

## Use of aluminium alkoxide and oxazolidine II to treat acid deteriorated historic leather

### Key words

Leather; conservation; acid deterioration; red rot; artificial ageing; shrinkage temperature

### Introduction

Acid deterioration in historic leather, commonly known as red-rot, occurs in vegetable-tanned leathers predominantly manufactured from the mid-nineteenth century onward.<sup>1</sup> Acid deterioration has been observed in a variety of leathers such as bookbinding, gilt leather, screens, wall hangings, upholstery and luggage. The deteriorated leather usually shows a lower pH (~3.0) and lower hydrothermal stability.<sup>2,3</sup> The visible changes include a powdery surface and a complete or partial loss of the grain layer.<sup>4</sup>

A number of research projects<sup>2-16</sup> have been conducted over the years. Various consolidants as well as acid and collagen stabilising compounds have been investigated in an effort to find a suitable way to conserve acid deteriorated historic leather. For example, a polyacrylate resin commercially known as Pliantex<sup>®</sup> or Plexisol<sup>®</sup>, was used by Waterer<sup>(1972)</sup> as a consolidant.<sup>6-8</sup> Organic solvents, such as 1,1,1-trichloroethane and toluene were used as diluents for Pliantex<sup>®</sup> or Plexisol<sup>®</sup>.<sup>12</sup> However, 1,1,1-trichloroethane is hazardous in nature and there is a potential health impact of toluene on humans. Use of an acrylate polymer, polymethyl acrylate was investigated by Phillips<sup>(1984)</sup><sup>8</sup> to consolidate deteriorated historic leather including acid deteriorated historic leather. Hydroxypropyl cellulose in isopropyl alcohol (IPA), generally sold under the trade name of Klucel G<sup>®</sup> (powder form only) or Cellugel<sup>®</sup>, has also been applied as a surface consolidant to acid deteriorated historic leather.<sup>9</sup>

Aqueous-based buffer salts (sodium citrate, potassium tartrate and lactate) have been used to buffer the acidity.<sup>10</sup> Deteriorated leathers darken and harden in contact with water due to the movement of salts and water soluble tannins within the leather.<sup>9, 11-13</sup> As a result aqueous-based buffer salts are unsuitable for the treatment. Imidazole in isopropyl alcohol (IPA) has also been introduced to buffer the acidity.<sup>14</sup> A disadvantage of using IPA is that damage may be caused to the leather by solubilising oils and tannins present in leather.<sup>11</sup> Moreover, buffers (aqueous or organic solvent-based) do not have the ability to stabilise collagen and therefore do not provide long-term protection.<sup>15</sup> Use of ammonia vapour to neutralise acidity in leathers with a pH below 3.0 has been used by van Soest *et al.*<sup>(1984)</sup>.<sup>14</sup> Ammonia may reduce the acidity by reacting with the acids in leather, forming ammonium salts. The ammonium salts produced could breakdown over time producing free ammonia and acids.<sup>12</sup> Therefore, similar to the buffers, ammonia may only be effective against acid deterioration for a limited period of time.<sup>15</sup>

Among the various products studied, aluminium di(isopropoxide) acetoacetate ester chelate (referred to as aluminium alkoxide in this study) was found to be the most effective as studies<sup>10, 15, 16</sup> showed that the reagent increases hydrothermal stability and pH of the aqueous extract when applied to the leather. Application of aluminium alkoxide was first introduced by Calnan<sup>15</sup> for the treatment of acid deterioration in historic leather and investigated further during the STEP<sup>16</sup> and the Environment Leather projects,<sup>10</sup> and was recommended as a

treatment [option](#). However, aluminium alkoxide may only provide a short-term stabilisation effect,<sup>10</sup> and therefore, conservation of acid deteriorated historic leather is still a concern.

This study was undertaken to develop a product that will increase the longevity of the acid deteriorated historic leather by delaying the deterioration rate. The ideal product should have collagen stabilising properties, with minimal visual and physical changes to the leather. The product should also provide long-term durability to the acid deteriorated historic leather along with a safe and easy application.

## Materials

### 1 Acid deteriorated historic leather

Samples of acid deteriorated historic leathers used in this study were supplied by various conservators and organisations within the UK and Europe. The acid deteriorated leathers were selected based on visual observations, that the selected samples consisted of a powdery and flaky surface.

### 2 White spirit

White spirit is a non-polar organic solvent and so reduces the probability of solubilising polar components (salts and water-soluble tannins) in leather. White spirit is proven to be a safe solvent option (when used correctly) and has been used in the cleaning of historic leathers.<sup>11</sup> Therefore in this study white spirit was selected as a diluent.

### 3 Aluminium alkoxide

Aluminium (Al) di(isopropoxide) acetoacetate ester chelate ( $C_{12}H_{23}AlO_5$ ), 9.6% w/w Al, was diluted to 1.5% w/w Al using white spirit. This dilution was based upon the study carried out during the Environment Leather project.<sup>10</sup>

### [Figure 1](#)

### 4 Oxazolidine II

Bicyclic oxazolidine (5-ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane) ( $C_7H_{13}NO_2$ ), 97% w/v, is generally referred to as oxazolidine II or E, and referred to as oxazolidine II in this study. The reagent was applied to the acid deteriorated historic leather samples without any dilution.

### [Figure 2](#)

Oxazolidine II was selected in this study as it has collagen-stabilising properties and confers a shrinkage temperature ( $T_S$ ) of approximately 80°C when native collagen is treated with oxazolidine II at a neutral pH.<sup>17, 18, 19</sup> Research<sup>18, 19</sup> has shown that it is possible to increase the  $T_S$  of vegetable-tanned leather from 80-85°C to 100°C or above if re-tanned with oxazolidine II. However, the reaction of oxazolidine II with vegetable tannins and vegetable-tanned leather depends on the chemistry of the vegetable tannins. Vegetable tannins are classified into two groups: condensed (catechol) and hydrolysable (pyrogallol). Leathers tanned with condensed tannins have been shown to be more liable to acid deterioration than the leathers tanned with hydrolysable tannins.<sup>3</sup> Research has also shown that oxazolidine II confers a higher  $T_S$  to a vegetable-tanned leather tanned with condensed tannins such as mimosa and quebracho than a vegetable-tanned leather tanned with hydrolysable tannins, such as sumac and chestnut.<sup>17</sup>

## 5 New formulation

The new formulation consisted of aluminium alkoxide and oxazolidine II. The exact formulation cannot be published due to commercial sensitivity.

## 6 Cellugel®

Cellugel® was applied directly to the experimental leather samples without any dilution.

## Method

### 1 Initial trial

For the initial trials the acid deteriorated leather samples were placed on Whatman No. 1 filter paper followed by the application of aluminium alkoxide, oxazolidine II and the new formulation separately. Cellugel® does not have a collagen stabilising effect and generally used as surface consolidant,<sup>11</sup> therefore Cellugel® was not included during the initial trial. The reagents were applied on three different acid deteriorated leathers using the same leather samples wherever possible. The reagents were applied to the grain side using cotton buds or brush until the samples were fully saturated. The excess of the reagents was absorbed by the filter paper. The treated samples were dried overnight at room temperature before further analysis. The hydrothermal stability of the leather and pH of the aqueous extract of the treated and corresponding untreated leather samples were determined to measure the effect of the treatments.

### 2 Determination of hydrothermal stability

Collagen is the main structural protein in hides and skins, and hence leather. The conversion of putrescible hides and skins into non-putrescible leather is known as tanning. Various types of vegetable, synthetic, organic and mineral tanning agents (tannins) are used to convert hides and skins into leather. Tanning causes permanent changes in the physical and chemical properties that include an increase in hydrothermal stability.<sup>17, 20-22</sup> The hydrothermal stability of collagen within the leather industry is expressed in terms of shrinkage temperature ( $T_s$ ) and is defined as the effect of wet heat on collagen/leather.<sup>17, 23</sup> Collagen undergoes denaturation if heated in the presence of water. During the denaturation process, the triple helical structure of collagen collapses and transforms into a random coil.<sup>17</sup> A reduction in the hydrothermal stability occurs due to the degradation of collagen, in this case leather.<sup>21</sup> Therefore, in this study the effects of the applied reagents were measured by determining the hydrothermal stability through thermal analysis.

Differential scanning calorimetry (DSC)<sup>22, 24</sup> was used to determine the hydrothermal stability of the treated and untreated leather samples. Samples for the DSC analysis were taken from the full structure of the leather samples. 5-10mg of fully hydrated samples<sup>25, 26</sup> were placed in aluminium crucibles (40µl) and sealed with an aluminium lid. Analysis was carried out with an initial temperature of 0-10°C and a final temperature of 150°C with a ramping rate of 5°C per minute. The onset temperature of the denaturation process was recorded as shrinkage temperature ( $T_s$ ) (Fig. 3).

### 3 Determination of pH

The pH of an aqueous extract was determined based on the British Standard BS1309:1974<sup>27</sup> method. According to BS1309:1974, 5 g leather sample should be soaked in 100ml of deionised water in order to measure the pH of

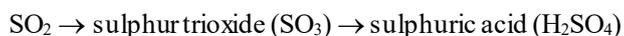
the aqueous extract. In this instance, due to the scarcity of the acid deteriorated sample, 0.25g leather sample was used.

Leather samples,  $0.25 \pm 0.002$ g, were placed in 5 ml deionised water (pH: 6-7, adjusted using diluted sodium hydroxide solution) and agitated mechanically for 24 hours using a horizontal shaker at  $20 \pm 2^\circ\text{C}$ . The following day the pH of the aqueous extract was measured using a standard pH meter.

Similar to the hydrothermal analysis, samples to determine the pH of the aqueous extract were collected from the acid deteriorated historic leather samples treated with various reagents mentioned previously as well as corresponding untreated samples.

#### 4 Accelerated ageing trial

It has been suggested that hydrolysis and oxidation is responsible for the deterioration of historic leather. However, it has also been suggested that acid hydrolysis is probably the main cause of acid deterioration in historic leather.<sup>13</sup> Environmental pollutants, particularly sulphur dioxide ( $\text{SO}_2$ ) and nitrogen dioxide ( $\text{NO}_2$ ), are considered as one of the factors responsible for acid deterioration in historic leather.<sup>2</sup> Environmental pollutants absorbed by vegetable-tanned leather may form acids when reacting with water:



The formation of a hydronium ion ( $\text{H}_3\text{O}^+$ ) in an acidic environment may cause acid hydrolysis of the collagen molecule in leather.<sup>2, 13</sup> Therefore, to investigate the long-term impact of the new formulation (aluminium alkoxide + oxazolidine II) on acid-deteriorated historic leather samples, **accelerated** ageing was carried out for up to 12 weeks in an acidic environment. Aluminium alkoxide only and Cellugel® were also applied to acid-deteriorated historic leather samples followed by the 12 weeks accelerated ageing.

In order to minimise the effect of the treatment due to variation among samples, three of the reagents (Cellugel®, aluminium alkoxide and the new formulation) were applied to leather samples obtained from the same leather object. Oxazolidine II was not included during the accelerated ageing trial as the initial trial showed that oxazolidine II was ineffective in increasing the shrinkage temperature as well as buffering the acidity of acid deteriorated historic leather when applied on its own (for details see 'results and discussion').

The trial was carried out in triplicate. Each sample was treated with Cellugel®, aluminium alkoxide, and the new formulation. Untreated corresponding samples were used as a control. Each of the treated and untreated samples was divided into 5 pieces, one of sample was not aged, each of the remaining four samples were removed following 3, 6, 9 and 12 weeks of accelerated ageing. Figure 4 is a diagram of this process.

Accelerated ageing was carried out based on the experiments conducted during the STEP leather project<sup>16</sup> and Environment leather<sup>10</sup> projects as well as experimental trials carried out within the Leather Conservation Centre (LCC).<sup>28</sup> The accelerated ageing was conducted by exposing the samples to a concentration of  $\text{SO}_2$  (40 ppm) and  $\text{NO}_2$  (20 ppm) at  $40^\circ\text{C}$  and 30% relative humidity (RH).

The authors would like to stress that the accelerated ageing was used as an indication on the longevity of the studied leather samples. The accelerated ageing will not reflect real life scenarios by any means as the storage conditions of any historic leather artefacts vary greatly.

## Results and discussion

The untreated samples of acid deteriorated historic leather exhibited a wide range of  $T_s$  from 43-75°C, indicating the variable nature of the acid deteriorated historic leather. However, some acid deteriorated historic leather samples analysed also showed an undetectable shrinkage temperature, possibly due to the high level of deterioration. The thermographs of such leathers showed no visible transition peaks indicating that deterioration of collagen had already taken place. Therefore, it was not possible to determine the effect of the treatments on the hydrothermal stability of these samples and hence they were excluded from this study. The pH of the acid deteriorated historic leathers used in this study was within the range of 2.5-3.5, although the pH levels of most of the leather studied were 3 or below.

## 1 Aluminium alkoxide

The results obtained showed that aluminium alkoxide increased the shrinkage temperature by an average of 20.7°C (Table 1) and increased pH by an average of 1.1 (Table 2) from the untreated acid deteriorated historic leather. This indicates that aluminium alkoxide has collagen stabilising and acid buffering properties.

A study carried out by Calnan<sup>15</sup> also showed that aluminium alkoxide increased hydrothermal stability of vegetable-tanned leather indicating it has a collagen stabilising ability. Alternatively, the increase in  $T_s$  shrinkage temperature may also be due to the hydrophobic properties of aluminium alkoxide. The  $T_s$  shrinkage temperature of collagen increases with a decrease in moisture content in the collagen fibres and leather.<sup>29, 30</sup> Research carried out by Miles *et al.*,<sup>30</sup> showed that crosslinking agents such as glutaraldehyde and hexamethylene di(isocyanate) stabilise collagen by reducing the distance between collagen molecules through dehydration. Due to the hydrophobic properties (Fig. 5b) imparted by aluminium alkoxide to the leather, water is repelled by the aluminium alkoxide-coated fibres, preventing the fibres from rehydrating and consequently showing an increase in hydrothermal stability. As mentioned in the introduction, it has also been reported that aluminium alkoxide may have a short-term stabilising effect against acid deterioration.<sup>10, 31</sup> Metal alkoxides are usually prone to hydrolysis, although chelation with various chelating agents is known to reduce the rate of hydrolysis,<sup>32, 33, 34</sup> however it may not prevent the hydrolysis of alkoxides altogether. Therefore, the increase in  $T_s$  and the hydrophobicity presented by the acid deteriorated historic leather following application of a chelated aluminium alkoxide may not be permanent and hence provide short-term protection only.

## 2 Oxazolidine II

In this study oxazolidine II was found to be ineffective as among the three samples trialled a negligible increase in shrinkage temperature  $T_s$  was observed in one sample, with the shrinkage temperature  $T_s$  decreasing in the two other samples (Table 3). Similar to the shrinkage temperature, an insignificant increase was observed for two samples when oxazolidine II was applied on its own, with the average being no change in pH (Table 4). The reaction between oxazolidine II and collagen is pH dependent. Although oxazolidine II can react with native collagen at a lower pH, a pH 7.5-8.0 is required for optimum reactivity.<sup>18, 19</sup> At pH 7.4 and pH 4.0 oxazolidine II confer a  $T_s$  of 82°C and 72°C respectively with a 5% (w/w) oxazolidine II offer.<sup>17</sup> In this instance the reaction of oxazolidine II was perhaps hindered by the low pH of the acid deteriorated historic leathers. Along with acidity, the nature of the breakdown products due to deterioration may also affect the reaction of oxazolidine II.

### 3 Aluminium alkoxide and oxazolidine II combination (new formulation)

The new formulation containing aluminium alkoxide and oxazolidine II increased the ~~T<sub>s</sub> shrinkage temperature~~ by an average of 33.6°C (Table 5). The pH was increased by an average of 1.2 (Table 6) on acid deteriorated historic leather samples.

The increase in ~~T<sub>s</sub> shrinkage temperature~~ following application of the new formulation could be due to the following reasons. It is apparent from Table 4 that oxazolidine II did not play a role in increasing pH of the acid deteriorated historic leather samples. Therefore the increase in pH following application of the new formulation is due to the presence of aluminium alkoxide, which confirms that aluminium alkoxide has acid buffering capacity. Aluminium alkoxide present in the formulation increased the pH of the acid deteriorated historic leathers on average from 2.9 to 4.1. This increase in pH may assist oxazolidine II to interact with vegetable-tanned leather resulting in the increase in ~~T<sub>s</sub> shrinkage temperature~~. Aluminium alkoxide may therefore provide conditions for oxazolidine II to exert a stabilising effect to the leather samples treated with the new formulation containing both the aluminium alkoxide and oxazolidine II.

Re-tanning vegetable-tanned leather with aluminium salts is known to increase the hydrothermal stability of vegetable-tanned leather.<sup>17</sup> Dasgupta<sup>18</sup> showed the ~~shrinkage temperature T<sub>s</sub>~~ of mimosa-tanned leather was increased from 76°C to 130°C, when the mimosa-tanned leather was re-tanned with an aluminium salt. Oxazolidine II in the formulation may react with the alkoxide to enhance formation of a stabilising matrix, which therefore allows the aluminium present in aluminium alkoxide to react in a similar way as vegetable-tanned leather re-tanned with aluminium salts.

An acid deteriorated leather sample treated with the combination of aluminium alkoxide and oxazolidine II has shown a reduced hydrophobicity (Figure ~~54c~~) when compared to the sample treated with aluminium alkoxide (Figure ~~54b~~) on its own. This indicates that the increase in hydrothermal stability in this instance may not necessarily be due to the increase in hydrophobicity of the treated leather.

An additional study was carried out where a number of acid deteriorated historic leather samples were treated with the new formulation only to observe the effect on T<sub>s</sub> and pH of a wide range of acid deteriorated historic leathers (Table 7). Although, the new formulation increased the T<sub>s</sub> and pH of majority of the samples, the formulation was however found to be ineffective when applied to a sample with a heavy surface finish or treated with leather dressings. The presence of a heavy surface finish or leather dressing may ~~have hindered~~ the penetration of the formulation through the cross section of the leather.

### 4 ~~Accelerated artificial~~ ageing

The results from the ~~accelerated artificial~~ ageing are shown in Tables 8 and 9, and the average values of all three acid deteriorated leather samples are shown in Tables 10 and 11. The results showed that instead of gradual changes, decreases in pH mostly occurred during the first 3 weeks of ageing and thereafter the rate of pH decline was reduced considerably. It was also interesting to observe that ~~the majority of the none of the~~ acid deteriorated leather samples had a ~~n-pH approximate pH below 2 or above~~, even after accelerated ageing.

#### 4.1 Untreated

It was observed that following the 12 weeks ageing the average shrinkage temperature of the untreated acid deteriorated leather decreased from 54.2°C to 47.7°C. Similarly, the average pH of the untreated leather sample reduced from 2.6 to 2.1.

#### 4.2 Cellugel®

The results show that Cellugel® did not provide the acid-deteriorated historic leather samples with long-term protection when subjected to the accelerated ageing. Among the three leather samples studied, increase in ~~shrinkage temperature~~  $T_s$  was observed in one sample only, when compared to the untreated samples following application of Cellugel® before aging. This was possibly due to the variation in the extent of deterioration rate within the same sample. After 12 weeks of ageing, the average ~~shrinkage temperature~~  $T_s$  of the acid deteriorated leather treated samples with Cellugel® decreased from 57.5°C to 46.6°C and the average pH decreased from 2.5 to 2.1. These were somewhat similar to the values obtained from untreated leather following 12 weeks accelerated ageing.

#### 4.3 Aluminium alkoxide and the new formulation

Both Aluminium alkoxide and the new formulation increased the average  ~~$T_s$  shrinkage temperature~~ of acid deteriorated historic leather from 54.2°C to 69.7°C and 76.5°C respectively. After 12 weeks of artificial ageing the acid deteriorated historic leather samples treated with the new formulation showed a higher  ~~$T_s$  shrinkage temperature~~ when compared with the untreated leather samples and leather samples treated with Cellugel®, and aluminium alkoxide on its own. The average  $T_s$  was 58.1°C whereas the samples treated with aluminium alkoxide only showed an average  $T_s$  of 50.0°C.

The pH of the acid deteriorated historic leather for both untreated and treated samples showed a similar pH of 1.92-2.3 within the first 9 weeks of artificial ageing. After 12 weeks ageing, the pHs of the acid deteriorated historic leather samples were 2.1-2.3, similar to the pHs obtained after 9 weeks artificial ageing.

During this study it was observed that the pH of the aqueous extract of the leathers did not always correlate with the degradation of collagen and hydrothermal stability. For example as shown in Table 7, samples 1, 2, 5, 16 and 17 all had a pH of 2.8, but the hydrothermal stability varied greatly. This confirms the speculation made by Thomson.<sup>13</sup> Florian<sup>11</sup> showed that the pH of leather is not the only indicative measurement of deterioration levels in historic leather. Acid deteriorated historic leather with a higher deterioration level may also show pH values higher than 3.0; this is understood to be due to the release of free ammonia.<sup>13</sup>

#### 4.4 Further ageing trials

Based on the above trial it was hypothesised that in order to allow oxazolidine II to react with vegetable tanned leather, and hence to obtain the optimum increase in ~~shrinkage temperature~~  $T_s$ , the pH of the acid deteriorated leather was required to be around 4. A higher pH may have a de-tanning effect<sup>35</sup> as vegetable tanning agents fixes at a lower pH.<sup>17</sup>

A quick trial was carried out using two acid deteriorated leather samples, where the leather samples were treated with Cellugel®, aluminium alkoxide, and the new formulation. ~~During this trial, Additionally, the area treated with the new formulation was then treated further to raise its pH to approximately 4 (average pH= 4.2)- the samples were treated with the new formulation and allowed to dry, this was followed by a further~~

application of the new formulation to raise the pH to approximately 4. It should be noted here that relatively thinner leather samples (e.g., thickness less than 1mm) may only require one application to raise the pH to approximately 4, however, this may also depend on the initial pH of the acid deteriorated leather subjected to treatment. The samples were then artificially aged for 6 weeks. The results obtained are shown in Tables 12 and 13, and the average results of the two acid deteriorated leather samples are shown in Table 14.

The average ~~shrinkage temperature  $T_s$~~  before ageing was 85.54°C following application of the new formulation with an average increase of pH to 4.2. This shows that a pH of approximately 4 assists in obtaining a higher shrinkage temperature. This also shows that oxazolidine II perhaps played a major role in increasing the ~~shrinkage temperature  $T_s$~~  when acid deteriorated leather samples were treated with the new formulation.

As shown in Tables 8 to 11, the greatest pH decrease in the first ageing trials was observed during the first 3 weeks of accelerated ageing. Similarly, in the second trials as shown in Tables 12-14, the greatest pH decrease was also observed during the first 3 weeks of accelerated ageing. However, the average pH in the second trials after 6 weeks' ageing was 3.1 whereas in the first trials the average pH was 2.6.

Additionally, in the second trials, after 6 weeks' ageing the leather samples treated with the new formulation showed the highest average shrinkage temperature (73.3°C) when compared to average ~~shrinkage temperatures  $T_s$~~  of the untreated leather (59.6°C), Cellugel® (61.7°C) and aluminium alkoxide (63.4°C) samples.

## 5. Visual observations

A change in appearance and firmness may occur due to the application of the new formulation to the acid deteriorated historic leather samples. Visual observations showed that the sample treated with the new formulation darkened when compared to the corresponding untreated samples (Fig. ~~65~~). The samples treated with the new formulation also felt firmer in comparison to the untreated samples. Humidification of the treated object may help to reduce the firmness. However, as always when humidifying historic leather, care must be taken.

## Conclusions

This study showed that although the new formulation consisting of aluminium alkoxide and oxazolidine II may cause a change in firmness and appearance following its application to acid deteriorated historic leather, the formulation does provide acid-buffering and collagen stabilising effects, as the formulation increases the pH and  ~~$T_s$  shrinkage temperature~~. The results obtained also showed that the new formulation was capable of providing long-term protection against an acidic environment created artificially using SO<sub>2</sub> and NO<sub>2</sub>. However, to ensure an optimal reaction between oxazolidine II and the vegetable tanning agent, a pH of approximately 4 is required.

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## **Abstract**

This study was undertaken to develop a product that will potentially delay the progress of deterioration of acid-deteriorated historic leather. Acid deteriorated leather samples were treated with a new formulation consisting of aluminium di(isopropoxide) acetoacetate ester chelate (aluminiumalkoxide) and 5-Ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane (oxazolidine II). The leather samples were also treated with oxazolidine II and aluminium alkoxide separately to compare the effectiveness of these reagents against the new formulation. Untreated leather samples were used as a negative control. Acid deteriorated leather samples treated with Cellugel<sup>®</sup>, aluminium alkoxide and the new formulation along with corresponding untreated leather samples were also subjected to accelerate ageing in order to investigate the longevity of the treated leather. The impact of the treatments and accelerated ageing were determined by measuring the hydrothermal stability of the leather and pH of the aqueous extract. The formulation showed a potential to provide the acid-deteriorated historic leather with long term protection against an artificially-created acidic environment.

### Der Gebrauch von Aluminium Alkoxid und Oxalidin II bei der Behandlung von abgebautem historischem Leder.

Diese Studie wurde unternommen um ein Produkt zu entwickeln, dass das Potential hat den fortlaufenden Zerfall von historischen, sauren Ledern aufzuhalten. Lederproben, die unter sauren Zerfall litten, wurden mit einer neuen Lösung behandelt, die aus Aluminium Diisopropoxid Acetoacetat Ester Chelat (Aluminium Alkoxid) und 5-Ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane (Oxazolidin II) bestand. Die Lederproben wurden auch separat mit Aluminium Alkoxid und Oxazolidin II behandelt, um die Effektivität der Einzelkomponenten gegenüber der neuen Lösungsformel zu differenzieren. Nicht behandelte Proben stellten eine Negativkontrolle dar. Proben von Leder mit saurem Zerfall wurden auch mit Cellugel<sup>®</sup>, Aluminium Alkoxid und der neuen Lösung behandelt und anschließend zusammen mit entsprechenden unbehandelten Proben künstlich gealtert, um die Langlebigkeit des behandelten Leders untersuchen zu können. Die Effekte der Behandlung und des künstlichen Alterns wurden durch Messungen der Temperaturbeständigkeit und durch pH Wert Messung im wässrigen Extrakt ermittelt. Die neue Lösung zeigte Potential zerfallenden, sauren Leder einen Langzeitschutz gegen eine künstlich herbeigeführte saure Umgebung zu gewähren.

### Materials and suppliers

Aluminium alkoxide:

Alfa-Aesar

Shore Road

Port of Heysham Industrial Park

Heysham

LA3 2XY

UK

Cellugel:

Preservation Solutions

33941 Skyline Drive

Golden

Colorado

CO 80403

USA

DSC822° differential scanning calorimeter, SevenMulti pH meter:

Mettler-Toledo

Langacher 44

8606

Greifensee

Switzerland

New formulation:

Leather Conservation Centre

Broughton Green Road

Northampton

NN2 7AN

UK

Oxazolidine II, white spirit:

Sigma-Aldrich

The Old Brickyard

New Road

Gillingham

Dorset

SP8 4XT

UK

Whatman No 1 filter paper:

Fisher Scientific

Bishop Meadow Road

Loughborough

LE11 5RG

UK

## **Biographies**

Anne Lama received her PhD degree from the School of Applied Sciences, University of Northampton, UK. She is currently working at the Institute for Creative Leather Technologies, The University of Northampton, UK and, involved in teaching and research activities. Her research interest includes clean technology and sustainability of the leather manufacturing process, deterioration of leather and historic leather, as well as collagen stabilisation chemistry.

A Paula M Antunes received her PhD degree from the Biochemistry, Microbiology and Biotechnology Department of Rhodes University, South Africa. Paula is now working for the Institute for Creative Leather Technologies, formerly known as the British School of Leather Technology at the University of Northampton, where she is involved in teaching and research activities within the subject of leather. She has published a number of articles in peer-reviewed journals on the subject of leather and associated fields. Her primary research interests focus on collagen, modification and application in biomaterials as well as chemistries and analysis of leather objects.

Anthony Dale Covington initially obtained his PhD from Stirling University, Scotland, and received his Doctor of Science (DSc) degree from the University of Northampton, UK, in 2011. Currently, he is Emeritus Professor of Leather Science at the Institute of Creative Leather Technologies, University of Northampton. He has been involved in leather research for over 30 years, publishing 270 technical articles, covering wide ranging subjects in tanning chemistry and theory, the biochemistry of leather making and clean technology. He is the author of the book *Tanning Chemistry. The Science of Leather*, for which ALCA gave him the 2011 Alsop Award.

Jeffry Guthrie-Strachan obtained a PhD in 2006 from Rhodes University, South Africa. After 11 years in the UK at the University of Northampton's leather division, Jeffry made the move to industry in 2014 to the German leather and paper chemicals supplier, Trumpler. Current activities include product communication and promotion, research and leather sustainability.

Yvette Fletcher has a BA (Hons) in History and Art History and a Masters Degree in Conservation of Historic Objects from De Montfort University (Lincoln). Following a six-month internship at The Leather Conservation Centre (the Centre) in Northampton, she has been working in conservation since 2001. She became a permanent member of the Centre in 2003 and was promoted to Head of Conservation in 2009. In addition to undertaking practical conservation, Yvette carries out training and research in leather conservation.