



Back to Basics: A Framework for Leather Manufacture

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Charge and fixation

The rate of fixation between the collagen structure and pre tanning/tanning/retanning agents, dyes, and many polymeric resins and fatliquors is determined by the charge of the collagen and the charge of the product.

An increase in alkalinity causes an increase in negative charge within the skin, due to losses of amino⁽⁺⁾ groups. Under these conditions, if a chemical with a strong positive charge is offered—such as chrome or aluminium salts—there is a very rapid reaction with the surface carboxyl⁽⁻⁾ groups and no penetration. Under the same conditions, a product with a negative charge—such as a syntan—will combine slowly and penetrate deep into the structure as there is a reduced number of available amino⁽⁺⁾ groups for fixation.

If the pH is gradually reduced more amino⁽⁺⁾ groups become available, until the IEP, when the charges are balanced. If the pH is reduced further, then carboxyl⁽⁻⁾ groups are removed. If the pH is sufficiently low, say pH 2.5, then the opportunity for reaction between carboxyl⁽⁻⁾ groups and positively charged (chrome/metal) tanning materials is thus reduced, so that deep penetration into the skin structure is possible before fixation. In practice a pH rise or basification to moderate levels of acidity (pH 3.5 or higher) is needed to make more carboxyl⁽⁻⁾ groups available and thus improve the efficiency of the tanning system. However, under similar conditions the uptake of anionic⁽⁻⁾ products such as syntans and vegetable tanning products would be very fast due to the high positive charge of the amino⁽⁺⁾ groups, resulting in an over fixation on the surface.

Liming causes a partial breakdown of certain amino acids in the collagen backbone. This moves the IEP, from around neutral to around pH 5.0.

But the introduction of anionic or cationic products within skin also shifts the charge. The fundamental mechanisms set out in *Panel E4/2* illustrates a loss of negative charge and an increase in positive charge as chrome fixation takes place. Although not the precise mode, this

Panel E4/1

Charges relating to groups and products

Positive charge ⁺	Negative charge ⁻
Cations	Anions
Protein amino groups	Protein carboxyl groups
Metal tanning agents: (Chrome, Aluminium, Titanium, Zirconium Iron)	Syntans
Specialty products: (Cationic Resins Cationic Fatliquors Cationic Dyes)	Vegetable tanning agents
	Polymeric resins
	Dyestuffs
	Fatliquors
	Sulfonated/sulfited products
	Surfactants

illustration shows condensation and full cross-linking. Aldehydes do not carry a charge, but remove positive charge from amino groups during fixation thus making the collagen more anionic in nature, as indicated in *Panel E4/3*. The uptake of vegetable tanning agents is by hydrogen bonding as illustrated in *Panel*

E3/4, however, because these products are anionic a negative charge predominates within the leather structure.

Due to the strong positive surface charge of a chrome tanned leather, an anionic⁽⁻⁾ dyestuff will rapidly fix on the grain and flesh surface. If the pH is raised, then the positive charge is reduced as less amino⁽⁺⁾ sites are available, so penetration is improved. Alternatively, pre-treatment with another anionic⁽⁻⁾ product—such as a syntan, or proprietary levelling agent—blocks many of the amino⁽⁺⁾ groups so that dye penetration is improved. In this event, the dyeing is lighter but more level.

Similarly, for controlled uptake of any anionic⁽⁻⁾ product such as a vegetable tanning agent, replacement syntan, or polymeric resin, then the positive charge must be reduced. In practice this is brought about by raising the pH in neutralisation, coupled with the offer of mildly anionic⁽⁻⁾ syntans. Products such as sulfited fatliquors⁽⁻⁾ can also be used to temporarily block available sites, before being displaced by anions⁽⁻⁾ of greater affinity, leading to deeper penetration of both products. The depth of penetration is therefore largely governed by the charge within the neutralised section.

In the case of a leather with a strong negative charge, the reverse applies. The shrinkage temperature of a vegetable tanned leather can be raised by retannage with aluminium or chromium tanning agents. In this event deep penetration is encouraged by acidification to reduce the negative charge.

At all stages the charge on the leather can be adjusted both by pH change and the use of suitable charged products. Products can also be modified by pretreatment. Cationic⁽⁺⁾ products such as chrome or aluminium can be masked by formate⁽⁻⁾ ion, or vegetable tanning extracts by sulfition.

In summary, the surface charge alters at each stage throughout wet processing. The uptake and penetration of products is strongly dependent upon the charge of the product and the prevailing charge throughout the leather section.

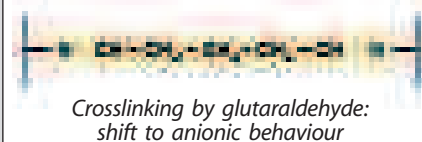
Generalised mechanisms of tannage

Panel E4/2



Crosslinking by chromocomplexes:
shift to cationic behaviour

Panel E4/3



Crosslinking by glutaraldehyde:
shift to anionic behaviour

Panel E4/4



Hydrogen bonding by vegetable or
synthetic tannins: shift to anionic behaviour