White tawed leather - aspects of conservation

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Abstract

For more than 150 years research has been done to solve the problems of leather deterioration, especially on bookbindings. Research has mainly focussed on vegetable tanned leather, which presents the most serious problems of deterioration. Generally white tawed leather is found to be in relatively good condition, and very little research is done in this area.

The present work includes a description of the tawing process. Deterioration of a set of historical samples from bookbindings, ranging from 14th to the 18th century, has been investigated and the results are discussed.

The results of the analysis show that white tawed leather is vulnerable to deterioration but the effect of this chemical deterioration does not have dramatic effects on the physical state of the leather structure like seen on vegetable tanned leather. The differences in tawing and tanning material have to be taken into consideration when interpreting the results of the analysis. If practical conservation treatments are necessary those differences are important, too. Also the level of deterioration has to be determined before any treatment is started.

Zusammenfassung

Seit 150 Jahren schon wird Forschung betrieben, um die Probleme von Lederzerfall, speziell an Bucheinbänden, zu lösen. Die Forschung hat sich hauptsächlich auf vegetabil gegerbtes Leder konzentriert, was die ersnthaftesten Probleme von Zerfall aufweist. Weißgegerbtes Leder wird meistens in gutem Zustand befunden, und dahingehend ist wenig untersucht worden.

Diese Arbeit beinhaltet eine Beschreibung des Weißgerbungsprozesses. Die Zerfallmechanismen von einer Gruppe historischer Muster von Bucheinbänden aus dem 14. bis 18. Jahrhundert sind hierbei untersucht worden, deren Testergebnisse besprochen werden.

Die Testergebnisse zeigen, daß weißgegerbtes Leder auch zum Zerfall neigt, aber die chemischen Zerfallmechanismen auf die physische Lederstruktur sich nicht so dramatisch auswirken wie auf vegetabil gegerbtes Leder. Die Unterschiede zwischen Weißgerbung und Pflanzengerbung müssen beim Interpretieren der Testergebnisse beachtet werden. Das müssen sie auch, was die praktische Restaurierung anbelangt. Bevor man eine Behandlung beginnt, muß festgestellt werden, wieweit der Zerfall fortgeschritten ist.

Introduction

White tawed leather was used as a binding material for books from medieval times to the end of the 18th century. In medieval times it was an important and frequently used material but with the production of printed books its significance decreased and most books were bound in vegetable tanned leather.

Deterioration of leather is a major conservation problem in libraries and archives. For more than 100 years research has been carried out to study the causes of deterioration and the conservation treatments for damaged leather [1-6]. The research on the deterioration and preservation of white tawed leather in particular has to a certain degree been neglected. This might be due to the fact that white tawed leather seems to be much better preserved than vegetable tanned leathers. Furthermore, white tawed leather bindings are much fewer in number than vegetable tanned leather bindings.

White tawed leather – production

The white tawing method was usually carried out on skins of sheep and goat, but also pig and calf skins were used. The following description of how the process was carried out is based on detailed descriptions from the 16th to the 18th century [7-9]. After slaughtering the skin was either dried or salted to preserve it and the tawer had to soak it in water before further processing. This was followed by unhairing the skin in a lime pit at a pH-value of 10-13. In this process hair and other epidermal structures were loosened and the remainings could subsequently be mechanically removed over a beam of wood with a blunt knife. A further purpose of the liming process was to clean, loosen and swell the fibre structure. Over the beam the skin was fleshed to clean and level the flesh side and the grain surface was ‘scudded’ with an unhairing knife, a process where the surface was cleaned of further remains of hair, lime, grease and dirt. Eventually unwanted pieces of the skin were cut off, a process called ‘trimming’. Afterwards some tawers used a process called ‘bating’, where the skin was immersed in warm water with dog dung. Others used fowl droppings, then the process was called ‘puering’. Enzymes in the dung digested and dissolved some of the proteins in the skin and with further scudding it resulted in a very smooth grain. Bating/puering could be replaced by ‘bran drenching’, where the skin was immersed in warm water with husks of cereals, a solution which liberated small amounts of weak organic acids. The effects of the process were similar to them of bating but with the advantage that any residual lime in the skin was neutralised. With additional scudding the skin was ready for

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the tawing process. An aqueous solution of alum and common salt was prepared together with egg yolk and flour, and with immersion and agitation of the skin in this paste mixture, it was absorbed by the skin. A solution of alum and salt alone could also be used, but this gave a rougher and more inflexible leather with less water resistance. The leather was hung to dry over weeks to age, a stage where the aluminium salts fixed better in the skin. At this stage the leather was stiff and inflexible. So the final process was a softening process, called 'staking', where the flesh side of the leather was mechanically stretched by pulling it over a blunt wooden or metal edge. The final result was a white leather, soft and stretchy and with a very smooth, silky grain. Some leathers were subsequently surface coloured in red, blue, green, or black [10].

Alum tawing is defined as a semi-tannage as the leather is not stable in water like a vegetable tanned leather. Right after tawing the aluminium salts can be washed out with water, but ageing for a long time or contents of grease or fat will improve the water resistance. Today more stable products are obtained by using aluminium chloride or sulphate instead of alum. Also the use of a pretannin or retannin with glutaraldehyde is used today [11].

Deterioration

The deterioration of white tawed leather was investigated through a study of 26 historical bookbinding leathers (12). Chemical deterioration of leather occurs through two competitive and interactive chemical mechanisms, acidic hydrolysis and oxidation. The hydrolytic breakdown is caused mainly by the acidic pollutants sulphur dioxide and nitrogen dioxides. The effects on leather will be a decrease of the pH-value and a break-up of peptide bonds in the main chain of collagen. Furthermore, the sulphate content of the leather will increase. Oxidation of the leather is caused by factors such as light, heat and oxidative pollutants. During this process the collagen chains will deteriorate so that the number of acidic side-chains will increase and the number of basic side-chains will decrease and the leather structure will destabilise. The break-up of the main chain of the collagen can also occur. These oxidative changes can be detected by amino acid analysis. Both oxidative and acidic deterioration is reflected in the measurements of shrinkage temperature and this method is therefore a valuable indicator for the total degree of deterioration of a leather sample.

Materials

New leathers

Three new white tawed leathers from wool sheep, goat and calf were produced as references for this project (sample 1, 2 and 3) by Lotta Rahme, Sweden. The skins were soaked in water, limed with calcium hydroxide, delimed in water, puered and bran drenched. Then the skins were cut into halves and one half (1a, 2a, 3a) treated with a mixture of alum and salt in water. The other halves (1b, 2b, 3b) were tawed with a mixture of alum, common salt, flour, egg yolk, neatsfoot oil and water. The mixture was worked into the skins by hand. Sample 4 was a commercially available alum-tawed wool sheep sample from Cowley's Parchmentworks, England. Sample 5 was from wool sheep, tawed by Roy Thomson, Northampton, with alum, common salt, egg yolk and flour. The tawing paste was worked into the skin by mechanical drumming. Samples 6 - 8 were from goat, calf and pig and commercially available alum-tawed leathers from Hewitt & Sons, Scotland. Sample 9 was from calf and produced in the Czech Republic. No information on the exact production methods of the samples 4 and 6 - 9 was available.

Historical leathers

The historical samples were sampled from bookbindings belonging to The Regional Archive for Northern Jutland, Viborg (samples 2, 8, 10, 11, 13, 16-18, 20-23, 26), The Regional Archive for Seeland, Copenhagen (samples 19 and 24), The National Archive, Copenhagen (samples 9,12,14, 15, 25), The Central Botanical Library of the University of Copenhagen (samples 3, 4, 6, 7), private owner, Copenhagen (sample 5), The National Library of the Czech Republic, Prague (sample 1) and The German Leather Museum, Offenbach (sample 0 taken from a coptic shoe). In some cases two or three leather samples were taken from a bookbinding, one from an area protected by the endleaf (sample a) and another sample from an area exposed directly to the atmosphere (sample b/c). The samples kept in Copenhagen represented an air-polluted environment and samples from Viborg, a rural environment with a lower level of air pollution.

Testing method

Determination of shrinkage temperature (hydrothermal stability): The measurement of shrinkage temperature demands only a very small sample of fibres (0.3 mg) which makes it very suitable for analysis of valuable historical leathers [13, 14]. A few fibres are heated in water on a microscope slide with a concavity positioned on a micro hot table, under a stereo microscope (Mettler FP90 Central Processor and FP82 Microscope Hot Stage). The temperature is increased with 2 C°/min. During heating the fibres will start to shrink at a certain temperature, which will depend on the stability of the collagen. New fibres before and after shrinkage are shown in figure 1 and 2. The shrinkage of the leather fibres is a temperature-dependent process which can be divided into temperature intervals occurring in the following order: A, B, C, B2 and A2 with different shrinkage activity as follows:

Interval A/A2: Distinct shrinkage activity in individual fibres.

Interval B/B2: Shrinkage activity in one fibre (occasionally more) is immediately followed by shrinkage activity in another fibre.

Interval C: At least two fibres show shrinkage activity simultaneously and continuously. The starting temperature of this main interval of shrinkage is the shrinkage temperature, Ts.

Shrinkage activity starts in individual fibres (interval A) and increases during the B-interval. The start of the main interval

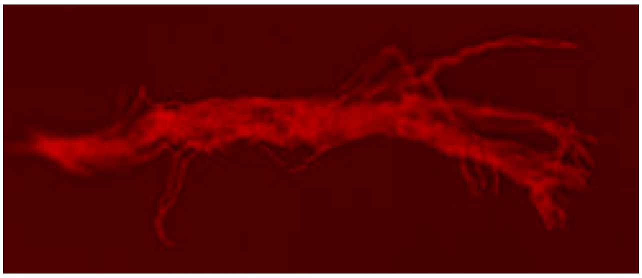

Figure 1. New fibres at 20°C, before shrinkage.

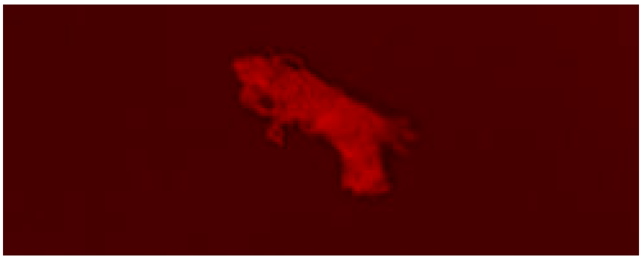

Figure 2. New fibres at 80°, after shrinkage.

(interval C) is the shrinkage temperature (Ts) and with the end of this interval the shrinkage activity will start to decrease again. The accuracy of the shrinkage temperature (Ts) measurements is ±2°C. With increasing deterioration of a sample the shrinkage temperature and the shrinkage activity will decrease. The C-interval can disappear and in a very deteriorated sample only very little shrinkage activity remains (interval A). All Ts measurements were performed in triplicates.

Results and discussion

New leathers

Raw skin has a shrinkage temperature (Ts) of around 65ºC and limed skin has a Ts of around 60ºC. In the literature the Ts-values of new white tawed leather are found to vary considerably from 49 - 63ºC [15] and from 70°C to 73°C [16]. This might be due to differences in tawing methods or the quality of tawing. The measured shrinkage temperatures of the new samples are presented in figure 3 and table 1.

The samples 1a, 2a and 3a, tawed with alum and salt, had a shrinkage temperature of 49.9 - 50.6°C. This is lower than the Ts for the samples 1b, 2b and 3b, tawed with the additional use of egg yolk and flour. They had a shrinkage temperature of 55.1 - 57.1°C, which might be higher because of the presence of fatty material, which can give an additional effect of fat-tanning [17]. The very first shrinkage is low for all six samples, 39.6 - 53.3°C, and the shrinkage activity in general is low, too. This could indicate a slight deterioration of the collagen taken place already during bran drenching of the skins.

The three-year-old sample 5 had a Ts of 67.2°C, but just after tawing the Ts was measured at 62 - 63°C. The higher Ts-value, compared to the samples 1b, 2b and 3b, might have been obtained by mechanical drumming to work in the tawing paste instead of doing it by hand and the larger amounts of egg yolk used. The effect of ageing, i.e. further stabilisation, just after production of tawed material is reflected in the increase of Ts between 4-5°C in the first years after production.

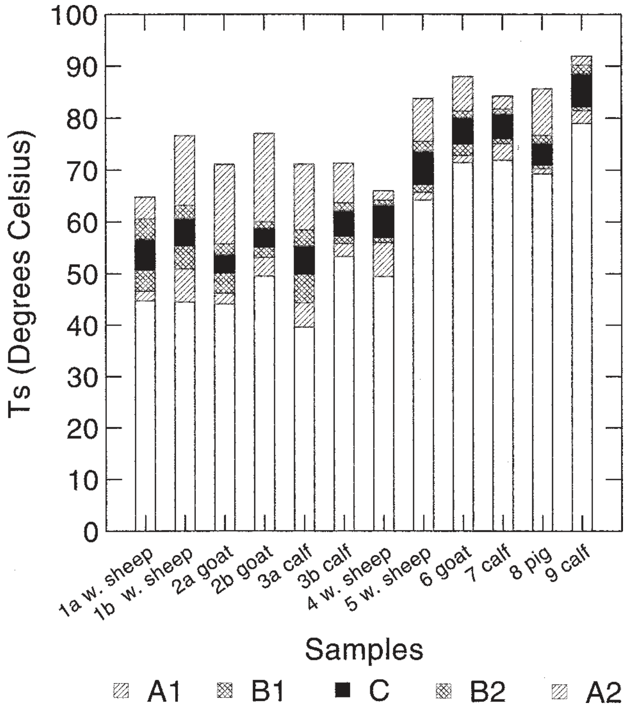

Figure 3. Shrinkage intervals for new alum tawed leathers.

The commercial samples had a Ts-value of 57.0°C (sample 4) and samples 6 - 9 had Ts-values between 75.0°C and 82.2°C. No information on the exact production method was available but for the samples 6 - 9 the high Ts-values could reflect the additional use of glutaraldehyde or the use of other aluminium compounds than alum used in traditional tawing.

Historical samples

The shrinkage temperatures of the historical samples were between 32.7°C and 62.7°C, close to or lower than the Ts for raw hide. The results are presented in table 2 and 3 and a selection are presented by a graph, see figure 4. The results reflect a wide variation in the state of deterioration. Some leathers have a Ts close to that for new leather (samples 16 and 20b) and others are in a progressive state of deterioration (sample 0,7 and 15b) with a Ts close to 30°C.

Although the shrinkage temperature in some cases is very low, all shrinkage intervals are still present. In very deteriorated vegetable tanned leather the shrinkage activity is normally lost with increasing deterioration. This indicates another deterioration pattern in white tawed leather compared to vegetable tanned leather.

The effect of an direct exposure to the atmosphere can be seen in the Ts-values of samples a/b. The exposed sample 15b has a Ts which is 5.8°C lower than the protected sample 15a (Ts 40.3°C) from the same bookbinding stored in Copenhagen. Also for the exposed sample 20b, the Ts is 5.1°C lower than for the protected sample 20a (Ts 62.7°C) from the same bookbinding kept in Viborg. In the case of the exposed/protected samples 6b/6a and 23b/23a the Ts-values of the exposed areas differ less than 2.2°C from the protected areas.

If the bindings are divided into groups depending on collection, differences in the mean Ts of the collections are found, see table 4. The mean Ts of 13 bindings kept in Viborg (low

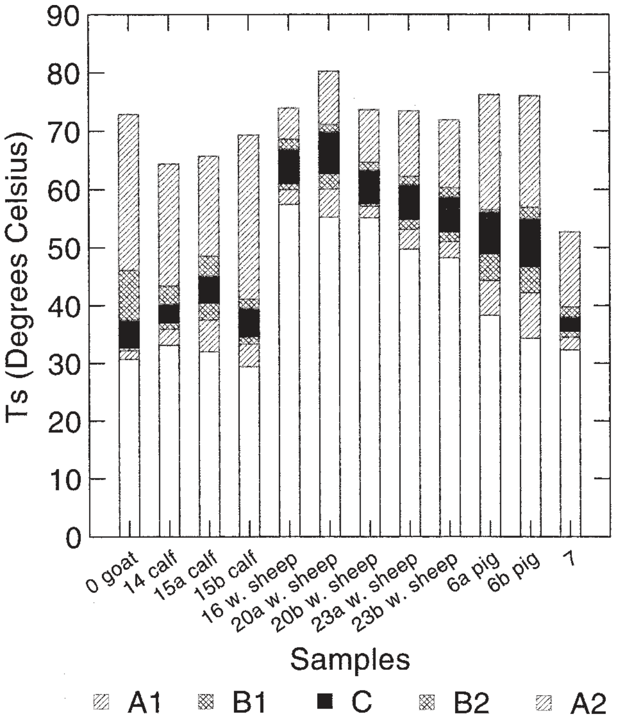

Figure 4. Shrinkage intervals for historical alum tawed leathers.

level of air pollution) is 54.0°C and four bindings kept at the National Archive in Copenhagen (high level of air pollution) have a mean Ts-value of 38.7°C.

These differences were tested statistically through a t-test. The results showed strongly significant differences in the Ts-values for the Regional Archive of Northern Jutland, Viborg, versus the National Archive, Copenhagen (probability = 0.002), i.e. a probability of 97.4% that the mean values are different. The mean Ts-values from Viborg and the Central Botanical Library of the University of Copenhagen were significantly different (probability = 0.026), i.e. a probability of 97.4% that the mean values are different.

Problems for conservation

The very low shrinkage temperatures close to room temperature of some historical white tawed leathers tells us that a water-based conservation treatment will cause irreparable shrinkage to the leather. This is especially dangerous, as a very high level of deterioration cannot be judged by visual examination. These leathers can also be damaged through short-term exposure to very high relative humidity in the air during storage. The samples can still be flexible and the fibres of the grain and corium layer coherent even though the samples have a low Ts. Besides a minor loss in strength the degree of deterioration is not reflected in the physical state of the leather structure and the leather shows none of the characteristics normally observed on very deteriorated vegetable tanned leather. Here the grain is flaking, looses connection to the corium layer and the fibres are brittle. The whole structure of a vegetable tanned leather can be extremely powdery so that handling is impossible, a stage which is obvious through visual examination.

White tawing is defined as a semi-tannage being unstable in water, but it has been demonstrated for new alum tawed leather that the stability reflected in Ts is increased by time. It is still not known to what extent water cleaning of historical alum tawed leather will wash out tawing material. Therefore it should be investigated further before a water-based treatment can be recommended without any risk for long-term damage to the leather.

Lubrication as a conservation method has been widely used for leather, including white tawed leather. Lubrication on white alum-tawed bindings often results in yellowing and the leather still feels 'wet' of lubricant even several years after lubrication. Such damaged bindings have no doubt received too much lubricant but another damaging factor could be the type of lubricant used. Examples of red alum tawed bindings lubricated with a mixture of neatsfoot oil and lanolin (60/40 w/w) in 1989 have so far not suffered from any visual damage to the leather caused by lubrication. Is seems that the type and amount of lubricant but also differences in tawing methods and surface colouring may influence the result of lubrication. Furthermore, the use of formaldehyde has been suggested for the conservation of historical alum tawed material [18].

New leather for conservation bindings

New white tawed leather is used for rebinding and restoring historical bindings. The quality of new leather can vary considerably, but it is still not known which set of minimum standards for Ts, pH, amounts of tawing material, etc. should be fulfilled to give the best possible leather for use in conservation. However, the historical white tawed leathers have in general shown a better long-term stability than the vegetable tanned leathers and therefore new material produced by traditional methods is recommended for conservation purposes. This has already been recommended by others [19].

Conclusion

New and historical white tawed leather samples were examined by measuring shrinkage temperature. The results for new material showed a considerable variation in the shrinkage temperature, the Ts ranging from 55.1°C to 82.2°C. These variations can be caused by differences in the traditional methods which have been used or by the use of modified methods.

The historical samples ranged from a very good state (Ts = 62.7 °C) to heavily deteriorated (Ts = 32.7 °C). In some cases the areas of a binding exposed to the atmosphere were clearly more deteriorated than the protected areas. Furthermore, bindings kept at a high level of air pollution were more deteriorated than bindings kept in a rural area. This difference in Ts was found to be strongly significant and shows that white tawed leather is damaged by environmental factors. Still, white tawed leather is less sensitive to deterioration than vegetable tanned leather.

Unlike vegetable tanned leather heavy deterioration of the white tawed leather is not reflected in the physical state of the leather structure. Very deteriorated leather can be damaged irreparably by shrinkage either through a water based conservation treatment or by short-term exposure to levels of high relative humidity during storage.

The knowledge of the effects of conservation treatments is small so far. Water-based treatments can be problematic and on the basis of empiric experience lubrication cannot be recommended. Therefore, further research has to be carried out in order to give some proper recommendations for the conservation of white tawed leather.

Tables

Table 1. Results of measurements of shrinkage temperature (Ts), the first observed shrinkage (Tf) and the length of the shrinkage intervals A1, B1, C, B2 and A2 for new alum tawed leathers.

Sample	Ts (SD)	Tf	A1	B1	C	B2	A2
1a wool sheep	50.6 (2.1)	44.7	1.9	4.1	6.0	3.9	4.2
1b wool sheep	55.3 (0.6)	44.5	6.4	4.5	5.3	2.5	13.4
2a goat	50.1 (3.3)	44.1	2.1	3.9	3.6	2.0	15.4
2b goat	55.1 (0.4)	49.5	3.6	2.0	3.6	1.3	17.0
3a calf	49.9 (1.1)	39.6	4.7	5.6	5.5	3.0	12.7
3b calf	57.1 (1.6)	53.3	2.5	1.4	5.0	1.5	7.6
4 wool sheep	57.0 (0.1)	49.4	6.6	1.0	6.3	0.9	1.8
5 wool sheep	67.2 (0.1)	64.2	1.5	1.5	6.4	1.9	8.2
6 goat	75.0 (0.2)	71.4	1.4	2.2	5.0	1.3	6.6
7 calf	76.1 (0.5)	71.9	3.2	1.0	4.7	0.9	2.5
8 pig	70.9 (0.7)	69.3	1.0	0.7	4.2	1.5	8.9
9 calf	82.2 (1.6)	79.0	2.4	0.8	6.3	1.7	1.7

Table 2. Results of measurements of shrinkage temperature (Ts), the first observed shrinkage (Tf) and the length of the shrinkage intervals A1, B1, C, B2 and A2 for 12 historical alum tawed leathers presented in figure 3.

Sample	Ts (SD)	Tf	A1	B1	C	B2	A2
0 goat	32.7 (0.6)	30.7	1.5	0.5	4.8	8.6	26.8
6a pig	48.9 (0.6)	38.3	6.0	4.6	7.2	0.4	19.7
6b pig	46.7 (1.1)	34.3	7.9	4.5	8.3	1.9	19.1
7	35.5 (0.1)	32.3	2.2	1.0	2.5	1.7	13.0
14 calf	37.0 (0.8)	33.1	2.8	1.1	3.3	3.1	21.0
15a calf	40.3 (0.1)	32.0	5.5	2.9	4.7	3.4	17.2
15b calf	34.5 (0.5)	29.4	3.9	1.3	4.9	1.6	28.2
16 wool sheep	61.0 (0.1)	57.4	2.6	1.0	5.9	1.7	5.3
20a wool sheep	62.7 (0.6)	55.2	4.9	2.6	7.2	1.2	9.1
20b wool sheep	57.6 (0.1)	55.1	2.0	0.5	5.7	1.3	9.0
23a wool sheep	54.7 (0.1)	49.7	3.4	1.7	6.0	1.4	11.2
23b wool sheep	52.6 (0.0)	48.2	2.8	1.7	6.0	1.6	11.6

Table 3. Results of shrinkage temperature measurements (Ts) and standard deviation (SD) for 26 historical alum tawed leathers.

Sample	Ts (SD)	Sample	Ts (SD)
0	32.7 (0.6)	15a	40.3 (0.1)
1a	49.9 (0.8)	15b	34.5 (0.5)
1b	43.3 (1.6)	16	61.0 (0.1)
2a	51.5 (0.6)	17	53.1 (0.1)
2b	46.0 (1.1)	18a	50.0 (1.7)
2c	47.3 (0.2)	18b	50.2 (0.2)
3	45.8 (1.6)	19a	37.9 (0.9)
4	47.0 (0.8)	19b	45.6 (0.4)
5a	45.7 (0.0)	20a	62.7 (0.6)
5b	43.6 (0.7)	20b	57.6 (0.1)
6a	48.9 (0.6)	21a	57.3 (0.5)
6b	46.7 (1.1)	21b	58.2 (0.0)
7	35.5 (0.1)	22a	57.1 (0.2)
8	51.7 (0.1)	22b	54.0 (1.0)
9a	37.4 (1.0)	23a	54.7 (0.1)
9b	38.7 (0.4)	23b	52.6 (0.0)
10	55.9 (0.4)	24a	54.1 (0.1)
11	55.0 (1.3)	24b	46.5 (0.9)
12a	42.7 (0.6)	25	46.5 (0.8)
12b	39.3 (0.6)	26a	57.7 (0.2)
12c	44.4 (0.5)	26b	48.9 (0.4)
13	56.4 (0.6)	26c	49.5 (0.6)
14	37.0 (0.8)		

Table 4. Mean values of shrinkage temperature measurements (Ts) and standard deviation (SD) for bookbindings grouped after collection.

Collection	Samples (one sample from each binding)	Ts (SD)
Regional Archive of Northern Jutland, Viborg	2c, 8, 10, 11,13, 16, 17, 18b, 20b, 21b, 22b, 23b, 26c	54.0 (3.85)
National Archive, Copenhagen	9b, 12c, 14, 15b	38.7 (4.20)
Central Botanical Library, Copenhagen	3, 4, 6b, 7	43.8 (5.52)

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Biography

Marie Vest finished her apprenticeship as a bookbinder in 1986. Afterwards she studied nearly one year at the bookbinding school Centro del bel Libro in Switzerland under Edwin Heim. From 1987-90 she studied at The School of Conservation in Copenhagen and graduated with a BS degree. She worked in different conservation workshops in book and parchment conservation and from 1991-96 Marie Vest was involved in the two European research projects on leather, STEP and Environment, on a full-time basis. In 1996 she graduated from the School of Conservation with an MS degree in white tawed leather conservation and the same year she was employed as a full-time lecturer at the School of Conservation.

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