



pH is used as a control for charge throughout the collagen or leather structure. This directly influences the penetration and fixation of materials within the matrix. However, the charge of collagen/leather depends on the relationship between pH and pI (IEP).

In practice, the lower the pH in relation to the pI, the greater the positive charge of the collagen/leather, the deeper the penetration of positively charged (cationic) products, and the slower or less secure their fixation. Conversely, the higher the pH in relation to the pI, the greater the negative charge of the collagen/leather, the deeper the penetration of negatively charged (anionic) products, and the slower or less secure their fixation. Moreover, cationic, anionic and neutral materials, which interact with charges on collagen/leather, can also influence pI. pI is central to many mechanisms of chemical penetration and fixation, but unfortunately it is difficult to measure. Nevertheless, the direction that chemicals shift the pI, and the effects that this has on leather charge, are essential to an understanding of wet end collagen/leather chemistry.

Protein and leather charge

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Definitions

- [1] **Polyelectrolyte:** generally polymers with many chemical groups which are charged or may become charged in water.
- [2] **Ionise:** the process where a chemical group becomes positively or negatively charged.
- [3] **pH:** a reflection of the acidity (H^+) or alkalinity (OH^-) of aqueous media. A scale running roughly from 0 to 14. pH from 0 to 7 is acidic (higher H^+ than OH^- content), pH 7 is neutral (H^+ equals OH^- content), and pH 7 to 14 is alkaline (higher OH^- than H^+ content).
- [4] **pI:** the pH at which the total number of positive charges present in a material equals the total number of negative charges present and the material has an overall charge of zero. This pH is commonly referred to as I.E.P.
- [5] **Cationic and anionic charge:** When a chemical group becomes charged and ionised, it may be positively charged—known as a cation, or negatively charged—known as an anion.

Collagen can be considered to be a polyelectrolyte^[1]. Chemical groups found on collagen can ionise^[2] to form positive or negative charges. This ionisation is possible in aqueous media.

The effect of pH on charge

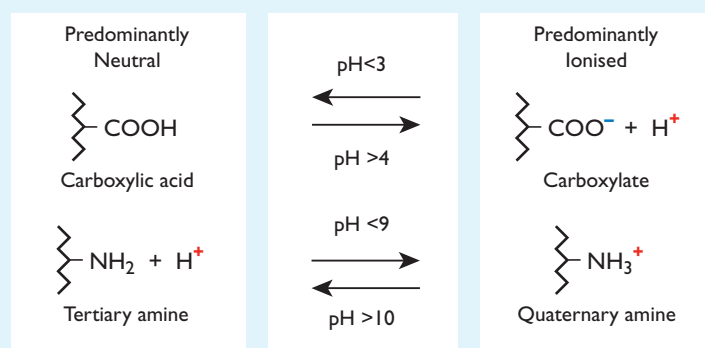
pH^[3] plays the most important role in collagen charge. A low pH (*acidic conditions*) indicates an abundance of H^+ in water, and a high pH (*alkaline conditions*) indicates a lack of H^+ and the presence of OH^- .

Specific chemical groups on collagen are able to bind H^+ , or release it, and become charged. For simplicity's sake, only two of these chemical groups are considered, the carboxylic acid and amine functional groups. The effect of pH change is indicated in *Panel 1*.

This can be seen as producing three general zones as ➤

Panel 1

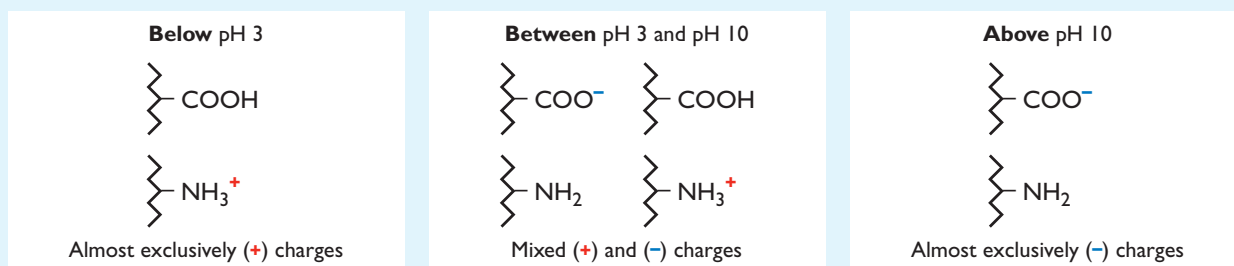
The effect of pH change





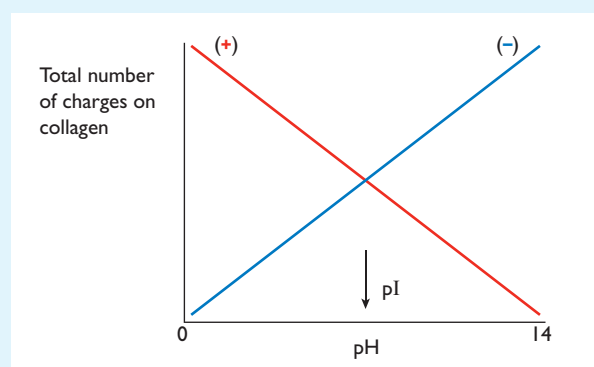
Panel 2

Generalisation of charges on collagen



Panel 3

Representation of charges on collagen



Graph showing the decreasing positive and increasing negative charge according to rising pH. The intersection of the lines shows the pI point.

shown in Panel 2.

The charges may be represented graphically as shown in Panel 3.

At the point of intersection, the total number of positive charges is equal to the total number of negative charges. The pH, which this correlates to, is the isoelectric point or pI^[4].

The effects of change in pI

The actual pI values of collagen and leather are a contentious issue but Panel 4 reflects representative values.

What is important to note is the direction of pI shift and what the shift indicates. All substances, which affect the total number of carboxylic acid/carboxylate and amine functional groups and therefore the relative number of positive and/or negative charges (or potential charges) on collagen, will affect the pI of the material.

There are four ways to influence pI:

- add positive charges or potentially positive charges to the collagen
- remove positive charges or potentially positive charges from the collagen
- add negative charges or potentially negative charges to the collagen
- remove negative charges or potentially negative charges from the collagen.

These modifications may be permanent or temporary and are represented in Panel 5.

Panel 4

Representative pI values of collagen and leather*

Condition	pI values	Charge of tanning agent	Effect on pI	Effect on collagen
Raw hide	6-8	n/a	n/a	n/a
Limed pelt	5-6	n/a	lower	Add (-),
Chromium tanned	~ 6.7	(+)	higher	Add (+), Remove (-)
Chromium tanned (masked)	~ 6.0	(+)	higher	Add (+), Remove (-)
Aluminium tanned	~ 7.2	(+)	higher	Add (+), Remove (-)
Zirconium tanned	~ 7.5	(+)	higher	Add (+), Remove (-)
Vegetable tanned	~ 4.0	(0) and (-)	lower	Add (-), Remove (+)
Aldehyde tanned	~ 2.0	(0)	lower	Remove (+)

* J.H. Sharphouse: *Leather Technicians Handbook*, pp236.
E. Heidemann: *Fundamentals of Leather Manufacture*, pp259.

The penetration and reaction of chemicals with collagen/leather

At pHs below pI, collagen/leather carries a net positive charge, and at pHs above pI, collagen/leather carries a net negative charge. This means that:

- Anionic⁽⁻⁾ chemicals, which interact with cationic⁽⁺⁾ charges on collagen/leather, generally struggle to penetrate at pHs below pI and bind to the collagen/leather.
- Cationic⁽⁺⁾ chemicals, which interact with anionic⁽⁻⁾ charges on collagen/leather, generally struggle to penetrate at pHs above pI and bind to the collagen/leather.

Conversely,

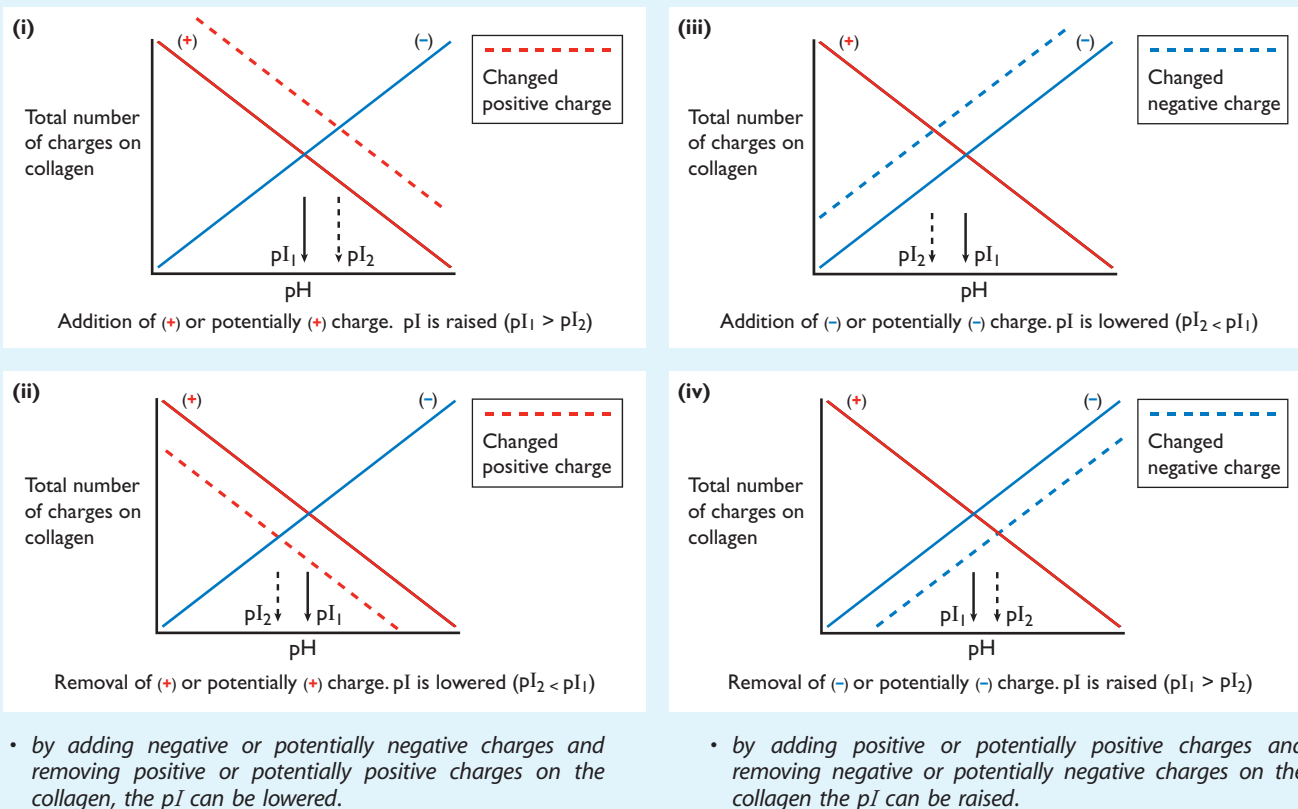
- Anionic⁽⁻⁾ chemicals, which interact with cationic⁽⁺⁾ charges on collagen/leather, generally penetrate well at pHs above pI with little or slow binding to the collagen/leather (e.g., conventional syntans, dyestuffs and fatliquors).
- Cationic⁽⁺⁾ chemicals, which interact with anionic⁽⁻⁾ charges on collagen/leather, generally penetrate well at pHs below pI with little or slow binding to the collagen/leather (e.g., chromium⁽⁺⁾, aluminium⁽⁺⁾, zirconium⁽⁺⁾).

This is illustrated in Panel 6.



Panel 5

Changing the pI



The balance between penetration and fixation

Many chemicals added to collagen/leather will raise or lower pI, however, changing the pH does not affect pI. This is because chemicals must add or remove charged (*and/or potentially charged*) groups on collagen/leather in order to affect pI. This may be permanent (*e.g., chromium tanning*) or temporary (*e.g., neutralising syntans*).

Panel 4 shows that mineral tannages are cationic(+), and raise the pI by adding positive charges and/or removing negative charges. Aldehydic tannages are neutral, but lower the pI by removing potentially positive charges. An understanding of the binding mechanisms of chemicals to collagen/leather is vital to interpret the effect of the chemical on pI.

Fatliquors, syntans and dyestuffs are predominantly anionic(-) in nature and mask positive charges when binding to leather, and hence, lower the pI. The lower pI results in better penetration of

other anionic(-) chemicals and is one of the key functions of the neutralisation and retanning stages prior to dyeing and fatliquoring in conventional processing.

However, anionic(-) chemicals require cations(+) on the collagen/leather to bind to when fixing—and there are a limited number of positive charges available. Whereas the addition of excessive amounts of anionic(-) chemicals will improve penetration of other anionic(-) chemicals, this will ultimately reduce the fixation of these chemicals. This may result in poor oil fixation (*fogging, fat migration*) and poor dyestuff uptake (*dull, pale colours, poor rub fastness values, dye migration*).

There is a fine line between good chemical penetration and poor chemical fixation.

Managing the penetration and fixation of chemicals

Chemical companies have identified the advantages of lowering the pI to enhance the penetration of anionic(-) chemicals at low pH and the necessity of cationic(+) fixing agents to enhance chemical uptake and fixation. This reduces and/or limits pH fluctuations during processing, being attributed to a reduction in looseness and therefore an increase in cutting yield.

Manipulation of the pI is a valuable tool and is used to increase chemical penetration or increase chemical fixation. Within the neutralisation process, in conjunction with the ➤

Panel 6

Penetration and Fixation in relation to pI

Below pI	Above pI
Collagen/leather carries a net (+) charge	Collagen/leather carries a net (-) charge
pH 0 ←	→ pH 14
• Good penetration of cationic(+) chemicals • Poor fixation of cationic(+) chemicals • Good fixation of anionic(-) chemicals • Poor penetration of anionic(-) chemicals	• Poor penetration of cationic(+) chemicals • Good fixation of cationic(+) chemicals • Poor fixation of anionic(-) chemicals • Good penetration of anionic(-) chemicals



Panel 7

Charges within neutralisation

(Colours shown as indicated by using Bromocresol Green.
Charges as shown are for indication purposes only)

7/1: Complete Neutralisation

Grain	-	-	+	-	-	pH 6.0 - 6.5
	+	-	-	-	+	
Middle	-	+	-	+	-	
	+	-	-	-	+	
Flesh	-	-	+	-	-	

Total (+) = 8, (-) = 17
Neutralisation ~ 60 mins, float pH ~ 6.5

7/2: Incomplete Neutralisation

Grain	-	+	-	+	-	pH 4.0 - 5.0
	+	-	+	-	+	pH 3.5 - 4.0
Middle	+	+	-	+	+	pH 3.0 - 3.5
	+	-	+	-	+	pH 3.5 - 4.0
Flesh	-	+	-	+	-	pH 4.0 - 5.0

Total (+) = 14, (-) = 11
Neutralisation ~ 30 mins, float pH ~ 5.0

7/3: Neutralising syntan-assisted complete neutralisation

Grain	-	-	+	-	-	pH 4.0 - 5.0
	+	-	-	-	+	
Middle	-	+	-	+	-	
	+	-	-	-	+	
Flesh	-	-	+	-	-	

Total (+) = 8, (-) = 17
Neutralisation ~ 60 mins, float pH ~ 5.0

An indication of pH can be gained by applying indicators such as Bromocresol Green. In no way does this reflect the state of neutralisation or pI.

manipulation of pI, the pH is normally raised towards the pI of the leather. This further reduces the cationic(+) content of the leather and allows anionic(-) chemicals to penetrate.

There are two main types of neutralisation processes:

Complete neutralisation: mainly used when complete penetration of anionic(-) dyes and fatliquors is required, for example, for softer leathers such as upholstery and garment. (Panel 7, Item 7/1)

Incomplete neutralisation: utilised to limit penetration and encourage surface fixation of anionic(-) dyes and fatliquors. This produces leathers which are firmer with a degree of roundness required in, say, shoe upper leathers. (Panel 7, Item 7/2)

However, neutralising syntans can be used to temporarily lower the pI to facilitate the penetration of retanning agents, dyes and syntans, even at lower pHs (Panel 7, Item 7/3). This is particularly important with thicker leather (> 2 mm) where looseness may be a problem. These three conditions are expressed in Panel 7.

The opposite effect is also possible, so that the pI may be raised by adding small amounts of cationic(+) products to increase the fixation of anionic chemicals. ⚙️

Panel 8

pI as a tool in leathermaking

The pI of a leather is influenced by the type of preparatory processes, the type of tannage, the crusting procedure used, and the extent to which these have been undertaken.

Beamhouse operations remove some neutral chemical groups, and replace these groups with groups that can become negatively charged (anionic(-)). The overall result is a decrease in pI as indicated in Panel 4 (Raw hide to limed pelt).

The tannage may cause the pI to:

- Decrease through the addition of anionic(-) chemicals such as vegetable tanning agents or syntans as these bind to cationic(+) fibre groups.
- Increase through the addition of cationic(+) chemicals such as metals, as these bind to anionic(-) fibre groups.

During crusting processes, pI shifts occur through the addition of chemicals with multiple chemical groups, some of which can ionise depending on the pH. Dyestuffs, vegetable tannins, resins, syntans, fatliquors and auxiliaries all have functional groups that ionise at differing pH values to become charged groups. By adding chemicals containing ionisable groups the overall leather charge is affected.

The pI can also be changed when a neutral chemical is added which binds to groups through a chemical bond. The charge that the fibre amino acid could have is thus cancelled. Examples of these chemicals include unmodified aldehydes and resins. These are neutral but they react with -NH₂, which could otherwise form -NH₃(+) cations at high pH values, so the pI is shifted downwards.

Changing the pH does not change the pI. Chemicals must interact directly with the collagen/leather and change the relative numbers (or ratio) of charges or potential charges in order to affect pI. As discussed in the main text, the following conditions cause shifts in pI:

- the binding of cations/cationic(+) groups to collagen (Cr, Al, Zr, Fe) results in an increase in pI.
- the binding of anions/anionic(-) groups to collagen (veg, syntans, acid dyes, anionic fatliquors) results in a decrease in pI.
- the removal of cationic(+) groups on collagen (by masking agents - formates, veg tanning agents, syntans, aldehydes, fatliquors) results in a decrease of pI.
- the removal of anionic(-) groups on collagen (by Cr, Al, Zr, Fe, and amphoteric resins) results in an increase of pI.

These shifts are indicated in the correspondingly numbered diagrams in Panel 5.

In practice, these shifts have major considerations. A controlled pH of the bath (and ultimately the pH of the leather) means that the charge balance of the leather can be defined. As indicated in Panel 7, the overall charge is determined from the total of one charge, e.g. cations(+), less the total of opposite charge, e.g.



Panel 8 cont

8/1

pI as a tool in leathermaking

	Chemical	Charge	Binding to collagen
Mineral	Chromium	Cationic ⁽⁺⁾	Binds to (-) irreversibly
	Zirconium and Aluminium	Cationic ⁽⁺⁾	Binds to (-) reversibly
Vegetable Tanning Agent	Hydrolysable (<i>Myrabolans, Sumac etc</i>)	Unmodified: non-ionic ⁽⁰⁾ to anionic ⁽⁻⁾ Modified (sulfited) anionic ⁽⁻⁾	Binds to ⁽⁰⁾ and ⁽⁺⁾ reversibly Binds to ⁽⁰⁾ and ⁽⁺⁾ reversibly
	Condensed (<i>Mimosa, Quebracho etc</i>)	Unmodified: non-ionic ⁽⁰⁾ to anionic ⁽⁻⁾ Modified (sulfited) anionic ⁽⁻⁾	Binds to ⁽⁰⁾ and ⁽⁺⁾ reversibly Binds to ⁽⁰⁾ and ⁽⁺⁾ reversibly
Aldehydic	Formaldehyde Glutaraldehyde	Non-ionic ⁽⁰⁾ Non-ionic ⁽⁰⁾	Binds to neutral groups ⁽⁰⁾ of potential ⁽⁺⁾ charge
Classic syntans	Phenolic	anionic ⁽⁻⁾	Binds to ⁽⁺⁾ reversibly
	Naphthalene sulfonate	anionic ⁽⁻⁾	Binds to ⁽⁺⁾ reversibly
	Mineral syntan	Overall anionic ⁽⁻⁾ but may contain ⁽⁺⁾	Binds to ⁽⁺⁾ reversibly
Resin/polymer	Acrylics	anionic ⁽⁻⁾	Binds to ⁽⁺⁾ reversibly
Dyestuffs	Acid	anionic ⁽⁻⁾	Binds to ⁽⁺⁾ reversibly
	Basic	cationic ⁽⁺⁾	Binds to (-) reversibly
Surfactants	anionic	anionic ⁽⁻⁾	Binding to ⁽⁺⁾
	cationic	cationic ⁽⁺⁾	Binding to (-)
	non-ionic	non-ionic ⁽⁰⁾	negligible binding
Fatliquors (<i>classification according to surfactant</i>)	anionic	anionic ⁽⁻⁾	Binds to ⁽⁺⁾ reversibly
	cationic	anionic ⁽⁻⁾	Binds to (-) reversibly
	non-ionic	non-ionic ⁽⁰⁾	Binds to ⁽⁰⁾ reversibly

NOTE: (-), (+), (0) indicates charge

anions⁽⁻⁾. The overall charge will be either anionic⁽⁻⁾ or cationic⁽⁺⁾ to a varying degree and is rarely perfectly neutral.

Placing another charged chemical into the leather results in either its penetration or fixation from a reaction with an oppositely charged ion. Fixation will therefore be overwhelming or partial depending on the overall charge and binding mechanism.

Frequently, the leather pH through the cross-section—as shown in *Panel 7 Item 7/2*—is not even, mainly as a result of incomplete neutralisation. The result is an uneven charge, which results in uneven fixation and unpredictable penetration. If the surface layers are partly anionic⁽⁻⁾, then anionic⁽⁻⁾ chemicals penetrate until they meet the overwhelmingly cationic⁽⁺⁾ layer. To reduce the fixation of anions⁽⁻⁾, the cationic⁽⁺⁾ charge is lowered by adding anionic⁽⁻⁾ masking agents or by raising the pH so that the cationic⁽⁺⁾ groups deionise.

The pI is thus manipulated to help create effects. Complete penetration is used to create soft leathers. Small amounts of cationic⁽⁺⁾ chemicals—e.g., aluminium⁽⁺⁾ compounds—may be added to increase the pI of the leather surface to encourage surface fixation of anionic⁽⁻⁾ dyes for intense, deep shades. Other

effects include the assistance of top fatliquoring, shrunken grain, and grain tightening by depositing resins on the grain junction. Cationic⁽⁺⁾ resins are also commonly used for the fixation of anionic chemicals—mainly dyes—already located within the leather to improve fastness.

The charge of typical tanning agents is given in this panel as *Item 8/1*. Complications may arise through the modification of typical chemicals to give them a charge (*to increase solubility*), as well as chemicals bearing two, oppositely-charged groups. Multi-charged chemicals such as polymers/ emulsions also blur the classification system.

The fixation of chemicals is highly dependent on the leather charge, and the processing of wet white leathers has highlighted this. A lack of cations⁽⁺⁾ in the leather, due to a non-ionic/anionic⁽⁻⁾ tannage or a poor number on leather fibres, means the dyeing will be pale and the fastness properties will be poor. Oils may also fix poorly resulting in a 'drying out' of the fibres due to migration or poor fogging values. Poor fixation during the wet processes often results in poor exhaustion. By manipulating the charge through low pH values or cationic⁽⁺⁾ fixing agent, this can be prevented.