CHAPTER 15

Post Tanning

15.1 DEFINITION

The term 'post tanning' refers to the wet processing steps that follow the primary tanning reaction. This might refer to following tannage with chromium(III), as is usually the case in industry, but equally it applies to vegetable tanning or indeed any other tannage used to confer the primary stabilisation to pelt. The combination of post tanning processes may not always be the same for all tannages: the choice of post tanning processes depends on the primary tannage and the type of leather the tanner is attempting to make. In all cases, post tanning can be separated into three generic processes:

1. Retanning: This may be a single chemical process or may be a combination of reactions applied together or more usually consecutively. The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. The effects are dependent on both the primary tanning chemistry and the retanning reactions.

   Retanning can involve many different types of chemical reactions. These include mineral tanning with metal salts [including chromium(III) applied to chrome tanned leather], aldehydic reagents, hydrogen bondable polymers, electrostatic reactions with polymers or resins or any other type of synthetic tanning agent (syntan).

2. Dyeing: This is the colouring step. Almost any colour can be struck on any type of leather, despite the background colour, although the final effect is influenced by the previous processes.

   Colouring almost invariably means dyeing. Applying dye in solution or pigment, to confer dense, opaque colour, can be performed in the drum or colouring agents may be sprayed or spread by hand (padding) onto the surface of the leather.

3. Fatliquoring: This step is primarily applied to prevent fibre sticking when the leather is dried after completion of the wet processes. A secondary effect is to control the degree of softness conferred to the leather. One of the consequences of lubrication is an effect on the strength of the leather (Chapter 17).

  Fatliquoring is usually conducted with self-emulsifying, partially sulfated or sulfonated (sulfited) oils, which might be animal, vegetable, mineral or synthetic. This step might also include processing to confer to the leather a required degree of water resistance.

15.2   RELATIONSHIP BETWEEN TANNING AND POST TANNING

In the whole of leather making, each step in the process affects all subsequent steps and none more so than the impact of tanning on the post tanning reactions. Table 15.1 illustrates the nature of tanning reactions and their possible effects by the following types of reaction.

Modification of collagen by the chemistry of the tanning agent(s) affects the following features of the properties of the new material:

1. The hydrophilic–hydrophobic balance of the leather is markedly affected by the chemistry of the tanning agent, because it is likely to change the relationship between the leather and the solvent, which in turn will affect the equilibrium of any reagent between the solvent and the substrate.
2. The site of reaction between the reagent and the collagen will affect the isoelectric point of the collagen and consequently there will be a different relationship between pH and charge on the leather. The lower the isoelectric point, the more anionic or less cationic the charge on the pelt will be at any pH value: the higher the isoelectric point, the more cationic or less anionic the charge on the pelt will be at any pH value.
3. The relative reactions at the sidechains and the backbone of the protein will determine the type of reaction and hence the degree of stability of the tannage: the fastness of the reagent will influence the interaction between reagents and the substrate. Here, the important factors are the effects of free tanning agent and charge on the leather: reactions by covalency, electrostatic interaction, hydrophobic interaction and hydrogen bonding will all have effects on leather properties.

The nature of the tanning agent will impact differently on the different aspects of post tanning:

1. Retanning may involve interaction with the first tanning agent or it may be independent, because the chemistries are incompatible or the reactions sites may be different.
2. Dyeing outcome depends on the chemistry of the dye and the chemistry of the substrate. They may work together, as is the case of metal mordanting, or colouring may be adversely affected by similarity of chemistry, such as

Table 15.1 Categorisation of tanning reactions.

| Tannage | IEP | HHB | | Charge | Reaction sites | Bonding |
		Tanning agent	Leather			
Mineral	Higher	Hydrophilic	Hydrophilic	Cationic	CO_2^-	Electrovalent
Chromium(III)	Higher	Hydrophilic	Hydrophobic	Cationic	CO_2^-	Covalent
Aldehydic	Lower	Hydrophilic	Hydrophilic	Neutral	NH_3^+	Covalent
Syntan	Lower	Hydrophilic/Hydrophobic	Hydrophilic	Neutral	NH_3^+, amide	Electrovalent, H-bonding
Vegetable	Lower	Hydrophobic	Hydrophilic	Neutral	NH_3^+, amide	H-bonding, hydrophobic
Oil	No change	Hydrophobic	Hydrophilic	No change	None	None, hydrophobic

syntan tanning, or the colour may be 'saddened'. The HHB (hydrophilic–hydrophobic balance) properties of the substrate will influence the uptake of dyes, because the dyes can exhibit the full range of HHB properties.

3. Fatliquoring has two aspects that can be influenced by the substrate. First, there is the question of depositing the neutral oil by damaging the emulsification mechanism. This is clearly affected by charge, but also by the availability of charged sites on the leather. Second, there is the degree of compatibility of the neutral oil with the HHB properties of the leather, modified by the particular chemistries of the previous process steps.

15.3   CHROME RETANNING

A common retannage for chrome tanned leather is more chrome tanning. This raises the question: why? It is not obvious why the leather should be rechromed, when the reaction could have been completed during primary tanning. Possible reasons are as follows:

1. To increase the shrinkage temperature.

    Since rechroming is typically conducted with an offer of about 1% Cr_2O_3 (4% chrome tan powder) or less, *i.e.* half or less than the original offer, usually over a period of about an hour, *i.e.* an order of magnitude shorter than the original tanning process, it can be understood that the effect of retanning is going to be much less than the original reaction. Moreover, the time allotted is unlikely to result in an effect through the cross section. Therefore, the retannage is more to do with an effect on the surfaces.

    It is a common experience that rechroming has little or no effect on the shrinkage temperature of the final leather. This is understandable, because of the conditions and the resulting change in chrome content contributes little to the tanning effectiveness.

2. To increase the chromium content.

    For many applications of chrome tanned leather, the specification typically includes the requirement for 4% Cr_2O_3 on dry weight, *e.g.* defence specifications. Note, this is a sort of quality assurance specification, because at that level of chrome the tannage is *likely* to be complete and the shrinkage temperature is *likely* to be $>100\,°C$. Note, too, there is no guarantee that those properties will be met – it is possible to fix that amount of chrome and still obtain a shrinkage temperature considerably lower than $100\,°C$.

    From the conditions of retannage set out above, the fixation of chrome is not going to be as effective as the primary reaction. Indeed, it is possible to discharge more chrome in the effluent stream than is offered in the retannage, by not fixing much chrome and by stripping chrome from the wet blue during retanning!

3. To even up the colour.

    When bovine wet blue is split, it is common to observe variations in colour over the split surface. Whilst this may not adversely influence the

overall properties and performance of the leather, cosmetically it looks better to make the colour more even or uniform.

Rechroming is often used if wet blue is purchased from different sources, in an attempt to make the colour more uniform between batches of leather.

4. To change the reactivity of the leather.

Incorporating fresh chrome into aged wet blue has the effect of creating new cationic sites, which might be useful in fixing anionic reagents later in the post tanning process. More fundamentally, the isoelectric point (IEP) will be moved to a higher value, so that at any pH the charge on the leather is either less anionic (negative) or more cationic (positive) than the unretanned leather. This too will influence the reactivity towards the post tanning reagents, which are often anionic.

Note, the effect of IEP is more important than the introduction of cationic charges, because they can be discharged chemically, whereas the influence of IEP with pH on the charge of the leather is a permanent effect.

5. To modify the properties of the leather.

Fixing chrome under conditions at the limits of basicity in solution means that polymeric chrome is bound to collagen (Chapter 11). In this way, a degree of filling and softening is achieved, without using reagents that might adversely affect light fastness or water resistance, *etc*. However, considering the amount of chrome likely to be fixed, the effect will be small.

15.4   SEQUENCE OF POST TANNING STEPS

Whilst there are very many variations on the procedures within post tanning processes, in general they tend to conform to the following sequence: retanning then dyeing then fatliquoring.

The rationale can be expressed as follows:

- Retanning may not only modify the properties of the leather, but will typically also modify the reactivity of the pelt towards other reagents. Even if the processes do not include specific reactions to assist uniform colouring, it is possible to achieve such a side effect as a bonus. Alternatively, if the retannage includes mineral reagents, they may also have a mordanting effect on the dyeing step, to achieve modified colour or better fixation (Chapter 16).
- Dyeing comes next, to take advantage of the changes to the reactivity of the pelt conferred by additional tanning. The relationship between dyeing and fatliquoring is controlled by the requirements of the dyeing compounds for reactivity towards the substrate. This reactivity is partly dependent on the HHB characteristics of the substrate, which can be positively or negatively modified by the presence of hydrophobic species such as fatliquors.

- Fatliquoring usually comes last, in order not to interfere with the colouring reaction. In particular, if the lubrication step includes reactions to confer water resistance, this can create a barrier to reaction of aqueous reagents with the collagen, so it must be done just prior to drying.
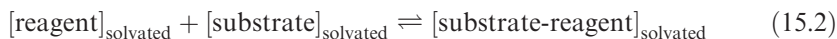
15.5 PRINCIPLES OF POST TANNING

15.5.1 Mechanisms of Post Tanning

All the post tanning process steps involve the fixation of a solute in solution onto a solid substrate. The reactions are made more complicated by the fact that the tanner is dealing with a substrate that has finite thickness. Therefore, to control the outcomes of these steps, it is necessary to understand the parameters that come into play. First, it is important to understand that there is a general mechanism that must be taken into account, which is the steps by which fixation occurs; this was introduced in Chapter 11. The steps involved in any general reaction in which a reagent in solution is fixed onto a solid substrate, *e.g.* in the heterogeneous system of post tanning, may be defined as follows:[1,2]

1. Transfer of the reagent from solution into the substrate;
2. Hydrophobic bonding;
3. Electrostatic interaction between the reagent and the substrate;
4. Covalent reaction between the reagent and the substrate.

The first controlling factor can be expressed as follows:

$$\text{reagent} + \text{solvent} \rightleftharpoons [\text{reagent}]_{\text{solvated}} \tag{15.1}$$

$$[\text{reagent}]_{\text{solvated}} + [\text{substrate}]_{\text{solvated}} \rightleftharpoons [\text{substrate-reagent}]_{\text{solvated}} \tag{15.2}$$

$$\text{favoured} \leftarrow \text{disfavoured}$$

$$\text{disfavoured} \rightarrow \text{favoured}$$

The position of the equilibrium for Equation (15.1) depends on the affinity of the reagent for the solvent. This is analogous to partitioning a solute between two immiscible solvents, where the equilibrium constant of transfer is analogous to the partition coefficient (see below). In the case of water as the solvent, the equilibrium is defined by the degree of hydrophilicity or hydrophobicity of the solute/reagent. This has been defined as the hydrophilic–hydrophobic (HHB) or hydrophilic–lipophilic (HLB) balance. This property is conventionally measured by chromatography in various solvents, ranging from water to petroleum ether (also known as 'light petroleum'), *i.e.* highly polar to highly non-polar. Figure 15.1 shows the principle of liquid chromatography, in which the solvent travels upwards, taking the reagent with it. The fraction of the way from the initial position of the reagent spotted on the paper or thin layer plate to the solvent front is referred to as the R_{f} value and this is a measure

Closed chromatography jar

Solvent front

Final position of reagent

y   x

Initial position of reagent

solvent

Rf = $\frac{x}{Y}$
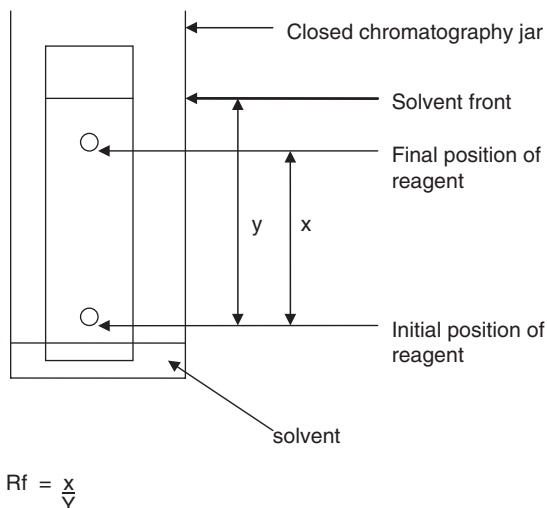
Figure 15.1   Representation of the liquid chromatography method for measuring the hydrophilic–lipophilic balance.

of the affinity of the reagent for the solvent. The closer the R_f value approaches 1.0, the higher the affinity of the reagent for the solvent.

Transfer from the solvent to the substrate will depend on whether the reagent is charged and whether the substrate is charged. This will affect the interaction with the solvent, particularly if the solvent is polar, such as water. Therefore, the relative charging of the reactants will influence the relative affinities of the solute for the solvent and for the substrate. This can be distinguished from the role of electrostatic attraction or repulsion, which determines the rate of fixation, following transfer from solution into the substrate.

It must follow that the equilibrium for Equation (15.2) can be altered by changes to each component of the equilibrium:

1. Changing the HHB/HLB value of the reagent will alter its relative affinity for the solvent *versus* the substrate. This might be done using the chemistry of the reagent itself or by changing the reagent for one with a more appropriate HHB/HLB value.
2. Changing the chemistry of the substrate will alter the relative affinity of the solute for the substrate *versus* the solvent. This might be achieved by manipulating the chemistry of the substrate: possibilities include chemical modification and charge change. Alternatively, the HHB/HLB value of the substrate may be changed by applying hydrophilic or hydrophobic reagents, *e.g.* water resistance fatliquor.
3. Changing the solvent will alter the position of the first equilibrium, with a consequent change to the relative affinity of the solute for the substrate. This change can be in either direction, depending on the nature of the change made to the solvent. Water can be made more or less polar by

the presence of neutral electrolyte. Similarly, any other solvent can be modified by the presence of other components, such as solutes or other solvents. Ultimately, the solvent itself can be substituted.

While reviewing the principles of tanning and advanced aspects of tanning, and especially post tanning, examples of all these possibilities will be encountered. An understanding of the variables in these reactions is a powerful tool for future developments in leather technology.

The equilibrium for Equation (15.2) depends on the relative affinities of the reagent/solute for the solvent and the environment within the substrate. That is, a hydrophilic reagent will tend to remain in solution, because it interacts favourably with water. In contrast, a hydrophobic reagent will not be as soluble in water and will tend to move into a more hydrophobic environment, into the substrate. The degree to which this happens and the rate of transfer depend on the magnitude of the HHB/HLB value of the solute and the properties of the solvent.

The concept of transferring a solute is familiar to chemists in the form of partitioning between two solvents in the technique of solvent extraction. The notion can be extended to the free energy of transfer between two solvents, which determines the degree of preferential solvation when a solute is dissolved in a binary solvent.[3]

The step of hydrophobic bonding is essentially a special case for aqueous solution. If the driving force for transfer is dominated by the hydrophilic nature of the reagent, the first mechanism of reaction may be hydrophobic bonding. This has been suggested as the route of plant polyphenol fixation (Chapter 13). Such bonding is likely to change to hydrogen bonding as its equivalent of the electrostatic interaction.

The concept of transfer from solvent to substrate should not be confused with the notion of penetration through the cross section of the substrate. Tanners are constantly dealing with heterogeneous systems and balancing the rate of penetration with the rate of fixation. This is consistent with the model of stepwise reaction between a reagent and a substrate. Penetration is a consequence of favourable reagent–solvent interaction. The more favourable this is, or the more soluble the reagent is in the solvent, the less favoured is transfer, so the reagent can penetrate through the substrate cross section. Fixation is a consequence of favourable transfer into the environment of the substrate. Since the rate of transfer of a reagent is affected by the HHB/HLB value, the reagent properties also affect the nature of the reaction. All reactions are dependent initially on some form of charge-charge interaction. So, because electrostatic interactions are fast, reaction between the substrate and the reagent is initiated by the rate-determining step of transfer. Therefore, fast uptake means surface interaction, rather than penetration into the cross section of the substrate. This has many implications in different processes in leather making, not only for the science of reaction efficiency, but also for the technological outcome.

The extent to which covalent reaction applies depends entirely on the chemistry of the reaction and may not apply at all. All chemical reactions result in bonding

that lies somewhere on the scale between pure electrostatic and pure covalent. Few lie at the extremes, but it is clear that most reactions can readily be designated as one or the other.

15.5.2 Role of the Isoelectric Point

The concept of an isoelectric point in proteins was introduced in Chapter 1, where it was shown that it could be defined as follows:

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

There are two points, relating to isoelectric point and its particular relevance to post tanning, that are very important and worth emphasising:

1. IEP is a point on the pH scale, so it does not change with changing pH of the system. The IEP of collagen is the same whether it is in the limed state or in the pickled state. The importance of this point is that the isoelectric point can only be changed if there is a chemical change that alters the availability of active groups.

   In the context of charge on leather, care must be taken in ascribing the influence of charged reagents. For example, treating collagen with cationic chromium(III) species may be regarded as altering the IEP, because it may introduce positive charge. Whilst the introduction of charge is true, notably, the charge can be lost by treatments other than pH change. From this point of view, the charge is immaterial as far as the IEP is concerned, although the binding of chromium(III) clearly impacts on the IEP, by removing some carboxyl function from the IEP determining ratio.

   In the context of charge as a function of pH, the definition of IEP must be applied correctly. The introduction of charged species into the substrate clearly can influence the overall charge and hence modify the reactivity of the substrate towards specified reagents. An example is polycationic species as dye intensifying agents (Chapter 16).
2. The charge on collagen is determined by the relative values of the IEP and the pH. If the pH is higher than the IEP, the collagen is negatively charged, and if the pH is lower than the IEP, the collagen is positively charged. Moreover, the further the pH is from the IEP, the greater the charge. The clear consequence is the effect on the affinity of reagents that rely on charge for fixation to the leather. This can be modelled as shown in Figure 15.2, which also shows the effect of moving the isoelectric point.

From the model in Figure 15.2, it can be seen that the effects of moving the isoelectric point are as follows:

- Change to higher IEP: at any pH value the charge on the protein/leather is either less negative or more positive, depending on which side of the IEP is considered.
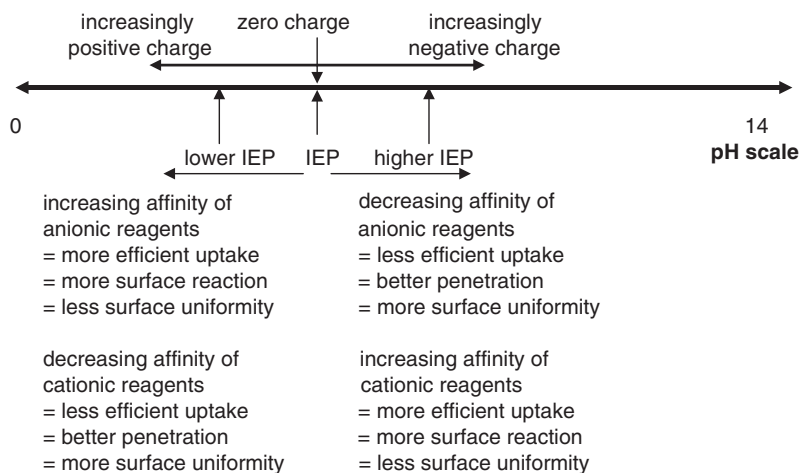
Figure 15.2 Relationship between pH and charge, governed by the isoelectric point.

- Change to lower IEP: at any pH value the charge on the protein/leather is either less positive or more negative, depending on which side of the IEP is considered.

The effects of charge on an electrostatic reaction can be understood from the simple relationship:

$$\text{rate} \propto [\text{reagent charge}]^{a}[\text{substrate charge}]^{b}$$

where the rate refers to the rate of the fixation reaction, which will be controlled by the magnitudes of the charges, because they determine the degree of attraction. Clearly, if the charges are different, the affinity is favoured: this results in fast uptake, with a limitation on the degree to which the reagent can penetrate the substrate. In contrast, if the charges are the same, the affinity is disfavoured: the reaction is slowed, because of the availability of reaction sites, so penetration is favoured. The measurement of the magnitude of the charge on leather is not easy. Attempts have been made to use charged dyes to determine charge interactions, but not with much success. In the context of processing, the best we can do currently is to estimate the overall effect of the accumulation of change. In native collagen, charge as a function of pH will reflect the swelling curve, since there is some cause and effect. The swelling is also influenced by osmosis and lyotropy, and may even be controlled by those mechanisms, depending on the specific conditions in solution.

The direction of change in IEP is known for most leather-making process steps or can be judged from the reaction if conflicting reactions occur, such as in dyeing with premetallised dyes. However, in the absence of direct data on the change in IEP, the change may be estimated from the nature of the reaction and bearing in mind the typical offers of the reagents. The starting point is the IEP

Table 15.2 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	Covalent bonding	Estimate $\Delta IEP=-1.0$
Vegetable tannin	Electrostatic bonding	Estimate $\Delta IEP=-0.5$
Syntan	Electrostatic bonding	Estimate $\Delta IEP=-0.5$
Resin	No effect	Estimate $\Delta IEP=0$
Dye reactions:		
Acid dye	Electrostatic bonding with NH_3^+	Estimate $\Delta IEP=-0.5$
1 : 1 Premetallised dye	Metal complexation at carboxyl, sulfonate reaction at amino	Estimate $\Delta IEP=+0.5$
Reactive dye	Covalent reaction with NH_2	
	Electrostatic reaction with NH_3^+	Estimate $\Delta IEP=-1.0$
Fatliquor, sulfo reaction at amino	Electrostatic bonding	Estimate $\Delta IEP=-0.5$

of raw collagen, the accepted change by liming and Gustavson's measurement of the effect of chrome tanning.[4] Table 15.2 gives estimates of the effects of post tanning. The numbers have to be estimates, because, although it can be accepted that covalent reaction will have a certain effect on the value of IEP, it is not known how electrostatic reaction influences the value. This is because it must be assumed that a pH change can have a reversing effect on the interaction and hence the group on the protein may still be counted in the calculation of the IEP ratio. In addition, the influence of introducing charge is also not known. Using the model of Table 15.2, the changes in isoelectric point might be estimated as shown in Table 15.3, starting with chrome tanned leather with IEP 7.0, retanning with only one reagent, dyeing with only one type of dye, then fatliquoring. Furthermore, the changes to IEP will depend on the amounts of reagents bound to the leather: here the estimates are generalised, assuming typical processing. It is assumed that the effects of reagents on IEP are accumulative.

The likely scenario in post tanning is that the IEP will gradually move down, from pH 7 to pH 5–6. Therefore, at any given pH, the leather will be less positive or more negatively charged than it was before. In other words, the leather has less and less affinity for anionic reagents, so penetration of these reagents is favoured. However, variations in this pattern must be recognised, especially when using premetallised dyes or if large offers are made in the process step.

Table 15.3 Estimated changes in isoelectric point, starting with chrome tanned leather at 7.0, then retanning, dyeing (1 : 1 premetallised dye, acid dye or reactive dye) and fatliquoring.

						Retan					
Aldehyde			*Syntan*			*Vegetable*			*Resin*		
6.0			6.5			6.5			7.0		
Dye											
1 : 1	**Acid**	**Reac.**	**1 : 1**	**Acid**	**Reac.**	**1 : 1**	**Acid**	**Reac.**	**1 : 1**	**Acid**	**Reac.**
6.5	5.5	5.0	7.0	6.0	6.5	7.0	6.0	5.5	7.5	6.5	6.0
Fatliquor											
6.0	5.0	4.5	6.5	5.5	6.0	6.5	5.5	5.0	7.0	6.0	5.5

15.5.3   Role of the Peptide Link

When considering the properties of collagen, reactions at the peptide link are important, since the link is the most common feature of protein structure. Hence, its susceptibility to hydrolysis is a feature of beamhouse processing. In the case of post tanning processing, its role depends on its ability to engage in fixation reactions. As described in Chapter 1, the bond can be drawn in two ways, showing that charge is separated between the amino and carbonyl groups. This means that the peptide link can engage in two types of bonding with incoming reagents (Figure 15.3):

- Hydrogen bonding: the presence of a negative charge on the oxygen allows hydrogen binding with an active hydrogen bearing group.
- Electrostatic bonding: the presence of positive charge on the nitrogen allows electrostatic bonding with anionic species.

The versatility of the reactivity of proteins originates from the partially charged nature of the peptide group. Despite the limitations of the partial charge, the peptide links have a powerful effect, because their concentration is higher than the other obvious reaction centres on the sidechains. The contents of carboxyl groups and amino groups in dry collagen are 1.0 and 0.6 moles per kg dry weight and may be compared with the amount of peptide links as follows.

The molecular weight of the triple helix is 300 000, containing 3000 amino acids. Consequently, collagen contains ten amino acids per kilogram, equivalent to nine peptide links. Therefore, there is an order of magnitude more peptide links than carboxyl groups and 15 times more than amine sidechains.

15.5.4   Role of the Sulfonate Group

A chemical theme that runs through the whole of the post tanning reactions is the role of the sulfonate group. This theme is expanded in the individual sections below. Reagents that typically carry sulfonate groups include:

- syntans;
- modified vegetable tannins;
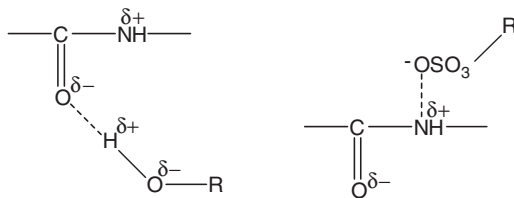
Figure 15.3   Illustrations of bonding at the peptide link.

- dyes: acid, basic, direct, premetallised, reactive;
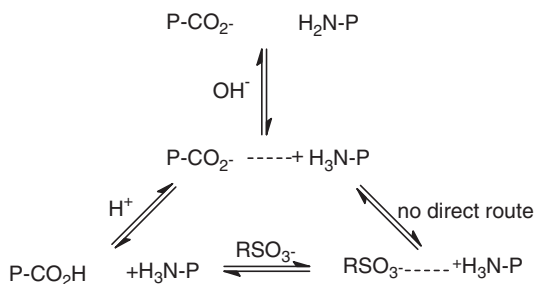- fatliquors: sulfated fatliquors included.

In each case, the mechanism of fixation is the same. An electrostatic reaction can take place between the anionic sulfonate group and the protonated amino group. However, this can only happen when the collagen is acidified, to create the cationic group. Above the isoelectric point, there are no cationic centres for reaction. At the isoelectric point, the cationic groups are locked together with the anionic carboxyl groups: it is only when the salt links are broken by acidification that reaction with sulfonate can occur. The carboxyl groups are not in competition with the sulfonate groups, because the weak carboxylic acid groups become protonated, as the mechanism of breaking the salt link. This is the reason that acid dyes are so-called, because they are fixed by acid. Figure 15.4 sets out the general reaction mechanism.

The mechanism of sulfonate fixation has sometimes been wrongly rationalised in terms of protonation of the sulfonate group, particularly as the mechanism for lowering the emulsifying power of the sulfo fraction of fatliquors (Chapter 17). However, it is important to recognise that the mechanism actually does not include protonation of the sulfonate group: it is much too strong for that to happen under the aqueous conditions of leather making (Chapter 9). A practical demonstration of the strength of sulfonate group is to try to create a non-swelling acid from an auxiliary syntan by acidification, *i.e.* the reverse of the reaction to create a syntan from a sulfonated compound. The reaction can only be made to work in concentrated sulfuric acid, a solvent that cannot be regarded as aqueous.

15.5.5   Coordinating Post Tanning Processes

Creating a process for post tanning is not a case of merely putting together the steps for applying the required reagents in the right order. The following considerations must be addressed, applying to every reagent that the tanner intends to fix onto the leather:

1. Surface reaction or penetration?
2. The required degree of penetration down the hierarchy of structure.
3. The requirement for uniformity of reaction: through the cross section and over the surfaces.

P-CO$_2$-   H$_2$N-P

OH$^-$

P-CO$_2$- -----+ H$_3$N-P

H$^+$ no direct route

RSO$_3$-

P-CO$_2$H   +H$_3$N-P ⇌   RSO$_3$------+H$_3$N-P

Figure 15.4 Mechanism of sulfonate fixation on collagen (P = protein).

4. The amount and suitability of the reagent necessary to achieve the requirement.
5. The rate of reaction, *i.e.* the process time yielding optimum efficiency and hence cost effectiveness.
6. The affinity of the reagent for the substrate and consequent fastness properties.

The specific nature of each reagent and its function must be considered, in the light of the following features of post tanning processing:

1. Is this the best reagent for the purpose, using any criteria – cost, efficiency, safety, environmental impact, *etc.*?
2. Are there any options for 'compact processing', *i.e.* combining more than one process step into a single step (Chapter 20)?
3. Do the process steps interact to create synergy, *i.e.* obtaining effects greater than the sum of the parts, *e.g.* one reagent influencing the fastness of another or together producing a new interacting species on the substrate that contributes to the leather stability in some way?

The following variables must be considered, to achieve the required outcome:

1. Compatibility of the reagent for the substrate, *i.e.* the status of the substrate at any point in the process: it is not enough to consider the tanned starting material, it is important to consider how previous processes have modified the leather.
2. Compatibility of the reagent not only for the leather modified by previous processes, but also for subsequent reagents.
3. Role of isoelectric point: although the relationship between processing and quantitative change to IEP is not known with any precision, the direction of change due to reagent reaction can be judged qualitatively.
4. Role of pH: The relationship between pH and the isoelectric point determines the charge on the leather. This controls transfer of the reagent onto the leather and the initial electrostatic interaction.

5. Role of HHB/HLB value: The value for the leather will change as post tanning progresses. Whilst value changes may not be available, qualitative judgements about the directions of change can be made.

15.6   COMPACT PROCESSING

The conventional components of post tanning are neutralisation, retanning, dyeing and fatliquoring: in each case, an industrial process will use one or more agents of that type. However, in post tanning it is possible to combine process steps, to create 'compact' processing.[5] Here the principles of compact processing will focus on simple combinations of agents. The permutations and combinations are as follows, limited to a degree by the order in which they might have to be applied:

- neutralise + retan
- retan + dye
- retan + fatliquor
- dye + fatliquor
- retan + dye + fatliquor

15.6.1   Neutralise and Retan

This is conventional technology, in which neutralising syntan can achieve both required outcomes at the same time. The mechanism relies on enough basifying power to raise the pH to the required level and sufficient tanning power to lower the isoelectric point enough to ensure the pelt is adjusted to be anionic.

15.6.2   Retan and Dye

The concept for this process is to colour the leather, whilst conferring a retanning effect. Here, it might be assumed that the neutralising process will be separate, as the chemistries of the processes are likely to be different. In post tanning the retanning process is usually applied to modify the leather properties, especially the handle and the uniformity of handle over the hide or skin. However, the consequence for hydrothermal stability is typically relatively unimportant, because that is taken care of by the chrome tanning.

A commercial option available is the use of vegetable tannin, modified by fixing dye to the polyphenol. This has been done by Forestal Quebracho. The range of colours is limited and the presence of the vegetable tannins inevitably saddens the colour struck on the leather. An alternative approach is to use the chemistry of melanin formation:[6] using model reactant polyphenols and the aid of polyphenol oxidase, it is possible to achieve a tanning reaction and develop colour at the same time (Chapter 16).

The chemistry of dyeing itself might be considered to be a retanning reaction, depending on the type of dye, which determines the nature of the binding interaction with leather, and the offer. The use of reactive dyes would

clearly constitute a form of retanning, because they bond to basic sidechains *via* one or two covalent links. The effect will depend on the amount of reactive dye and the ability of the structure to interact with the aqueous supramolecular matrix.

15.6.3 Retan and Fatliquor

The concept in this combination is for the retanning reaction to lubricate the fibre structure, to prevent fibre resticking during drying and to soften the leather. To a degree this can be considered conventional technology, because polymeric tanning agents often confer softness, *e.g.* vegetable tannins, replacement syntans, resins and acrylate polymers. However, in some cases the tanning effect is weak: synthetic resins and polymers can bind to the collagen in a useful way, but may contribute nothing to the stability of the leather. Some specialist polymers, *e.g.* the water resistance acrylic esters, certainly confer softness and their complexing reaction with bound chromium(III) might be considered to be a version of retanning.

15.6.4 Dye and Fatliquor

The concept of this combination is to colour the leather at the same time as introducing lubrication. To date, there is no industrial product available to do this. However, such a concept is not impossible. It might be accomplished by using highly hydrophobic dyes (which do exist) and delivering them through the cross section by an appropriate emulsification system. The drawback is the use of expensive dyestuff deep within the fibre structure, where its presence does not contribute to the perception of colour. However, such a combination might be useful in the contexts of grain layer or suede leather lubrication.

   If this type of combination is desirable, using conventional dyes and fatliquors together, the compatibility of the components must be considered. One way of looking at the problem is to consider the impact of one reagent on the other:

> current operation: → compact processing: → alternative processing :
> dye then fatliquor → dye with fatliquor → fatliquor then dye

   Looking at the problem in this way highlights the effect of hydrophilic–hydrophobic balance (HHB) on the affinity of the dye for the substrate. Any change from current processing will tend to make the substrate more hydrophobic than before, therefore changing the outcome of dyeing. Therefore, if compacting means merely combining the two steps of dyeing and fatliquoring, it is clear that the dyes will have to be changed to meet the new requirements of the substrate.

15.6.5 Retan, Dye and Fatliquor

The concept of this combination is to conduct the whole of post tanning in a single step. It is possible that all these requirements could be met in a single

chemical reagent. As a beginning, Gaidau *et al.*[7] have described a compatible mixture for aqueous processing.

However, the concept does raise the question of the role of the solvent. If the tanner could use a more exotic solvent, to solubilise simultaneously a wider range of reagents than is possible in water, it might be feasible to apply all of them at once. A candidate solvent is liquid (supercritical) carbon dioxide. According to the choice of solvent, there may be no need for neutralisation. Alternatively, neutralisation may have to be retained as an aqueous process, to achieve the charge required by the new mixed process.

15.7   ROLE OF PROCESSING ON LEATHER PROPERTIES: DYNAMIC MECHANICAL THERMAL ANALYSIS

Although the basic properties of leather are created by the earlier processes in the beamhouse and in tannage, the properties are considerably modified by the latter processes of retanning and fatliquoring. Collagenous materials are viscoelastic:[8] that means they exhibit viscous properties, when they resist shear forces, and elastic properties, when they return to the original state when a stress is released. These properties can be measured by dynamic mechanical thermal analysis (DMTA) (Figure 15.5), which is introduced in Chapter 13.

Figure 15.5   Working head of DMTA apparatus, showing the sample locked at each end and the oscillating mechanism operating in the middle.

The technique is based on measuring the way in which the response or strain of a material lags behind a deforming stress: the modulus of the material, λ, is measured as the conditions change:

$$\lambda = \text{stress/strain} = \text{(force per unit area)/(ratio of change to original state)}$$

When the stress in sinusoidal, the lag phase, δ, will lie between $0°$ for a perfectly elastic material and $90°$ for a perfectly viscous material. The time lag between the displacement and response, the damping effect, is measured as $\tan \delta$. If the amplitude of the applied stress is σ_0 and the amplitude of the subsequent strain is ε_0, the storage modulus, E', is calculated as follows:

$$E' = (\sigma_0/\varepsilon_0) \cos \delta$$

The loss modulus, E'', a measure of the irrecoverable energy due to internal molecular motion is calculated as follows:

$$E'' = (\sigma_0/\varepsilon_0) \sin \delta$$

$$\tan \delta = E''/E'$$

Proteinaceous materials can exhibit glass transitions, when there is a change in physical properties at a particular temperature: above the T_g, the material has liquid/rubbery properties and consequently the molecules have high mobility; below T_g, the material has amorphous/solid, glassy properties and consequently the molecules have low mobility. Glass transitions can be detected by a shift in the baseline of differential scanning calorimetry, when endothermic and exothermic changes in a sample can be measured as a function of temperature or heating rate (Figure 15.6).

Collagen has been regarded as a semi-crystalline material due to the presence of disordered regions, revealed by X-ray diffraction.[9,10] For this reason, leather may be expected to show thermal properties associated with both crystalline and amorphous materials. Some researchers regard the shrinkage temperature as melting of the crystalline regions, whereas the glass transition temperature is associated with amorphous region of leather fibres.[11–13] Recently, Cot *et al.* have reported the presence of a glass transition in leather tanned with chromium(III) salt: it was found to be approximately 45 °C, for leather conditioned at 65% relative humidity at room temperature.[14,15] Odlyha *et al.* have reported two transitional events below the shrinkage temperature and they associated these transitions with relaxation of the polypeptide chains of collagen, considering collagen as a block copolymer.[16,17] The viscoelastic transition temperatures of leather, which may give practical information regarding physical performance, have typically not been measured and characterised.

Figure 15.7 displays a typical DMTA response of a leather conditioned at 0% RH and shows three tan δ peaks of interest, labelled α, β and γ, associated with energy dissipation during stressing. Here, the β peak is assigned to the glass transition and the α peak is assigned to the shrinking related transition.[18]

^exothermic
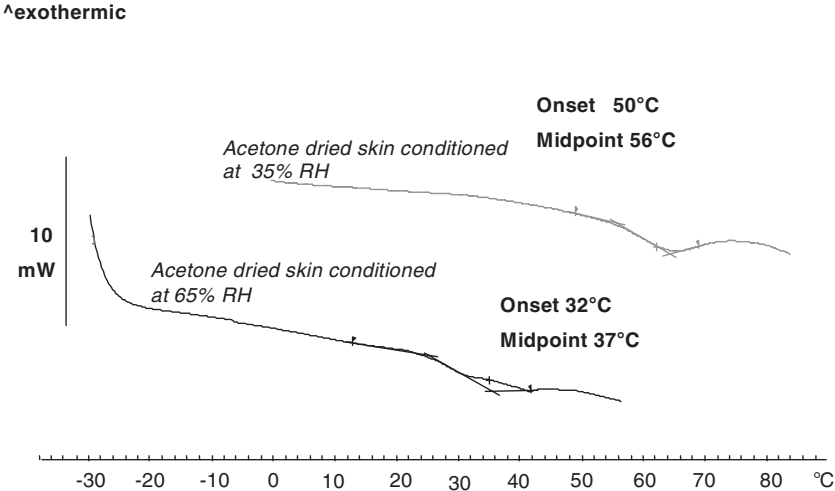
Figure 15.6   DSC thermograms of acetone-dried skins, conditioned at 35% and 65% RH, heated at $20\,°C\,min^{-1}$, showing the base line shift indicating the glass transition temperatures.
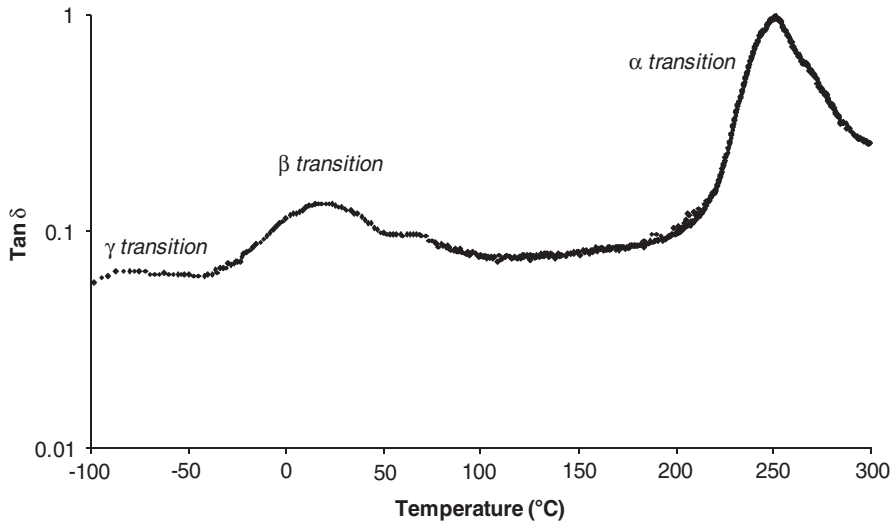

Figure 15.7   Typical DMTA thermogram of a leather tanned with vegetable tannin, conditioned at 0% RH.

When α and β peak temperatures are plotted against wet shrinkage temperature obtained by DSC only the α peak temperatures show a correlation with shrinking transition (Figure 15.8).

Figure 15.9 presents the dynamic mechanical properties of chrome and vegetable tanned calfskin leathers, compared with acetone-dried untanned
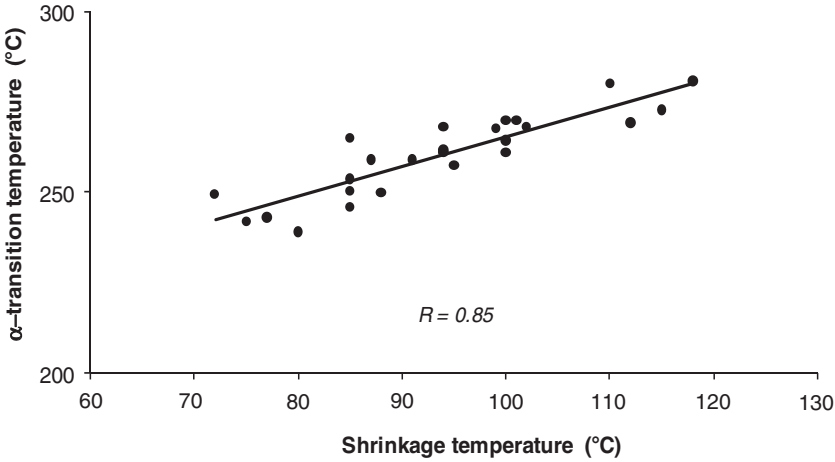
Figure 15.8 Relationship between wet shrinkage temperature measured by DSC and the α-transition temperature measured by DMTA (samples conditioned at 65% RH) for various leathers with different shrinkage temperatures.
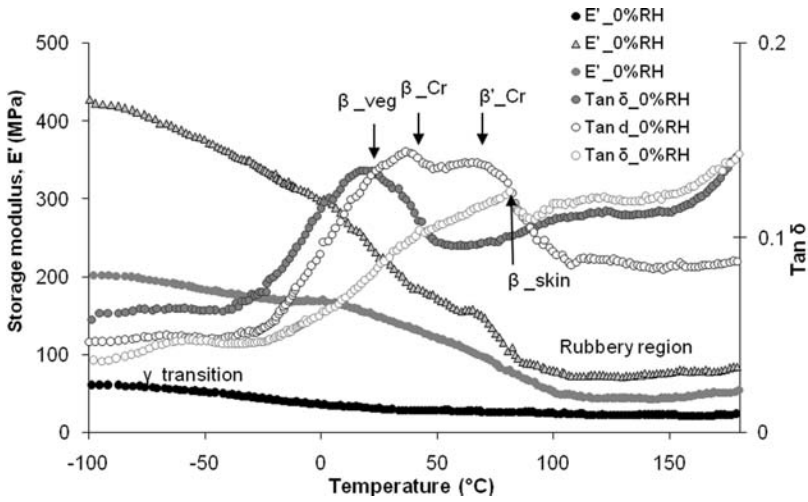
Figure 15.9 DMTA thermograms of chrome tanned skin, vegetable tanned skin and untanned skin, all preconditioned at 0% RH.

calfskin. The progressive decrease of storage modulus from –100 to +100 °C indicates a broad viscoelastic transitional region for all samples. However, the magnitude of the decrease in modulus is dependent on the tanning chemistry and corresponds to the regions where the β transition is observed. The tanned leathers show the β/glass transitions at a lower temperature than that of

Table 15.4 Transition temperatures of tanned and untanned skin, conditioned at 0% RH.

Tannage	Collagen content (%)	γ Transition temperature (°C)	β Transition/glass transition temperature (°C)	β′ Transition temperature (°C)
None	93	-53 ± 7	81 ± 5	–
Chromium(III)	89	-66 ± 4	38 ± 8	65 ± 3
Vegetable	67	-78 ± 5	20 ± 3	–

untanned skin. This demonstrates that tanning molecules are acting as a plasticiser:

1. From Table 15.4, hydroxyproline analysis of leathers conditioned at 0% RH shows that the chrome tanned leather has 89% collagen content, whereas vegetable tanned leather contains 67% collagen. A greater presence of vegetable tannins inside the collagen structure leads to greater depression of T_g.
2. Vegetable tannins are high molecular weight polyphenols and will give multipoint reactive sites for hydrogen bonding and hydrophobic interaction with the fibre. Thus, they are effective in reducing the chain rigidity of collagen by intermolecular hydrogen bonds.
3. Chromium(III) binds to carboxyl groups, which occur along the surface of tropocollagen molecules: as a result, the temperature at which segment motion of collagen molecules becomes thermally activated is increased. However, chromium complexes that form an interpenetrating network between the collagen molecules act as 'spacers' and thus T_g is depressed to lower temperature.

Tanning agents are conventionally understood to preserve collagen by introducing crosslinking between collagen molecules. Viscoelastic transitions would then be expected to move to higher temperatures. Because this was not observed for any of the leathers examined, it suggests that the mechanism of tanning is matrix or interpenetrating network formation around the collagen molecules. This is in line with the latest thinking of the tanning mechanism, presented in Chapter 19.

The identification of the glass transition temperatures of leathers has several practical implications. This is especially so for post tanning, where it may be suggested that processing above the glass transition temperature will be beneficial. This is because fibres are much more flexible and hence the uptake and fixation of dyes, fatliquor and retanning chemicals will be optimised.

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