



Saving our past for the future

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This paper is based on the 43rd J Arthur Wilson Memorial Lecture. Using techniques derived from the research described, the Leather Conservation Centre undertakes specialist projects. The photographs set illustrate examples of conservation and restoration performed in the Centre's workshops.

John Waterer⁽¹⁾ was the first to carry out detailed studies on the conservation of leathers. Many of these techniques had been developed and applied in previous decades for the care and preservation of leather bookbindings. These include the application of fungicides and insecticides, the use of buffer salts to impart resistance to acidic atmospheric pollutants and 'feeding' the leather with mixtures of oils such as the 'British Museum Leather Dressing'. In addition there were recommendations for measures, such as the control of temperature, humidity and light levels, designed to reduce the rate of deterioration of precious historic items.

The use of biocides, such as DDT, Lindane, pentachlorophenol, p-nitrophenol and orthophenyl phenol is no longer acceptable for health and safety reasons, and the efficacy of routine applications of buffer salts and oils to leather has been brought into question. Nevertheless, this systematic examination of a field which, up to then, had been approached in a random manner, could be considered as the foundation of leather conservation as a specialist area.

The effects of sulfuric acid on bookbinding leathers

Since the second half of the nineteenth century, the restoration of leather had been concentrated almost entirely on

bookbindings. This is because, unlike the majority of products made from leather, these are expected to last almost indefinitely.

If a pair of shoes breaks down after five years' wear, few people complain. If a briefcase or wallet collapses after ten years use, the owner is perhaps sad at the loss of a friend but accepts the situation. It is only in the somewhat artificial world of the museum and the collector that objects are expected to last for ever.



*Leather hoods and upholstery:
A Victorian coach from Hull Transport Museum, a red 1911
Renault AX, and (top) a blue 1899 Panhard et Levassor
from the Gressenhall Museum, Norfolk.
The latter was owned by the Hon Charles Stewart Rolls
before he founded Rolls Royce with Sir Henry Royce.*



With books it is different. Books generally spend most of their lives sitting unused on library shelves. They are, however, expected to be there, ready, when the owner or borrower wishes to use them. When, in the middle of the nineteenth century, it was discovered that many new bindings were deteriorating rapidly without, in some cases, the book ever having been used, an explanation was sought.

The major factor for this deterioration was found to be the presence of sulfuric acid, either absorbed from polluted atmospheres or added to the leather during various stages of the manufacturing process. The acid attacks vegetable tannins, particularly those of the condensed group, breaking down the collagen-tannin complex and leading to what has become known as red rot⁽²⁾.

Protection by buffering salts

Work carried out at the beginning of the twentieth century highlighted the particularly resistant properties of leathers prepared from native Nigerian tanned stock, and this led to the practice of adding protective buffer salts during the final stages of the dressing process. It was a direct transfer of this technology that led Plenderleith^(3,4), Werner⁽⁵⁾ and Waterer to recommend that museum objects made from vegetable tanned leather are treated in a similar manner with solutions of potassium lactate or other buffer salts. It was found, however, that when applying such aqueous-based treatments to museum objects, there is a danger that the water will react with highly acidic, partially degraded leather. This causes a darkening and embrittlement before the protective action of the buffer salt can take effect. This is why solutions of organic bases, such as imizadole in non-aqueous solvents have been suggested⁽⁶⁾.

In 1940, Frey and Beebe at the US Department of Agriculture discovered that vegetable tanned leathers retanned with aluminium salts combined the excellent ageing properties of chrome tanned materials with some of the handling characteristics of pure vegetable tanned leathers⁽⁷⁾. This work was developed further in the 1970s, leading eventually to the drawing up of a British Standard Specification for Archival Quality Bookbinding Leathers⁽⁸⁾. It also led indirectly to the development of a conservation treatment for red rotted leather, which is employed today as an alternative to Waterer's procedure.

Addressing red rot

Initially, it was argued that if retanning vegetable tanned leathers with aluminium salts can prevent the development of red rot, the use of solutions of the same aluminium salts on red rotted objects might halt the deterioration of the



Top to bottom:

Leather bucket decorated with Royal coat of arms, originally containing sand for fire prevention; Working on eighteenth century panelling at Levens Hall near Kendal, which houses one of Europe's most important collections of gilt leather (on site); Magnificent sedan chair belonging to the Museum of Leathercraft founded by John Waterer.



leather and prevent further breakdown. Unfortunately, as with the buffer salts, in some cases the aqueous solvent damaged the leather before the beneficial reactions could take place.

A search was therefore made for aluminium compounds, which are both soluble in non-polar organic solvents and give the required stabilising action. After some time, a compound from Alcan Chemicals Ltd., AOC 1010 X — described as a derivative of aluminium isopropoxide containing ethyl aceto acetate as a chelating agent — was found to have the desired combination of properties⁽⁹⁾.

Typically, leathers from the late nineteenth century, which are exhibiting symptoms of red rot, have a pH value of 2.0-2.5 and a shrinkage temperature of 50-53°C. After treatment with a solution of AOC 1010 X in white spirit containing 2% aluminium, the pH is increased to 3.3-3.7 and the shrinkage temperature to 80-90°C.

The Thermo Lignum process for pest irradiation

Until recently, infestations of museum objects by moulds and insects were treated with the types of biocides described by Waterer. However, as the dangers associated with the use of these materials have become apparent, investigations have been made into alternative, non-poisonous methods. These have included the use of heat, cold, radiation or anoxic atmospheres. A recent review by Pinniger⁽¹⁰⁾ has shown that each of these systems has its own set of disadvantages.

In 1995, Thermo Lignum (UK) Ltd. launched its pest eradication process⁽¹¹⁾. It is based on the fact that the majority of insects in all of the various stages of their life cycle — egg, larva, pupa, nymph and adult — are killed if they are held at a temperature of 50°C or more for an extended period of time. Most moulds are also killed under these conditions⁽¹²⁾. The problem associated with this type of process in the past, however, has been that, at these elevated temperatures, moisture is driven out of the object. In the case of wooden furniture this resulted in splitting, warping and twisting.

The secret of the Thermo Lignum process was that as the temperature is increased, the moisture content of the atmosphere is controlled so that there is no exchange of ➤





Figure 1

Effect of Thermo Lignum Process

	pH		Ts (°C)		Softness low=firm, high=soft		Tensile Strength N/mm ²	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
New Material								
Mimosa calfskin	4.0	4.1	78	78	14	13	18	25
Sumac calfskin	3.9	3.9	74	73	16	13	13	16
Oak hide	5.4	5.4	77	76	2	2	18	21
Parchment calf	8.5	7.1	57	56	12	11	87	95
Alum calf (Cowleys)	4.6	4.5	50	50	19	19	34	26
Alum calf (Hewits)	5.0	5.1	79	78	20	20	27	34
Brain/smoke deer	6.7	6.0	58	58	74	68	42	37
Untanned calf	6.7	6.6	60	60	6	6	30	29
Old Material								
Chrome side	4.3	4.2	86	88	21	21	12	13
Russian seat cover	4.7	4.4	68	68	15	17	4	4
Parchment	7.4	6.5	56	56	12	11	27	25
Vegetable bookbinding	4.1	4.0	54	52	18	20	5	7
Hide bucket	3.7	3.3	62	59	8	9	3	3

	Lastometer Extension at burst (mm)		Lastometer Pressure at burst (Kg force)		Tear Strength (N/mm)		Flexes to Break	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
New Material								
Mimosa calfskin	9.71	920	55	52	35	34	14380	17129
Sumac calfskin	776	801	31	35	29	25	15436	14723
Oak hide	1064	783	>80	>80	41	50	-	-
Parchment calf	669	744	31	35	74	86	76959	68673
Alum calf (Cowleys)	959	1256	47	55	105	88	44061	44584
Alum calf (Hewits)	859	900	57	38	31	32	20144	19028
Brain/smoke deer	1279	1871	>80	>80	219	204	123696	1328231
Untanned calf	934	1321	73	66	61	62	6096	6628
Old Material								
Chrome side	971	947	26	22	21	22	20805	14216
Russian seat cover	634	584	9	7	13	18	519	965
Parchment	508	572	12	17	61	59	20144	23156
Vegetable bookbinding	600	350	4	3	23	13	5	13
Hide bucket	840	800	15	15	32	24	360	120

moisture between the object and its surroundings. The process was so successful with wood that, later, the Victoria and Albert Museum treated all the carvings displayed at a major Grinling Gibbons exhibition in this way⁽¹³⁾.

Thermo Lignum process for historic leathers

Accordingly, a research programme was put into effect to examine the effects of this technique on leathers and samples of new and historic leathers were obtained. These included skins newly tanned with mimosa, sumac, oak bark, brains/smoke or alum, parchment and rawhide, as well as historical leathers and parchment.

After cutting out pieces for physical and chemical testing before treatment, they were put through the Thermo Lignum process. In this, the temperature was increased gradually from an ambient of 20°C to 52°C over a period of 11 hours, held at this

temperature for two hours and allowed to cool back to 20°C over a further 11 hours. During this period, the relative humidity in the chamber was increased following the appropriate isotherm on

Panel 1

The effects of moisture on shrinkage⁽²¹⁾

As Nayudarnma points out⁽¹⁵⁾, the shrinkage temperature of leather is critically dependent on its moisture content. At a moisture content of less than 20%, vegetable tanned leathers and untanned hides shrink at temperatures in excess of 100°C⁽¹⁶⁾. In atmospheres of 50-60% RH the moisture content of leather is only of the order of 15%⁽¹⁷⁾, so the conditions of the Thermo Lignum process are well within the area of safety.



Left: Book from the private collection of Anthony Blunt, one time Keeper of the Queen's pictures - and spy - bequeathed to the Courtauld Institute London.
Right: Product of early twentieth century working craftsmanship.

the Keyworth diagram from 50% RH to 60% RH and then decreased back to 50% RH.

Further samples were then cut out and a range of physical and chemical tests undertaken. These included measurement of shrinkage, pH, shrinkage temperature, softness, tensile strength, stitch tear strength, lastometer and flexibility⁽¹⁴⁾. The results all indicated that the Thermo Lignum process had no deleterious effect whatsoever, and the most significant results obtained are presented in *Figure 1*.

As a result of this work, large numbers of leather objects, including saddles, books, buckets and furniture, have been successfully treated in this manner (Re: Panel 1).

Figure 2: Changes in shrinkage temperature over time

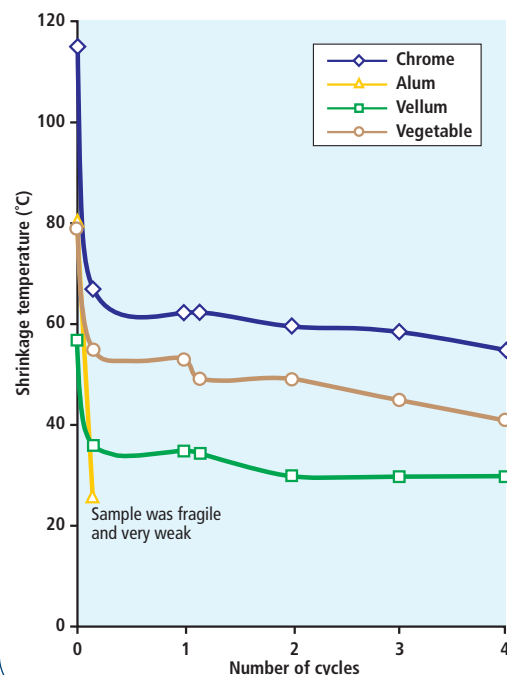
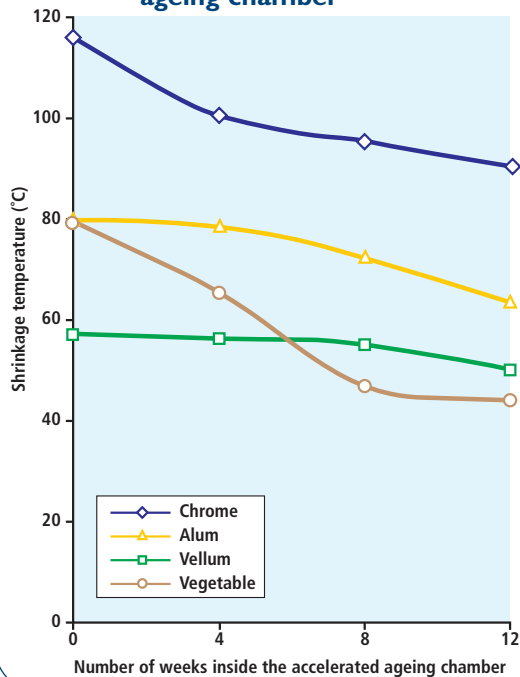




Figure 3: Changes in shrinkage temperature over time in ageing chamber



Fine example of a leather case to carry travelling clock. The front protective panel slides out to reveal the clock face through a glass window.

Artificial ageing systems

Accelerated artificial ageing systems have existed for over a century, most of which attempt to reproduce the combined effects of oxidation and hydrolysis that appear to take place in real life. The most recent system, partially funded by the European Commission⁽¹⁸⁾, was developed as part of the EU STEP⁽¹⁹⁾ and ENVIRONMENT⁽²⁰⁾ leather projects. In this, the leathers are first heated at 120°C for 24 hours to simulate oxidative deterioration. They are then subjected to an atmosphere of 25ppm sulfur dioxide + 10ppm nitrogen oxides at 40°C, 25% RH for six days to give accelerated hydrolytic breakdown. This cycle is then repeated a further three times.

In the final phase of the project, evidence began to emerge that, while this artificial ageing system caused chemical changes to the leathers similar to those observed with historic leathers, the physical changes were much more drastic. Nor did the system rank leathers in the order of resistance to ageing found in real life where experience shows that chrome tanned leathers, parchment and alum tawed skins last significantly longer than vegetable tanned products.

A much wider range of products was therefore subjected to the artificial



ageing process and the effects on their physical properties examined.

In all 72 commercial products were examined. They included calf, goat and sheepskins, full vegetable tanned, semi chrome, chrome retan and semi alum as well as alum tawed skins and vellums. Samples were examined for shrinkage temperature, pH, tensile strength, tear strength and resistance to flexing whilst under strain at each stage of the ageing regime.

In general, the findings indicated that the order of resistance to ageing is chrome>vegetable>vellum>alum as shown in *Figure 2* - but this does not correlate with what is found in real life.

A similar series of tests were therefore carried out with the heating stages omitted. These and the other results measured indicate the order of resistance to ageing is chrome>alum>vellum>vegetable as shown in *Figure 3* — being the order found in real life.

Based on this amended technique it was concluded that the leathers with the optimum combination of properties were made by retanning vegetable tanned crust with masked aluminium



Nineteenth century hunting scene in the form of a leather screen.

salts, a development of the work of Frey and Beebe⁽¹³⁾.

One British tannery member of the consortium has taken the work forward and, using its experience with the fatliquoring and finishing of semi alum leathers, has converted one of its product ranges completely to this process. From the artificial ageing results it is predicted that books bound with these leathers will remain sound for a hundred years or more even in heavily polluted city atmospheres - true preventive conservation. 

References:

1. Waterer, J.W. *The Conservation and Restoration of Objects made Wholly or In Part of Leather*. London: G. Bell & Sons, 1972.
2. Thomson, R.S. *Bookbinding leather: Yesterday, Today and Perhaps Tomorrow*. JSoc. Leather Technologists & Chemists. 2001, 85, 66.
3. Plenderleith, H.J. *The Preservation of Leather Bookbindings*. London: British Museum, 1946.
4. Plenderleith, H.J. *The Conservation of Antiquities and Works of Art*. London: Oxford University Press, 1956.
5. Werner, A.E. *The conservation of leather, wood, bone and ivory, and*



- archive materials. In: *The Conservation of Cultural Properties*. Lausanne: UNESCO, 1968.
6. van Soest, H.A.B. and Hallebeeke, P.B. *Chemical Solutions of Problems Encountered in the Conservation of Old Leather*. Postprints of the ICOM-CC 7th Triennial Meeting Copenhagen. 1984.
 7. Frey, R.W. and Beebe, C.W. *The Permanence to Acid Deterioration of Vegetable Leather Retanned with Aluminium*. JALCA. 1940, 35, 440.
 8. *British Standard 7451:1991, Specification for Archival Quality Bookbinding Leather*.
 9. Calnan, C.N. *Retannage with Aluminium Alkoxides - A Stabilising Treatment for Acid Deteriorated Leather*. Postprints of the ICOM-CC International Leather and Parchment Symposium, Offenbach am Main. 1989.
 10. Pinniger, D. *Insect Pests in Museums*. London: Archetype Publications, 3rd edition, 1994.
 11. Barrington, R. *The Treatment of Objects Affected by Pest Attack*. Conservation News, 1995, 56, 44.
 12. Florian, M-L. *Heritage Eaters: Insects and Fungi in Heritage Collections*. London: James & James, 1997, 149.
 13. Anon. *V&A Puts Its Faith in Novel Bug Busters*. Antiques Trade Gazette. 24th October 1998.
 14. Thomson, R.S. *The Effect of the Thermo-Lignum Pest Eradication Treatment on Leather and Other Skin Products*.



Early nineteenth century hall porters chair
now housed at the Hall of the Leathersellers
Company of the City of London.

- Postprints of the ICOM-CC Leathercraft Working Group Conference, Amsterdam. 1995, 67.
15. Nayndamma, Y. *Shrinkage Phenomena*. In: O'Flaherty, F. et al (eds). *The Chemistry and Technology of Leather*, vol 2. New York: Reiff'-old, 1958, 28.
 16. Bienkiewicz, K. *Physical Chemistry of Leathermaking*. Malabar: 1983, 249.
 17. Balfé, M.P. and Humphreys, F.E. *The Effects of Heat and Moisture on Leather*. In: *Progress in Leather Science*. Egham: British Leather Manufacturers' Research Association, 1948.421.
 18. EC BRITE-EURAM ift - CRAFT Contract No. BRST-CT98-5535.
 19. Larsen, R. (ed). *STEP Leather Project - Final Report*. Copenhagen: Royal Danish Academy of Fine Arts. 1994.
 20. Larsen, R. (ed). *ENVIRONMENT Leather Project - Final Report*. Copenhagen: Royal Danish Academy of Fine Arts. 1996.
 21. "A case of shrinkage temperature" & "Moisture and shrinkage temperature", *World Leather*, August/September 2003.