

The theory of tanning

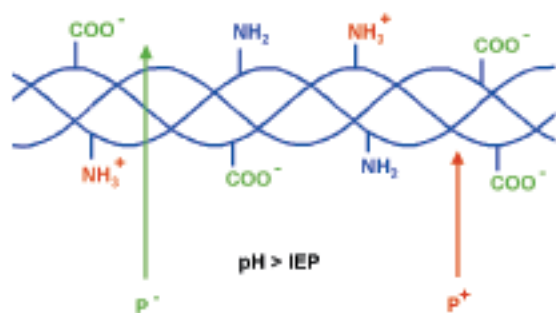
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For thousands of years the knowledge of tanning was passed from generation to generation. But it is only in the last 150 years that serious research started. This is because a better understanding was needed to ensure a more rational and economic production and more consistent quality.

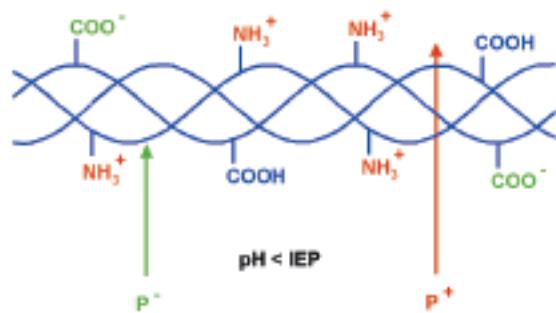
In the last 50 years fundamental findings have brought a wider

insight into the structure of the protein collagen,^{1,2} being the basic material for leather. The common interest of medical science and leather chemistry brought contributions from both sides, but medical interests supported research to a much greater extent. For this reason today's knowledge goes far beyond the level necessary to understand the reaction between collagen and

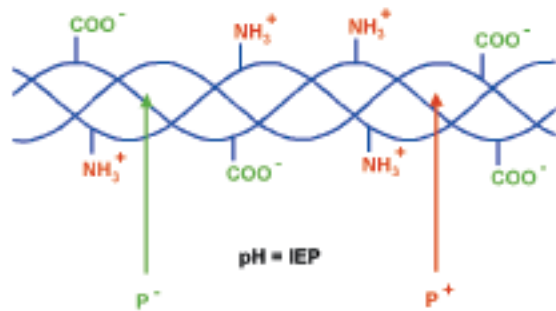
Figure 1: The correlation between the iso electric point, the pH value, and the fixation of cationic and anionic products.



a) Fixation at a pH below the iso-electric point.



b) Fixation at a pH above the iso-electric point.

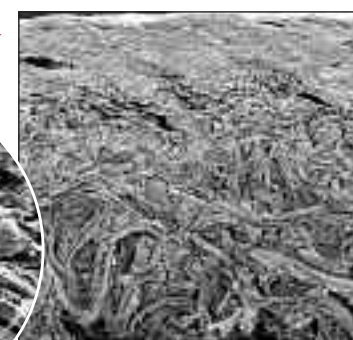
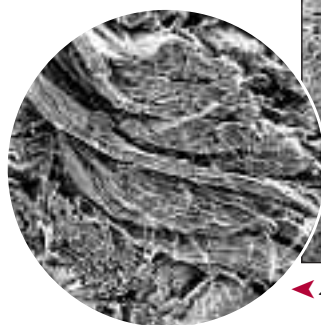


c) Fixation at a pH being the iso-electric point.

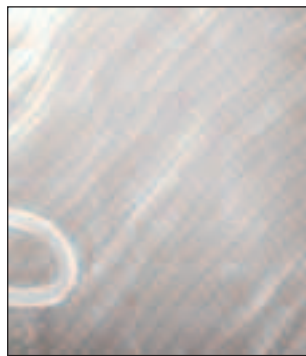
Courtesy: Fixation of leather dyes - a new concept: Jens Fennan, Jon McHugh & Campbell Page, World Leather, April 2003-11-14

Figure 2

2a) Fibre bundle viewed at x50.



2b) Cross section of fibre bundle showing bundles of fibrils viewed at x500.



2c) Individual fibrils viewed at x50,000. Each fibril is approximately 100nm in diameter. The banding patterns are characteristic of collagen fibrils and a function of the triple helix.

Micrographs courtesy of BLC, Leather Technology Centre, UK

chemicals used in the tanning process.

However, in the latest few decades the understanding of the chemical and physical structure of collagen has been mainly due to medical studies. This has made theoretical studies of tanning – the theory of tanning – easier.^{3,4,5,6}

This is summarised in *Figure 1*, where the collagen model of three protein chains in the form of a triple helix is shown, and the fixation of cationic and anionic products under different conditions.

However, it is the three dimensional network of fibrils and fibres that gives leather its strength. When processed as soft leather its behaviour is very similar to natural skin, providing ideal protection.

A definition of leather

A definition of leather is “a material which is resistant to putrefaction and enzymatic destruction and that after repeated wetting and drying returns back to its former soft characteristic.”

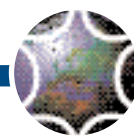
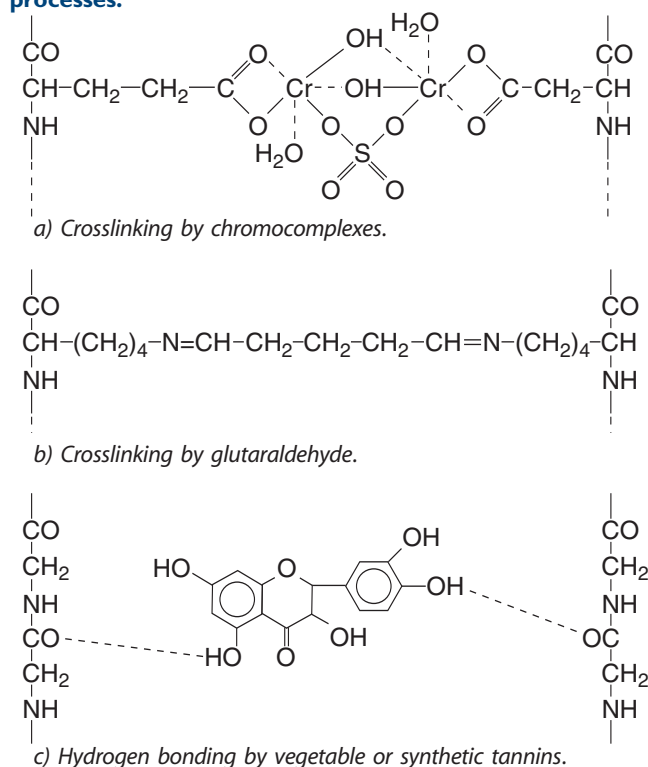


Figure 3: Ecological aspects of important tanning processes.



G. Reich, Jan 2000: Publication by German Tanners Council.

This has been valid for a long time, and this is what the tanning process is all about. Everything in the leathernaking process - from the preliminary work in the beamhouse, through the tanning, retanning, fatliquoring/ softening and finishing process - must be orientated to this objective.

However, there are many definitions, and another general description that is appropriate is: "a material formed from a network of collagen fibres of hides and skins, prepared by appropriate chemical and physical processes to the properties necessary for its final use."⁷ Tannage therefore has to change the properties of collagen, either by chemical reaction or by covering the fibres against outside influences.

Different tannages and tanning mechanisms⁸

There are many different types of tannage, and they provide different properties.

OIL TANNAGE

This is probably the oldest tanning method. It was possibly discovered when it was noticed that animal skins under the influence of air and smoke became softer and more pliable. This kind of tannage was used until recently recorded times by some primitive races in Asia and some American Indian Tribes. The Eskimo also practised a kind of oil tannage using natural animal grease. Ancient pictures showed how they softened the skins by chewing, the enzymes contained in the spittle helping to disperse the fat.

Modern oil tannage, still in use but limited to certain articles, use highly unsaturated fish oils that are oxidised after skin penetration under controlled conditions. The major tanning reaction comes from oxidised fractions of the oil reacting in a similar manner to aldehydes. This is the so-called Chamois

tannage. Relative little "tanning agent" is necessary to obtain a permanent (even washable) tannage and the remaining oxidised oil acts as the lubricating agent.

ALDEHYDE TANNAGE

Aldehyde tannages are well investigated, the aldehyde group reacting with the amino group of the collagen to form a covalent bond. Formaldehyde use is well known in this role as a preservative within anatomical preparations. Although considerable quantities of very soft leathers were made, the use is now very restricted for reasons of toxicity. Glutaraldehyde has become increasingly important, as it forms covalent bondings, and can provide good crosslinking action between reactive groups on different chains

VEGETABLE TANNAGE

For thousands of years vegetable tannage was the most important method. It probably evolved from observing that when skins came in contact with leachates from certain fruits and barks (with a high tannin content), they were transformed into a form of leather.

Vegetable tannins contain phenolic groups, and after skin penetration forms hydrogen bonds with the collagen peptide groups. This bond is dependent on pH of the tanning system and is intensified under acid conditions. However, if vegetable extracts are sulfited the affinity to collagen is lowered. A reduction in affinity - or bond weakening - also occurs under higher pH conditions. For this reason E.I. goatskins can be detanned under alkali conditions and vegetable leathers suffer from perspiration.

CHROME TANNAGE

The tanning properties of trivalent chrome tanning salts were discovered about 150 years ago, but have been in use for about 100 years. This is because of both economy in use and versatility in the production of leathers of high quality. Today more than 80% of all leathers are chrome tanned, and has created an intermediate product as a commodity, the so-called "wet blue".

Chrome tannage has a special advantage due to the complex chemistry of the trivalent chrome. Very stable cross-links are formed between the carboxyl groups of the collagen side chain as they enter the chromium complex. By raising the pH basification and condensation occur to form complex molecules of higher weight. These are particularly suited for crosslinking, being the reason for the high heat resistance of chrome tanned leather. However, it may be reversed if the carboxylic group is replaced within the complex by other ligands of greater affinity.

SYNTHETIC TANNINS

These are either dispersing or bleaching agents or replacement syntans, and are mainly based on phenol-formaldehyde condensation products.

Replacement syntans have larger molecules and are used to a degree as replacements for vegetable tannins. These are irreplaceable for white leathers and in special combination tannages, but the full replacement of vegetable tannins has failed so far.

POLYMER RESINS

These are the fastest growing products and used mainly for retanning purposes. In addition, modified products with lubricating chains can provide superior qualities to ordinary fatliquors.



OTHER ORGANIC AND INORGANIC PRODUCTS

These are of minor importance and includes cationic resins, aluminium salts, speciality products such as zirconium and titanium salts, and recently re-introduced iron compounds. However, phosphates and silicates seem to be gaining importance for chrome-free pretannages.

COMBINATION TANNAGES

Combination tannages are of growing importance. As the final goal is not simply tanned collagen, but a 'high tech' material with very special properties, different tanning materials have to be used in the right sequence and quantity to obtain an optimal result.

Examples of the different cross-linking systems and their role in tannage are illustrated in *Figure 3*.

Heat stability and product quality

A valid theory for all types of tannages has been the objective of many investigations and will remain an interesting target. Hydrothermal isometric tension measurement is one of the latest promising attempts.

However, there are many different types of tannages. The tanning mechanisms vary, and each provides different properties. Nevertheless, heat stability or shrinkage temperature is often used as a scale for "tannage" reflecting one important characteristic. This is certainly useful for leathers subject to higher temperatures, such as in footwear construction, certain industrial safety articles, or even car upholstery. As such it is an excellent tool within quality control for measuring the consistency of a defined process.

Scientific theory plays a central role in understanding the complex process of tanning. This is important. However, it does not explain how to produce a very soft leather without weakening or loosening the grain, or how to keep the butt as flat as possible and still fill the empty flanks. Tanners still await helpful theories that can be applied to the problems that they permanently face. 

Acknowledgements

This paper is based on the latest publications as set out in "Literature", and conversations with Professor Gunter Reich to whom I wish to express special thanks.

Legends

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