Paper B17

Investigation of Acid-Deterioration in Leather Leading towards Finding a Suitable Product for Treatment

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Abstract
Acid-deterioration occurs in vegetable-tanned leathers that were predominantly manufactured from the mid-19th Century onward, and has been observed in a variety of leathers (e.g., bookbinding, gilt leather, screens, wall hangings, upholstery and luggage). The deteriorated leathers are characterised by a lower pH (≤3.0) and shrinkage temperature (T_S), acrid odour and a powdery surface. Both the leather manufacturing processes and environmental pollutants, particularly sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), are thought to be responsible for the deterioration. Conservation of acid-deteriorated historic leather is a concern due to the lack of suitable products for the treatment of acid-deterioration. The purpose of this research was to undertake further investigation into acid-deterioration in leather in order to develop a product that will delay the progress of the decay in acid-deteriorated historic leather. Desk-based research was conducted to review the products used in the past for the treatment of acid-deterioration. Based on the research and personal communication, various compounds were selected and trialled using new mimosa-tanned leather, artificially-aged mimosa-tanned leather and acid-deteriorated leather. New mimosa-tanned leather was artificially aged through exposure to 80 parts per million (ppm) SO_2 and 40ppm NO_2 at 40°C and 30% relative humidity for 6 weeks. Differential Scanning Calorimetry (DSC) was used to determine T_S and a pH test was used as an indication of acidity in the leather (new and artificially aged mimosa-tanned leather and acid-deteriorated historic leather) samples. The results obtained from the experiments showed interesting outcomes. The ideal product should have collagen-stabilising properties, acid-buffering capacity, be capable of providing a long-term conservation effect to the acid-deteriorated leather, along with a safe and easy application.

Introduction
Acid-deterioration occurs in vegetable tanned leather, particularly manufactured from the mid- 19th Century onwards.[1] Acid-deterioration is observed in a variety of leathers including bookbinding leather, gilt leather, screens, wall hangings, upholstery and luggage. The deteriorated leather shows a lower pH, sometimes below 3.0,[2] and lower shrinkage temperature (may be as low as low as 30°C[3]), indicating the loss of collagen structures. The visible changes in the deteriorated leather usually include fine cracking, a powdery surface (often reddish/brownish and hence the common term for acid-deterioration is red-rot) and complete or partial loss of the grain layer.

Causes of acid-deterioration
The first recorded investigation of acid-deterioration of armchairs and books was conducted by Faraday in 1842-43, who was appointed by the Athenaeum Club.[4,5] Faraday concluded that the heat and sulfur gas due to the burning of coal-gas was responsible for the rapid deterioration of the leather.[4,6] However, current research showed[2,5,7,8] that the changes in the leather manufacturing process in the 19th Century; such as, introduction of alternative tanning agents, use of synthetic dyestuffs, use of imported raw materials from Indian subcontinent, Middle East or Africa and

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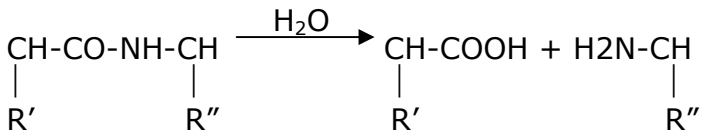
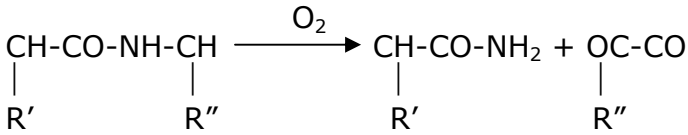
increased use of acids, particularly sulfuric acid as well as environmental pollutants (e.g., nitrogen dioxide and sulfur dioxide) are responsible for the rapid deterioration of acid-deteriorated leather. It has also been found that leather tanned with condensed (catechol) tannins is more susceptible to acid-deterioration than the leather tanned with hydrolysable (pyrogallol) tannins.[3,9] The presence of a higher amount of non-tannins in hydrolysable tannins may provide the leather with some degree of protection against acid-deterioration.[9]

Mechanisms of acid-deterioration

Collagen is the main structural protein in leather. The triple helical structure of the collagen is stabilised by hydrogen bonds.[10] Environmental pollutants such as sulfur dioxide (SO_2) is absorbed by the vegetable-tanned leather and eventually forms sulfuric acid (H_2SO_4) when it reacts with water: $SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$. The formation of a hydronium ion (H_3O^+) in an acidic environment may cause acid hydrolysis and breakdown of the hydrogen bonds, weakening the helical structure.[11] Hydrolytic and oxidative breakdown of the peptide bonds in the collagen molecule in leather are shown in equations 1 and 2.[2] Oxidative and hydrolytic reactions are influenced by the environmental conditions such as water, heat, pH, light and gasses.[12] Acid pollution is thought to be responsible for hydrolytic breakdown, whilst light, heat and oxidative pollution may cause oxidative breakdown. The deterioration due to the acid hydrolysis may be faster than oxidation.[3]



Equation 1: Hydrolytic breakdown of peptide bond



Equation 2: Oxidative breakdown of peptide bond

Reagents that have been used previously for the treatment of acid-deterioration

Research[2, 13,14, 15] has been carried out to find a suitable solution to conserve acid-deteriorated leather. Aqueous-based buffer salts[7] (e.g., sodium citrate, potassium tartrate and lactate) and solvent (isopropyl alcohol)-based buffer, imidazol[16] had been used to buffer the acidity in acid-deteriorated leather. Acid-deteriorated leather was found to darken and harden in contact with water[17,18,19] due to the movement of water soluble materials in the leather[17] and therefore aqueous-based buffers are unsuitable for the treatment of acid-deterioration. Moreover, buffers (aqueous- or organic solvent-based) provides short-term protection against acid-deterioration.[15] Ammonium vapour has also been used to neutralise the acidity in leather.[16] Similar to the buffers, ammonium also provides a short-term protection against acid-deterioration,[15] as the reaction of ammonium with acids in leather produces ammonium salts, which may breakdown over time producing free ammonia and acid.[18] A polyacrylate resin known as Pliantex® or Plexisol® was also used for the treatment of acid-deterioration.[6,20] However, due to the toxic effect of the solvents (1,1,1-trichloroethane[18] and toluene) used to dilute the compound, use of Pliantex® or Plexisol® on acid-deteriorated leather is no longer recommended. Aluminium diisopropoxide acetoacetate ester chelate (referred to as aluminium alkoxide in this study) was introduced by Calnan (1989)[15] followed by further investigation during the STEP[21] and ENVIRONMENT[8] leather projects, and was recommended to treat acid-deterioration in leather[8,15]. Aluminium alkoxide may also provide a short-term protection against acid-deterioration.[22] In a previous study,[23] the effect of aluminium alkoxide and an Organic Stabiliser was trialled. In this study various reagents including the Organic Stabiliser and aluminium alkoxide, L-arginine, DL-phenylalanine, gelatine, Zirconium(IV) propoxide and Titanium diisopropoxide (bis) acetylacetonate

have been trialled to identify the most suitable products for the treatment of acid-deterioration in leather.

Materials and methods

Mimosa-tanned leather (new and artificially-aged) and acid-deteriorated historic leather were used for this study. Figure-1 shows representative thermographs of new mimosa-tanned leather, artificially-aged mimosa-tanned leather and acid-deteriorated historic leather. During a previous study[23] as well as in this study, variable levels of degradation in acid-deteriorated leather were observed when the T_S of the leather was determined. Therefore mimosa-tanned leather was used as a control to maintain consistency of the obtained results. Mimosa tannins (classified as condensed tannin) are also known to be sensitive towards acid-deterioration.[24]

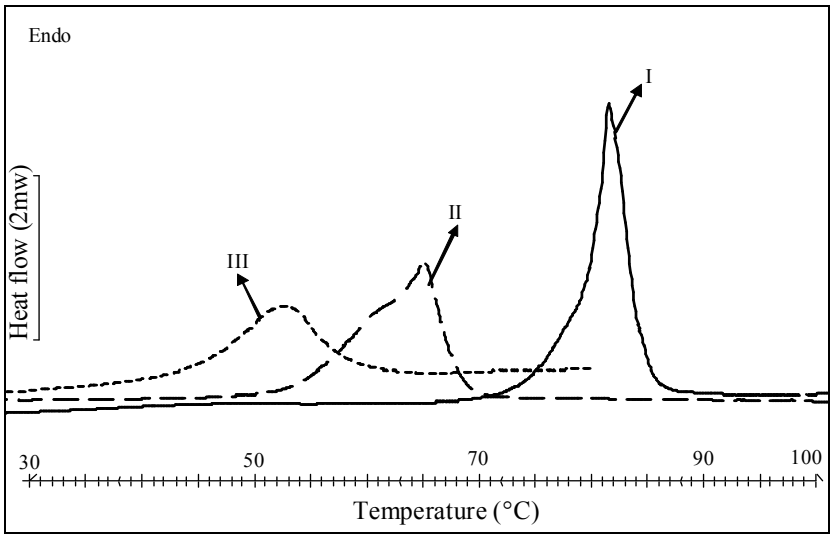


Figure 1: Thermographs of new mimosa-tanned leather: I, artificially-aged mimosa-tanned leather (aged for 6 weeks): II and acid-deteriorated historic leather: III (representative curves).

New mimosa-tanned leather

Goat skins (Lacto Ltd., UK) were used as raw materials and tanned using mimosa extract (Mimosa ME, Mimosa Extract Company Ltd., South Africa) to manufacture new mimosa-tanned leather. The detailed process is given in the Appendix.

Artificially-aged mimosa-tanned leather

New mimosa-tanned leather samples were artificially aged through exposing the sample to a concentration of 80 ppm sulfur dioxide (SO_2) and 40 ppm nitrogen dioxide (NO_2) at 40°C and 30% relative humidity [25-28] for 6 weeks.

Acid-deteriorated historic leather

Acid-deteriorated historic leather used in this study was supplied by various organisations, conservators and book binders.

Solvents

White sprit and Isopropyl alcohol (IPA) were selected for this study. These selected solvents have been used within the conservation field to clean historic leather. [17]

Reagents Trialled

The following chemicals were trialled

1. Amino acids (L-arginine and DL-phenylalanine)
2. Gelatine
3. Metal Alkoxides: the following metal alkoxides were investigated.

Aluminium diisopropoxide acetoacetate ester chelate (9.6% w/w Al)
Aluminium diisopropoxide acetoacetate ester chelate (9.6% w/w Al: Alfa-Aesar, UK) was diluted to 1.5% w/w Al using white spirit.

Zirconium(IV) propoxide solution (18.1-22.3% w/w Zr)
Zirconium(IV) propoxide solution (18.1-22.3% w/w Zr: Sigma-Aldrich, UK) was diluted to prepare a solution that consists of 1.8-2.2%, 2.5-3.5%, 5-7% and 9-11% w/w Zr, using white spirit. Preliminary experiments showed that application of a higher Zr concentration (2.5% w/w Zr and above) on leather produced a white powdery layer. Therefore, further experiments were carried out using a Zirconium(IV) propoxide solution that consists of 1.8-2.2% w/w Zr.

Titanium diisopropoxide (bis) acetylacetonate (9-10.5% w/w Ti)
Titanium diisopropoxide (bis) acetylacetonate (9-10.5% w/w Ti: Sigma-Aldrich, UK) was applied on leather without any further dilutions.

4. Organic Stabiliser: The formulation of this product, at the time of writing this article, cannot be disclosed. The compound is capable of providing an additive stabilisation to the vegetable-tanned leather. The compound was applied on leather samples directly without further dilution.

Solubility of each reagent in the selected solvents was determined. A preliminary experiment was then carried out to determine the effects of the reagents on new mimosa-tanned leather. The products were then trialled on new mimosa-tanned leather that was previously artificially-aged for 6 weeks and on acid-deteriorated historic leather. Approximately 1ml of each reagent was applied on per gram of leather samples. The reagents were applied on leather samples using an individual cotton bud and dried overnight at room temperature. Shrinkage temperature (T_S) and pH of the treated samples were determined. T_S and pH of the corresponding untreated samples were also determined.

Determination of shrinkage temperature (T_S)
The leather samples were cut into small pieces (≈3 mg), placed in deionised water for a minimum of 16 hours at 20±2°C. The following day the excess of water was removed using Whatman No.1 filter papers and 5-10mg[30] were placed in aluminium crucibles (40µl). The samples were analysed using Differential Scanning Calorimetry (DSC)[31,32] (DSC822e, Mettler-Toledo, Switzerland). The initial and final temperatures during the analysis were 0°C and 100-150°C respectively at a ramping rate of 5°C/minute. The onset temperature of the denaturation process was recorded as T_S.

Determination of pH
The pH of aqueous extract was determined following a British standard method (British Standard Institution; BS1309, 1974).[33] A leather sample, 0.25±0.002g was placed in 5ml deionised water (pH: 6-7; adjusted using diluted sodium hydroxide) and agitated mechanically for 24 hours using a shaker at 20±2°C and 65±2% relative humidity. The following day the pH of the aqueous extract was measured using a standard pH meter.

Results and discussion
L-arginine, DL-phenylalanine and gelatine were insoluble in the selected organic solvents and therefore it was decided that these reagents are unsuitable to use to treat acid-deterioration in leather. No further experiments were undertaken using these products.

The selected metal alkoxides and the Organic Stabiliser were found to be soluble in both white spirit and IPA. A disadvantage of using IPA is that it may cause damage to the leather by solubilising oil and tannins present in leather. On the other hand, White spirit is a non-polar solvent and so reduces the probability of solubilising polar components (salts and water soluble tannins) in leather when applied.[17] Therefore, further experiments were carried out using white spirit.

The results obtained when new mimosa tanned leather was treated with metal alkoxides are given in Table 1. Table 1 shows T_S and pH of new mimosa-tanned leather following application of aluminium alkoxide (1.5% w/w Al), titanium diisopropoxide (bis) acetylacetonate (9-10.5% w/w Ti) and zirconium(IV) propoxide (1.8-2.2% w/w Zr). In this study, the change in T_S and pH due to the application of the reagents will be referred to as ΔT_S and ΔpH respectively. The thermographs obtained are shown in Figure 2.

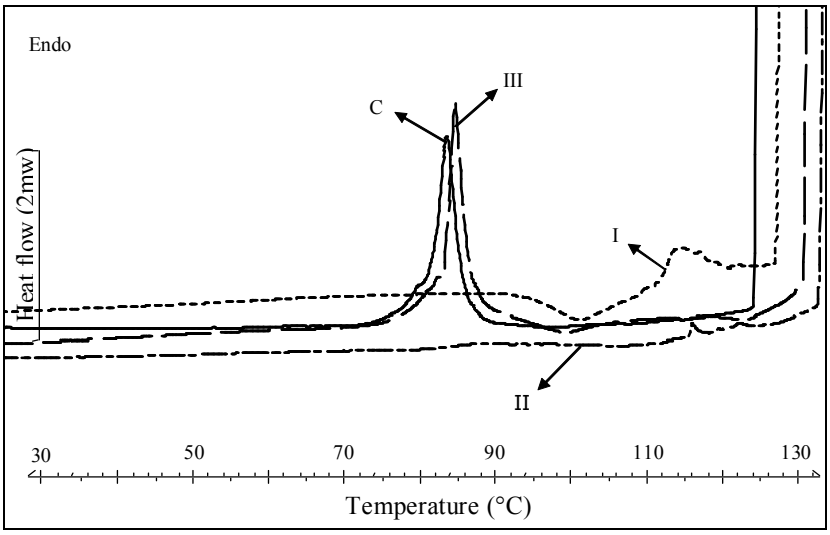


Figure 2: Thermographs of new mimosa-tanned leather: C and new mimosa-tanned leather treated with aluminium alkoxide (1.5% w/w Al): I, Titanium diisopropoxide (bis) acetylacetonate (9-10.5% w/w Ti): II and Zirconium propoxide (1.8-2.2% w/w Zr): III (representative samples).

A slight increase in T_S was observed following application of Zirconium(IV) propoxide on new mimosa-tanned leather (see Table 1) and may be considered negligible. Formation of a white powdery layer was observed on the Zirconium(IV) propoxide-treated leather samples even when a lower concentration (1.8-2.2% w/w Zr) was used. Metal alkoxides are susceptible to hydrolysis. Atmospheric moisture may be sufficient to initiate the hydrolytic process resulting in the formation of a metal hydroxide and occasionally a hydroxy-alkoxide.[34] The white powdery layer following application of zirconium(IV) propoxide may be due to the formation of zirconium hydroxide through hydrolysis reaction. Due to the deposition of white powder and the negligible effect on T_S of the treated leather, it was therefore decided not to undertake further experiments with this compound.

Inconclusive results were obtained when the T_S of Titanium diisopropoxide (bis) acetylacetonate-treated mimosa-tanned leather samples were measured. Titanium diisopropoxide (bis) acetylacetonate had a yellowing and hardening effect on leather, and so no further experiments were conducted using this chemical. Moreover, the average increase in pH of the new mimosa-tanned leather was found to be below 0.5.

A previous study[23] showed that aluminium alkoxide both increased the T_S and pH of the new mimosa-tanned leather (Table 1), artificially-aged mimosa-tanned leather (T_S increased by 25.8±8.7 and pH

increased by 1.3), and acid-deteriorated historic leather (Table 2). The increase in T_S and pH of new mimosa-tanned leather following the application of aluminium alkoxide indicates that the product has a collagen stabilising effect and acid buffering capacity. As metal alkoxides are moisture sensitive[35-37] and therefore aluminium alkoxide may breakdown over time providing a short-term preservation effect when applied on its own.

Table 1: Effect on T_S and pH of the new mimosa-tanned leather following application of aluminium alkoxide (1.5% w/w Al), Zirconium(IV) propoxide (1.8-2.2% w/w Zr) and Titanium diisopropoxide (bis) acetylacetonate (9-10.5% w/w Ti).

Sample name	T_S°C	ΔT_S	pH	ΔpH
Control	82.0±1.0	0.00	3.7±0.08	0.00
Aluminium alkoxide	116.5±7.8	34.5±6.8	4.5±0.00	0.81±0.04
Titanium diisopropoxide (bis) acetylacetonate	-		3.9±0.25	0.22±0.08
Zirconium (IV) propoxide	84.1±1.4	2.2±0.5	3.8±0.15	0.10±0.04

Table 2: Effect on T_S and pH of acid-deteriorated leather following application of an Organic Stabiliser, aluminium alkoxide (1.5% w/w Al) and a formulation containing aluminium alkoxide and the Organic Stabiliser. [23]

Sample name	T_S (°C)	Δ T_S	pH	ΔpH
Control	45.4±6.4	0	2.7-3.1	0
Organic Stabiliser	45.2±4.8	-0.2±3.7	2.5-3.6	-0.2 - 0.6
Aluminium alkoxide	64.5±14.9	19.1±10.3	3.7-4.2	0.7 - 1.5
Aluminium alkoxide + Organic Stabiliser	76.2±2.4	27.4±0.9	4.0-4.3	1.0 – 1.4

During the study, it was observed that aluminium alkoxide suppressed fungal growth on leather. Figures 3 and 4 show fungal growth on untreated leather samples (new mimosa-tanned leather and acid-deteriorated historic leather) whilst no or low growth of fungi was observed on the corresponding leather samples that were treated with aluminium alkoxide. It was also observed that aluminium alkoxide prevented movement of water-soluble materials (tannins and non-tannins) from the leather to water when soaked (Figure 3). Aluminium alkoxide may coat the collagen fibre preventing water soluble material to transfer from leather to water.

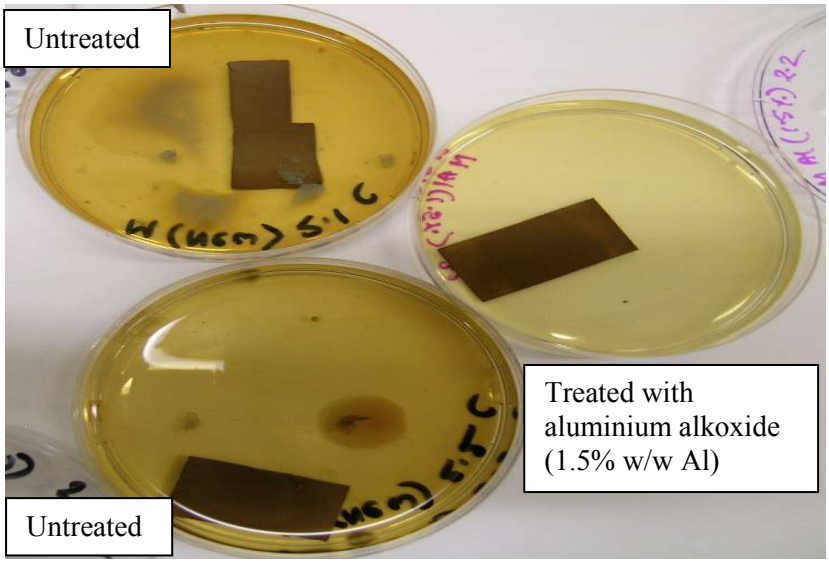


Figure 3: No fungal growth and low percolation of water soluble tannins and non-tannins in the petri-dish when new mimosa-tanned leather samples were treated with aluminium alkoxide (1.5% w/w Al).

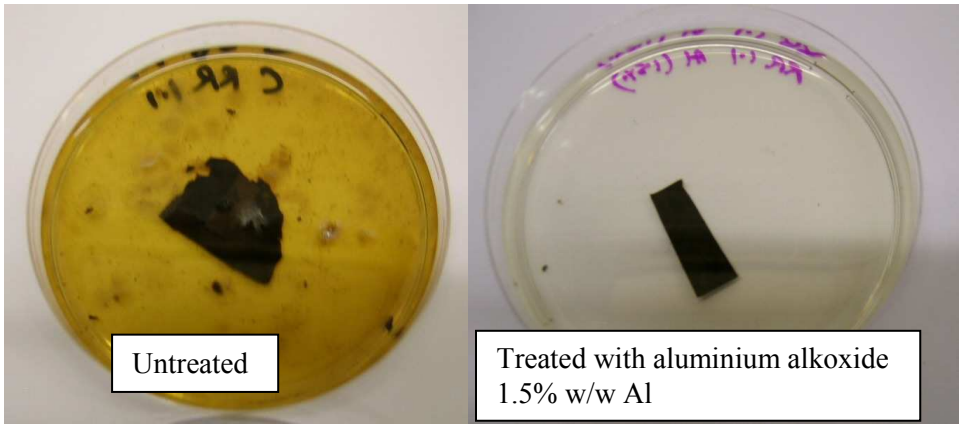


Figure 4: No fungal growth and lower percolation of water soluble tannins and non-tannins in the petri-dish when acid-deteriorated leather samples were treated with aluminium alkoxide (1.5% w/w Al).

In a previous study conducted by the authors[23] it was shown that the Organic Stabiliser increased the T_S and pH of new mimosa-tanned leather and artificially-aged mimosa-tanned leather (Table 3). The previous study also showed that the Organic Stabiliser on its own failed to chemically stabilise the acid-deteriorated leather. However, experiments carried out in this study showed that the Organic Stabiliser is capable of increasing the T_S of acid-deteriorated leather when applied on its own (Figure 4). The reaction of the Organic Stabiliser with the vegetable tannins, and vegetable-tanned leather depends on the nature of vegetable tannins along with the pH. The degradation states, the nature of the breakdown products and the acidity in acid-deteriorated leather due to the acid-deterioration, may affect the reaction of the Organic Stabiliser producing inconsistent results when the Organic Stabiliser was applied on its own.

Table 3: Effect of the Organic Stabiliser on new mimosa-tanned leather and artificially-aged mimosa-tanned leather.[23]

	New Mimosa tanned leather		Artificially-aged mimosa-tanned leather	
	Control	**Organic stabiliser**	**Control**	**Organic stabiliser**
T_S	81.7±2.1	91.1±3.8	62.6±4.9	71.8±1.1
ΔT_S	0.00	8.9±3.0	0.00	11.9±3.7
pH	5.0±0.4	6.2±0.6	2.1±0.1	2.7±0.0
ΔpH	0.00	1.3±0.3	0.0	0.6±0.0

Conclusions

The study showed that the aluminium alkoxide has an acid-buffering capacity and collagen stabilising property, as it increased the T_S and pH of new mimosa-tanned leather, artificially-aged mimosa-tanned leather and acid-deteriorated historic leather. However, the highest increase in T_S and pH was obtained following the application of a formulation containing aluminium alkoxide and Organic Stabiliser on artificially-aged mimosa-tanned leather, also on acid-deteriorated leather. Therefore the formulation has the potential to treat acid-deterioration in leather. Further experiments are still required to recommend the product for the treatment of acid-deterioration in historic leather.

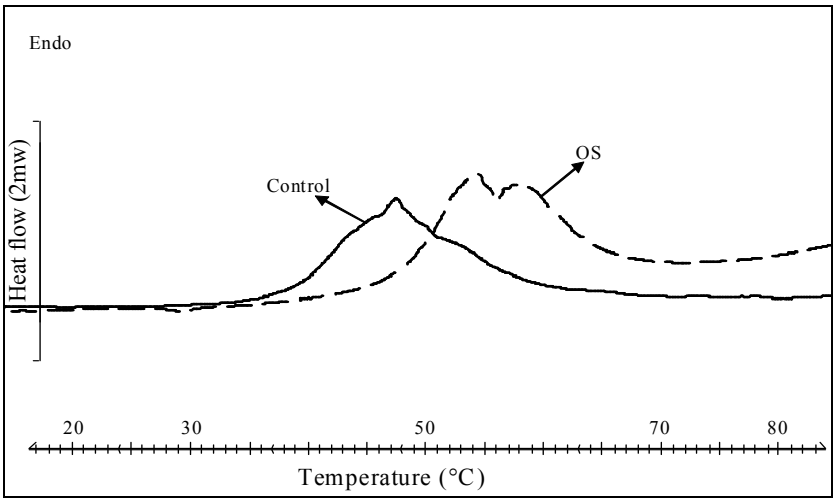


Figure 5: Thermographs of acid-deteriorated leather (untreated): control and treated with the Organic Stabiliser: OS

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Appendix: Leather-making process that was followed to manufacture mimosa-tanned leather from raw goat skins in this study.

Process stages	Chemicals	Amount (%w/w)*	Time	Remark
Pre-soaking	Water	300	1 hr	
	Bactericide (Trupsept BA; Trumpler Germany)	0.2		
Soaking	Water	300	Overnight	
	Bactericide (Trupsept BA)	0.2		
	Surfactant	0.5		
Fleshing				
Unhairing/ liming	Water	200	18-24 hrs	
	Lime	2		
	Sodium sulfide	3		
Washing (twice)	Water	250	10 mins	
Deliming	Water	100	45 mins	pH 8.5
	Ammonium chloride	2		
Bating	Protease (Oropon ON2, TFL, Germany)	0.2	30 mins	Temperature 35°C
Washing (twice)	Water	250	10 mins	
Pickling	Water	80		pH was adjusted to 4.7 using sodium citrate
	Salt	6-8	10 mins	
	Sulfuric acid	0.5	2 hrs and left overnight	
	Formic acid	0.5		
Tanning	Mimosa ME (Mimosa Extract Company Ltd, South Africa)	20%		

***Note:** Percentage of the added chemicals was based on the weight of the calf skins; min=minute and hr=hour.