# AGING PROCESSES AND CHARACTERIZATION METHODS FOR HISTORICAL BOOK BINDING LEATHER

Katarzyna Marcula[1], Katharina Schuhmann[1], Manfred Anders[1, a]

1 ZFB Zentrum für Bucherhaltung GmbH, Germany

*a Corresponding author: anders@zfb.com*

**Abstract.** The original substance of a book binding leather provides information about the place of origin, storage and user history of the book, which is why the preservation of this material in its original form is of crucial importance for research in the field of bookbinding. In a current research project in cooperation with FILK Freiberg, a newly sustainable treatment for historical leather book covers will be developed. The aim is to introduce a long-term mild care agent to increase leather flexibility and stability, which will remain in the structure and to stabilize the pH value at an optimal level with a buffer introduced in the form of deacidification agent. Preliminary research showed, that aging processes of vegetable tanned calf leather, which has been mainly used for leather book bindings in the past centuries, haven't been fully explored yet. Further, essential characterization methods like the determination of the acid content and methods for accelerated aging tests are not yet defined for leather. For a systematic development and evaluation of the newly treatment, the project had to be focused on accelerated aging and characterization methods first.

## 1 Introduction

Book binding leather not only has a decorative character in book bindings, but above all fulfills the protective and mechanical functions of the book. Therefore, it must have certain strength and flexibility. The original substance of a book binding provides information about the place of origin, storage and user history of the book which is of important scientific interest. For this reason, the preservation of this material in its original form is of fundamental importance for research in the field of bookbinding. The functionality of the leather book bindings is endangered because, like other organic materials, they undergo the continuous and unavoidable aging processes over the time. In recent decades in the various national libraries, special leather treatments have been developed, which, however, without exception, have been proven to be more destructive than stabilizing in long term. Components of these mixtures harden over the time and the leather becomes fragile and brittle. Partially they also migrate to the surface of the material, making it sticky. Looking at the issues of protection of leather book bindings, there are two main aspects to be dealt with: introducing long-term mild care agent to boost leather flexibility, which will remain in the structure and stabilize the pH value at the optimal level with the buffer introduced in the form of deacidification agent. One reason why there is still no solution to these problems is the inhomogeneity of the leather and difficult analysis of this material.

In a current research project in cooperation with the Forschungsinstitut für Leder und Kunststoffbahnen FILK, a newly sustainable treatment for the chemical stabilization and flexibilization for historical leather book covers will be developed.

Within the preliminary research, it turned out that the aging processes of vegetable tanned calf leather, which has been mainly used for leather book bindings in the past centuries, hasn't been fully explored yet. Therefore, the main degradation processes oxidation and acid-catalyzed hydrolysis have been investigated further to determine the most dominant process. Furthermore, standardized characterization methods and methods for accelerated aging tests are not defined yet and had to be developed, regarding the results of the degradation investigations. The analytical approach to leather aging processes was focused on chemical and mechanical collagen assessment.

The analysis of change of tannins has not been conducted, as it would have exceeded the limits and possibilities of the current project.

## 2 Materials and Methods

### 2.1 Production of homogeneous collagen and leather samples

Animal skin itself, and accordingly book binding leather as well, is a very inhomogeneous material. Depending on the specific animal, applied leather manufacturing technologies, the sampling point, the storage and usage history of a book, especially the mechanical properties of book binding leather varies a lot. This inhomogeneity is a very challenging aspect for comparative studies, investigating degradation processes or evaluating new developed care treatments. As there is no suitable completely non-destructive test method available yet, a novel approach for the use of possibly homogeneous samples for comparative experiments has been developed.

To determine the chemical effect of the developed treatments on collagen, “Freiberger Hautpulver”, a slightly chromium tanned collagen powder, has been used for analysis. For the current project, the powder did undergo a vegetable tanning, like it has been used extensively for the production of historic book binding leather. Experiments on the tanned collagen powder allow to investigate the effect of the care treatment without being limited by diffusion effects of the product into the leather matrix.

To investigate the diffusion processes into a physical collagen matrix and the effects of the developed treatment on the mechanical behaviour of leather, real leather samples had to be examined as well. To receive possibly comparative results in that case as well, defined and reproducible model leathers have been produced at FILK. According to historic book binding leather, a vegetable tanning has been applied to calf skins to produce a so-called restoration leather. For the treatment development, accelerated aging experiments have been performed on the model leathers to achieve a reproducible state of degradation. To compare different initial states, some of the model leathers have been produced with a specifically higher acid content.

### 2.2 Sampling

In initial experiments, selected mechanical and chemical parameters of the model leathers have been examined in defined reference spots of small distances over the total skin area of all produced model leathers. The results delivered a defined set of reference values for further tests on the one hand, as well as an overview of the comparability in between the model leathers on the other. For a further improvement of the comparability of results before and after a treatment, samples of the model leathers have been taken in a possibly small distance after a defined scheme (Fig. 1).

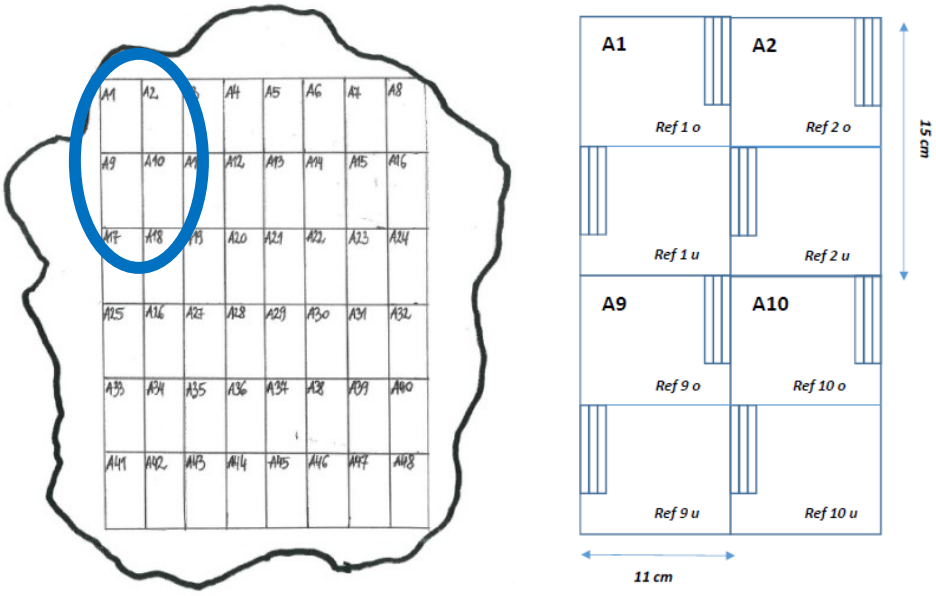


**Fig. 1.** Sampling on model leather skins

### 2.3 Accelerated Aging

The developed accelerated aging method is based on ISO 5630-5 for paper aging which provides a heating of the samples in a closed vessel of a defined volume at 100 °C for five days. For the model leather samples, a two-step aging procedure has been developed. Within a first step, a typical state of degradation like it can be found in historical book binding leathers, shall be simulated. This can be achieved by triggered acidic catalyzed hydrolysis reactions by the addition of acid(s) to the sample in the closed vessel. After the care treatment which has to be tested has been applied, its sustainability shall be proven in a second aging step.

With this objective, numerous versions of aging methods with varied aging time, temperatures and acid additives have been tested.

### 2.4 Analysis of Amino Acids

A qualitative and quantitative analysis of the included amino acids has been performed by FILK within the project. Therefore, acids have been dissolved out of the leather samples by acidic hydrolysis and separated by ion exchange chromatography. Subsequently, the single amino acids have been identified by a post-column derivatization with ninhydrin which enables a photometric detection and after calibration a quantitative analysis of α amino acids.

### 2.5 Warm water solubility

The warm water solubility of the samples has been determined by giving 1.00 g of a sample in 50.0 ml water of 60 °C for 120 minutes. The weight decrease of the dry sample allows information about the content of hydrolyzed or denatured collagen in the sample. The determination of this value is especially important for historical samples, which are characterized by high solubility in warm water (30-50%), due to a far-reaching hydrolysis. This value has become the main indicator for determining the degree of hydrolysis in the study of historical leathers, and serves as a guideline value for the development of methods of artificial aging.

### 2.6 Shrinkage temperature

The shrinkage temperature of collagen fibers is a well-known measure for the degree of denaturation. Within the project, it has been visually determined with the micro hot table (MHT) method, where the samples are heated in water at a constant rate of 2-4 °C/min and observed under a light microscope. Two states have been documented per sample:

$T_I$ – first motions of single fibers
$T_S$ – majority of the fibers is shrinking

The shrinkage temperature allows qualitative information about the state of degradation of the collagen fibers – the further the degradation process, the lower $T_S$. The $T_S$ of a single and complete hydrated triple helix is about 37 -38 °C. With the natural arrangement of the triple helices to fibrils and collagen fibers and finally their physical intertwining, $T_S$ increases to about 60°C. A vegetable tanning leads to a $T_S$ of 75-80°C. If a triple helix is heated over its $T_S$, it will be irreversible degraded. Another method to determine the shrinkage temperature of collagen is the differential scanning calorimetry (DSC) which has been carried out within the project for selected samples by FILK. An acceptable accordance between $T_I$ (MHT) and $T_{onset}$ (DSC) as well as between $T_S$ and $T_{max}$ could be found which allows both measurements to be used in comparative studies. The DSC method delivers the denaturing enthalpy as a further interesting parameter.

### 2.7 pH value and differential number

The measurement of the pH value has been carried out following DIN EN ISO 4045 in an extract of 1.00 g sample in 20.0 ml water. Each sample has been measured in a three-fold determination.
Further information on the acidity composition of the sample gives the measurement of the differential number (only for samples with pH below 3.5 or above 9.0). Therefore, the sample extract has to be diluted 1:10 after the initial pH measurement and measured again. The differential number corresponds to the difference between both pH values.

A differential number below 0.7 indicates the presence of either free strong acids in combination with a large amount of buffering salts or the presence of mainly weak acids. A differential number above 0.7 is a sign for mainly strong acids and the presence of buffering salts. [1]
With a pH below 4.0 and a differential number below 0.7, major acid-caused damages within the leather can be foreseen.

Both measurements have been made with a METTLER TOLEDO Five Easy pH meter and deionized water (< 10 µS/cm).

### 2.8 Acid-base titration

In addition to the determination of pH value and differential number, which deliver information about the acidity of the samples, an acid-base titration allows quantitative statements about the acid amounts. This information is decisive for the development of an accelerated aging method and in particular for the development of the sought pH adjustment. As the leather industry usually refers to the pH value and differential number, a standard method for the quantitative determination of the acid content surprisingly doesn't exist yet and had to be developed within the project first.

A titration method for the quantitative determination of the leather's acid content has been developed on the basis of ISO 10716, a back titration with NaOH after addition of HCl, developed for the alkalinity determination of paper. To adapt the method for the analysis of leather samples, several alkalimetry and acidimetry methods have been tested on extracts of leather samples with varied extraction and filtration parameters, different extraction media ($H_2O$, NaCl or KCl solution),

sample amounts and titration volumes. Furthermore, the influence of $CO_2$ presence has been investigated. A METROHM DMS Titrino 716 has been used for titration.

### 2.9 Ion chromatography

To gain more information about the contained acids in typical historical leather samples and the produced and accelerated aged model leathers, a semi-quantitative ion chromatography on selected leather samples has been performed at HTWK Leipzig. In three different test sets, inorganic anions ($F^-$, $Cl^-$, $NO_3^-$, $PO_4^{3-}$, $SO_4^{2-}$), inorganic cations ($Na^+$, $NH_4^+$, $K^+$, $Mn^{2+}$, $Ca^{2+}$, $Mg^{2+}$) and organic anions (lactate, formate, acetate, oxalate) have been detected.
For the comparison of the total detected acid content with the results of the developed acid-base titration, the following equation 1 has been applied under consideration of the ions valence:

$$Acid\ content\ \left[\frac{mmol}{g}\right] = \sum anions - \sum cations \qquad (1)$$

## 3 Results and discussion

### 3.1 Leather degradation

The aging of leather is a complex of related chemical reactions and physical processes. The chemical processes that destroy vegetable tanned leather are generally subdivided into reactions caused by oxidation and hydrolysis (mainly acid catalyzed hydrolysis). All major components of the tanned leather: collagen, tannins and fats are undergoing these degradation processes. Due to hydrolytic degradation, the cleavage of the peptide bond –CO-NH-, the protein chain separates into two parts as a result of binding of water molecule. Gradual breakdown of the collagen chain at different places simultaneously causes severe shortening of the collagen, which on the macroscopic scale is expressed as powdering and gelatinizing. As a consequence, the collagen becomes water soluble. For this reason, the determination of warm water solubility is a suitable indicator for the degree of hydrolysis degradation.

The oxidation of the fats, tanning agents and other substances contained in leather is favored by the presence of light. In the process of photo oxidation, the photon absorbed by the material reacts with an oxygen molecule to form a free radical, which after reaction with water produces hydrogen peroxide – a very powerful oxidant. However, the oxidation does not have to take place only with the contribution of light. The auto-oxidation of unsaturated fatty acids can also lead to damaging degradation processes [2].

According to Larsen, both oxidation and hydrolysis occur simultaneously, however hydrolysis seems to be more aggressive and faster than oxidation. Moreover it could be noticed that the less acidic the sample, the more important are oxidation processes. [3]

Oxidative damage is well detectable by a reduction of the methionine residues in the collagen. Methionine is easily oxidized by hydroxyl radicals, so the amount of methionine is a suitable marker for oxidation. From the amino acid analysis of collagen, the ration of basic and acidic acids (B/A) can be determined. The relationship between the two groups of amino acids has been used by Larsen to predict the denaturation temperature of historical leather samples and to describe the state of degradation processes. [4]

The methionine content of several historical leather samples was analyzed. The amount of methionine remains stable or only slightly reduced towards the newly tanned model leather. Especially natural aged samples with the typical powdering effect, known as “red rot”, showed no

change in the methionine content. The amino acid analysis results therefore support the hypothesis, that oxidation processes play only a subordinate role in leather degradation.

**3.2 Accelerated aging method**

In order to be able to work on samples that imitate the historical leather and to influence their properties in a controlled manner, the focus was initially placed on the development of the artificial aging method.

The aim of accelerated ageing was to reproduce as precisely as possible acid catalyzed hydrolysis as main degradation mechanism in the natural aged leather. To induce the hydrolysis and then to examine the efficacy of the newly developed care agent used to prevent it, a two-step aging process has been developed. The first stage is to introduce the acid into the material to initiate this type of degradation and thermal aging in closed vessel. The second thermal aging after treatment verifies its effectiveness by comparing treated and untreated leathers at this stage of aging.

Both stages of aging were carried out in closed 250 ml glass vessels, in which 9,01 – 9,05 g of leather were aged. Keeping the amount of leather constant in the defined volume of the glass vessels, allows to control the moisture content of equal level by all aging trials. Two methods of introducing acids into the skin structure have been tested: gas phase (in case of volatile acids) and impregnation (in case of strong inorganic not volatile acids). In case of aging in gas phase an intermediate/double bottom was used to avoid direct contact between the leather and the liquid volatile acid.

In estimating the amount of acid required for this aging method, it was assumed that the acid would be adsorbed by the leather in the vapor phase and thus removed from the gas phase. In order to achieve equilibrium, the acid has to change continuously from the liquid to the gaseous state. Therefore, it has been worked with excess of liquid phase to ensure the continuously exchange-dynamic balance between these two phases.

These aging tests by absorption of acids from the gas phase shows a significant dependence on the water content in the system. The use of 1 M formic acid resulted in the complete destruction of the leather, while the use of concentrated formic acid had a less destructive effect. Moreover, not pre-dried leather shrinks greatly and loses its shape already at about 70 °C when closed in the glass vessel without the addition of acid. Accordingly, the amount of water needs to be significantly reduced, to avoid denaturing reactions or the temperature must be maintained at a level at which no shrinkage under the given conditions occurs. It should be noted, however, that even pre-dried leather still contains water in the triple helix which should be sufficient to provide enough water for slow hydrolysis under acidic conditions. These artificial aging tests have shown that the acid amount of 1.8 mmol / 1 g of leather is sufficient to achieve the hydrolytic leather degradation when keeping the aging temperature below the denaturation temperature $T_S$. It was further confirmed that the denaturation temperature increases with decreasing moisture content. The water content in the closed vessel can be controlled by pre-drying the sample and then adding a defined amount of water or by using samples with a water content of between 9.5 and 11.0%. To determine the effectiveness of accelerated aging, the focus was placed on the analysis of the following skin properties: visual assessment, loss of mechanical properties, lowering the shrinkage temperature (but without reaching the state of denaturation), reducing the pH to about 2.5 - 3.5 and in a later stage determining the acid amount in the structure using titration methods. Among the tried-and-tested acids such as formic acid, acetic acid and mixtures of these acids with hydrochloric acid, which were tested at temperatures of 35 to 70 °C in different molar ratios, concentrations and for a different time, one method has been chosen which gave the best results. The selected method is based on 7 days aging in a closed vessel in a gas atmosphere of formic acid at a temperature of 60 °C. This way of aging allowed to obtain samples, which had reduced mechanical strength (loss of tensile strength of approx. 50 % compared to the reference sample), shrinkage temperature at about 55-60 °C, pH value of 3.0 and increased solubility in warm water by approx. 25 % compared

to the reference sample. In addition, the long-term observations were made to examine the stability of this method by testing the pH value over time. Multiple measurements of artificial aged samples revealed a time-dependence of the pH value, especially in the first weeks after aging (Fig. 2 and Fig. 3).

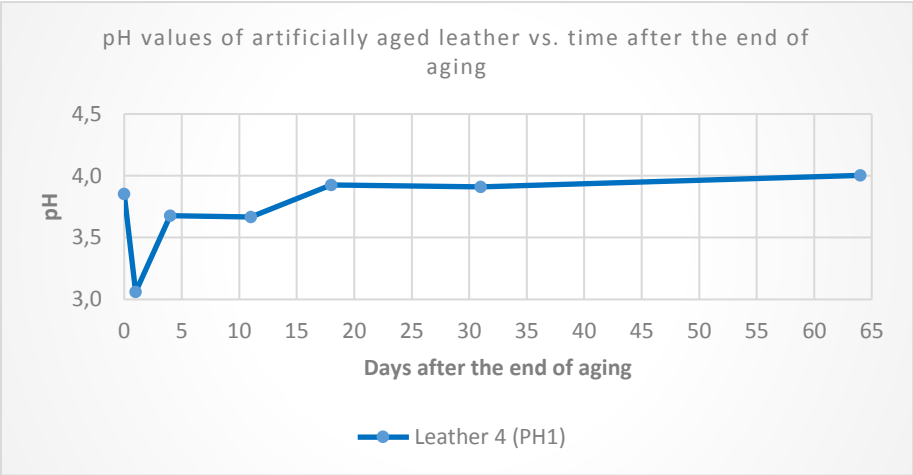


**Fig. 2.** pH values of artificially aged leather vs. time after the end of aging

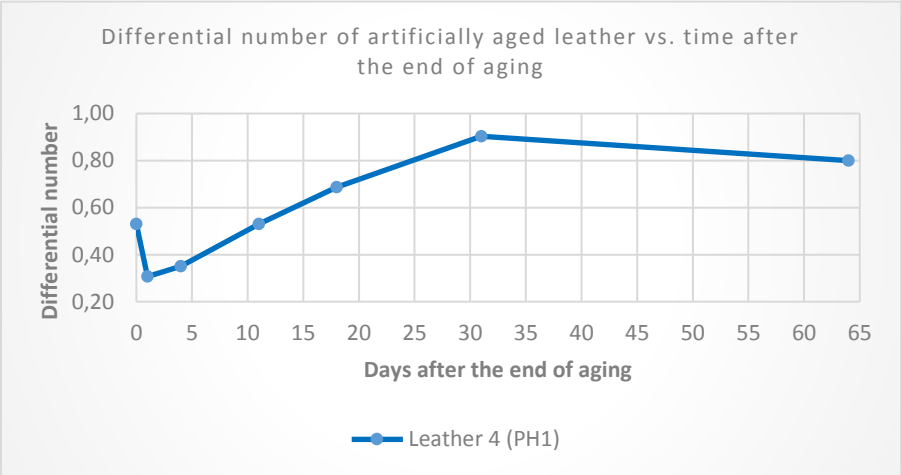


**Fig. 3**. Differential number of artificially aged leather vs. time after the end of aging

After artificial aging, the pH drops almost one unit to about 3.0. When samples have been stored under standard conditions, the pH values increase after 14-18 days and reach their original value after this time. The pH increases over time as the volatile formic acid desorbs from the collagen. Because the pH of these samples does not remain stable after aging and no further damage can be achieved in the second (thermal) stage of aging, this type of artificial aging had to be modified. Nevertheless, these experiments have proven that weak organic acids are able to lead to very significant leather damage.

A new aging method was developed based on the introduction by soaking in the leather structure mixture of two acids used in tanning: sulfuric acid and formic acid. The samples were soaked in a bath of acid solution in water for 10 minutes, air-dried and then aged for 7 days at 60 °C in a closed glass vessel. 0,1 M sulfuric acid was used with 1 M formic acid in a proportion 1:1. Conducted experiments for the first stage of aging yielded very satisfactory results and were subsequently subjected to second stage thermal aging at 60 °C for next 7 days. The results of pH values and

differential number after two aging stages remained stable and amounted 2.3 and 0.97 subsequently.

**Table 1.** pH and differential number values – reference and after two stages of artificial aging

| Sample | pH value/ difference number- reference leather | | pH value/ difference number- leather after I-st stage of aging | | pH value/ difference number- leather after II-nd stage of |
|---|---|---|---|---|---|
| 1 | 3,7 / 0,61 | Aging - I stage | 2,3/ 0,97 | Aging - II stage | 2,3/ 0,97 |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | 3,7/ 0,70 | | 2,3/ 0,98 | | 2,4/ 0,99 |
| 6 | | | | | |
| 7 | | | | | |
| 8 | | | | | |

The shrinkage temperature for the reference samples was within 72-74 °C, dropped after the first stage of aging to 53-60 °C, and after the next stage to the value of 49-55 °C.

**Table 2.** Shrinkage temperatures (in °C) and color difference ΔE*ab (2000) for reference leather and after two stages of artificial aging

| Sample | Shrinkage temp. | | ΔE*ab (2000) | | Shrinkage temp. | | ΔE*ab (2000) | | Shrinkage temp. | | ΔE*ab (2000) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (TI) °C | (TS) °C | | | (TI) °C | (TS) °C | | | (TI) °C | (TS) °C | |
| 1 | 74,0 | 78,0 | x | Aging - I stage | 52,7 | 60,0 | 1,8 | Aging - II stage | 49,0 | 55,2 | 2,1 |
| 2 | 74,0 | 78,0 | x | | 53,8 | 60,8 | 1,2 | | 49,7 | 56,7 | 1,4 |
| 3 | 74,0 | 78,0 | x | | 54,2 | 60,7 | 1,4 | | 51,0 | 56,8 | 1,5 |
| 4 | 74,0 | 78,0 | x | | 53,7 | 60,8 | 1,4 | | 48,5 | 55,0 | 2,0 |
| 5 | 72,0 | 79,0 | x | | 55,2 | 64,0 | 1,3 | | 43,3 | 54,7 | 1,5 |
| 6 | 72,0 | 79,0 | x | | 58,0 | 63,7 | 1,1 | | 48,8 | 56,2 | 1,4 |
| 7 | 72,0 | 79,0 | x | | 59,7 | 65,3 | 1,0 | | 55,3 | 61,3 | 1,2 |

The difference between the tensile strength in relation to the reference sample after the first stage of aging was from 20 to 74 % and after the second stage it decreased by another 10-20 %.

This type of ageing made it possible to distribute acids in leather evenly. Moreover, sulfuric acid is not volatile and remains in the structure, which is necessary in order to realize the second stage of aging at all. Although, the amino acid analysis has shown that this aging does not alter the amino acid composition, indicating a pure hydrolytic damage, which is a main chain cleavage.

**Table 3.** Mechanical properties of leather – reference and after two stages of artificial aging

| Sample | Tensile strength σ | Elongation at max. force D | | Change of tensile strength Δσ | Change of elongation at max. F | | Change of tensile strength Δσ | Change of elongation at max. F |
|---|---|---|---|---|---|---|---|---|
| | N/mm2 | % | | % | % | | % | % |
| 1 | 8,0 | 15,4 | Aging - I stage | -36,7% | -9,1% | Aging - II stage | -46,1% | -27,7% |
| 2 | 17,0 | 17,7 | | -43,7% | -23,2% | | -50,7% | -32,4% |
| 3 | 9,8 | 22,0 | | -46,8% | -9,7% | | -49,0% | -18,1% |
| 4 | 18,2 | 26,7 | | -19,9% | -14,1% | | -45,8% | -27,1% |
| 5 | 21,2 | 22,2 | | -46,5% | -18,7% | | -52,9% | -28,7% |
| 6 | 25,5 | 20,8 | | -26,7% | -5,9% | | -89,8% | -69,0% |
| 7 | 29,5 | 22,8 | | -73,4% | -43,9% | | -85,4% | -62,1% |

### 3.3 Acid content determination

The main objective of the experiment was to use titration to perform quantitative analyses of acids in modern as well as artificial or naturally aged leather. The determination of the exact amount of acids contained in the structure of the leather is of great importance in characterizing the modern skins for artificial aging and afterwards pH adjustment, as well as for determining the acidity level of historical samples. In order to get the most accurate picture of skin response to titration, all three possible titration options were used for the initial analysis: back-titration with 0.1M NaOH, back-titration with 0.1 M HCl and direct titration with 0.1 M NaOH. In the case of leather, several equivalence points (EP) were detected during the titration. The result (amount of acid) is the amount of acid / base used, which is consumed at the maximum value of the first derivative (dE/dV). At the same time, the pH value for each EP at the maximum of the first derivative is determined. As an additional result, the amount of acids at a constant pH of 5.5, which is considered to be the isoelectric point of the skin, has been listed as well. For the development of this method, several different modern leathers and artificially aged skins with a different amount of acids were used. The results that are discussed in this publication refer only to one type of modern leather, which during the tanning was intentionally (over)acidified with sulfuric acid.

Fig. 4 shows the titration curves during the titration for all tested methods listed above. These curves correspond to the titration of the same amount of leather sample (1.00 g) extracted in 20.0 ml of water, decanted/filtered and supplemented with 90.0 ml of distilled water. Titrations were carried out under nitrogen to minimize the influence of carbon dioxide. The Leather was extracted in pure distilled water, free from $CO_2$.

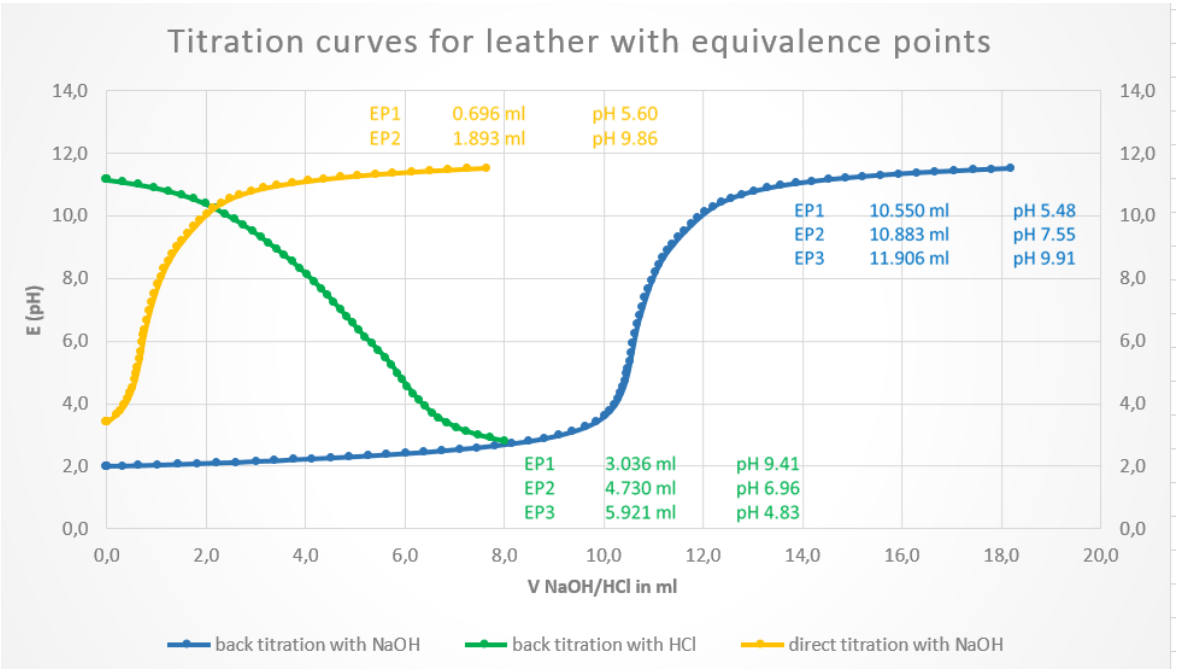


**Fig. 4.** Titration curves with equivalence points for three different types of titration

In case of each of these methods, modifications were made, which were aimed at selecting the best method for the objectives set in the project. Results of each of these modifications are collected in Table 4. The experiments in which extracts were boiled were excluded for further development, since the volatile organic acids evaporate during heating. In back titration with HCl, where NaOH was added to the extracts, higher amount of acids were obtained compared to other results, which

is probably related to swelling of the collagen by higher pH values. After careful analyses of these results two options were selected for further development of these methods – method no.4 and 7. It was found that filtration had no effect on the measured acid amount by modern leather compared to the values obtained from decanted extracts. The influence, however, can be seen in the measurements of the historical leather and for this reason filtering is recommended.

It was also attempted to investigate whether collagen acts as an ion exchanger. The acidic and basic side chains in collagen carry both negative and positive charges. In the acidic pH range, the corresponding amino groups are protonated and present in the solution as cations. In the basic pH range, the amino acids perform as an anion with an excess of negative charges. The electric charge depends on the pH of the surrounding eluent. The addition of acids or alkalis in the leather leads to a dissociation or charging of the collagen molecule and thereby also to a swelling. The collagen acts as an ion exchanger in this case, which can falsify the results, since the charge state is kept constant over a wide pH range. To minimize these undesirable effects extracts in aqueous NaCl and KCl solution were tested (variation: 0.3 M and 1.0 M). By presence of $Na^+$/ $K^+$ and $Cl^-$ ions, a diffuse double layer should be introduced. These effects were tested using the direct titration with 0,1 M NaOH method.

**Table 4.** Titration: Method development 1

| Method number | Modern leather - acidified with 0,8% $H_2SO_4$ | Acid content by max. EP in mmol/gDM | pH by max. EP | acid content by pH approx.= 5.5 |
|---|---|---|---|---|
| 1 | Back titration with 0,1N NaOH - Mettler-Toledo (according ISO 10716 for determination of alkali reserve in paper) | 0,10 | 5,7 | 0,09 |
| 2 | Back titration with 0,1N NaOH +$N_2$ - Metrohm - Water(-$CO_2$) (A) (20ml extract+ 10ml 0,1N NaOH (10 min) + decanting + 90ml $H_2O$) | 0,02 | 5,8 | 0,02 |
| 3 | Back titration with 0,1N HCl +$N_2$- Metrohm (20ml extract+ 10ml 0,1N NaOH (10 min) + decanting + 90ml $H_2O$) | 0,33 | 4,9 | 0,35 |
| 4 | Back titration with 0,1N HCl +$N_2$- Metrohm - Water(-$CO_2$) (C) (20ml extract+ 10ml 0,1N NaOH (10 min) + decanting + 90ml $H_2O$) | 0,46 | 4,8 | 0,51 |
| 5 | Back titration with 0,1N HCl +$N_2$- Metrohm- Water(-$CO_2$)/ extracts boiled (F) (20ml extract+ decanting+ 90ml $H_2O$+ boiling+ 10ml 0,1N NaOH) | 0,48 | 4,8 | 0,51 |
| 6 | Back titration with 0,1N HCl +$N_2$- Metrohm- Water(-$CO_2$)/ extracts in NaOH solution (D) (20ml extract in NaOH-solution + decanting+ 90ml $H_2O$) | 0,88 | 5,0 | 0,96 |
| 7 | Direct titration with 0,1N NaOH +$N_2$ - Metrohm - Water(-$CO_2$) (B) (20ml extract+ decanting + 90ml $H_2O$) | 0,08 | 5,8 | 0,08 |
| 8 | Directe titration with 0,1N NaOH +$N_2$ - Metrohm - Water(-$CO_2$)/ extract boiled (E) (20ml extract+ decanting+ 90ml $H_2O$+ boiling) | 0,05 | 5,0 | 0,06 |

The evaluation of the results leads to the conclusion that the preparation of the extract in NaCl solution has a very low and from leather to leather different influence on the amount of acid, which in turn does not confirm the statement that collagen acts like an ion exchanger. However, it seems to have an influence on the pH at the equivalence point, which could confirm the ion exchange theory. A shift in the EP could also be due to the heterogeneity of the leather. After a thorough examination of the reasons for the lowering of the pH value it turned out that it is related to the discalibration of the electrode under the influence of the measurement in NaCl. In order to test the negative effects of the NaCl solution again, a similar series of measurements in KCl was carried out. It could be confirmed that collagen does not act as ion exchanger in this case. In addition, measurements in 1 M KCl solution were found not to interfere with the electrode – the calibration remained stable during the measurement time. Comparable amounts of acid were measured in extracts in $H_2O$, 1 M NaCl and 1 M KCl. It is worth emphasizing that the result of the measurement is influenced by the ratio of leather weight to the amount of extraction medium (compare Table 5). The less leather sample is subjected to an extraction in a given amount of solution, the larger amounts of acid will be measured. Therefore, it is extremely important to maintain a constant proportion between these two factors. For these studies, the proportions of 0.1 g of the sample per 10.0 ml of solvent will be the standard procedure for sample preparation.

**Table 5.** Comparable measurements of acid in $H_2O$, NaCl and KCl extract

| Method number | Modern leather - acidified with 0,8% H2SO4 | Sample amount in 50 or 110 ml extract | Acid content by max. EP in mmol/gDM | pH by max. EP | acid content by pH approx.= 5.5 |
|---|---|---|---|---|---|
| 7.8A | Direct titration with 0,1M NaOH (110ml extract+ filtering) | 1g | 0,15 | 5,8 | 0,14 |
| 7.8G | Direct titration with 0,1M NaOH (50ml extract+ filtering+ 60ml H2O) | 0,5g | 0,14 | 5,6 | 0,13 |
| | | | | | |
| 7.2(A) | Direct titration with 0,1M NaOH / 1M NaCl (110ml extract in 1M NaCl + filtering) | 1g | 0,13 | 2,5 | 0,29 |
| 7.2A repeated | Direct titration with 0,1M NaOH / 1M NaCl (110ml extract in 1M NaCl + filtering) | 1g | 0,11 | 3,9 | 0,17 |
| 7.2B | Direct titration with 0,1M NaOH / 1M NaCl (110ml extract in 1M NaCl + filtering) | 0,5g | 0,16 | 3,5 | 0,27 |
| | | | | | |
| 7.2C | Direct titration with 0,1M NaOH / 1M KCl (110ml extract in 1M KCl + filtering) | 1g | 0,13 | 5,2 | 0,14 |
| 7.2D | Direct titration with 0,1M NaOH / 1M KCl (110ml extract in 1M KCl + filtering) | 0,5g | 0,16 | 5,3 | 0,17 |
| 7.2E | Direct titration with 0,1M NaOH / 1M KCl (50ml extract in 1M KCl + filtering+ 60ml H2O) | 0,5g | 0,13 | 5,4 | 0,13 |

To determine the amount of acid in the skin structure, aqueous extracts (0.1 g of skin per 10.0 ml of water) were used, which were directly titrated with 0.1 M NaOH. Using this method, the acid quantity was determined for reference leather, over acidified skins during the tanning, artificially aged leather and historical samples (Table 6).

**Table 6.** Acid content, pH value and differential number for some of measured samples – reference, over acidified reference, artificial aged samples and historical leather

| Sample | Acid content by max. EP in mmol/gDM | pH by max. EP | acid content by pH approx.= 5.5 | pH | differential number |
|---|---|---|---|---|---|
| ***Modern leather, arificial aged reference leather*** | | | | | |
| 8 - reference leather | 0,05 | 5,7 | 0,05 | 3,8 | 0,64 |
| 8 after 1st stage of aging | 0,28 | 5,2 | 0,29 | 2,4 | 0,80 |
| 8 after 2nd stage of aging | 0,28 | 6,1 | 0,27 | 2,5 | 0,74 |
| ***Modern leather over acidified during the tannage*** | | | | | |
| overacidified with HCOOH | 0,07 | 4,8 | 0,09 | 3,5 | 0,81 |
| overacidified with H2SO4 with rinsing | 0,14 | 5,8 | 0,14 | 2,8 | 0,88 |
| overacidified with H2SO4 without rinsing | 0,25 | 5,5 | 0,25 | 2,4 | 0,84 |
| ***Historical leather from book covers*** | | | | | |
| HL1 | 0,55 | 6,7 | 0,48 | 3,0 | 0,48 |
| HL2 | 0,38 | 6,8 | 0,30 | 3,3 | 0,45 |
| HL3 | 0,45 | 6,7 | 0,39 | 3,0 | 0,54 |

Results obtained from titration were compared with the results of the acid content determined by the IC method. A very strong correlation between these two methods has been found for reference and artificial aged samples. The history of the samples was known and it could be predicted which acids should be found in the structure of leather.

**Table 7.** Comparison – acid content calculated from IC analysis/ acid content titrated for reference and artificially aged leather

| Sample | Acid content calculated (anions-cations) in mmol/gDM | Acid content in mmol/gDM |
|---|---|---|
| | "H+" mmol/gDM | titrated |
| Ref 1.2 | 0,11 | 0,09 |
| Ref 2.2 | 0,00 | 0,04 |
| Ref 4 | -0,01 | 0,03 |
| artificial aged 119 | 0,21 | 0,23 |
| artificial aged 123 | 0,33 | 0,38 |

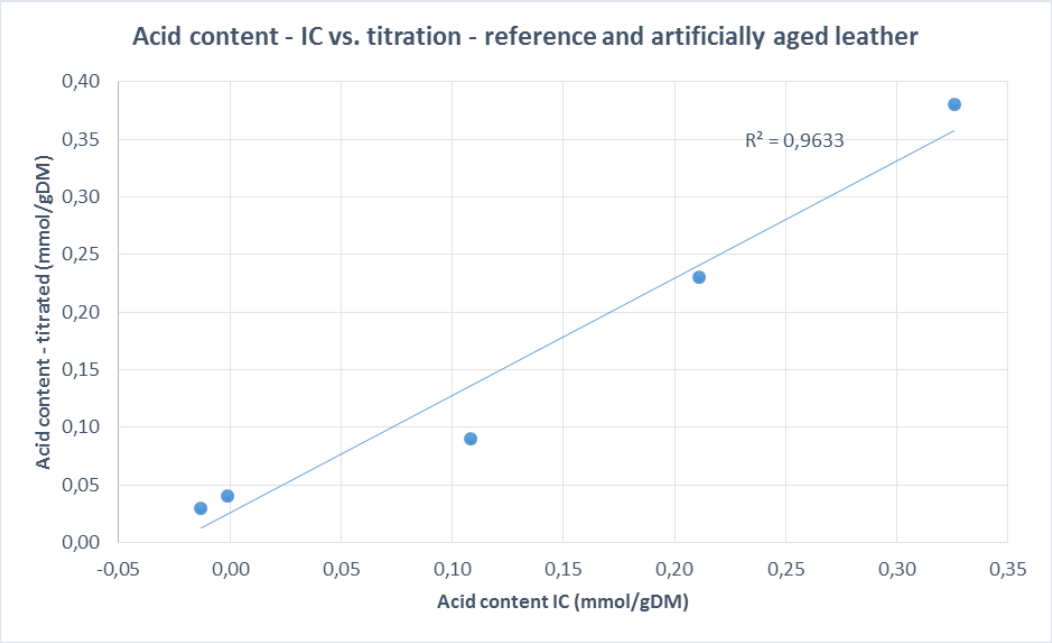


**Fig. 5.** Comparison – acid content calculated from IC analysis/ acid content titrated for reference and artificially aged leather

The comparison within the historical book cover leathers was also satisfactory with a coefficient of determination of 89 %. Differences between both analyzing methods can be traced here to further possible contained acids, which haven't been included in the IC analysis.

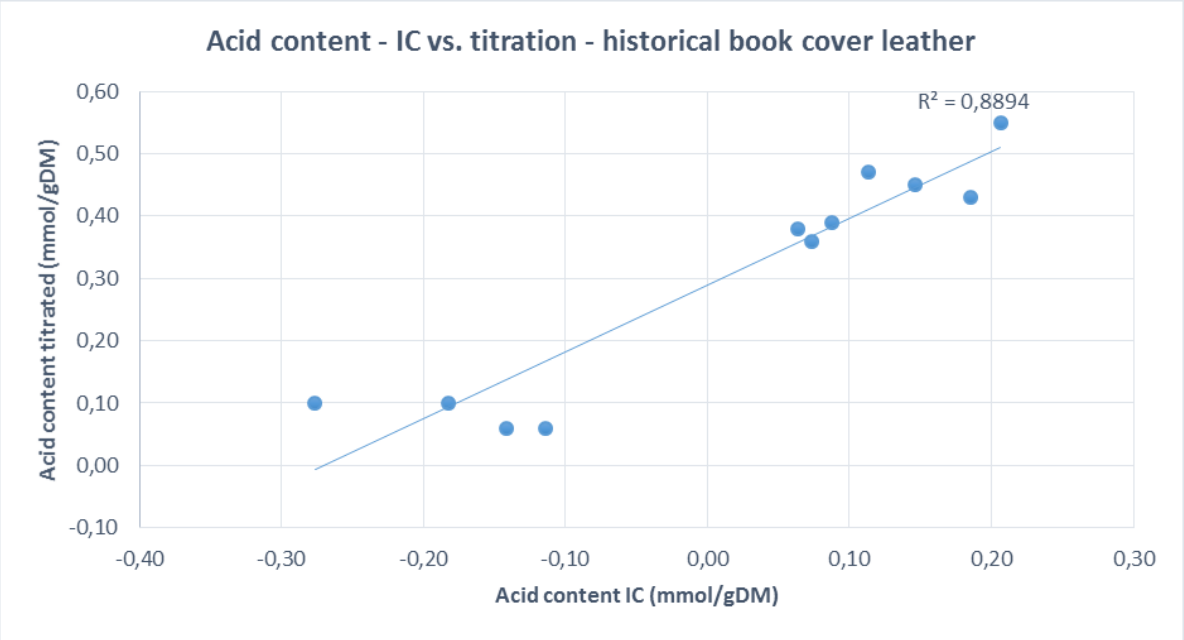


**Fig. 6.** Comparison – acid content calculated from IC analysis/ acid content titrated for historical samples

While comparing the acid contents obtained from these two methods for all types of examined leather together, it was not possible to find a significant correlation. But regarding the measurement of the reference and artificial aged samples with a known history, the IC results support the confirmation of the developed titration method.

## 4 Conclusion

Oxidation and acid-catalyzed hydrolysis have an enormous impact on the state of the leather. Both take place simultaneously and affect each other. The executed investigations have confirmed the hypothesis that the damage by acid hydrolysis is much more dominant than the damage by oxidation. Since oxidation plays only a minor role and can be slowed down only preventively by storage conditions, the project focused on the hydrolysis as the significant degradation mechanism. The aim of accelerated aging was to reproduce as precisely as possible observed and identified degradation mechanisms in the natural aged leather. Therefore, a two-step aging process has been developed. The first stage is to introduce the acid into the material that is to be used to simulate the acid catalyzed hydrolytic degradation. The second step is to verify the effectiveness of the newly developed care products by comparing treated and untreated leathers at this stage of aging. It has been proved that not only strong acids but weak organic acids also have a very destructive effect on the leather degradation. The aging was evaluated by optical/haptic tests, shrinking temperature, mechanical properties, hot water solubility, pH value and differential number. The influence of the alteration of the tanning agent has not been studied yet.

Regarding the leather characterization, the determination of the exact amount of acid introduced by the artificial aging is of great importance for the development of the aging method as well as for the pH adjustment of the leather for conservation purposes. For the method development, an acid-base titration was selected, which allows quantitative results of the acid content in the examined material. The developed method is easy to carry out and allows the measurements of different sample quantities (0,1 g - 1,0 g).

## 5 Acknowledgement

The authors want to thank for generously support of the project by EU funds (ESFR) and administration by Sächsische Aufbaubank – Förderbank (SAB).

Further, we acknowledge the Forschungsinstitut für Leder und Kunststoffbahnen, especially Dr. Anke Mondschein and Dr. Michael Meyer for the constructive project cooperation, the production of model leather, all conducted analysis and numerous discussions and consultings.

Large gratitude is offered to HTWK Leipzig, especially Dr. Jürgen Gebhardt for the further development and provision of the ion chromatography methods.

## References

1. *A. Küntzel (1943) Gerbereichemisches Taschenbuch, Verlag von Theodor Steinkopff, Dresden und Leipzig, p. 265*
2. *M. E. Florian (2006) The mechanisms of deterioration in leather in: Conservation of Leather and Related Materials (M. Kite, R. Thomson), Amsterdam, p.38- 40.*
3. *R. Larsen (14-15.06.2018) Oral presentation during the interdisciplinary workshop in Freiberg/ Germany*
4. *A. Mondschein (2017) Interim report. Procorium: Nachhaltig wirkendes Pflegemittelsystem zur Behandlung von vegetabil gegerbtem Bucheinbandleder.*