

THE PH OF LEATHER

Topic #1

Acid and alkaline. Alkaline and acid. Two words commonly used in our vocabulary. Some of the products used daily have different levels of acidity and alkalis. For example, some foods like bananas and coffee are acidic. Whereas eggs and the toothpaste used are more alkali. Even different parts of our bodies have different levels of acidity and alkalis, depending on the function. The stomach is more acidic as it helps to break down the food we consume, whereas blood is slightly more alkalis. Acid and alkaline are measured by the pH scale.

pH scale

Simply put, the pH is a calculation of the amount of hydrogen ions in a system. In 1909, a Danish chemist called Søren Sørensen, coined the pH scale which runs from 0 to 14. The pH of distilled, degassed water at 25°C should be pH 7. This is referred to as pH neutral. Below the pH 7 a solution is called acidic and above pH 7 a solution is called alkaline (or basic).

The pH is calculated by taking the negative logarithm (base 10) of the concentration of the hydrogen ions, see Equation 1. In other words, the higher the number of hydrogen ions the lower the pH value will be.

 $pH = -log_{10}[H^+]$ Eq. 1

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To measure the pH value, a glass electrode is often used or a dyestuff that changes colour according to the pH (a pH indicator). The Nernst equation in Equation 2 is used to calculate the pH from a measured electric potential of a solution. That is, a measure of the electrical activity of a solution linked to the Faraday number (F), the standard potential (E⁰) of the electrode, the temperature (in Kelvin) and the gas constant give a number directly proportional to the natural logarithm of the concentration of hydrogen ions.

$$E = E^0 + \frac{RT}{F} ln[H^+]$$
 Eq. 2

The Nernst equation becomes inaccurate at pH values below 2.5 and above 10.5 due to limitations in the glass electrode method. pH indicator paper or specially constructed electrodes are required for these extremes.

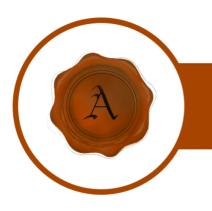
pH of skin

Even our skin has a pH level. It was 130 years ago when scientists started looking at the pH of human skin. A researcher by the name of Heuss conducted some of the first work on this subject in 1892 (Heuss, 1892). Since then, there has been a lot of research into the subject of skin pH, which has seen the development of the "acid mantle" theory.

The "acid mantle" is found in the statum corneum (the outer layer of the epidermis), which has a pH of between 4.2 and 6.5 (Schmid-Wendtner and Korting, 2006).

The most commonly quoted pH of the epidermal surface is pH 5.2 and is often said to be instrumental in helping to control healthy skin free from infection and dryness (Lambers et al, 2006). In their review in 2006, Schmid-Wendtner and Korting claim that the average pH of human skin is 4.7, particularly in the ear canal and on low moisture areas. High moisture areas have a marginally higher pH, as do female skins. These researchers go on to state that healthy skin can protect itself if the pH is held low, as bacteria cannot easily colonise low pH skin (Lambers et al, 2006; Schmid-Wendtner and Korting, 2006).

The "acid mantle" is more remarkably robust. Researchers working on human skin creams and cleansers note that consistent changes to the skin pH (notably when adding alkalis) are often returned to normal acidic pH values after as little as 3 hours (Takagi et al, 2015), but normally within 24 hours of some extreme change to pH.



pH and dermatitis

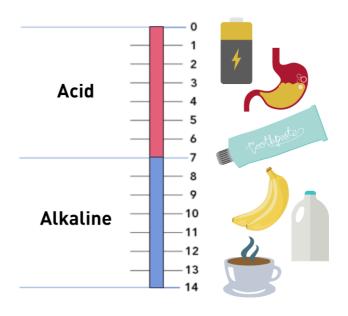
Eczema or dermatitis is the development of a rash or lesion on localised region in the skin because of a skin biochemical change such as a change in pH levels. There are three types of dermatitis:

- Stasis dermatitis is one of the rarer conditions and is fundamentally related to venous supply and drainage.
- Atopic dermatitis is the development of a rash in response to some skin change. The cause of atopic dermatitis is not known, but genetic predisposition, immunosuppression, permeability of the skin or environmental stimuli are causes often cited.
- **Contact dermatitis** is a skin reaction caused by a specific substance landing on the skin. These substances could be allergenic or a chemical substance that is causing an irritation that is not dependent on a histamine response.

Many dermatological researchers implicate the pH increase of the skin as a mitigating (sometimes causal) influence in the development of dermatitis. Irritant contact dermatitis in cement workers (who work with lime-based products, which are alkaline) is well documented and elevated skin pH often results in contact eczema. High pH cleansing using powerful soaps also has an impact in increased incidence of dermatological sensitivities. The "acid mantle" is reported to be a result of the enzymatic maintenance of the low pH value (in human skin) through hydrolysis of phospho- and other lipids to produce free fatty acids (Takagi et al, 2015).

Leather pH

Acids and alkalis are used throughout the tannery process, and unsurprisingly, the finished leather will have its own pH level. See Figure 1.





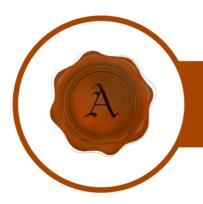
To determine the pH in leather the BS EN ISO 4045:2008 or ASTM D2810-07 are commonly used. Both methods entail some agreed sample preparation of the leather. For BS EN ISO 4045:2008 the sample is ground according to ISO 4044 and the pH of the sample is equilibrated with distilled water in a shaker for a short amount of time, see method.

This method varies from the determination of pH in textiles, in that textiles are rarely ground up. Leather that is not ground up will equilibrate much slower in the stipulated time frame of the test. A low pH value of the leather indicates a high concentration of hydrogen ions in the sample. If the pH is less than 4 or greater than 10 then a difference figure is calculated. The difference figure is a calculation of the difference between the measured pH according to the BS EN ISO 4045:2008. This means that the extracted solution is diluted 1:10 and the pH is measured again. The difference figure should be less than 1, and a figure between 0.7 and 1 indicates the presence of a strong acid (or strong base/alkalis). Presence of a strong acid or strong alkalis could present difficulty to sensitive skin users of the leather.

Final leather is highly unlikely to have a strong acid present and leather found with strong acids should be sanctioned. Healthy human skin will cope with moderate levels of acidity, especially weak acids as they are congruous with the "acid mantle". Dermatological studies, like Takagi et al (2015) and Lambers et al (2006) suggest that lower pH values will in fact help with skin health. Of course, the presence of large quantities of strong acid, like any chemical, may give rise to contact dermatitis. Safety of the leather for the human skin seems to rest, not in the actual pH value, but in the presence of acidity levels that would cause an imbalance in the "acid mantle" of the human skin.

Current leather specifications

Very few of the accepted leather specifications have a final leather pH requirement that is based on any human health science. This may be a research priority going forward. Generally, tanners keep the final leather pH below 4, but higher than 3 (some would say higher than 3.5). The BS EN 16419:2014 (chamois leather standard) specifies the leather should be above pH 6.5 and this is because the type of tannage requires a high pH. This is a great exception to the general final leather pH values. Chromium, organic tannages, and vegetable tannages and their corresponding post tannages will culminate in the fixation of the chemicals (normally with the addition of acid). The iso-electric point and the type of tannage will determine how low the pH will need to go in order sufficiently fix the chemicals. Tannages that result in the leather having a low iso-electric point may need the



fixation pH to go lower than usual. The addition of fixing chemicals, other than formic acid may be required to provide more binding sites for the anionic chemicals. Dyestuffs that have been extended (or stabilised) with neutral salts may also need a lower pH if the dyes are to fix to correct level of rub-fastness.

Safety and stability of the tannage may be called in to question if the pH is raised higher. It is well known that vegetable tanning materials is easily stripped off as the leather pH is raised. A high pH will also result in loose chemicals (especially fatliquors) that can move around the leather. Looseness, resulting from fatliquor moving to the grain junction can increase when the pH is not lowered below 4.

Conclusion

A few brands and retailers have started specifying the final leather pH to be between 4 and 7. However, these are often taken directly from textile standards and have not been set specifically for leather. The implementation of these specifications is very seldom done with any consultation with leather scientists and leather technologists that are not biased by commercial decisions linked with any tannery.

An increased number of technological quality problems, productions issues

and environmental sustainability issues have arisen from these decisions. A high final leather pH will result in poorer environmental performance due to less chemical fixing to the collagen (and subsequently going into the effluent plant).



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