ISO Electric Point is essential in tanners' toolbox

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As a fundamentally central concept to the wet-end of the tannery, the principles of iso-electric point (IEP) is an essential part of the tanner's toolbox. The effective penetration and fixation of the post-tanning chemistry into/onto the leather cannot take place unless the tanner understands how IEP works and how it can be manipulated. Most leather makers have a very basic grasp of this concept and are frustrated when they try the obvious things to manipulate the leather charge, and then find the leather still not behaving in the way they require. This effect is often due to a tanner failing to grasp the innuendoes of charge manipulation in the leather and only applying first principles.

Protein charge

A 2017 scientific paper demonstrates the complexity of leather charge and their work can be traced back to seminal work (done on leather protein charge) performed back in the early part of the 20th century (Wang et al., 2017). In 1929, Gustavson began sharing what happened to leather charge as the effect of tanning was imposed (McLaughlin and Theis, 1945). Since then several papers can be consulted for what the pH needs to be for the leather to have an overall nett charge of zero.

Figure 1 shows how the acidic sidechains and terminal groups of the leather collagen can be affected by the introduction of an acid. A similar diagram can be drawn to show a charged chemical effect on the amino containing protein side chains. To be clear, the addition of acid or alkali into the leather results in the charging of the protein which creates a cationic (positively) or anionic (negatively) charged protein surface. Carboxylic groups (-COOH) lose their hydrogen atom to become anionic (-COO-) when they are in the presence of an alkali. Amine groups ($-NH_2$) will gain a hydrogen atom in acidic conditions to become cationic ($-NH^{3+}$). In other words, the leather will become more positively charged in the presence of acid, and more anionic in the presence of alkali. Technicians who say leather is cationic at low pH and anionic at high do not understand the difference between adding acid and being at a low pH.

The distinction that these groups ionize when acids or alkalis are added means that at any pH the charge of the chains is often more complex than just being one charge state. At any one time there are both cationic and anionic groups, a theoretical calculation can be made that determines the zero-sum of the number of cationic, balanced by anionic charge; a tanner introducing a chemical knows whether the collagen is overwhelmingly cationic or anionic. Knowing if a charge dominates allows the tanner to dictate whether the chemical (of a certain charge) will bind to its opposite or will penetrate deep into the leather structure.

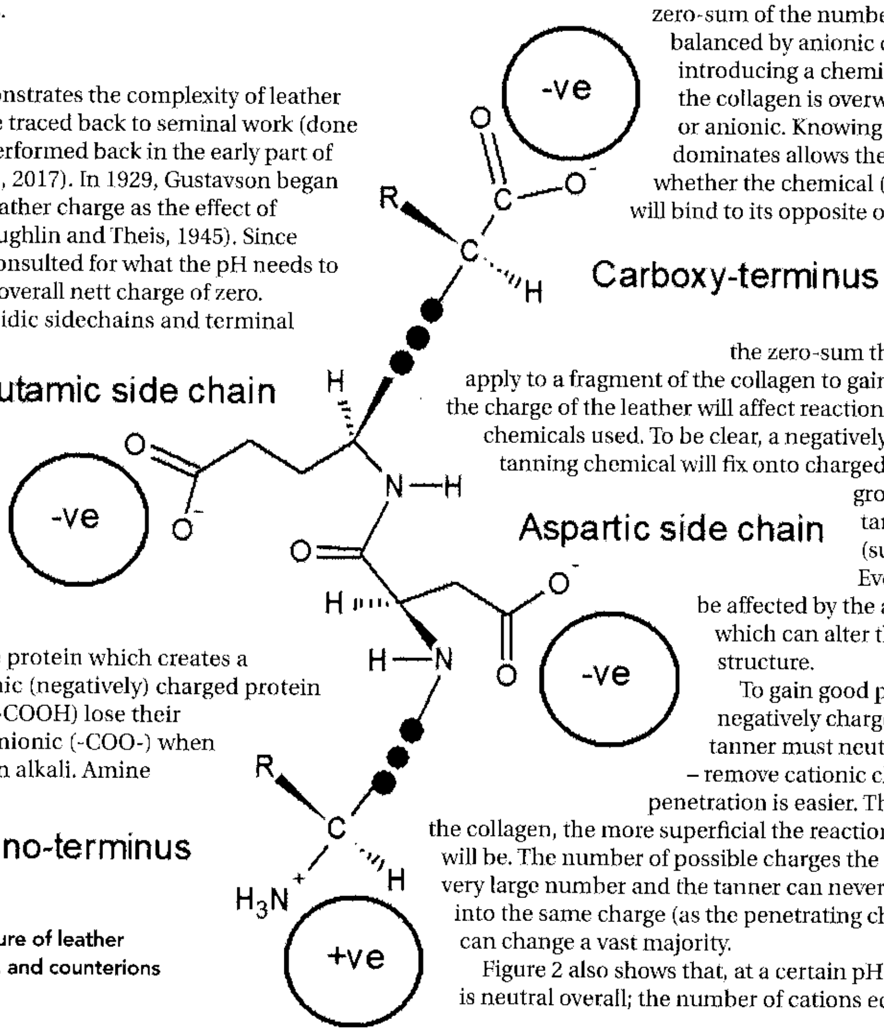

Figure 1. The chemical structure of leather collagen showing the charging, and counterions associated with the protein.

Figure 2 shows the zero-sum theory that one can apply to a fragment of the collagen to gain an idea as to how the charge of the leather will affect reaction of the post-tanning chemicals used. To be clear, a negatively charged post-tanning chemical will fix onto charged amino ($-NH^{3+}$) groups or cationic tanning materials (such as chromium). Even the metals can be affected by the addition of alkalis which can alter their charge structure.

To gain good penetration of a negatively charged chemical, a tanner must neutralise the leather – remove cationic charge so that the penetration is easier. The more cations on the collagen, the more superficial the reaction of the chemical will be. The number of possible charges the collagen has is a very large number and the tanner can never change them all to into the same charge (as the penetrating chemical), but they can change a vast majority.

Figure 2 also shows that, at a certain pH value, the protein is neutral overall; the number of cations equals the number

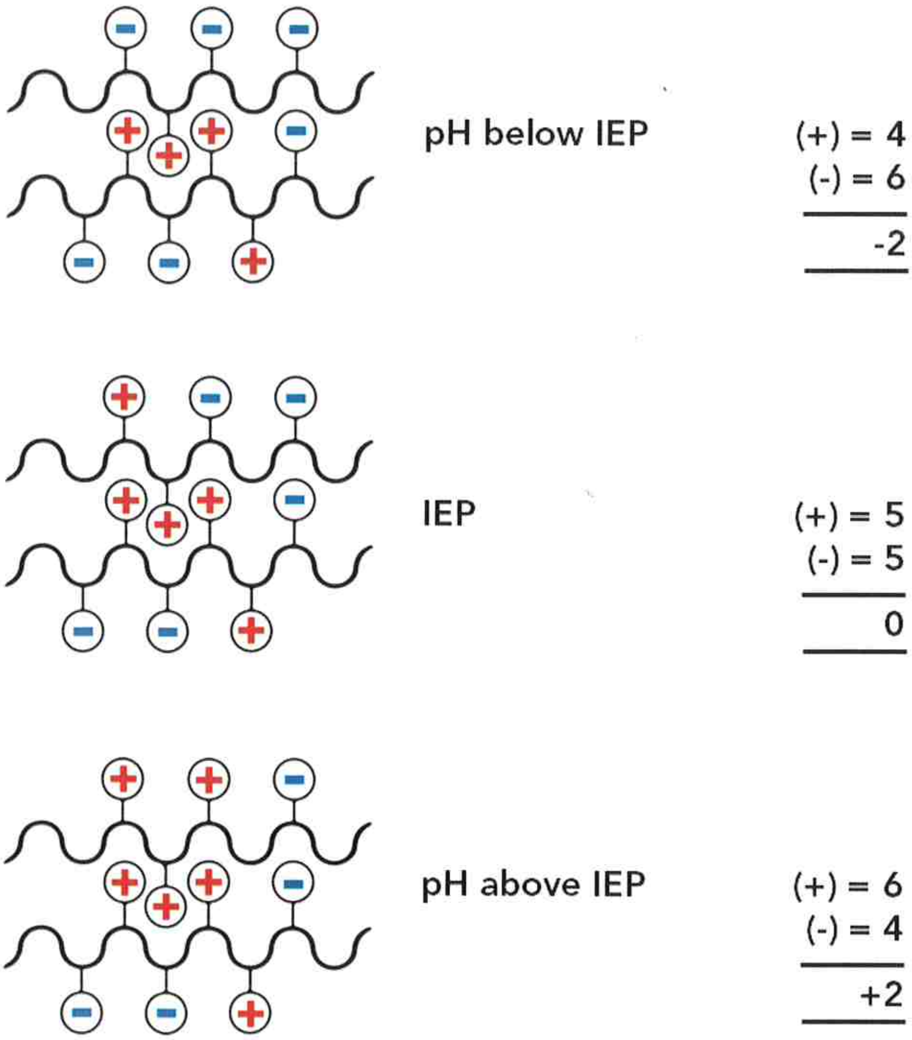

Figure 2. The theoretical calculation that can be performed to determine overall charge.

of anions. This is the simplest definition of iso-electric point and will be expanded on later. Another common error tanners make is to assume that at pH values below the IEP the leather is cationic (with no anionic groups), and above the IEP the leather is anionic (with no cationic groups). This is simply not true. As Figure 2 shows, both charges are present, but at pH values above and below one type of charge dominates. Practically, this means that a tanner must use masking chemistry that will cover the opposite charge groups when attempting to penetrate the leather deeply; a common practice for assisting dye penetration.

Changing the IEP

The tanner during the beamhouse can alter the collagen chemistry and this will permanently change the IEP of the material. Groups that can become charged if removed will not enter into the zero-sum calculation and the IEP shifts up or down. Specifically, if a tanner removes side chain groups that can become positive the IEP shifts down. The decrease takes place when liming and bating is done on the skin. Deamidation of the collagen removes potential cationic groups. These are permanent changes and cannot be undone if the pH of the leather is changed.

Some tanners say that the IEP can be shifted using tannins and other chemistry. Technically, a perceived shift of the IEP occurs but, practically, it is slightly more complicated. Determination in the shifts that take place in the protein during leather-making can be done theoretically; to an extent, the number of groups makes the calculation for the whole leather complex, virtually impractical. Practical measurement of the leather charge is possible but difficult. A snap-shot of the charge is easier to do than what most tanners are interested in – the actual determination of the IEP.

One method commonly used by leather scientists to try and measure the IEP is to change the pH of leather, and then measure the amount of dye absorbed when the dye and leather is mixed. This will give an indication of how charged the leather is and will lead one to believe how close to the IEP the leather is. The measurement of the zeta potential is a slightly more accurate way of doing it. The typical output of a zeta potential screening is given in Figure 3. These types of graphs show the measurement of the charge in the leather, but they must be taken as relativistic as, for example, they interfere with the charge of the leather during the measurement. They are the leather industries version of Shrodinger's cat.

Shrodinger is associated with the thought experiment that hypothesises that if a cat is placed in a cupboard and the door is closed, the cat will be inside the cupboard and can either be alive or dead. An experimenter would not know which until the door is opened and the observation is made. The observation however is influential as it may be the determining factor that causes the cat's life or death. This thought experiment is fundamental to quantum physics, but is also informative in allowing an experimenter, particularly in IEP determination, to understand that very often the act of measuring changes the outcome.

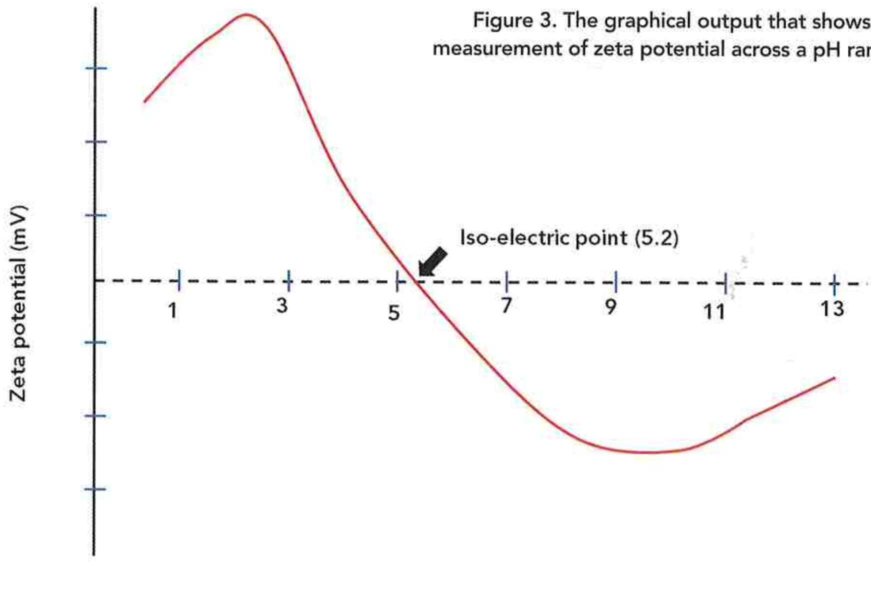

Figure 3. The graphical output that shows the measurement of zeta potential across a pH range.

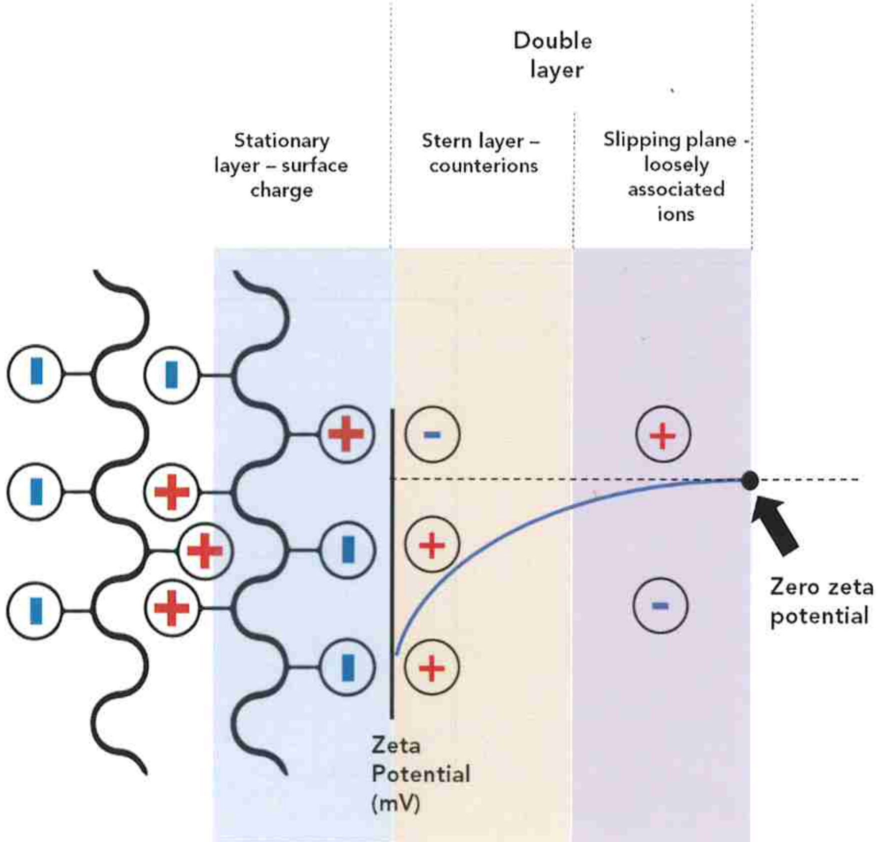

Figure 4. A schematic illustration showing surface charge and the changing zeta potential as one moves through the double layer.

Zeta potential

Zeta potential is the measurement of the charge seen on the surfaces of molecules. Electroacoustics is the most common form of this technique and it "hears" the vibration of the surface, when the surface is "pinged," with an electrical signal. Most commonly, the detection starts at the molecule surface and the signal received back will usually show that the leather is in a highly charged state. The layer closest to the protein backbone/sidechains is commonly called the stationary layer (charges there are static).

Figure 4 shows that at the stationary layer the leather has the highest zeta potential. As the detection moves towards the bulk medium the zeta potential decreases, through the double layer. In the Stern layer, the counterions or masking agents are found. These opposite charges are often closely bound to the stationary layer. Tanning materials like chromium will be covalently bound here and they will have such a profound effect on the IEP that it will seem like it has shifted in a manner, similar to the permanent effects seen in the beamhouse modification.

In the outer layers of the double layer is an area referred to as the slipping plane. In this plane the zeta potential is often zero and is often referred to as the zero-zeta potential. It does not have to be zero, however. If the measurement of the charge is done here, it may seem like the surface charge is at the IEP or not. The associated ions in the double layer are highly changeable in that, if a dye enters the double layer, it can bind to molecules in the Stern layer or can even displace or easily bind to the stationary layer if no counterions are present. All these are dependent on how high the zeta potential of the charged surface and Stern layer gets.

Simply put, the aim of neutralisation is to consider the extent of the surface charge either at the double layer or molecule surface and then attempt to neutralise the opposite charges (opposite to the chemistry of the substance you are trying to penetrate). It is also important to remember that throughout the cross-section of the leather thickness this charge will vary. A good tanner will have an idea of where stratigraphically the chemical needs to go, and they will then add an alkali or masking that can influence the surface charge at any part of the molecule surface or double layer.

Many tanners have been frustrated by the addition of alkali which can change the slipping plane or Stern layer, or part of the stationary layer, only to be intrigued why the dye still fixes on the outside first. Remember, the associated or bound chemistry are constantly in flux and this can result in charge neutralisation by hydrogen, sodium, or potassium ions, that are then easily displaced by an electronegative dye. Chromium and other metals will also complicate things because the can hybridise their outer valence shells and can then perform ionic or co-ordinate interactions that tanners just simply cannot neutralise with an alkali.

Good thorough neutralisation, through alkali manipulation of the molecule surface, and strong masking of the double layer by anionic neutralising syntans, will give easy penetration of dyes and fatliquors. If the binding of these masking agents is too tight, the tanner will then experience another problem, namely, the lack of binding sites later for the chemicals you do want to fix; for example, the bleaching effect on intense dyeings. A balance needs to be struck.

Conclusion

The Shrodinger's cat effect in IEP determination cannot be overstated. When the researcher adds hydrochloric acid or sodium hydroxide to the leather to create certain pH conditions for the experiment, the stationary layer is influenced, but so is the double layer. Sodium from the hydroxide and chlorine from the acid will be counterions that will change the zeta potential of the Stern layer and slipping plane. If the zeta potential of the interface is measured, the counterions may influence the measurement. Of course, the effect is relative, but it is very dangerous to claim absolute values for IEP – the very reason previous textbooks will give an approximation.

How do tanners use this detailed understanding? The IEP of metal tanned material is high (pH 6-8) as one moves from chromium through to zirconium. This means difficult penetration for anionic chemicals into these leathers at low pH values. Fixation of anionic chemicals at low pH values (3.5-4) will be good, subject to the double layer losing its temporary masking agents.

For chromium-free leathers, including vegetable tanned leather, the IEP is low (pH 3-5). These leathers will struggle to bind anionic chemicals at pH 3.5 – 4. They will allow easy penetration of anionic products, unless the double layer contains charges that are cationic in nature.

Washing and neutralisation of leathers are focussed on the removal of opposite charge in all layers surrounding the collagen. When fixation is needed then the layers around the collagen need to be switched into full opposite charge, so that the binding will be tight and permanent. Much more research on how this can be optimised is needed. ■

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