ELSEVIER

Thermochimica Acta 365 (2000) 85–99

thermochimica acta

www.elsevier.com/locate/tca

Experiments and observations in the study of environmental impact on historical vegetable tanned leathers

René Larsen

Det Kongelige Danske Kunstakademi, Konservatorskolen, Esplanaden 34, 1263 København K., Denmark

Abstract

The hydrothermal stability in the form of the shrinkage temperature (Ts) is a fine measure of the deterioration of vegetable tanned leathers. Previously, it has been demonstrated that the Ts can be predicted by multiple regression modelling based on parameters for the chemical breakdown of the collagen and tannin structures, the sulphate content and acidity of the leather as well as the interaction of these four parameters. In the present paper, several deterioration profiles are suggested for both the natural and artificial aged leathers based on significant regression analyses of the grouped data. The possible existence of several deterioration profiles is supported by more than 100 years of observational and experimental studies of natural and artificial ageing, and is probably mainly due to difference in tannin type and storage conditions. On this basis the problems in using simple standard artificial ageing systems are discussed, and improvement of more complex systems suggested. The latter based on continuation of combined observational and experimental studies using the multiple regression modelling of the Ts as an instrument for adjusting and developing the ageing system.

Keywords: Vegetable tanned leathers; Artificial ageing; Shrinkage temperature; Multiple regression analysis; Standardised coefficients; Breakdown profiles

1. Introduction

The combination of comparative observational and experimental research in the study of the causes of the deterioration of cultural heritage leather objects has, from the very beginning, been the leading principle. Not least this is due to the fact that the studies are complicated by the restricted possibility in getting access to samples of the often precious cultural heritage objects. The leather itself represents a very complex material composition. Its surroundings are likewise a very complex and dynamic dimension constantly varying with respect to the quantity and degree of their interaction with each other and with those materials which are being stored within them. Moreover, the production and ageing history of cultural heritage leathers are in most cases unknown. In general, this is the situation in observational studies, which can be supported by experimental studies based on well defined material and artificial ageing conditions. In previous papers, it has been demonstrated that the hydrothermal stability, expressed by the shrinkage temperature of the leather, can be predicted by means of multiple regression modelling [1–4]. The prediction is based on a few chemical characteristics of the leather, and may be used in the study of the environmental impact and the breakdown patterns of vegetable tanned leathers. Moreover, it may form the basis for improving the methods of artificial ageing.

2. Materials

The observational studies were performed on European historical vegetable tanned leathers dating from

0040-6031/00/$ – see front matter
PII: S0040-6031(00)00616-X

Table 1
Description of samples

Sample code	Type including plant origin of tannins
H	Random historical leathers samples in Europe
B	British Library
W	The National Library of Wales
B, W	A, L2 (acacia); M (mimosa); C (chestnut); G (gambier); Q (qebracho); QS (sulphated qebracho); S, L9, L10, L11 (sumac); SF (filtered sumac); O, L3, L4, L7 (oak)
F29A3, F29B3, V18A1, V18D1	Newer experimental leathers tanned with condensed tannins sampled in France
M0, S0	New experimental leathers (blank): M (mimosa); S (sumac); 0 (0 weeks or days of ageing)
EM18–24, ES18–24, FM16–22, FS16–22	New experimental mimosa and sumac leathers artificially aged 1–8 weeks
MA1–8, MAA2–10	New experimental mimosa leathers artificially aged 1–8 weeks and 2–10 weeks, respectively

ca. 1600 to ca. 1980. Information on the sample code and type are listed in Table 1. Moreover, the code, dating and main tannin type of the historical and new experimental samples are shown in Tables 2 and 3. The sample codes are the same used in earlier publications where more details on the samples can be found [5,6].

The H samples were sampled in Denmark, France, the Netherlands and the UK. The B, BL and W samples are part of a major investigation started in the 1930s by the British Bookbinding Industry, in cooperation with Leather and Paper Research Associations, to determine the causes of leather deterioration and to establish which tannages and treatments conferred long-term durability on a leather [7,8]. The BA, WA, etc. originally originate from the same piece of leather divided into two. These were bound on books stored in the Library of The British Museum (British Library) in London and The National Library of Wales in Aberystwyth to test the durability of the leathers stored in a polluted and a clean environment, respectively. In total, 120 pairs of leathers were stored as part of this trial. The BL samples belong to those leathers stored in British Library. The F and V samples are from a recent storage trial in France. The samples used in the artificial ageing experiments were mimosa (condensed tannin type) and sumac (hydrolysable tannin type) tanned leathers prepared especially for the experiments by the British School of Leather Technology [5,6]. In general, the condensed tannins (plant polyphenols mainly consisting of the flavanol-3-ol oligomers) are more sensitive to oxidative deterioration and absorb sulphur dioxide easier than the hydrolysable tannins (plant polyphenols consisting of esters of glucose and gallic acids or ellagic acids or derivatives of these).

3. Experimental

3.1. The hydrothermal stability (shrinkage temperature)

The hydrothermal stability of collagen fibres (shrinkage by heating in water) is a particularly good measure of the strength or quality of leather and skin materials and the degree of their deterioration [7–13]. A sample of around 0.3 mg fibres from the corium part of the leather is wetted with distilled water for at least 10 min on a microscope slide with a concavity. The fibres are separated, any air bubbles are removed with a needle and the fibres are well dispersed on the slide. The fibres are covered with distilled water and secured with a microscope slide. The microscope slide is placed on the hot table (Mettler FP82 Hot Stage, Mettler-Toledo, Switzerland) and heated at a rate of 2°C/min. The hot stage is thermostatically controlled through a Mettler FP90 Central Processor. Two crystals are used for calibration, azobenzene with a melting point of 68°C and benzil with a melting point of 95°C. To record the shrinkage process, the micro hot table is placed under a stereo microscope with transmitted light. When heated in water the collagen fibres will deform over a distinct temperature interval. The deformation is seen as a shrinkage of the fibres, and can be described in three temperature intervals where interval A/A2 is distinct shrinkage activity observed in individual fibres, interval B/B2 is shrinkage activity in

Table 2
Analytical data on naturally deteriorated historical vegetable tanned leathers dating from ca. 1600 to ca. 1980[a]

Sample	Date	Group	Tannin	Ts (°C)	*B/A*	% Sulphate	% Monomers	pH	$[H^+] \times 10^4$
H1	ca. 1838	N1	C	57.2	0.55	1.0	7.0	5.10	0.08
H3	19th century		H	55.7	0.55	1.5	6.3	3.25	5.62
H5	1700–1730		H	42.1	0.51	2.0	8.6	3.40	3.98
H7	18th century		(C)	48.2	0.52	1.8	6.7	3.00	10.00
H13	ca. 1730		(C)	44.5	0.52	5.1	8.9	2.55	28.18
H15	ca. 1890		C	43.9	0.54	4.8	4.1	2.55	28.18
BL7	1932		H	65.7	0.63	2.6	2.6	2.76	17.38
BL9	1932		H	68.5	0.63	1.9	1.9	2.78	16.60
BA	1932		H	67.3	0.65	2.7	1.4	2.86	13.80
BM	1932		C	55.3	0.63	5.2	1.7	2.66	21.88
BQ	1932		C	60.1	0.64	4.8	3.8	2.55	28.18
WM	1932		C	76.6	0.59	0.5	1.2	4.33	0.47
F29A3	1982		C	76.4	0.64	0.4	1.4	3.2	6.30
F29B3	1982		C	53.4	0.60	2.0	6.5	2.6	25.10
V18A1	1982		C	80.8	0.65	0.4	2.2	3.7	2.00
V18D1	1982		C	64.7	0.63	0.8	5.5	3.0	10.00
H8	16th century	N2	C	36.9	0.51	4.8	4.6	2.65	22.39
H9	18th century		C	33.1	0.51	1.6	7.3	3.10	7.94
H10	?		C	53.4	0.60	1.7	3.8	2.70	19.95
H11	ca. 1660		(C)	32.6	0.49	5.6	4.4	2.85	14.13
H12	18th century		H	37.7	0.55	2.8	8.1	3.25	5.62
H14	ca. 1830		C	57.2	0.58	0.2	2.7	5.20	0.06
H18	ca. 1740		(C)	51.3	0.56	1.6	2.1	4.25	0.56
H19	1880		(C)	47.4	0.56	0.8	6.4	3.20	6.31
H20	1700		(C)	43.7	0.53	2.0	6.8	3.85	1.41
BL3	1932		C	35.7	0.58	6.8	2.4	2.52	30.20
BC	1932		C/	44.8	0.62	3.5	2.5	2.92	12.02
BO	1932		C	39.8	0.59	4.8	2.3	2.73	18.62
BQS	1932		C	52.2	0.65	4.7	3.7	2.80	18.85
WC	1932		C	65.6	0.59	0.5	1.1	4.23	0.59
WO	1932		C	62.9	0.59	0.5	1.8	4.29	0.51
H2	ca. 1882	N3	H	51.9	0.49	0.8	13.5	3.80	1.58
H6	?		C	39.1	0.45	5.5	5.0	2.80	15.85
H16	18th century		(C)	60.6	0.52	0.3	7.0	4.25	0.56
H17	1850		C	78.3	0.60	0.9	2.8	3.10	7.94
BL2	1932		H	62.5	0.64	3.9	0.7	2.53	29.51
BL4	1932		C	60.8	0.55	6.6	2.4	2.79	16.22
BL10	1932		H	68.4	0.60	2.3	0.2	2.73	18.62
BL11	1932		H	64.8	0.60	3.5	3.5	2.95	11.22
BG	1932		C	70.0	0.61	5.6	3.5	2.58	26.30
BS	1932		H	68.7	0.62	2.6	1.7	2.83	14.79
BSF	1932		H	75.3	0.64	2.4	1.3	2.91	12.30
WA	1932		H	83.7	0.61	0.4	1.2	4.08	0.83
WG	1932		C	81.1	0.59	0.4	1.5	4.19	0.65
WQ	1932		C	84.5	0.58	0.5	1.8	4.07	0.85
WQS	1932		C	81.5	0.61	0.6	1.7	4.62	0.24
WS	1932		H	80.0	0.58	0.4	1.4	4.11	0.78
WSF	1932		H	85.7	0.62	0.6	1.0	3.82	1.51

[a] Uncertain identification of tannin type is marked by parenthesis. The grouping of the samples refers to the regression analysis (see Section 5).

Table 3
Analytical data on artificially aged new experimental vegetable tanned leathers[a]

Sample	Group	Ageing cycles	Tannin	Ts (°C)	*B/A*	% Sulphate	% Monomers	pH	$[H^+] \times 10^4$
M0	A1	0	C	78.0	0.69	0.2	0.0	3.26	5.50
EM18		1		68.1	0.63	0.4	0.0	2.76	17.38
EM20		2		55.0	0.62	0.8	0.5	2.55	28.18
EM22		4		45.2	0.60	1.4	0.9	2.35	44.67
EM24		8		40.0	0.56	2.4	1.8	2.35	44.67
FM16		1		58.2	0.62	0.4	0.2	2.82	11.14
FM18		2		55.2	0.59	0.4	0.5	2.81	15.49
FM20		4		43.1	0.56	1.0	1.0	2.51	30.90
FM22		8		25.6	0.51	1.6	1.8	2.41	38.90
S0	A2	0	H	76.0	0.69	0.1	0.6	3.16	6.92
ES18		1		71.1	0.65	0.2	0.6	2.87	13.49
ES20		2		60.9	0.65	0.4	0.7	2.74	18.20
ES22		4		52.7	0.62	0.8	0.9	2.51	30.9
ES24		8		40.5	0.60	1.0	0.9	2.50	31.62
FS16		1		69.5	0.65	0.2	0.7	2.95	11.22
FS18		2		59.8	0.62	0.3	0.7	2.88	13.18
FS20		4		45.3	0.62	0.6	0.8	2.66	21.88
FS22		8		36.7	0.57	0.8	0.8	2.64	22.91
MA1	A3	1	C	64.1	0.63	0.5	0.9	2.88	13.18
MA2		2		51.9	0.60	0.8	2.0	2.70	19.95
MA4		4		40.9	0.57	1.4	5.1	2.54	28.84
MA8		8		35.1	0.45	2.3	8.0	2.35	44.67
MAA2		2		54.1	0.53	0.4	4.3	3.06	8.71
MAA4		4		48.6	0.51	0.4	4.6	2.99	10.23
MAA8		8		42.0	0.47	1.0	6.5	2.68	20.89
MAA10		10		39.8	0.44	2.3	10.9	2.39	40.74

[a] M: mimosa, S: sumac. The grouping of the samples refers to the regression analysis (see Section 5).

one fibre (occasionally more) immediately followed by shrinkage activity in another fibre and the main interval C where at least two fibres show shrinkage activity simultaneously and continuously. As a function of temperature a sample of new unaged fibres undergoes the following changes:

$$\text{no activity} \rightarrow \text{A} \rightarrow \text{B1} \rightarrow \text{C} \rightarrow \text{B2} \rightarrow \text{A2} \rightarrow \text{complete shrinkage}$$

The start temperature of this main interval of shrinkage is the shrinkage temperature, Ts. The accuracy of the measurement of the Ts is ±2°C. In the present paper, only the recorded Ts is used in the calculations. The Ts of new vegetable tanned leathers varies from 70 to 90°C depending on the tannin type and quality of production. The Ts of historical leathers falls with increasing deterioration. It may vary from more than 80°C to below room temperature.

3.2. Amino acid analysis

For amino acid analysis of vegetable tanned leather around 0.2 mg of corium sample is taken. The sample is hydrolysed for 24 h in an evacuated and sealed glass ampoule at 110°C in a solution consisting of 300 μl 6 M redistilled HCl, 15 μl 2% 3,3′-dithiodipropionic acid (DTDPA) in 0.2 M NaOH and 15 μl 1% phenol in water. After hydrolysis the amino acids are separated by ion exchange HPLC (Waters, USA) with two Waters high pressure pumps, equipped with high sensitivity pulse dampers and microflow modules, an auto/manual solvent select switch for four solvents, Waters M 710, refrigerated autosampler, a Rheodyn six-port valve, two Eldex reagent pumps, a column oven. Separation takes place on a 12.5 × 0.46 steel column packed with MCI CK 10 U resin (Mitsubishi Chemical Industries) using a pH gradient system with two buffers (A: 0.20 sodium citrate containing 0.05%

phenol and 5% isopropanol, B: 0.210 M sodium borate, 5% isopropanol). The eluated amino acids are quantified after derivatisation with *ortho*-phthaldialdehyde (OPA). The detector is a Waters M 420 fluorescence detector with 338-nm bandpass excitation filter and 455-nm long-pass emission filter. The amino acids are identified and quantified on the basis of an external standard mixture of amino acids (Beckman No. 33 8088, hydroxyproline from BDH) The deviation of the total analysis is normally below 3%. Further details on the method and equipment can be found in Refs. [14–17]. In the following are used the value of the ratio of the sum in mol% of basic (B) and the sum in mol% of acidic (A) amino acids $B/A = \sum \mathrm{Arg, Hyl, Lys} / \sum \mathrm{Asp, Glu}$ [2]. The *B*/*A* value is about 0.7 for intact hide and leather collagen and the value decreases with increasing oxidation. Thus, *B*/*A* values below 0.5 have been observed in very deteriorated leathers.

3.3. Measurement of pH, sulphate and tannin analysis

Measurements of pH, sulphate as well as tannin analysis were performed on the same leather sample by Wouters and co-workers according to the procedure of Wouters [18–22]. The analyses are performed on between 2200 and 1000 mg of leather (grain and corium) cut into 1 mm^2 fragments. The relative amount of volatile matter is calculated with reference to the conditioned leather [23]. The leather fragments are extracted in water for 24 h at room temperature, under constant agitation in a closed polyethylene vessel. The extraction volume is always 50 times the weight of the leather sample. Up to 2% by volume of the aqueous extract is used for pH measurements and ion chromatography. To the aqueous extract, containing the leather fragments, is added an equal volume of acetone and extraction is continued a further 24 h under the same conditions [24]. The pH in historical leather may vary between about 2 and more than 5. In the calculations presented $[H^+] \times 10^4$ is used, calculated from the observed pH values.

3.3.1. Measurement of pH

The measurements were performed directly on the aqueous extract using a pH meter (PHM62, Radiometer, Copenhagen) with a combination electrode and calibrated between pH 3 and 7, at 21°C. To make the method available to small samples, the dilution condition of the leather extract (1 g/50 ml) differs by a factor of 2.5 from the standard procedure (2.5 g/50 ml [25]). This makes the present pH readings of strong mineral acid solutions about 0.4 higher as compared to the standard procedure. Historical vegetable tanned leathers normally have a pH between 2 and 6 depending on the conditions under which they have been stored.

3.3.2. Measurement of sulphate

A small aliquot of the aqueous extract is properly diluted with potassium phthalate buffer, pH 5.8 and subjected to anion chromatography on an ionosphere-A column (100 × 4.6 mm, 5 μm; Chrompack, Antwerp, Belgium). The eluent used is the same phthalate buffer, pumped at 1.0 ml/min (model 510 HPLC pump, Waters, USA). The sulphate is detected with a conductivity detector (Model 430, Waters, USA) and quantified with the help of a calibrated standard curve for sulphate. The amounts of sulphate is expressed as percentage by weight of dry leather. Between less than 1% and up to and around 6% of sulphate has been measured in historical leathers depending on the storage conditions.

3.3.3. Analysis of vegetable tannins

A small sample of the water–acetone extract (1/1, v/v) is diluted fivefold with water–methanol (1/1, v/v) and analysed by reversed phase liquid chromatography on a sperisorb ODS2 column (100 × 4.6 mm, 3 μm; Alltech, Laarne, Belgium). For the elution a water/methanol linear gradient from 90/10 to 10/90 (v/v) is used in the presence of 0.5% (w/v) phosphoric acid at 1 ml/min (Waters 625 LC System, Waters, USA). The detection is performed using an UV–VIS diode-array detector (model 996, Waters, USA) at 280 nm. The amount of extractable tannins and specific tannin components (monomers, gallic acid and ellagic acid) is expressed as the optical density at 280 nm obtained if 100 mg of leather were extracted with 1 ml of water–acetone and measured with an optical path-length of 1 cm (total tannin, OD/100 mg). The general term ''monomers'' indicates those fractions which appear as distinct peaks in front of the main tannin pattern and which display spectral characteristics resembling those of other small tannin

Table 4
Ageing systems used in the artificially ageing of new vegetable tanned leathers

Sample	Tannin	Cycle system	Ageing conditions
EM	C	$(H_{120} + 6P)_n$, $n = 1, 2, 4, 8$ weeks	H_{120}=dry heat at 120°C for 24 h; $P = 45$ ppm SO_2, 10 ppm NO_2, 10 ppm NO at 40°C and 30% RH for 6 days
ES	H		
FM	C	$(H_{120} + 6P)_n$, $n = 1, 2, 4, 8$ weeks	H_{120}=dry heat at 120°C for 24 h; $P = 45$ ppm SO_2, 20 ppm NO_2 at 40°C and 30% RH for 6 days
FS	H		
MA	C	$(H_{150} + 6P) + (H_{120} + 6P)_n$, $n = 1, 3, 7$ weeks	H_{150}=dry heat at 150°C for 24 h; H_{120} dry heat at 120°C for 24 h; $P = 25$ ppm SO_2, 10 ppm NO_2 at 40°C and 30% RH for 6 days
MAA	C		

components with known chemical structure such as gallic acid and protocatechuic acid. The monomers become more prominent in extracts from aged leather, especially in condensed tannins. In the present calculations the relative amount of monomers expressed as percentage of extractable tannins is used. The amount of monomers may vary from 0 to more than 13%.

3.4. Artificial ageing experiments

The artificial ageing experiments were performed on experimental mimosa and sumac tanned leathers. The ageing method was selected for the purpose of imitating an ''average deterioration'' observed for historical leathers [26–30]. Exposure with sulphur dioxide and nitrogen oxide were performed under constant relative humidity and temperature in specially designed chambers (acid ageing) [26–28]. Dry heat ageing (oxidative) was performed in standard laboratory ovens with ventilation. The selection has been made to perform the ageing in cycles due to practical reasons, as it is not possible to carry out the gassing at the high temperatures used. The high starting temperature of 150°C is necessary to create oxidative changes in both the collagen and the vegetable tannins which correspond to those which are observed in natural deterioration. The ageing conditions are given in Table 4.

4. Multiple regression analysis

The prediction of the Ts (Ts_{pre}) of the leathers is performed as a common multiple regression based on the classical least-squares method [31–33] using the general linear model

$$Y = \beta_0 + \beta_1^* X_1 + \beta_2^* X_2 + \beta_3^* X_3 + \cdots + e_1$$

where the observed Y is expressed as the expected value plus the random error e. The X_1, X_2, X_3, etc. are the independent variables termed regressors or predictors. The established regression model for the prediction of the Ts of vegetable tanned leather is [1]:

$$Ts_{pre} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_1^* X_2^* X_3^* X_4$$

where X_1 is the *B*/*A* value, X_2 the percentage content of tannin monomers, X_3 the percentage content of sulphate, and $X_4 = [H^+] \times 10^4$. The expression can be understood as a model of the expected event (the Ts of a piece of leather that has been exposed to the decompositional directly or indirectly expressed by the factors X_1, X_2, X_3 and X_4). The calculated multiple correlation coefficient R measures how well the dependent variable is related to all regressors at once ($R = 1.0000$ by perfect correlation). R^2 gives the sum of squares that is explained by all the predictors (SS_{exp}) in proportion to the total sum of squares (SS_{tot}). Thus, $R^2 = SS_{exp}/SS_{tot}$ denotes the part of the variance of the dependent variable which can be explained by the regression equation. The goodness of the fit of the entire model (H_0: $\beta_1, \ldots, \beta_p = 0$) is tested by the analysis of variance expressed by the F-ratio which is the variance explained by the regression

Table 5
Observed Ts, predicted Ts and ΔTs ($Ts_{obs}-Ts_{pre}$) of the ungrouped and grouped naturally deteriorated leathers

Sample	Number of samples (n)	Observed Ts (°C)	Ungrouped data		Group	Grouped data	
			Predicted Ts (°C)	ΔTs (°C)		Predicted Ts (°C)	ΔTs (°C)
H1	48	57.2	55.4	−1.8	N1 ($n = 16$)	56.5	−0.7
H3		55.7	53.8	−1.9		54.2	−1.5
H5		42.1	43.0	0.9		43.8	1.7
H7		48.2	47.8	−0.4		47.4	−0.8
H13		44.5	44.5	0.0		45.2	0.7
H15		43.9	45.3	1.4		44.3	0.4
BL7		65.7	66.4	0.7		65.6	−0.1
BL9		68.5	69.5	1.0		68.5	0.0
BA		67.3	68.1	0.8		68.4	1.1
BM		55.3	55.3	0.0		55.6	0.3
BQ		60.1	58.2	−1.9		58.2	−1.9
WM		76.6	74.9	−1.7		75.7	−0.9
F29A3		76.4	78.0	1.6		78.2	1.8
F29B3		53.4	55.0	1.6		53.2	−0.2
V18A1		80.8	79.0	−1.8		80.2	−0.6
V18D1		64.7	65.4	0.7		65.3	0.6
H8		36.9	41.5	4.6	N2 ($n = 12$)	37.2	0.3
H9		33.1	46.4	13.3			
H10		53.4	60.1	6.7			
H11		32.6	37.0	4.4		29.4	−3.2
H12		37.7	46.1	8.4		38.1	0.4
H14		57.2	71.7	14.5		60.7	3.5
H18		51.3	65.2	13.9		52.9	1.6
H19		47.4	56.7	9.3		47.1	−0.3
H20		43.7	49.5	5.8			
BL3		35.7	44.4	8.7		37.4	1.7
BC		44.8	61.0	16.2		48.3	3.5
BO		39.8	52.4	12.6		40.6	0.8
BQS		52.2	59.5	7.3		50.8	−1.4
WC		65.6	75.0	9.4		62.9	−2.7
WO		62.9	73.5	10.6		61.7	−1.2
H2		51.9	34.4	−17.5	N3 ($n = 14$)	50.2	−1.7
H6		39.1	31.9	−7.2		38.7	−0.4
H16		60.6	54.6	−6.0		64.6	4.0
H17		78.3	68.1	−10.2		75.9	−2.4
BL2		62.5	58.0	−4.5		63.2	0.7
BL4		60.8	42.4	−18.4			
BL10		68.4	63.8	−4.6		67.2	−1.2
BL11		64.8	62.0	−2.8			
BG		70.0	52.6	−17.4		67.0	−3.0
BS		68.7	64.3	−4.4		71.0	2.3
BSF		75.3	68.7	−6.6		75.3	0.0
WA		83.7	77.3	−6.4		83.9	0.2
WG		81.1	74.5	−6.6		80.7	−0.4
WQS		81.5	75.6	−5.9			
WS		80.0	73.6	−6.4		79.3	−0.7
WSF		85.7	77.8	−7.9		84.4	−1.3

divided by the unexplained variance (to reject the null hypothesis probability p should be <0.0500). The probability for the null hypothesis that the individual predictors do not influence the dependent variable (H_0: $\beta = 0$) is found on the basis of the t-ratio=b_i/S.E., where S.E. is the standard error of the coefficient. The H_0 is rejected by a p (two tail)<0.0500. The standardised coefficients are the partial or more strictly ''semi-partial'' correlations between each independent variable (predictors) and the residuals from the regression of Ts on all the other predictors. The standardised coefficients are used to compare the influence of each predictor (deterioration factor) on the prediction. The standardised coefficients are found by performing the regression calculation on the standardised variables $=X-\mu$/S.D., where X is the observed value, μ the mean of the variable values and S.D. the standard deviation on the mean.

5. Results

Tables 2 and 3 show the results of the analysis and measurements, and Tables 5 and 6 the observed Ts (Ts_{obs}), Ts_{pre} the difference ΔTs of the naturally and artificially aged samples, respectively. The results of the multiple regression analysis are given in Tables 7 and 8. These show that in both the naturally and artificially aged leathers, the overall correlation and degree of explanation of the model is insignificant when basing the model calculation on the total number of samples. Apart from the acidity, however, the coefficient conditions are significant to highly significant in the case of the naturally aged leathers, whereas only the B/A coefficient is satisfactory in the artificially aged leathers.

Figs. 1 and 2 show the plots of Ts_{obs} versus Ts_{pre} for the two sets of samples. The distributions of the events

Table 6
Observed Ts, predicted Ts and ΔTs ($Ts_{obs}-Ts_{pre}$) of the ungrouped and grouped artificially aged leathers

Sample	Number of samples (n)	Observed Ts (°C)	Full regression model		Group	Reduced regression model	
			Predicted Ts (°C)	ΔTs (°C)		Predicted Ts (°C)	ΔTs (°C)
M0	$n = 26$	78.0	75.9	2.1	A1 ($n = 8$)	77.8	−0.2
EM18		68.1	58.9	9.2			
EM20		55.0	51.4	3.6		55.7	0.7
EM22		45.2	38.9	6.3		46.4	1.2
EM24		40.0	34.3	5.7		37.6	−2.4
FM16		58.2	61.3	−3.1		60.6	2.4
FM18		55.2	54.2	1.0		52.7	−2.5
FM20		43.1	40.7	2.4		41.5	0.7
FM22		25.6	29.1	−3.5		28.1	1.2
S0		76.0	75.7	0.3	A2 ($n = 9$)	75.8	−0.2
ES18		71.1	65.3	5.8		71.7	0.6
ES20		60.9	62.5	−1.6		58.0	−2.9
ES22		52.7	50.3	2.4		53.7	1.0
ES24		40.5	46.6	−6.1		39.6	−0.9
FS16		69.5	66.7	2.8		69.5	0.0
FS18		59.8	60.7	−0.9		60.7	0.9
FS20		45.3	55.6	−10.3		46.4	1.1
FS22		36.7	46.8	−10.1		37.1	0.4
MA1		64.1	62.6	1.5	A3 ($n = 8$)	61.8	−2.3
MA2		51.9	55.0	−3.1		50.8	−1.1
MA4		40.9	49.5	−8.6		45.5	4.6
MA8		35.1	42.3	−7.2		35.0	−0.1
MAA2		54.1	53.0	1.1		56.4	2.3
MAA4		48.6	49.2	−0.6		48.0	−0.6
MAA8		42.0	39.0	3.0		40.7	−1.3
MAA10		39.8	31.8	8.0		38.2	−1.6

Table 7
Standardised coefficients, correlation coefficients and overall variance conditions for the grouped naturally deteriorated leathers[a]

Group	n[b]	Standardised coefficients					R	R^2	F-ratio	p
		β_1 (B/A)	β_2 (% sulphate)	β_3 (% monomers)	β_4 ($[H^+] \times 10^4$)	β_5 ($X_1X_2X_3X_1$)				
All	48	0.3588 (0.0094)	−0.5044 (0.0045)	−0.4291 (0.0014)	−0.2639 (0.1474)	0.3104 (0.0431)	0.8398	0.7053	20.0999	0.0000
N1	16	0.5171 (0.0000)	−0.48134 (0.0000)	−0.5488 (0.0000)	−0.5122 (0.0000)	0.6187 (0.0000)	0.9963	0.9925	265.9295	0.0000
N2	15	0.4139 (0.0053)	−0.9504 (0.0022)	−0.3867 (0.0056)	−0.4803 (0.0627)	0.7477 (0.0391)	0.9638	0.9289	23.5261	0.0001
	12	0.37658 (0.0040)	−0.9300 (0.0041)	−0.3553 (0.0038)	−0.7801 (0.0289)	1.0147 (0.0096)	0.9850	0.9702	39.0029	0.0002
N3	17	0.6962 (0.0003)	−0.3661 (0.0814)	−0.2610 (0.0442)	−0.6115 (0.0021)	0.4347 (0.0054)	0.9729	0.9466	38.9798	0.0000
	14	0.6152 (0.0007)	−0.5884 (0.0024)	−0.3172 (0.0058)	−0.2917 (0.0223)	0.2684 (0.0344)	0.9924	0.9849	104.4636	0.0000

[a] Values in parentheses are probability p (two tail) for the coefficients of the predictors (H_0: β=0).
[b] Number of observations.

Table 8
Standardised coefficients, correlation coefficients and overall variance conditions for the grouped artificially aged new reference leathers[a]

Group	n[b]	Standardised coefficients					R	R^2	F-ratio	p
		β_1 (B/A)	β_2 (% sulphate)	β_3 (% monomers)	β_4 ($[H^+] \times 10^4$)	β_5 ($X_1X_2X_3X_1$)				
All	26	0.7493 (0.0019)	−0.0036 (0.9917)	−0.2349 (0.4706)	−0.5555 (0.0553)	0.1086 (0.7035)	0.9191	0.8448	21.7703	0.0000
A1	9	0.4695 (0.1248)	−1.1219 (0.4529)	−0.5717 (0.2536)	0.1942 (0.7372)	1.0488 (0.3014)	0.9914	0.9829	34.5552	0.0075
	8	0.7692 (0.0003)			−0.2851 (0.0186)		0.9913	0.9827	141.8895	0.0000
A2	9	0.1205 (0.3226)	−2.4918 (0.0058)	−0.0773 (0.6274)	0.5696 (0.0713)	1.2517 (0.0148)	0.9975	0.9949	117.6710	0.0012
	9		−2.8693 (0.0000)		0.5854 (0.0336)	1.4533 (0.0003)	0.9958	0.9917	198.7062	0.0001
A3	8	−1.3087 (0.0484)	7.9873 (0.0192)	−3.9694 (0.0186)	−6.9177 (0.0140)	0.8176 (0.0734)	0.9978	0.9956	89.9845	0.0110
	8		7.1257 (0.0259)	−1.7231 (0.0115)	−6.5634 (0.0217)		0.9694	0.9397	20.7840	0.0067

[a] Values in parentheses are probability p (two tail) for the coefficients of the predictors (H_0: β=0).
[b] Number of observations.

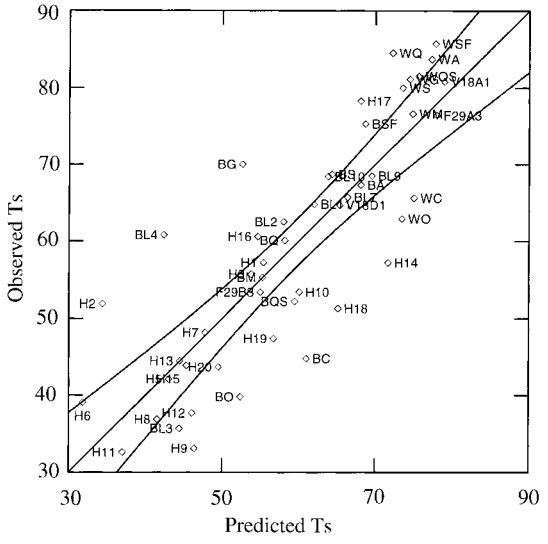

Fig. 1. Plot of Ts_{obs} versus Ts_{pre} (°C) with 95% confidence interval on the regression line. Naturally aged leathers.

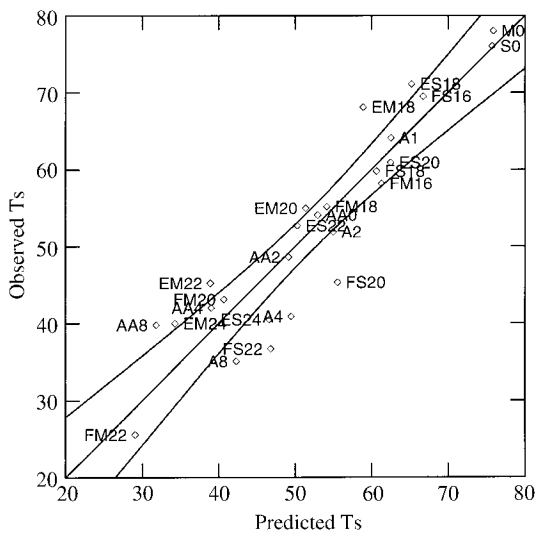

Fig. 2. Plot of Ts_{obs} versus Ts_{pre} (°C) with 95% confidence interval on the regression line. Artificially aged leathers.

indicate in both cases the presence of several sub-populations of samples. Based on the assumption that these have different overall ageing profiles, the two sets of samples were each grouped into three groups. These are indicated in Tables 2, 3, 5 and 6 in the column marked ''group''. The grouping of the naturally aged leathers is performed simply attributing those samples with a ΔTs within ±2°C (the accuracy of the measurement method) to one group (N1). The samples with a ΔTs above and below 2°C N2 and N3, respectively. With respect to the artificially aged samples the grouping (groups marked with an ''A'') is performed on simple trial and error performing the regression analysis on different combinations based on the two tannin types of the leathers and the ageing systems. It was easily found that the data clustered in three main groups. The E and F samples which were aged in very similar conditions can be grouped into two groups (A1 and A2) according to the tannin type. The MA and MAA samples cluster in a group of their own (A3).

The results of the regression model prediction of the three N groups are presented in Table 7. For group N1 the results are highly significant with respect to both the overall correlation and variance conditions as well as to the coefficient conditions. The correlation coefficient is 0.9963 and the model explains 99.25% of the changes in the Ts_{obs}. The correlation of group N2 is significant and apart from the acidity, coefficient conditions are fine. All regression conditions are improved to significant and highly significant by excluding the three samples with a ΔTs outside ±4°C. For N3 the overall prediction is significant and apart from the sulphate coefficient, the coefficient conditions are from satisfactory. As for N2, the regression conditions are improved considerably by excluding the three samples deviating by a ΔTs of ±4°C. The conditions now become significant to highly significant.

Using the full regression model, highly significant results on the overall conditions are obtained for the three groups of artificially aged samples. However, the coefficient conditions are especially bad for A2 and A3. These are improved first of all by reducing the numbers of predictors in the regression model. Table 8 shows the results of the regression model prediction. For A1 only the *B*/*A* and acidity values are used as predictors. The prediction is improved by exclusion of the one sample with a ΔTs of −5.9°C. Using the sulphate, acidity and the interaction term as predictors the conditions of A2 become in almost all cases highly significant. For N3 the conditions are significant.

6. Discussion

The study of the environmental impact on vegetable tanned leather like bookbindings and other cultural heritage objects is not of a recent date. The earliest known work on leather decay was published in 1843 by Faraday [34], who attributed the ''rotted'' conditions to the sulphur compounds in the coal gas burnt for illumination. In 1900, the Royal Society of Arts in England became so concerned about the effects of polluted industrial atmospheres on leather bookbindings in libraries that they appointed a committee to consider the whole question [35]. Based on examinations of naturally aged leathers in several libraries as well as artificial ageing of new leathers, a scientific sub-committee of the Royal Society of Arts reported in 1901 [36]: ''*The new red decay affects nearly all leathers, and in extreme cases, seems absolutely to destroy the fibres*.''...''*This leather, in most of the cases examined, was found to be absolutely rotten in all parts exposed to light and air; so that on the very slightest rubbing with a blunt instrument, the leather fell into a fine dust*.'' In the late 1920s and in the 1930s, several publications on investigations into artificially and naturally ageing leathers were published [37–40]. In later publications the causes and mechanisms of deterioration of natural vegetable tanned leathers have been discussed [41–45]. More recent experimental and observational studies have clarified that the chemical deterioration is caused by two competing and interacting mechanisms namely, a hydrolytic and an oxidative breakdown [1,2,46].

In general, past observations and recent studies have clarified that the hydrolytic breakdown is chiefly due to acidic air pollution with sulphur dioxide and nitrogen dioxides, whereas the oxidative breakdown is due to factors such as heat, light and oxidative contaminants. Moreover, it has turned out that air pollution has an inhibitory effect on the oxidative decomposition of the collagen. Likewise, it turns out that the vegetable tanning agents themselves decompose under oxidative and acidic conditions. Furthermore, the vegetable

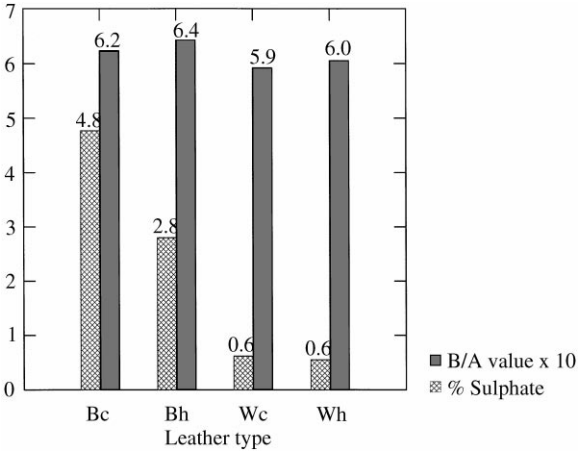

Fig. 3. Bar chart of the average sulphate content and the *B*/*A* value (×10) in leathers stored since 1932. Bc: condensed tanned leathers; Bh: hydrolysable tanned leathers stored in British Library, Wc: condensed tanned leathers stored in The National Library of Wales; Wh: hydrolysable tanned leathers stored in The National Library of Wales.

tannins promote both the oxidative as well as the acidic decomposition of the collagen. However, the sensitivity to these breakdown factors as well as the ability to absorb sulphur dioxide from the environment depend on the type of tannins as illustrated in Fig. 3. The figure shows the mean values of % sulphate and the *B*/*A* values (×10) for the leathers stored in British Library and The National Library of Wales. For the British Library, the sulphate content (4.8%) in the condensed tanned leathers are on average 42% higher than in the hydrolysable tanned leathers (2.8%). The mean sulphate content in the Welsh leathers are the same for both tannin types (0.6%) and several times lower than the British Library leathers. In both sets of samples the *B*/*A* value is lower for the condensed leathers reflecting the higher sensitivity to oxidation of these. Moreover, the leathers from The National Library of Wales leathers have lower *B*/*A* values as a result of the lower pollution. The inhibitory effect of acid pollution on the rate of oxidation on the leather collagen is clearly illustrated in Fig. 4. The plot shows the *B*/*A* values of experimental mimosa leathers artificially aged in dry heat at 120°C with and without prior pollution in a SO_2 and NO_2 containing atmosphere. The *B*/*A* value of the unpolluted leather decreases from 0.69 to 0.60 after only 1 day of ageing. The value of the polluted sample is still above 0.6 after 4 days of ageing.

That the mechanisms and pattern of breakdown are influenced by external (environmental) as well as internal factors are clearly indicated by the multiple regression analyses. On the basis of the calculated

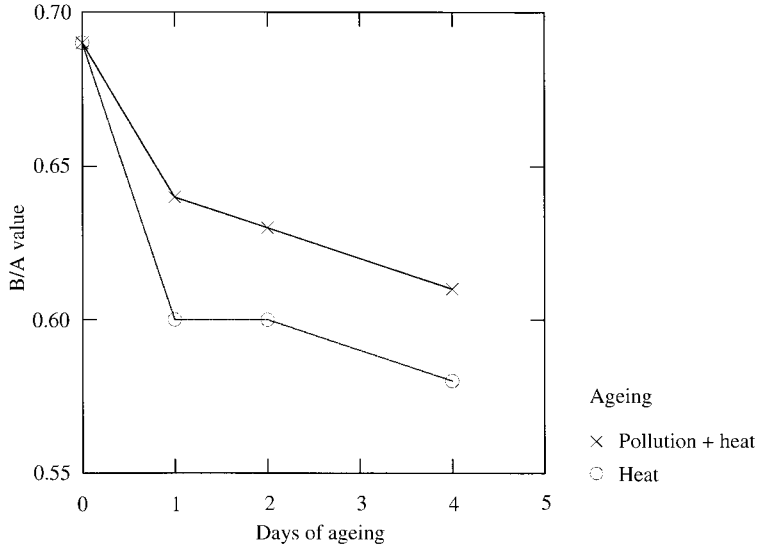

Fig. 4. Plot of *B*/*A* value versus ageing time of artificially aged leathers treated with dry heat (120°C) and dry heat and pollution (sulphur dioxide and nitrogen dioxide), respectively.

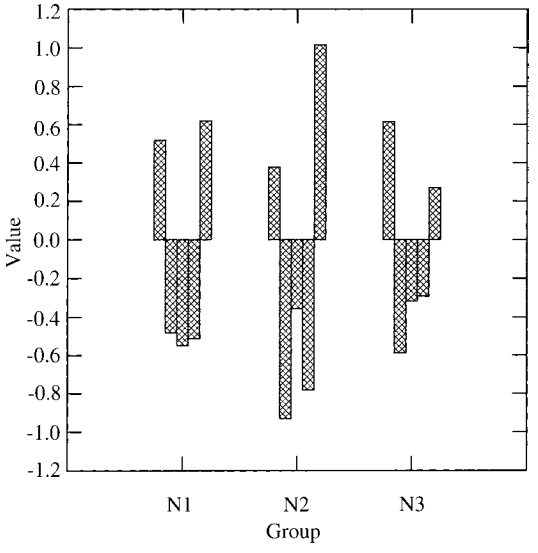

Fig. 5. Bar chart of the standardised coefficient ("value" on the vertical axis) from the regression analysis for the three groups N1, N2 and N3 of naturally aged leathers. The bars from the left to the right represent the coefficients for the *B/A* value, % sulphate, % monomers, $[H^+] \times 10^4$ and the interaction term, respectively.

standardised coefficients for each of the group of naturally and artificially aged leather samples it is possible to establish their individual average breakdown profile. Fig. 5 shows a bar chart of the standardised coefficients (labelled as "value" on the vertical axis) for the groups N1, N2 and N3 obtained from the analyses with the best regression conditions. The influence of the predictors in group N1 are of the same magnitude giving an even profile indicating equal parts of oxidative and hydrolytic breakdown. The largest influence on the Ts comes from the interaction followed by the breakdown of the tannins. The influence from the oxidation of the collagen and the actual acidity is equal. A somewhat smaller influence comes from the sulphate content representing the long-term pollution and hydrolysis of the leather. Apart from one sample, group N2 consists of condensed tanned leathers. The ageing profile is very representative for this type of leathers. Also here the interaction term represents the highest influence on the Ts. However, the acid hydrolysis, represented by the sulphate content and acidity of the leather, is clearly dominating the oxidation of the collagen and changes of the tannins. Finally, group N3 shows a profile with a high degree of oxidation closely followed by the influence from the pollution. On the other hand, the influence from the deterioration of the tannins, the acidity and the interaction are clearly smaller. As ammonia is produced by the oxidation of the collagen, this will reduce the acidity introduced by the pollution and thus this may explain the low influence from the actual acidity on the Ts.

With respect to the ageing profiles of the three groups of artificially aged leathers, the claim for significance of the overall and coefficient conditions of the regression model does not allow a deterioration profile to be based on all standardised coefficients. The regression analysis shows that the changes in Ts of group A1 (condensed tanned samples) is primarily dominated by oxidation compared to the acidity. Despite the lack of significance of the coefficients in the full regression model it is interesting to compare the profile of A1 with the one of N2 (mainly condensed), which, apart from the acidity, are alike (Fig. 6). The A2 group (hydrolysable tanned) in Table 8 is dominated by pollution, a relatively small influence from the acidity and a high influence from the interaction of all the deteriorative factors. Group A3 (condensed tanned) in Table 8 is dominated by a

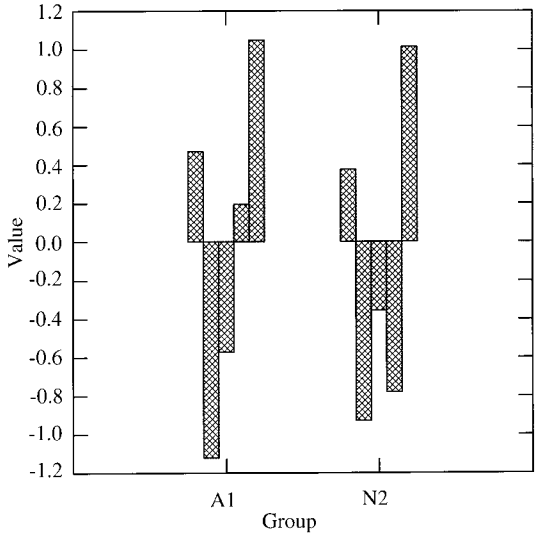

Fig. 6. Bar chart of the standardised coefficient ("value" on the vertical axis) from the regression analysis for group A1 (artificially aged) and group N2 (naturally aged) leathers. The bars from the left to the right represent the coefficients for the *B/A* value, % sulphate, % monomers, $[H^+] \times 10^4$ and the interaction term, respectively.

very high influence on the Ts from pollution and acidity and a relative small influence from breakdown of the tannins.

The present analysis clearly indicates the difficulties in imitating the natural ageing by artificial ageing methods. In the present ageing methods the high temperature needed to introduce oxidative changes in the collagen and tannin structures comparable to those obtained by natural ageing, is a problem. It probably causes evaporation of sulphur dioxide from the leather giving rise to a smaller accumulation of sulphate compared to what is observed for natural aged leathers. However, the breakdown pattern may be improved by adjusting the ageing conditions and parameters as indicated by the similarity between the profiles of A1 and N2. In this connection, it should be reminded that even if a predictor is not significant at a 95% significance level it is not the same as it does not have an actual influence on the ageing (in this case the Ts). The cause of the insignificance may be due to traditional variations or errors in the data, either from the measurements or due to material in homogeneity. This is a situation one very often has to face in observation studies in general, and more specifically, in conservation studies where there is access to only a few original very different and inhomogeneous samples. However, it may also reflect the presence of more sub-populations with different ageing patterns. This can only be clarified through further analysis and more data.

It should be emphasised that testing of the reliability of the ageing system cannot be based on the present model analysis alone. It demands detailed studies of the qualitative and quantitative changes in the collagen and tannin structures (e.g. changes in the amino acid distribution, tannin HPLC profile, type and number of breakdown products produced, etc.) as well as changes in other chemical and physical characteristics of the leather. The possible existence of several ageing profiles, and the difficulties with imitating these by the complex ageing systems used also puts questions to the use of simple ageing methods. Such ageing systems, based on a few standardised environmental conditions and measurement methods, are often used in, e.g. conservation studies of paper and photographic materials [47,48]. With regard to vegetable tanned leathers, both oxidative and pollution conditions are needed to produce breakdown characteristics like those obtained by natural ageing. Furthermore, both the observation and experimental studies have shown that no single standard method of ageing, no matter how many parameters it may be based on, can imitate the complex real life situation. The conditions and parameters of an ageing method has to be set according to kind of environment one wishes to simulate. Moreover, the conditions and parameters have to be set on the basis of observation studies of natural aged materials and the environment in which they have been stored. Therefore, more studies based on the combination of observations and experiments are needed to produce more detailed knowledge about the nature of the natural ageing and on the environmental impact on leathers. These may lead to more reliable ageing methods for testing new leathers, conservation methods and storage conditions for cultural heritage leather objects.

7. Conclusions

Beyond being a fine measure of the state of deterioration of vegetable tanned leathers, the Ts is a useful parameter in the modelling of the average breakdown profile of leathers. The prediction is performed on the basis of parameters reflecting the chemical changes of the collagen and tannin structures, the pollution and acidity as well as the interaction of these factors. By grouping of the samples, highly significant and significant predictions of the observed Ts are obtained. Together with the observed ageing characteristics of aged leathers in general, the regression analysis thus suggest the existence of several ageing profiles dependant on the type of tannins and storage conditions. This indicates that the conditions and parameters of artificial ageing systems have to be adjusted according to the environmental conditions to be simulated. Moreover, the analysis of the data from the observational and the experimental studies indicates the difficulties in imitating the natural ageing by artificial means. The ageing profiles, based on the standardised coefficients of the multiple regression model, may be used to test how well artificial ageing matches the profile of natural ageing and as basis for adjusting the ageing parameters. Thus the multiple regression analysis and modelling used in the combined observation and experiment study may

be a useful tool in improving the reliability of the artificial ageing.

Acknowledgements

I am very grateful to Jan Wouters, Johan Claeys and An Oostvogels, The Royal Institute for Artistic Heritage, Brussels; Claire Chahine, Christine Rottier and Daniel Floréal, Centre de Recherches sur la Conservation des Documents Graphiques, Paris; Chistopher Calnan, Tony Lochmuller and Roy Thomson, The Leather Conservation Centre, Northampton; Marie Vest, Ulla B. Kejser and Dorte V. Poulsen, School of Conservation, The Royal Danish Academy of Fine Arts; Arne L. Jensen, Department of Protein Chemistry, University of Copenhagen for their great work with performing the analysis, measurements and artificial ageing. I like to thank also the European Commission, DG XII for Science, Research and Development; The Danish Ministry of Culture; The Danish Research Councils; School of Conservation, Denmark for their financial support without which these studies could not have been realised.

References

[1] R. Larsen, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 165.
[2] R. Larsen, Fundamental aspects of the deterioration of vegetable tanned leathers, Ph.D. Thesis, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1995, p. 35.
[3] M. Odlyha, G.M. Foster, N.S. Cohen, R. Larsen, in: ICOM Committee for Conservation, 12th Triennial Meeting (Preprints), Lyon, 1999, p. 702.
[4] M. Odlyha, G.M. Foster, N.S. Cohen, R. Larsen, J. Therm. Anal. Calorimetry 59 (2000) 587.
[5] R. Larsen, M. Vest, C. Calnan, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 11.
[6] R. Larsen, J. Wouters, C. Chahine, C. Calnan, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 7.
[7] R.F. Innes, J. Int. Soc. Leather Trades Chemists XV (1931) 480.
[8] J.E. Taylor, Long-Period Test for Durability of Leather Bookbindings, Chemical Investigation of Used Bookbinding Leathers Removed after the Fifth (Interim) Inspection, BLMRA, LR 50, London, 1971.
[9] R. Larsen, M. Vest, K. Nielsen, J. Soc. Leather Technologists Chemists 77 (1993) 151.
[10] C. Chahine, C. Rottier, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 117.
[11] R. Larsen, M. Vest, K. Nielsen, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 151.
[12] C. Chahine, C. Rottier, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 129.
[13] R. Larsen, M. Vest, D.V. Poulsen, U.B. Kejser, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 145.
[14] V. Barkholt, A.L. Jensen, Anal. Biochem. 177 (1989) 318.
[15] R. Larsen, V. Barkholt, K. Nielsen, Das Leder 40 (1989) 153.
[16] R. Larsen, M. Vest, K. Nielsen, A.L. Jensen, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 39.
[17] R. Larsen, M. Vest, D.V. Poulsen, U.B. Kejser, A.L. Jensen, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 39.
[18] J. Wouters, The calculation of pH of aqueous solutions containing sulphuric and nitric acids and which may be partially titrated with ammonium hydroxide, KIK, Brussels, Unpublished.
[19] J. Wouters, in: ICOM Committee for Conservation, 10th Triennial Meeting (Preprints), Dresden, 1993, p. 669.
[20] J. Wouters, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 91.
[21] J. Wouters, J. Claeys, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 87.
[22] J. Wouters, M.V. Bos, J. Claeys, A. Oostvogels, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1997, p. 103.
[23] Determination of volatile matter in leather, SLC 3:1966 (I.U.C./5).
[24] H.B. Merill, D.H. Cameron, H.L. Ellison, C.P. Hall, J. Am. Leather Chemists Assoc. 42 (1947) 536.

[25] Determination of pH value and difference figure of an aqueous leather extract, SLC.13:1966(I.U.C./11).
[26] C. Chahine, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 31.
[27] R. Thomson, T. Lochmuller, in: STEP Leather Project, European Commission DG XII, Research Report No. 1, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1994, p. 35.
[28] C. Chahine, C. Rottier, in: Environment Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1996, p. 33.
[29] R. Larsen, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1996, p. 174.
[30] R. Larsen, J. Wouters, C. Chahine, P. Brimblecombe, C. Calnan, in: ENVIRONMENT Leather Project, European Commission DG XII, Research Report No. 6, The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, 1996, p. 167.
[31] T.H. Wonnacott, R.J. Wonnacott, Introductory Statistics, 5th Edition, Wiley, New York, 1990, p. 369, p. 496.
[32] K.N. Kirby, Advanced Data Analysis with SYSTAT, Multiscience Press/Van Nostrand Reinhold, New York, 1993, p. 165.
[33] L. Wilkinson, in: SYSTAT: The System for Statistics, SYSTAT, Evanston, IL, 1990, p. 146.
[34] M. Faraday, Repertory of Patent Inventions (London), Enlarged Series, Vol. 2, No. 5, 1843, p. 174.
[35] D. Cockerell, J. Soc. Arts (Lond.) 48 (1900) 401.
[36] J.G. Parker, H.C. Procter, A. Seymour-Jones, Appendix II in Report of the Committee on Leather for Bookbinding, The Society for the Encouragement of Arts, Manufactures and Commerce, London, 1901.
[37] R.F. Innes, J. Int. Soc. Leather Trades Chemists XIV (1930) 624.
[38] R.W. Frey, I.D. Clarke, J. Am. Leather Chemists' Assoc. 26 (1931) 461.
[39] R.F. Innes, J. Int. Soc. Leather Trades Chemists XVII (1933) 725.
[40] R.C. Bowker, E.L. Wallace, J. Am. Leather Chemists' Assoc. 28 (1933) 125.
[41] J.H. Bowes, Final Technical Report to United States Department of Agriculture, Agricultural Research Service, British Leather Manufacturers' Research Association, London, 1963, p. 49.
[42] L. Seligsberger, C.W. Mann, in: F. O'Flaherty, W.T. Roddy, R.M. Lollar (Eds.), The Chemistry and Technology of Leather, Vol. 2, Krieger Publishing Company, Huntington, 1978, p. 494.
[43] B.M. Haines, Br. Library J. (Lond.) 3 (1) (1977) 59.
[44] B.M. Haines, in: Proceedings of the Conference on the Conservation of Library and Archive Materials and the Graphic Arts, Part 3, Institute of Paper Conservation, Cambridge, 1980, p. 261.
[45] B.M. Haines, Leather, its Composition and Changes with Time, The Leather Conservation Centre, Northampton, 1991, p. 66.
[46] R. Larsen, Eur. Cult. Heritage Newslett. Res. 7 (1–4) (1993) 19.
[47] Workshop on the effects of ageing on printing and writing papers, in: Proceedings of ASTM Institute for Standards Research, 2nd Edition, Philadelphia, PA, 1994.
[48] Research techniques in photographic conservation, The Royal Danish Academy of Fine Arts, The School of Conservation, LP Nielsen Bogtryk, Denmark, 1996.