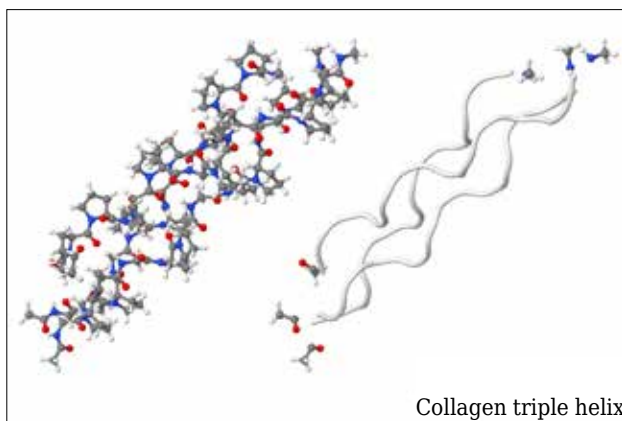




# The Leather Industry: A Chemistry Insight

## Part I: an Overview of the Industrial Process

Valentina Beghetto, Aurora Zancanaro, Alberto Scrivanti, Ugo Matteoli, Giorgio Pozza



***A panoramic overview of the industrial tanning process is reported, giving a general outline of how an animal skin (Collagen, image on the left) is transformed into a durable material by industrial processing***



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# The Leather Industry: A Chemistry Insight

## Part I: an Overview of the Industrial Process

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**ABSTRACT:** A panoramic overview of the leather world market is given. The industrial tanning process is schematically explained giving a general outline of how an animal skin is transformed into a durable material having many different characteristics according to its specific future use. All the tanning industrial steps are overviewed starting from soaking, liming and after various steps ending up with finishing. An insight of collagen chemistry is also given.

**KEYWORDS:** Skin, Leather, Tanning process, Collagen.

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### 1. Introduction

The leather industry is a world-wide leading market concerning the processing of skin or hide of animals, which by tanning are transformed into a durable material preventing its decay and making it persistent and flexible. Since the Prehistoric Age, primitive people have preserved pelts with smoke from wood combustion, ash and animal fat to craft garments, shoes, sheds, etc. It is of 2010 the discovery of the oldest shoe ever, found in Armenia dating back to 5500 years ago [1].

In the centuries, the tanneries gradually abandoned the labour-intensive production for a modern industrially feasible leather processing [2,3]. Currently, Asia is the world leader in leather production and in particular China is the most prominent representative in this industry, along with India and Hong Kong. However, according to market overviews, Italy leads both the garment and the fashion industries compared to Asia and South America [4].

From yearly Euroleather statistics, the over 3000 tanneries scattered around Europe, are at all rights leaders in the international leather producer and consumer markets, with an income of nearly € 5 billion corresponding to over 25% of the world market

(Table 1). Generally, European tanneries are companies of small to medium size and are specialized in the production of all kinds of leather for different goods such as footwear, garment, furniture, automotive.

The consequent flexibility, adaptability and the quick response to demand constitutes one of the industry's most important assets. Larger companies, however, excel thanks to their capacity to be at the forefront of technological developments and to constitute reliable partners in global business activities.

It is important to remember that the Leather Industry market is strictly connected to the meat market. In fact, this industry is able to convert a by-product of the food industry into a noble material which otherwise should be disposed into waste. Nowadays the average of cattle slaughtered every year is roughly 300 million, corresponding to 15 million tons of hides.

As a matter of fact, the outcome of the tanning process is highly dependent on the quality of the original raw hides, with special regard to the conservation status. Autolysis of collagen, in fact, starts just following the death of the animal due to the activity of spoilage bacteria producing proteolytic enzymes. Since any impairment of the collagenous network

Table 1. European leather market in 2009.

2009	Employment	Companies	Turnover (1.000 Euro)	Exports (%)	Production (1.000 m <sup>2</sup> )	
					Cattle/Calf	Sheep/Goat
France	1.529	53	217.792	33	2.663	2.306
Germany	1.925	18	286.968	60	7.000	450
Italy	16.717	1.378	3.800.000	68	96.921	29.295
Netherlands	325	5	100.000	71	4.000	-
Portugal	1.980	63	180.000	31	-	-
Spain	1.689	118	602.830	45	14.414	7.686
Sweden	260	4	40.000	90	1.100	30
UK	1.000	23	180.000	70	5.000	1.500
Romania (est)	900	15	16.250	-	300	1.250
Bulgaria	190	17	2.900	90	55	176
Norway	78	2	-	-	-	-
TOTAL	25.613	1.633	5.246.740		131.453	42.693

leads to severe losses in terms of final leather quality, a proper conservation of the hides represents one of the major issues in the leather making industry.

The most common preservation systems act by reducing the bacterial activity by means of drying, salting or refrigerating the substrate as soon as possible since flaying. Among these methods, salting techniques are the most viable and, therefore, industrially widespread, although a high load of chloride ion is inevitably released into the waste water [5].

Mammalian skin is an organ fulfilling many physiological functions such as regulation of body temperature, protection, elimination of waste products, sensory detection, etc. The aim of the tanning process is to enhance some of its natural properties, remove any unwanted matter, to stabilise its structure and at the same time to prevent putrefaction. The most important component of hide in the leather making view is collagen.

The approximate composition of a bovine hide is 64% of water and 33% of structural and non-structural proteins. In particular, structural proteins are collagen (29%), keratin (2%), elastin (0.3%) while non-structural proteins are albumins, globulins (1%), mucins, mucoids (0.7%). As minor components, fats (2%) and other substances (0.5% inorganic components, 0.5 % pigments, etc.) are contained in the skin [6]. In Table 2

are reported the average amino acid composition of collagen and keratin (see also Fig. 1).

Table 2. Amino acids contents in collagen and keratin.

Type	Amino Acid	Collagen Type I	Keratin
Non Polar	Glycine	330	81
	Alanine	110	50
	Valine	22	51
	Leucine	26	69
	Isoleucine	12	28
Hydroxy	Serine	34	102
	Threonine	18	65
	Tyrosine	5	42
Carboxy	Aspartic acid + asparagines	47	60
	Glutamic acid + glutamine	73	121
Basic	Lysine	38	23
	Hydroxylysine	6	0
	Arginine	48	72
	Histidine	4	7
Imino	Tryptophan	0	12
	Proline	126	75
Sulfur	Hydroxyproline	93	0
	Cystine	0	112
Aromatic	Methionine	4	5
	Phenylalanine	14	25
	Tyrosine	5	42

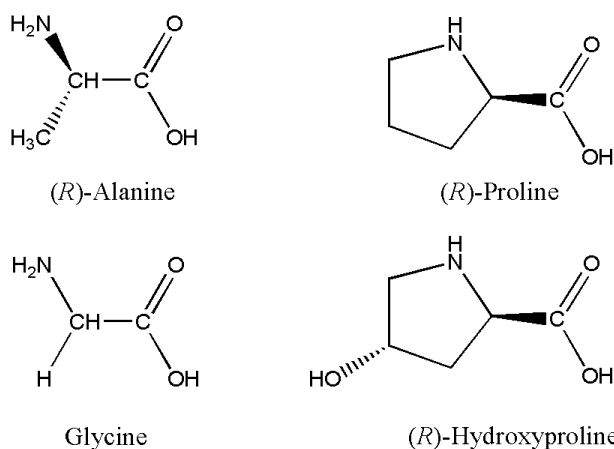


Figure 1. Molecular formula of the most abundant collagen amino acids.

The process, albeit its complexity, is very flexible and adaptable to the raw materials and the characteristics of the final products wanted. In Scheme 1 are reported only the tanning steps involving relevant chemical transformations of collagen; mechanical treatments such as fleshing or splitting are discussed only in the text.



Scheme 1. Simplified scheme of the tanning process.

In the first step of the process (soaking) the animal skins are soaked with water in the presence of additives in order to remove the excess of salt, dirt, dung, blood, and restore a suitable water content inside the skins. In some Countries the solid fraction of the salt used for conservation is removed by mechanical or manual treatment prior to the addition of water, in order to reduce the concentrations of chlorides in the wastewater [7]. Salt can be recovered for other uses after appropriate purification [8]. In the second step (liming) the soaked skins are steeped in an alkali and sulphide solution that breaks down the structure of the hair at the root (its weakest point) by a reduction of an important constituent of keratin, cystine sulphur-sulphur linkages, in order to facilitate hair removal. In this phase most of the unwanted substances (non-structured proteins, fats, hyaluronic acid, etc.) are removed and the proper-

ties of the skin protein are altered [9]. The collagen becomes chemically modified and swells, leaving a more opened structure. Adhering flesh and subcutaneous tissue are mechanically cut off by fleshing.

In the deliming-bating step the skin structure is opened up further by controlled enzymatic digestion, and further unwanted material (residual epidermis, etc.) is removed.

The pickling stage prepares the skins for the subsequent tanning by treatment with acids (formic and sulphuric acid are the most used). Since pH is driven well below the isoelectric point, sodium chloride is added to prevent a dangerous acid swelling of the pelt [10,11].

For historical reasons, all the preparative stages before the proper tanning step are collectively called *beamhouse*.

With the tanning process the skin is chemically stabilised and converted into a putrefaction-resistant material. This transformation may be operated by a wide range of chemistries; however, for a number of reasons chromium(III) basic sulphate is the predominant tanning agent used in the leather industry worldwide.

Despite all the scientific investigations in this field, the chemistry of tanning reactions still remains somewhat unclear. For decades the most credited tanning theory explained the stabilisation of the collagen with the formation of cross-links within its triple helix structure [3]. It actually seems that a modification of the supramolecular water sheath also plays a key role in this transformation [12]. All tannages results in an increase of the hydrothermal stability of the collagen, the extent of which depends mostly on the chemical nature of the tanning agent.

Tanned hides are neutralized with alkali and dyed. During this step leather is also retanned and treated with fatty substances that prevents leather fibres from sticking and make the leather softer. Unbound water is finally removed from the leather by drying and the look of the resulting leather is modified by finishing of the surface.

## 2. Discussion

### 2.1. Process details

Here below the steps of the process are illustrated.

#### 2.1.1. Soaking

One of the main purposes of the soaking stage is to remove dirt (blood, body fluids, mud, soil, dung, etc.) and salt from the raw hides. Actually a residual concentration of sodium chloride is still desirable in the process bath, as it helps diffusion of water down the hierarchical structure of skin fibres. In fact, absorption of water helps opening up the fibres preparing the collagen to the subsequent liming step. When fresh raw stocks are processed the salinity of the float may be adjusted by addition of sodium chloride. Soaking is generally carried out at pH values between 9 and 10 by addition of sodium carbonate or sodium sulphide, which leads to moderate swelling of the hides, beneficial for rehydration. Swelling of collagen is a very important phenomenon intimately involved with the tanning of hides and is observed when the pH of the surrounding matrix differs from the isoelectric point (I.P.) of the protein which is defined as the pH at which a particular molecule carries no net electrical charge; typically for native collagen I.P. is around 7.4. Thus, during the tanning process both acid and basic swelling are observed according to the trend outlined in Fig. 2 [11].

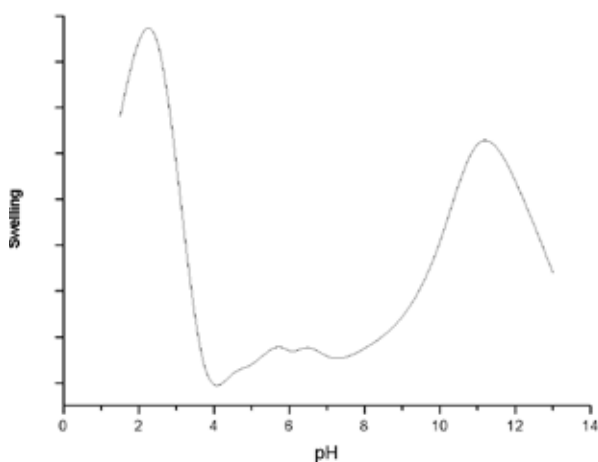
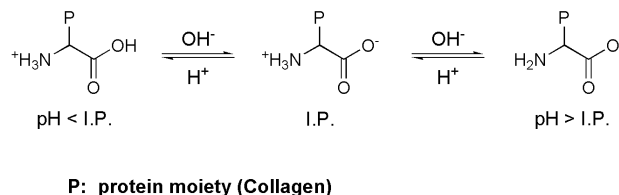


Figure 2. Dependence of swelling on pH.

For example at high pH values the amino groups of collagen are uncharged while the carboxylic group are quantitatively in their anionic form; the repulsive forces between the negative charge of

the anions are no more counterbalanced by amino cations, and produce a modification of the structure that allows more water molecules to accommodate inside. An opposite behaviour is observed when pH is below I.P. (Scheme 2).



Scheme 2. Effect of pH on the charge status of collagen protein.

The substantial difference between basic and acid swelling is the high risk of denaturation of the protein which can suddenly occur when pH is around 2.0-2.5, while a much more gradual swelling occurs when I.P. < pH although denaturation is observed when pH is higher than 13. Soluble proteins, hyaluronic acid, dung and other components are partially dissolved by the diffusion of water inside the cross section of the skin. The processing float is discarded and substituted with fresh water three or more times in order to optimise the cleaning action. The temperature is adjusted in the optimal range 20-30 °C; particular care is taken to avoid overheating (possibly by friction), as this can irreversibly damage the hide structure. Soaking usually requires 6 to 24 or more hours according to the size and the degree of drying of the raw stock. Detergents are added to mostly accelerate wetting of the fibre surfaces and, to a lesser extent, to remove fat. As long as rehydration of the organic substrate takes place, microorganisms, initially inactivated by salting and drying, begin to proliferate. Therefore, the addition of bacteriostatic or bactericide chemicals is necessary to prevent rapid collagen degradation. Proteolytic enzymes may be used to help removal of non-structural proteins, although their action can irreversibly damage the collagen structure; for this reason many tanners are extremely cautious regarding the use of enzymatic soaking.

#### 2.1.2. Liming

It is nowadays a common industrial practice to run unhairing and liming in one step. Unhairing is the process of removing the hair from the pelt. Once the hair shaft detaches from the hide surface it is free to float in the bath and can be separated



with ammonium salts (chloride or sulphate) that have an appreciable buffering effect at the pH of interest and quickly penetrate into the cross-section of the pelts. However, the employment of ammonium sulphate salts has two important drawbacks. In the first place, ammoniacal nitrogen concentration in the effluent should be limited due to its toxicity to aquatic life [21]. Secondly, sulphate anions may form sparingly soluble  $\text{CaSO}_4$  by reaction with calcium cations or limeblast left over from the previous liming step. *In situ* formed calcium sulphate crystals produce a distortion of the fibre structure and negatively affects the quality of dyeing. On the other hand, chloride ions have a greater lyotropic effect and can further open up the collagenous structure [19].

Other acidic chemicals, both weak and strong, can be effectively used for deliming, paying attention to the fact that strong acids may lower the pH enough to cause undesirable acid swelling (see Fig. 2). Although a variety of formulations containing dicarboxylic acids, synthetic tannins and inorganic buffering salts are commercially available under various brand names, the employment of a certain amount of ammonium salts is still unavoidable in practical industrial processes.

The subsequent bating process makes use of enzymes (usually proteases) to catalyse hydrolysis of non-structured proteins. To optimize the biochemical reactions, pH should range in the interval 8.0-9.0 and temperature set around 37 °C. Enzymes are of animal (pancreatic) or bacterial origin and are formulated with inert materials in order to better modulate their activity. It is worth to remember here that historical sources of enzymes were bird guano and dog puer, thus contributing to the collective perception of the tanning process as a dirty job across the centuries.

Bating is stopped by lowering pH and temperature when the desired degree of softening is reached. This assessment is very difficult to standardise and is still based on the empirical evaluation by experienced personnel.

#### **2.1.4. Pickling**

The industrial main tanning operation, requires a preventive treatment of the pelts at low pH, typically in the range 2.8-3.5. Lower values of pH can be reached to preserve small skins from putrefaction when traded in pickled state. Unless appropriate precautions are taken, acid swelling occurs in this pH region since it lies below the I.P. Unlike alkaline swelling, that determines the opening up of the

structure and allows removal of unwanted substances during liming, acid swelling must be accurately avoided as it causes a non-reversible disruption of hierarchical structure of collagen. Fortunately, this behaviour can be effectively inhibited by a suitable value of osmotic pressure in the aqueous solution, regulated by the addition of sodium chloride. Typical values of NaCl concentration in the pickling float are around 8-10% wt. Once the salt is dissolved, formic acid and, subsequently, sulphuric acid are added after previous dilution [3]. In order to avoid further discharge of chlorides in the effluent, salt can be avoided by using non-swelling acids, that combine acidity and osmotic effect in one single chemical species. These are based on naphthalensulphonic acids.

The temperature of the float should be kept around 20°C to inhibit acid hydrolysis of collagen; in hot Countries ice may be used to this scope. Time and mechanical action are necessary for the acid solution to permeate the whole cross section of the hides, although a certain pH gradient may be allowed for specific needs.

#### **2.1.5. Tanning**

At the end of beamhouse operations the main component of hides is structured collagen, that is ready to be transformed into leather. Once a skin is tanned some typical properties are expected to appear. The first feature is an outstanding resistance to putrefaction (it is common knowledge that some leather artifacts dated back to thousands years ago are still preserved); in a more general perspective a tanned skin is awaited to be softer than it was in the raw state, often with a typical colour and smell; all the changes given by tanning should be permanent. Technically speaking, an increase in shrinking/denaturation temperature also accompanies the transformation of skin in leather, measured as resistance to wet heat (hydrothermal resistance). The transition to leather requires permanent incorporation of chemical species into the collagen network; however, until the twentieth century, few tanning chemistries were known and applied by fellmongers. Among all, plant materials have certainly been the most commonly used: leaves, bark, galls, sawdust were put in strict contact with raw hides and allowed to stand for months or years before the transformation was deemed complete (vegetable tanning). The reaction site was often a pit in the ground (*pit tanning*), and the final leather was generally stiff and typically coloured depending on the plant.

Potash alum was also renowned as tanning agent and was often used in combination with vegetable tanning (semi-alum leather) [22]. Wood fumigation was also known to stabilize animal skins and was practised by some communities [23].

Fish oil tannage also represents an historical technique that is nowadays almost abandoned [24]. The resulting leather is typically yellowish and shows an extraordinary capacity to absorb water. Before synthetic materials, it was used for car-wash cleaning, fuel filtration and for sweat absorption in long term-patients.

With the progress of chemical science the active principles of the historical treatments outlined above were discovered and isolated: plant polyphenols, both hydrolysable and condensed, for vegetable tanning, aluminium salts, aldehydes in smoke from wood combustion [23]. In modern times all these substances are used on industrial scale; plantations are specifically grown for extraction of vegetable tannins, aluminium potassium sulphate is available for tanning purposes as well as glutaraldehyde and oxazolidine I and II [25] (Fig. 3) (although extensively used for decades, formaldehyde is ruled out as tanning agent due to safety restrictions [26]).

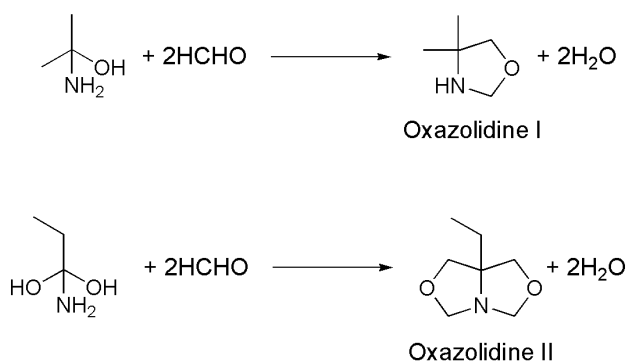


Figure 3. Oxazolidine I and II.

But the revolution in the tanning industry took place when chromium salts entered the tanners' venues; the discover of its extraordinary properties is reported by Knapp back in 1858 [27] and, although for various reasons it took some fifty or more years to gain proper industrial relevance, currently over 80% of the leather worldwide is tanned with Cr(III), mostly in the form of chromium basic sulphate.

It can be stated that almost the whole periodic table has been explored searching for other possible tanning agents; some metals other than chromium

and some non-metallic anions actually show interesting properties, but their use is limited by either cost or low effectiveness, or remains of purely demonstrative interest due to toxicity (e.g.  $\text{OsO}_4$ ,  $\text{UO}_2\text{Ac}_2$ ,  $\text{Pu}(\text{NO}_3)_4$  all have a good tanning effect [28]). Among metal ions only aluminium, titanium and zirconium have a role in the modern tanning industry. An effective iron tanning was developed around the mid of the twentieth century, but its industrial use has been very limited [29].

Special classes of synthetic tannins (syntans) have been created with tanning properties similar to the vegetable ones, which offer some important advantages like white colour and fastness to light.

A sizeable discover in tanning chemistry regards methylol phosphonium salts, and in particular tetrakis(hydroxymethyl)phosphonium sulphate (THPS) (Fig. 4) [30].

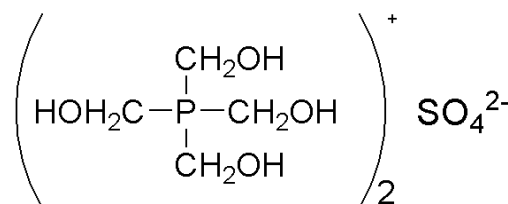


Figure 4. THPS.

This latter shows powerful tanning properties, with a mechanism similar to aldehydes chemistry [3].

Albeit a detailed discussion on the interaction between collagen and the tanning agent is beyond the scope of the present paper, nevertheless it is generally accepted that a common feature of tanning molecules is their ability to interact with the triple helix of collagen and its supramolecular water layer [31]. These interactions may differ in their character, ranging from strong covalent to much weaker hydrogen and Van der Waals bonding, and may involve acid or basic side chain groups of the aminoacid series. As a consequence, the isoelectric point of the leather will result raised or lowered compared with that of pelt, respectively. From a theoretical point of view, cross-linking of the tanning agent within the triple helix of tropocollagen is believed to be the main responsible of the typical features of leather especially with regard to its stabilisation [32]. This model is still considered fully working by many scientists and technicians, although Gustavson, one of the pioneers of



tanning science, expressed some degree of criticism [33] about this theory.

Collagen is a peculiar protein, characterized by an uncommon hydrothermal stability even in its native state. Quite exceptionally, its primary structure is a replication of the sequence Gly-X-Y, very often of the type Gly-Pro-X and Gly-Y-Hyp (where Gly=glycine, Pro=proline and Hyp=hydroxyproline), making Hyp one of the most abundant components of collagen. Through the determination of the quantity of hydroxyproline present it is possible to distinguish dermal proteins from others [34].

Collagen structure is a characteristic right-handed triple helix generated from three different helices of amino acids (Fig. 5).

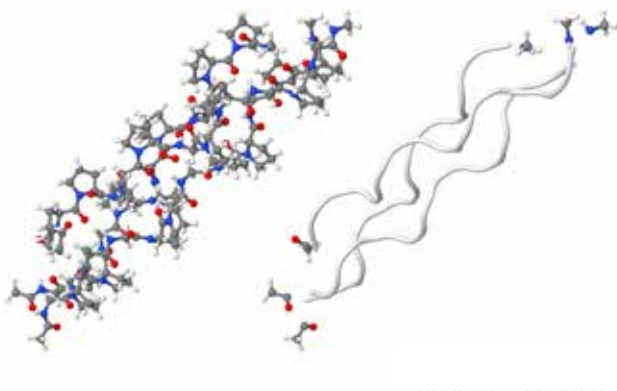


Figure 5. Structure of Collagen triple helix.

Collagen then aggregates into higher structures called microfibrils, that in turn pack in fibrils with the help of other classes of proteins like glycoproteins and proteoglycans. These latter are bonded together to constitute collagenic fibres, typically organized in a complex network. This kind of bottom-up steric organization is called “hierarchical structure” and, to a large extent, accounts for the remarkable stability of collagen. For steric reasons the ring of Hyp points outward the helix and constitutes an aggregation point for water molecules, that bond to the prolyl hydroxyl group via hydrogen bonding [35]. As a consequence, a solvating cylinder of supramolecular water originates around the triple helix by nucleation at the Hyp sites, that is the region where the tanning reactions occur. This water arrangement, although labile, constitutes a stable structure [36] onto which hydrothermal stability relies [37]. A stabilization effect of the tanning species on the water matrix must be then responsi-

ble for the enhancement of hydrothermal stability. A further consequence is a correlation between the hydrothermal stability and conformational changes at the fibrillar level, with an effect on biochemical resistance [38]. This interpretative model is known as “link-lock” concept [3], and should be included together with the crosslinking effect in a comprehensive theory of tanning.

#### **2.1.6. Retanning, neutralising, dyeing & fatliquoring**

At the end of tanning leather is generally at pH around 4.0. With chromium tanning, the pH tends to further decrease since protons are released by hydroxy bridges of chromium complexes (olation [39]). Since the isoelectric point is higher, the hide protein is in cationic form and is too reactive with regard to the dyestuffs and fatliquors, all in anionic form, employed in the subsequent steps. The pH value is then raised from 4.5 to 6.5 by using a mild alkaline salt such as sodium formate.

After the pH is uniformly adjusted along the cross-section, a retanning process is normally performed to tune the properties of the leather, thus defining its ultimate character. Such a transformation is mainly aimed to obtain the desired handle in terms of fullness of the final article and different tanning chemistries can be used here with respect to the main tannage. Although they do not strictly enter the tanning agent definition, hydrogen bondable polymers may be employed for this purpose, often in order to fill up the weaker areas of the hides (flanks) and produce a more even leather, or a particular handle.

The crusted leather is then coloured with dyestuffs, which are mainly of azoic nature. The introduction of one or more sulphonic functional groups is necessary to make the molecule water soluble and to allow an electrostatic bonding with the cationic amino groups of collagen. For a good penetration the reactivity of the substrate should be minimized by raising the pH value, while fixation is obtained by lowering it, typically with formic acid. In the fatliquoring process the leather is treated with fatty matters, often sulphonated or sulphated oils, that react with the fibrous structure of collagen and prevent them from sticking. This results in giving leather softness and suppleness.

### 2.1.7. Drying

All reactions are conducted in an aqueous medium. Therefore at the end of processing the leather is drenched and water needs to be removed. The drying technique (vacuum drying, toggling, etc.) has a considerable influence on the leather properties and area yield.

### 2.1.8. Finishing

Finishing consists in a group of surface operations aimed to enhance the natural qualities of the skin and cover imperfections eventually present on the surface. Mechanical protection, evenness of colour and touch properties are the main requirements for finishing. A number of acrylic, polyurethane and other film-forming synthetic polymers are common ingredients of finishing recipes; they are mixed with natural substances, both native or modified, like oils, waxes, caseins, albumins, cellulose esters and others. The colour is regulated by the use of dyes and pigments.

## 3. Conclusions

Leather is recognized and valued as one of the most ancient natural products still surviving in the industrial era, and is even more appreciated as it still brings in itself a degree of emotion that technology is hardly ever able to classify. Despite a certain degree of scepticism still around, the modern leather industry is deeply involved in chemical sciences, and is extremely demanding in terms of research and innovation. Leather making owes a lot to many branches of organic, organometallic and coordination chemistry, physics of surfaces and phases, inferential statistics, environmental sustainability, ethics and many other fields. It should be clear that processing of leather involves a continuous interplay of different disciplines that must keep abreast with a turbulent market, environmental restrictions, safety regulations, customers' needs, cutthroat competition, and many other aspects, representing a growing challenge for new generations of chemists and technologists [40].

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