Research on Materials Appropriate for Restoration – Impacts of Ancient and Modern Tanning Techniques on Leather Character

by

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Abstract

There now exist a large number of investigations on leather decay and its effect on cultural heritage; however, appropriated and sustainable sources of restoration leather are missing. Simple test methods and agreements regarding the quality assurance of commercial restoration products are not available. Many of the outstanding properties of ancient leather like long-term stability are attributed to the method of manufacture and the processing auxiliaries' common for the period of origin. The pure replication of the ancient techniques in detail is neither possible nor economically viable. Every step of tannage causes an anticipated step of collagen degradation. Is it possible to obtain a restoration leather of outstanding quality also under modern conditions? The Saxon States Authority for the Care of Monuments, the Research Institute for Leather and Plastic Sheeting (FILK Freiberg) and the Department of Conservation & Restoration of Moritzburg Castle co-operate in research on material appropriated for restoration of baroque leather wall hangings. The paper presents different characteristics of ancient and modern tanning techniques, practical experiences, test methods and recommendations for the manufacturing of restoration leather.

Resumen

Cuantiosas investigaciones sobre la degradación del cuero y sus efectos sobre la herencia cultural existen; sin embargo fuentes apropiadas y sostenibles de restauración hacen falta. Simples métodos de pruebas y consenso en asegurar la calidad de productos comerciales restaurados no existe. Muchas de las sobresalientes propiedades del cuero antiguo tal como la perduración de la estabilidad son atribuidas al tipo de fabricación y a los auxiliares existentes durante el período de su origen. La absoluta replicación en detalle de la técnica antigua no es ni posible o económicamente factible. Cada paso en el curtido causa un anticipable paso en la degradación del colágeno. ¿Es posible acaso obtener un cuero restaurado bajo condiciones modernas? La Autoridad de los Estados Sajones para el Cuidado de Monumentos, el Instituto de Investigaciones del Cuero y Coberturas de Plástico (FILK Freiberg) y el Departamento de Conservación y Restauración del Castillo de Moritzburg han cooperado en la investigación de materiales apropiados para la restauración de colgaduras de cuero barrocas. La obra presenta diferentes características técnicas de curtición del cuero tanto antiguas como modernas, experiencias prácticas, métodos de prueba, y recomendaciones para la manufactura de cuero para restauración.

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MORITZBURG CASTLE GILT LEATHER WALL HANGINGS — A CHALLENGE FOR RESTORATION

The world-wide trading volume of hide, skin, leather and leather goods outperform significantly other consumer products like coffee, cotton or tobacco.[8] Nevertheless leather appropriated for restoration is a niche market that is characterized by weak demand and extraordinary terms of delivery. A system of quality control does not exist. The conservator has to trust in the quality of the conventional merchandise. In the last years different national and European projects were carried out to solve the problem of the availability of high quality conservation leather. In these projects commercial leather have been exposed to artificial aging procedures and tested with analytical methods with unsatisfying results.

In Moritzburg Castle and other baroque palaces there is a steady demand for restoration leather for gilt* leather wall hangings. The gap between the demand and availability of reliable restoration material was the trigger of the pilot project "Development of long-term and emission stable leather for conservation and restoration of gilt leather wall hangings at Moritzburg castle" funded by the Deutsche Bundesstiftung Umwelt promoted by the Freistaat Sachsen. The project duration was of 30 months and has been conducted in co-operation of:

- Moritzburg Castle, Department of Conservation
- Saxon States Authority for the Care of Monuments
- Research Institute for Leather and Plastic Sheeting (FILK Freiberg).

The aim of the project was to establish vegetable tanned calf and goat leather suitable for conservation and restoration purposes, taking into account all application requirements as well as aspects of quality management and environmental sound manufacture.

Moritzburg Castle named for Herzog Moritz of Saxony is an impressive monument of Saxonian baroque. The dukes and later kings of Saxony expanded the hunting lodge to a royal palace and a summer residence. In the halls and rooms of Moritzburg Castle is preserved the world largest stock of 18^{th} century gilt leather as part of its original interiors (figure 1). From the 60 gilt leather rooms of this castle in 1733 the visitor will find today altogether two halls with huge paintings on gilded leather (figure 14) and 11 rooms with ornamental decorated gilt leather. A large number of additional panels and fragments exist in non-public rooms and in the depots of the museum. According to the recent research the origin of the punched gilt leather seems to be Venice, and of the embossed ones the Flemish region.

The maintenance of this cultural heritage needs continuously care. The leather substance shows a lot of serious damages like tears, holes, cuts, missing parts or damaged edges (figure 2) which have been caused in many cases by visitors. The conservation concept consists in repairing mechanical damages using vegetable tanned leather and the genuine technique of silvering and gluing to guarantee isotropic mechanical action of the hangings on changing climatic conditions. Therefore high quality leather for restoration is requested. It should meet special demands regarding chemical parameters and long-term behavior, defined e. g. by the European ENVIRONMENT project, as well as concerning its workability in restoration.

* *(The editor chose to continue using the authors original terms of gilt, past tense of gild, as used in conservationist literature to refer to ancient gilded wall hangings.)*

Figure 1: Front view of Moritzburg Castle nearby Dresden

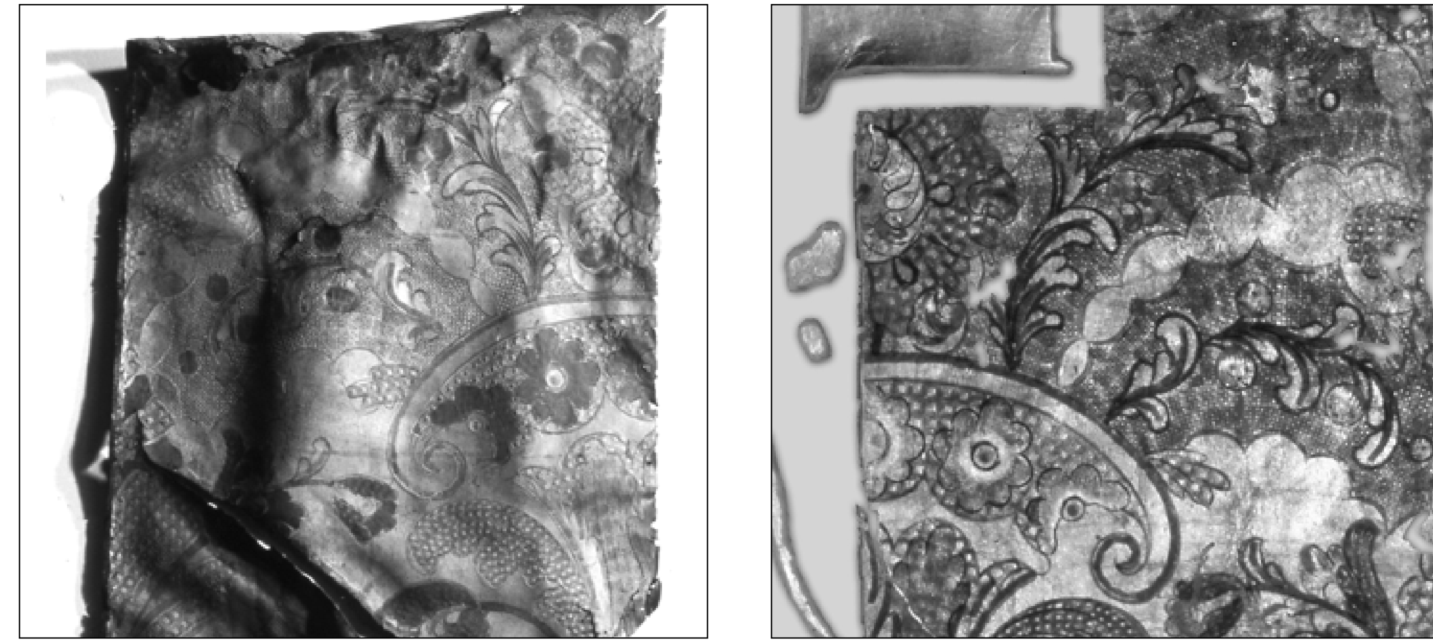

Figure 2: Example of the conservation concept of Moritzburg Castle

HANDICRAFT AND INDUSTRIAL LEATHER MANUFACTURE

Influence of raw material and provenience

What are the main differences between the ancient handicraft made leather and modern industrial products? What are the influencing factors of leather quality and how the modern technology can be adapted in order to meet the demands for restoration?

Two of the most important factors for the leather quality are the status (age, gender, season, veterinary state) and the origin (species, race and provenience) of the raw hide or skin. A lot of ancient domestic animal species are threatened species today or do not exist anymore. In the former time the domestic goat was dismissed as the "poor man's cow" for its ability to cope with very different and often harsh environments; which explain the comprehensive biodiversity of the ancient sources of raw material. The kind of the current agriculture and livestock husbandry, population density, the relationships between urban consumers and rural producers of animal products etc. are not comparable with the farming of the 17^{th} or 18^{th} century. Intensive animal husbandry, animal transport and highly automated meat-packing plants cause a number of special hide and skin defects. Industrial feed-up processes produce collagen that is younger and with weaker bonding properties.[6]

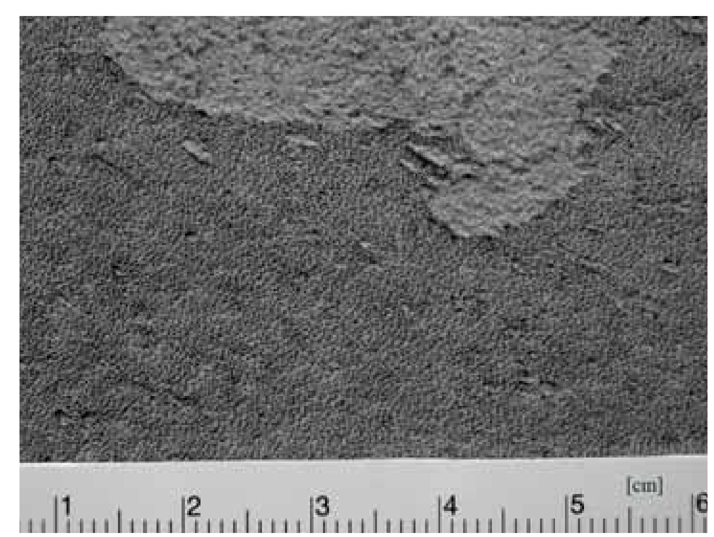

Figure 3: Leather defects caused by Sarcoptes mites on cattle hide

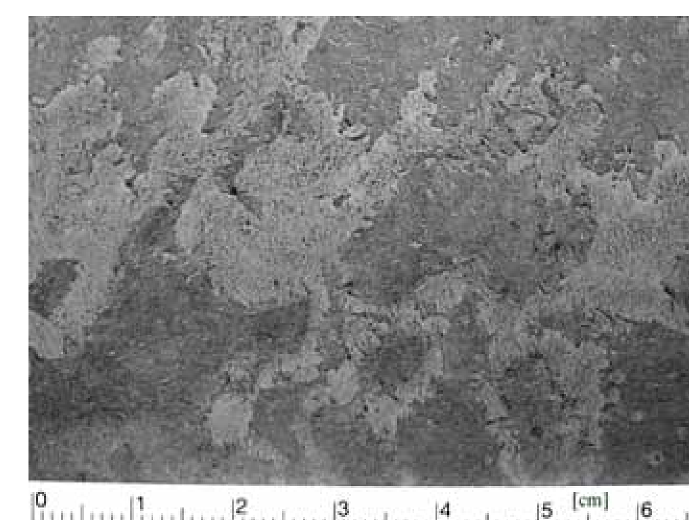

Figure 4: Vegetable tanned calf skin with storage defects

TABLE I

Examples of relationship between leather type and raw hide provenience

Leather type, application	Favored raw material, provenience
Bookbinding leather	
Morocco, saffian cover maroquin, marocchino, Saffianleder, Knirschsaffian, squeak morocco	Goatskins from Thuringia, Saxony (Germany), sheepskins, East-Indian bastards, Cap bastards, South Africa
Red saffian cover, Rote Saffianeinbände	Niger goat skins
Hand gilded cover, handvergoldete Einbände	Oasis goat skins
Glazed and punched cover, glanzgestoßene und punzierte Ledereinbände	Calf skins ≤ 4,5 kg from South and Central Germany, France, Poland, Scandinavia
Glove leather	
Gloving kid, chevreau pour ganteríe, Handschuhzickel	Lamb skins from Tuscany and Torino region
Mocha leather, Mochaleder, moca	Arabian black faces (hair sheep)
Bottom leather	
Sole leather, Bodenleder, cuir à semelle	Ox hides
Footwear uppers	
Shell cordovan, Korduanleder	Butts from plowhorses or mules
Box-calf, Boxkalb, vitello box	European calf skins
Chevreau, capretto, cabrito Chevrette (chevreau imitation made from ovine skins)	Goat and kid skins from Northern France, Piedmont, Thuringia, Saxony, Northern Bulgaria, Croatia, Maghreb, India
Saddlery, harness leather, bag maker, upholstery leather	
Box side, harness leather, sleek leather, Vachetten, Blankleder	European cow hides, dry kips (East India), bovine grain splits

The manufacture of traditional leather types for special application was bound to selected raw material respectively to raw hides of certain provenience. Some examples are written in table I. The commercial jargon of the trader and tanner was growing for a long time and in different languages which is difficult to understand today.

The majority of hides and skins for leather production are purchased either salted, sun dried or fresh from the slaughterhouse. Hides and skins are globally traded and are favored business of speculation in raw stock which means preservation and storage defects are permanent risks of the modern leather manufacture.

Dung and ectoparasits defects, goad damages during transport deteriorate the quality of the raw material significantly already in vivo. Figure 3 shows mange defects caused by mass infestation of housed cattle with Sarcoptes, Chorioptes and Psoroptic mites. Psoroptic mites can spread all over the body of cattle. Figure 4 shows calf leather with storage defects caused from a long-term salted raw stock. Preservation defects are mostly not visible at the raw material but can extensively decrease the resulting leather quality. Stricter regulations concerning the raw material already existed during the heyday of the Spanish leather manufacture in the medieval times. A royal edict banned knacker hides for leather manufacture was given to the Guadamacileros of Toledo (producer of gilded leather) in 1502.[3]

Beam-house work
The first step of the ancient leather manufacturing was done in watercourse beside the workshop of the tanner. Today's industrial scale soaking is usually done in rotating drums, mixers or paddles. The next step of unhairing and liming was conducted in the ancient techniques as pit liming, painting or sweating; which were slow-going static processes. The removed hair was saved as a by-product. In the modern beam-house most of the non-collagen components of the hide like keratin undergo a complete decomposition leading to highly loaded effluents and sludge. The traditional bating was performed with excrements of dogs or pigeons. It was substituted in modern technologies by highly efficient industrial auxiliaries like proteolytic enzymes.

The crossed fleshing and unhairing knifes became emblem of the tanner everywhere in the world. All former handmade operations which accompanied the wet processes, like fleshing, unhairing or scudding, are today machine-made by rotating tools. The principle of the rotating cylinder equipped with more or less sharp blades arranged in V-manner is well approved and have speeded up the work, but the machine pressure of knife cylinders affect hides and pelts by high tensile and shearing forces and printing pressure.

Vegetable Tanning
The ancient leathers for wall hangings were tanned by pure vegetable materials that contained high amounts of non-extractives and non-tannins. The numerous non-tans like sugars, acids and their salts, hemicelluloses, pectin, lignin, as well as compounds containing nitrogen and phosphorus combined with a slow-going tannage generated the long-term stability of the leather. The modern leather production process has speeded up considerably through the use of mechanical agitators and the application of concentrated tannin liquors.

Sumac is a plant which was extensive cultivated on the Mediterranean area especially in Sicily until the seventies of the last century. Tanning matter in the leaves of the Rhus species belongs to the group of hydrolysable gallotannins. Its antioxidant activity prevents the development of red rot. This kind of decay is greatly feared and infests leather which containing tannins of the condensed type. Red rot is induced by air pollution.

Table II shows the analysis of milled Turkish sumac (Rhus cotinus) and industrial Quebracho extract. The great amount of the non-extractive matter present in the milled sumac leafs was a great inconvenience and expense factor for the former tanner and the reason why chrome sulfate, syntans and spray-dried extracts became successful substitutes for sumac. The dominating tannage at the present time is chrome tannage combined with vegetable, synthetic, polymeric and other tanning materials and auxiliaries.

TABLE II

Analysis of vegetable tanning materials by the filter-bell method (VGCT /5/)

	Sumac powder, milled	Quebracho extract, spray dried
moisture	8,9 %	9,9%
non-extractives	52,5%	0,0%
insoluble (semi colloids)	0,0%	0,8%
tannins	22,9%	78,1%
non-tannins	15,7%	11,2%
purity figure	59,3%	87,5%

Tanneries which still practice pure vegetable tanning mostly apply high concentrated spray dried extracts. Sources of the products are mostly condensed tannins (catechin type) e.g. extracts of mimosa or quebracho. The wood of the quebracho three (Schinopsis balansae and S. lorentzii) is used as sulphited product with a very high tannin content and a very good solubility. Simple handling, high degree of tannage and shrinkage temperature ≥ 80 °C are additional advantages compared to the ancient tanning materials like sumac leafs or oak bark. The quebracho extract includes a whole series of condensation products. Modern extracts have a very high purity figure and very good water solubility that provide fast penetration. Condensed tanning materials are subjected to the sulphiting process in order to solubilize the less soluble fraction. The combination with synthetic tannins (syntans) enhances conversion of insoluble phlobaphenes in the liquor to tannins.

The modern use of concentrates prepared from vegetable sources causes the risk of over-tannage. This overloading of the pelt with tanning matter provokes a brittle and cracked grain. Condensed tannins are not appropriated for long-term application because the risk of red rot.

The vegetable tannage starts with a swelling or pickling of the pelt. Sulfuric acid was not available in the pre-industrial period and only organic acids were used for the traditional manufacture. Sulfuric acid became the common auxiliary of the industrial process. The preservation of goat or sheep pelts by a sulfuric acids pickle is also widely-used today. The uptake of a strong inorganic acid by collagen and its acid-binding capacity cause permanent risk of a long-term hydrolyses. The degree of tannage influences the acid-binding capacity of collagen only in a small range.

Mechanical operations, fat-liquoring and drying
The group of mechanical operations after tannage aims to make the leather stretched and the grain flat and smooth. In early stages leather was sammed, set out e. g. with a spud knife, slicker or setting out knife in a stretched out state and tacked by hand to wood boards or was hang-dried. The free hanging is accompanied with a loss of area up to 15 %. The most important criteria of modern leather manufacture is a maximum possible area yield. Sammying and setting-out are often completed by vacuum drying. Industrial drying apparatus e. g. drying chambers, racks, channels, tunnels etc. are well equipped with devices for the application of stretching that influence the final properties of leather. Modern drying is performed under a high in-put of energy for efficiency reasons and provokes thermo-mechanical stress. The ancient air drying without supply of energy has gentle effects.

Splitting and shaving operations guarantee a constant leather thickness and smooth surfaces which was done in ancient time manually by means of shaving and doling knife. The industrial manner is performed mechanically by splitting, shaving, buffing and ironing machines accompanied by high input of mechanical and thermal load. The cross section of the skin suffers from the rough intervention.

Fat assures an appropriate friction coefficient between the leather fibers. The attraction mode of fat with the leather fibers is mainly by ionic or polar bonds. The fatty matter can be introduced into leather by different ways. The directly and dry process e. g. by hot stuffing are ancient techniques. The use of oil-in-water emulsion by the help of anionic fat liquor products is the dominating form of the modern wet fatting in rotating drums. Leather for wall-hangings do not need a fat liquor or only on a small scale. The misuse of lubricants for restoration is a reason for large and irreparable area defects on gilt leather (figure 5).

Figure 5: Restoration damage due to misuse of grease (Moritzburg gilt leather, detail of tapestry in the Kurfürstenzimmer II)

Leather for the Conservation and Restoration of Gilt Leather Wall Hangings

Manufacture of vegetable tanned leather for the pilot plant project
Different technologies and tanning agents were applied at the Research Institute for Leather and Plastic Sheeting (FILK Freiberg). In Table III is present the types of raw materials and auxiliaries which were processed in semi-industrial scale and the shrinkage temperature of the resulting leather.

Salted goat and calf skins from local sources were used for the trials. In the common beam-house process the hide structure undergoes swelling and opening-up and rapid hair destruction by chemical burning. The most widely used liming agents are sodium sulfide and calcium hydroxide. The combined unhairing and liming operation requires 20 to 48 hours. A new environmental sound beam-house technology was introduced. A sweating was combined with a modern catalytic oxidative liming. The sweating is a traditional process without hear pulping. The hair is removed by an enzymatic autolysis. The second step of the process was developed by FILK Freiberg.[10] This alternative oxidative technology is based on practical experiences with a catalytic induced opening-up of the pelt with hydrogen peroxide. The process works without any lime in alkaline liquor with sodium hydroxide. The oxidative step with hydrogen peroxide is controlled by organic or inorganic catalysts. Very low quantities of tannery sludge and pollution load of dissolved parameters (organic nitrogen, ammonia, COD) are released by the combination of the sweating and oxidizing liming.[9]

Different tanning materials were tested. Chrome tannage and vegetable tanning with quebracho and mimosa extract became the blind test group for further trials. Samples for restoration were tanned with hydrolysable tannins, a combination of hydrolysable and condensed tannins and Dongola techniques which means retannage with mineral tanning agent e.g. alum has been tested. The use of strong mineral acids was strictly avoided neither during the tanning process nor for pickling. Tanning matter from gallotannin or ellagitannin type like sumac, valonea and chestnut were preferred. Sumac powder consists of dried and crushed leafs of Rhus species. The leaves of Sicilian Sumac is one of the oldest and well-known vegetable tans for white or light colored soft and supple leathers. It was very largely employed in ancient times. The quality of sumac products can suffer from impurities or blends with low grade condensed tannins. These problems existed already in ancient time. A modern spray-dried Sumac extract was tested too. It did not show the tanning characteristics of gallotannins compared with milled sumac.

TABLE III

Leather Manufacture for the Moritzburg Castle Pilot Project

Raw material	Tanning matter	Shrinkage temperature
Chrome tannage/ tannage with condensed tannins (comparative specimens)		
goat	chrome sulfate, powder, syntan (replacement tannin)	98°C
goat	quebracho, spray dried extract	86°C
goat	quebracho, spray dried extract, mimosa, spray dried extract	90°C
calf	mimosa and gambir (catechu, inorganic modification), spray dried extracts	83°C
calf	gambir (catechu), spray dried extract, inorganic modification	79°C
Tannage with hydrolyzable tannins, combination tannage		
goat	sumac, milled powder	75°C
calf	tara, milled powder	70°C
calf	sumac, spray dried extract, myrabolane, spray dried extract	65°C
calf	sumac, milled powder, valonea, spray dried extract	76°C
calf	valonea, spray dried extract, chestnut, spray dried extract	74°C
calf	valonea, spray dried extract, chestnut, spray dried extract, zirconium salt	85 °C
Tannage with hydrolyzable and condensed tannins, combination tannage		
calf	tara, milled powder, gambir (catechu), spray dried extract, modified	69°C
goat	tara, milled powder, sumac, spray dried extract, aliphatic glutaraldehyde, inorganic aluminum salt	79°C
goat	tara, milled powder, syntan, dispersing, replacement tannin, organic aluminum salt	—
goat	sumac, spray dried extract, gambir (catechu), spray dried extract, modified aliphatic glutaraldehyde, syntan (replacement tannin), inorganic aluminum salt combined with syntan (combination tannin)	107°C

Valonea represents tannins from Quercus species. Commercial valonea extract is made from acorn cups of Quercus aegilops. It causes leather to be dense and heavy with a high water resistance. Valonea belongs to the pyrogallol type tannins with a large amount of ellagitannic acid that is the weight-giving property of the leather even so chestnut.

Sumac powder was favored for the tannage of goat skin. Valonea and chestnut were suited for the tannage of calf skin. All skins were hang-dried and slightly toggled at room temperature.

Processing of the test leather at Moritzburg Castle
All leathers of the pilot plant tannery were tested regarding its characteristics for the restoration of wall hanging by the project partners in Dresden and Moritzburg. Every lot was sampled and checked with the Vanillin-spot-test to exclude the presence of condensed tannins in the leather. The conservation concept for

the hangings of Moritzburg castle provides silver-plated leather because of better upgrading of holes or missing parts. This method was applied very successfully in the former projects in Moritzburg Castle. For this purpose the leather was plated with silver leaf using parchment glue. This is the genuine technology of gilt leather wall-hangings. A sudden problem appeared on the fresh silvered surface of the first samples. In a very short time numerous brown dots spread out (Figure 6).

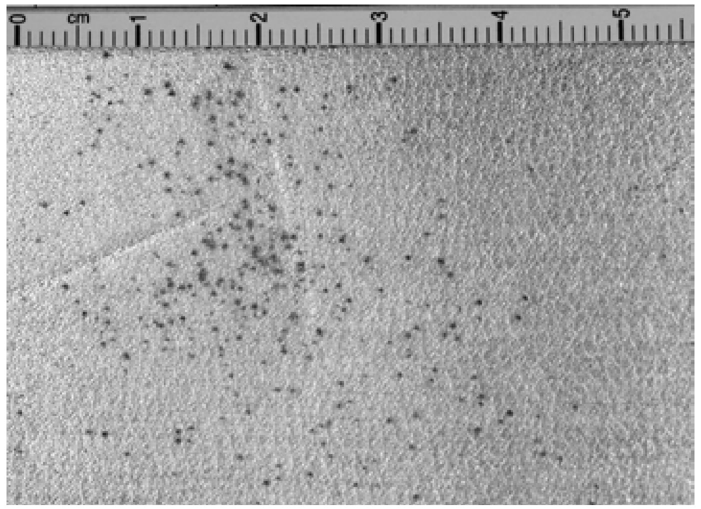

Figure 6: Sulphide dots on silvered leather surface

Despite of a protecting lacquer coat the silver was darkened after some weeks due to sulfidation. This, in hitherto existing researches disregarded aspect was an important one, because such corrosive influences from a restoration leather could darken not only the new retouches, but could be harmful also for the original silver layer of the historic artifacts. It was quite obvious that the sulfidation must be brought by the leather. To investigate the reasons for this phenomenon all produced leather samples were tested on their effects on pure silver leafs. All samples were shielded from environment influences. All the new leathers showed more or less intensive sulfidation effects on the silver. But also the different tanning materials and the lubricants were exposed to similar tests. It was very instructive to see, that also some lubricants caused darkening. The main reason of the staining and darkening was a polluted atmosphere in the drying chamber of the pilot plant tannery. A permanent emissions load of hydrogen sulfide was detected. After the solution of this problem the obtained leather were tested concerning their mechanical properties for the conservation and restoration steps like skiving, punching and embossing. Finally sumac tanned leather has been found to be particularly suitable for punching and calf leather was preferred for embossing techniques.

Quality Control of Leather for Wall Hangings

Mechanical and chemical testing

Leather is an upgraded natural product. 35 to 65 % of vegetable tanned leather consists of natural hide substance. The other leather matrix components are quite uneven distributed over the skin area and its cross section. When characterizing leather, topographic distribution of strength, histological composition and anisotropic properties have to be considered. Accurate sampling (DIN EN ISO 2418, DIN EN ISO 4044) and conditioning in a standard atmosphere (DIN EN ISO 2419) are the basics of every measurement and analysis but can not fully equalize the difference between species and even individuals. A typical example is mechanical strength which is characterized by a pronounced variability. For the selected leather types the following parameters have been proved:

- Volatile matter, "moisture content" (DIN EN ISO 4684)
- Sulfated total ash, water-insoluble ash (DIN EN ISO 4047)
- Matter soluble in dichlormethane, "fat content" (DIN EN ISO 4048)
- Water-soluble matter (organic and inorganic), "wash out" DIN EN ISO 4098)
- Nitrogen content and "hide substance" (ISO 5397)
- Hydroxyproline content (FILK-P-2003)
- Determination of pH, difference figure (DIN EN ISO 4045)
- Shrinkage temperature (DIN EN ISO 3380)
- Tensile strength and percentage extension (DIN EN ISO 3376)
- Tear load (DIN EN ISO 3377-1)

Figure 7 and 8 present the composition of two leather of the project. The calf leather of figure 7 was a comparative specimen tanned with gambier extract. Gambier is well established tannin of the condensed type. The calculated degree of tannage was 38 %. The total ash content of the leather was unusually high for a vegetable tannage and resulted from a tanning extract modified with mineral additives. The modified extract led to a pH 6.5 and an uncommon difference figure of -0.4 of the aqueous leather extract which refer to the presence of free alkali.

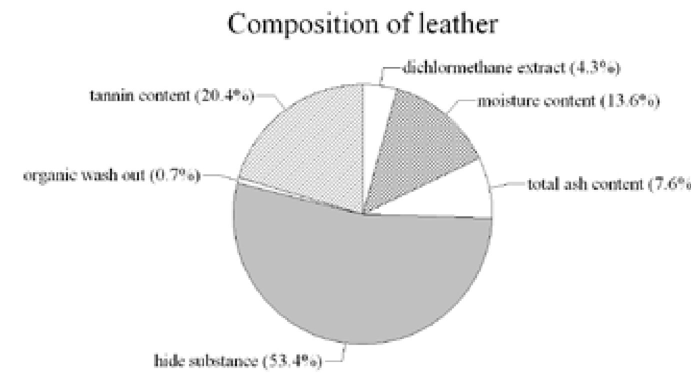

Figure 7: Test leather, calf skin tanned with modified gambier extract

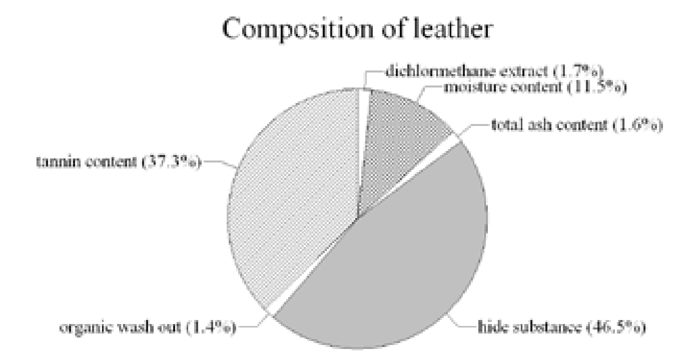

Figure 8: Test leather, goat skin tanned with sumac powder

The composition of a sumac tanned goat skin is presented at figure 8. The pH value 5.4 and difference figure of +0.2 were measured. The leather was not lubricated. The soluble matter in dichloromethane was only 1.7 % but nevertheless the leather showed a sufficient softness and strength resulting from the sumac tannage. The obtained degree of tannage of 80 % means approximately twice higher tannin binding then the gambier tannage. With sumac tanning degrees up to ≥ 100 % are feasible.

Figure 9 is showing the composition of genuine gilt leather from Moritzburg castle. Components of the gilt finish on the opulent punched grain layer were mechanically removed from the sample before analysis. The leather was sumac tanned goat skin with a degree of tannage of 45 %. The aqueous extract of the sample showed a pH 3.9 and a difference figure +0.3.

Enthalpy studies by differential scanning calorimetry (DSC) are appropriated to characterize the conservation respectively degradation status of leather. The enthalpy should be calculated on the true collagen content of the leather with respect to the inhomogeneous sample constitution and technological variances of vegetable tanning. The onset temperature correlates with the shrinkage temperature. A specific denaturation enthalpy from 13.5 to 24.0 Jg^{-1} collagen can be calculated, depending on the heat flow integral. Figure

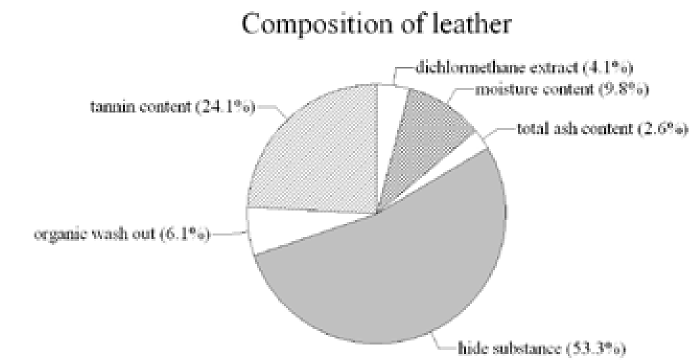

Figure 9: Genuine gilt leather from Moritzburg, sumac tanned goat skin, sample n° 1b

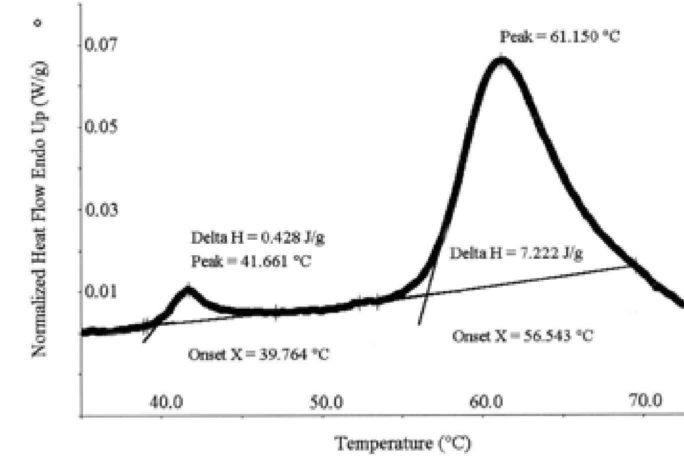

Figure 10: DSC measurement of gilt leather from Moritzburg Castle, sample n° 1b

10 is demonstrating the hydrothermal stability of the Moritzburg gilt leather. The delivered results show a partial degraded leather matrix and correspond to a normal state of aging.[11]

Test of long-term behavior

The European ENVIRONMENT and STEP leather project have clarified that the natural aging and the accelerated deterioration of the leather matrix due to environmental pollution are dominated by oxidative mechanisms. Pollution studies and artificial aging methods presented by these projects as well as numerous older scientific publications[1, 2, 7] require a very expensive and complex equipment that are available neither for leather manufacturer nor for the conservator.

A simple test method for accelerated oxidative and environmental induced aging by sulfur dioxide was developed as a result of a FILK research project about the manufacture of organ leather with long-term stability. Samples are stored one week at 30...40 °C and > 90% rH above sulfurous acid (6 % SO_2). After reconditioning the humidity of the specimens is diminished to ≤ 2 %. The dried samples are stored at 90...95 °C and ≥ 0 % rH for 18...24 hours. The dehydration of the specimen by desiccant avoids hydrothermal shrinkage and accelerated hydrolysis during the heating. The detailed description of the procedure is provided in[12]. The specimens were analyzed before and after the aging. Following tests were carried out:

- Volatile matter, "moisture content" (DIN EN ISO 4684)
- Sulfated total ash, water-insoluble ash (DIN EN ISO 4047)
- Matter soluble in dichloromethane, "fat content" (DIN EN ISO 4048)
- Water-soluble matter (organic and inorganic), "wash out" (DIN EN ISO 4098)
- Nitrogen content and "hide substance" (ISO 5397)
- Hydroxyproline content (FILK-P-2003)
- Determination of pH, difference figure (DIN EN ISO 4045)
- Shrinkage temperature (DIN EN ISO 3380)
- Differential scanning calorimetry of leather samples DSC[11].

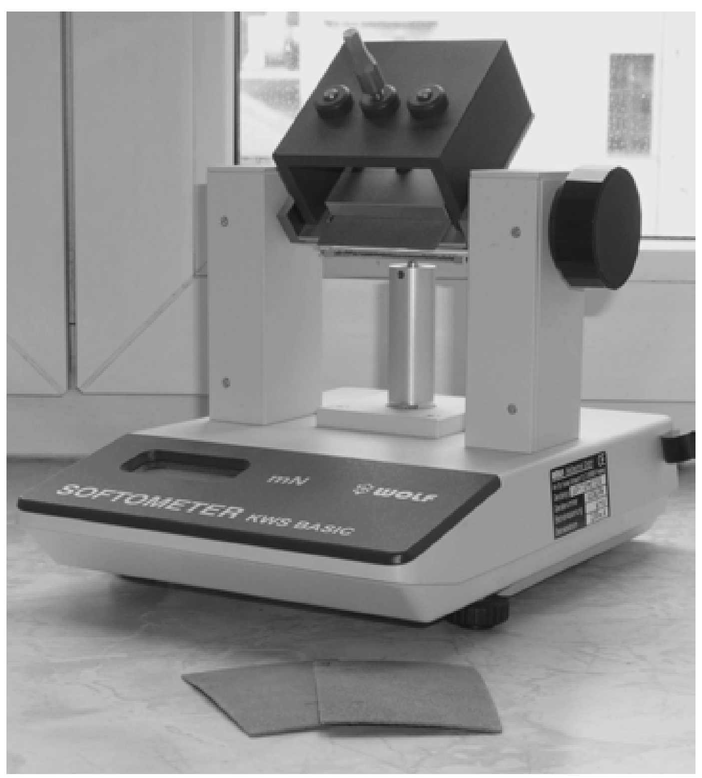

Figure 11: Softometer with leather samples

Significant information about the aging process was provided by the additional analysis of the water-soluble matter (DIN EN ISO 4098). The aqueous extract (total wash out) was analyzed regarding:

- Acid and base-neutralizing capacities (DIN 38409-H7)
- Dissolved ammonia NH_4^+-N (Merck Spectroquant photometric cell test n° 14544)
- Total dissolved nitrogen TKN (Merck Spectroquant photometric cell test n° 00613)
- Dissolved nitrate NO_3^--N (Merck Spectroquant photometric cell test n° 14542)
- Dissolved sulfate SO_4^{2+}-S (Merck Spectroquant photometric cell test n° 14548)

Tensile strength and tear resistance are destructive tests with a great variability. Therefore a non-destructive method of strength measurement is desirable for analysis of leather aging. The non-destructive Softometer test was implemented (figure 11).

For the test a piece of leather strip 60 X 75 mm is clamped on the one side and pushed 30 ° for 10 s to a sensor. The bending force is measured and the flexural stiffness is calculated by equation (1):

(1) $${}_B = \frac{M_B}{W_L} = \frac{6 \cdot F_B \cdot l}{b \cdot h^2}$$

σ_B … Flexural stress (MPa]	F_B ... Bending force [N]
M_B … Bending moment [Nmm]	l ... Bending distance [mm]
W_L … Section modules [mm^3]	b ... Sample width [mm]
(cross section sample)	h ... Sample thickness [mm]

A relaxation test has been run at the same test specimen before and after accelerated aging (figure 12). The measured response $\sigma_B = f(t)$ was fitted and linearized by a rezipro-Y/ square root-X transformation in an interval from 10 to 600 s (equation 2):

(2) $$\frac{1}{\sigma_B(t)} = C_0 + R^* \cdot t^{1/2}$$

C_0 … Y-intercept of the fitted model for t = 0 min

R^* … slope of fitted model (= specific relaxation modulus)

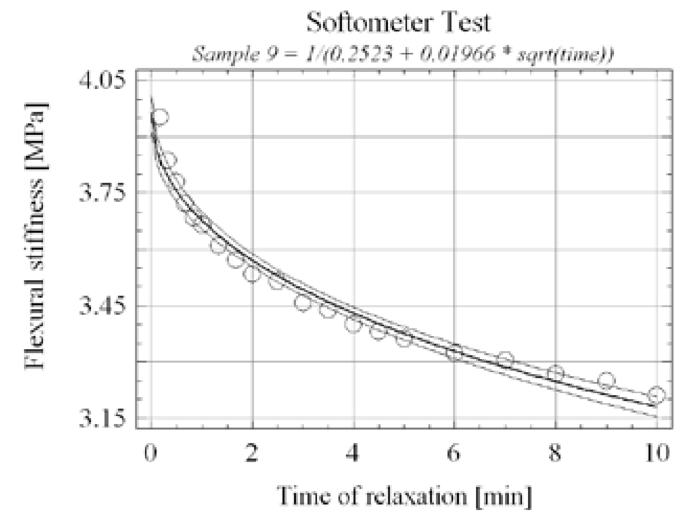

Figure 12: Relaxation curve with a sample of aged calf leather (gambir tannage)

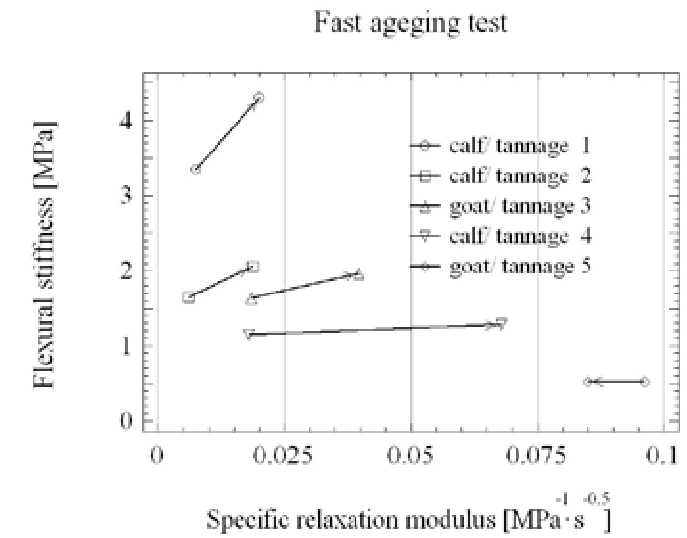

Figure 13: Mechanical response of the fast aging test on leather
1: calf, tannage with gambier extract
2: calf, tannage with valonea/ chestnut extract
3: goat, tannage with tara powder sumac/ gambier extract, aluminum salt
4: calf, tannage with mimosa extract
5: goat, tannage with sumac powder

The slope R of the quasi-linear regression was used as a description of a specific relaxation modulus. The Parameter σ_B and R* provide information about the static and visco-elastic behavior of the tested material. Several specimens of each leather type were tested. The arithmetic averages of both parameters before and after aging were used for the modeling of a simple vector of the "micro mechanical aging" of the leather matrix. The vector connects the starting and endpoint of the fast aging test by a line. Figure 13 presents the resulting vectors of 5 leather types. The most significant changes regarding stiffness and relaxation behavior showed leather samples tanned with gambir and mimosa extracts (tannage 1 and 4).

The aging behavior of the goat leather tanned with sumac powder (tannage 5) shows completely different behavior compared to the other test specimens. No change of stiffness was measured. The vector showed a contrariwise alignment. Table IV present the most pronounced differences between the sumac tanned goat skin (tannage 1) and the gambier extract tanned calf skin (tannage 5). For the unaged calf leather a negative difference figure was measured which means free alkali. This special feature was caused by the alkaline character of the extract additives. The ash content of the leather was 9 %. This is completely atypical for vegetable tanned leather and caused the high stiffness of the sample. A significant amount of aluminum and silica were detected by an EDX analysis as well in the extract as in the tanned leather. The big difference between the initial and final difference figure and pH-value of the aqueous extract indicate strong aging effects. Alkali causes a dark leather color and accelerates oxidizing effects on condensed tannins. The increasing amount of leachable sulfate and the reduction of the shrinkage

TABLE IV

Analysis of vegetable tanned leather before and after fast aging test

	Calf leather tanned with modified gambier extract		**Goat leather tanned with milled sumac powder**	
	Before	**After simulation**	**Before**	**After simulation**
pH value (aqueous extract)	6,5	3,0	5,4	4,7
Difference figure	- 0,4	+0,5	+ 0,2	+ 0,1
Dissolved sulfate SO_4^{2+}-S [% dry substance]	0,2	1,5	0,2	0,7
Shrinkage temperature [°C]	83,0	74,0	76,0	72,0