying, with a secondary purpose of conferring the required degree of softness to the product. Reagents may be of animal, vegetable or synthetic origin, made emulsifiable in aqueous solution by partially sulfating or sulfiting. With the exception of discontinuing the use of sperm whale oil in the latter part of the 20<sup>th</sup> century, the technology has changed little. There are alternative approaches known, each based on the principle of preventing fibre sticking, such as fixing hydrocarbon or derivative chains to collagen or physical separation with inert microspheres, but no technology has superseded the traditional options. (Covington and Wise, 2020a)

#### *Prediction of processing outcome or tanning requirements for desired outcome*

Tanners can to a great extent predict the outcome of experimental processes, providing they understand the principles of multicomponent reactions, the chemistries of the reagents and the technological properties conferred by the reagents. This new view of processing, as a series of interacting fixation reactions, is useful because it means the traditional sequence of reagent additions to the system may not be the most efficient and effective – all process steps should be candidates for change.

Creating new materials, which includes hybrid biomaterials, is most efficiently and effectively achieved by applying a mechanistic approach to proposed processes, which allows accurate prediction of experimental outcomes. By reversing the analysis of predicting process goals, it is possible to start with an idea of desired properties and performance in a new product and to design an appropriate process to achieve those outcomes. (Covington, 2011) This can extend to the development of new reagents and new chemistries, delivered in new solvent media. However, there are limits to what is possible, since the basis of all such developments is the organic substrate collagen.

#### *Finishing*

It is recognised in the leather industry that finishing is a separate technology to the rest of the process. The application of a coating to leather creates a two-component material, in which each contributes to the properties and performance: the finish provides protection to the vulnerable grain surface and can confer a wide range of aesthetic effects to enhance the

commercial viability of the leather, while the leather itself defines the properties that make it a desirable consumer product.

The technology is fundamentally the same as all other coatings – basecoat + topcoat. In leather making, the crucial step is the adhesion between the basecoat and the leather substrate: the chemistries must be compatible to ensure they function as one, then the chemistries of the two components of the finish must be compatible for the durability of the finish layer. The difference between leather finishing and painting for example is the requirement for leather to move and flex in use, making greater demands on the properties of the finish.

Modern options for both layers are urethanes, acrylates, nitrocellulose and proteins: within each type there is a wide range of chemical modifications offered by the supply houses. (Covington and Wise, 2020a) It is a feature of surface coatings that rapid product developments and availability lead to fast changes in leather finishing technology, so this is an area of leather production which cannot be easily defined at any one time.

The big change in finishing technology came towards the end of the 20<sup>th</sup> century, with the elimination of solvent based chemistry in favour of aqueous reagents. The leather industry quickly converted, although development was initially hampered by the total reliance on aqueous chemistry. However, the coming of non-aqueous solvents, ionic and deep eutectic solvents, opens up the possibility of using new and more reactive reagents in finishing for new leather properties.

## **Overview**

The keys to success in the modern leather industry are getting the science right and providing practitioners with the understanding of how that science can lead to workable new technologies.

A feature of the technology currently defining the sustainability of the global leather industry is keeping ahead of the competition, by maintaining the economic viability and constantly rebuffing the attacks directed at the industry from many sides. In order to do so, the environmental impact of processing must be constantly addressed, properties and performance of leather products must be improved to conform to the increasingly discerning market and new collagenic materials for new markets must be devised and created. Understanding the principles of leather science will allow these developments to be undertaken efficiently and effectively.

Whilst it is not yet necessary for the leather industry to undergo a revolution, nevertheless it is useful to know that we have the paradigm tools for it to happen ...if and when required.

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