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# A New Formulation for the Treatment of Acid-Deterioration (Red Rot) in Historic Leathers

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## Abstract

Conservation of acid-deteriorated historic leather (also commonly known as red rot) is an on-going concern as current treatment options are limited. Various products such as aqueous-based buffer salts, imidazole, ammonia vapour and aluminium di(isopropoxide) acetoacetate ester chelate (referred to as aluminium alkoxide in this study) have been used to treat acid-deterioration in historic leathers. Among the various products studied, aluminium alkoxide was found to be the most effective. However the effect of aluminium alkoxide when applied on its own may be limited due to its short-term stabilisation effect. A new formulation consisting of aluminium alkoxide and 5-ethyl-1-aza-3, 7-dioxabicyclo [3.3.0] octane (oxazolidine II) was used to treat acid-deterioration in historic leather. Acid-deteriorated leathers were treated with the new formulation and aged further by exposure to an acidic environment at 40°C and 30% relative humidity for up to 12 weeks. The acidic environment was created using sulfur dioxide and nitrogen dioxide. Corresponding untreated acid-deteriorated historic leathers were used as a negative control. The impact of the treatments and artificial ageing was determined by measuring the hydrothermal stability of the leather samples using differential scanning calorimetry (DSC) and pH of the aqueous extract. The results obtained showed that the formulation has collagen-stabilising properties, acid-buffering capacity as well as the capability to provide long-term protection against an artificially-created acidic environment.

**Keywords:** acid deterioration, historic leather, aluminium alkoxide, oxazolidine II, artificial ageing.

## 1 – Introduction

Acid-deterioration or red rot in leather is observed in vegetable-tanned leather manufactured from the mid-19th Century onward (Hulme *et al.* 1905), on various objects including bookbindings, gilt leather, screens, wall hangings, upholstery and luggage (Figure 1 shows few examples of acid-deteriorated historic leather). Historic leathers suffering from acid-deterioration generally show the following changes.

- Powdery surface, often reddish or brownish, and therefore the deterioration is commonly known as red-rot.
- Grain crack with complete or partial loss of grain structure.
- Low pH, sometimes below 3 (Haines 1980). Lama *et al.*, 2015 determined the pH values of a number of acid-deteriorated historic leather and found that although they varied greatly, the majority of the acid-deteriorated historic leathers exhibited pH <3.

- Low hydrothermal stability. The hydrothermal stability of acid-deteriorated historic leather studied by Lama *et al*. (2015) was within the range 43 - 75°C. However, Larsen (1995) reported that the hydrothermal stability of such leather could be as low as 30°C.
- Due to deterioration the leather may lose firmness.
- The leathers also have a distinct acrid odour.

Figure 1: examples of historic leather artefacts suffering from acid-deterioration (courtesy of Karen Vidler and The Leather Conservation Centre, Northampton, UK).

## 2 – Deterioration of historic leather

A number of factors may be associated with the deterioration of historic leather and are as follows.

- Microbial deterioration: bacteria, mainly *Actinomycetes* spp., and fungi are reported to cause deterioration to historic leather (Strzelczyk *et al*. 1987). Although fungi may not directly attack collagen, it may, however, attack other substances present in leather such as vegetable tannins, non-tannins and fatty substances and eventually may cause deterioration to the leather (Thomson 2006 and 2002).
- Various insects (such as booklice or silverfish) and vertebrates mainly rodents may also cause damage to historic leathers (Thomson 2006).
- Physical deterioration, such as wear and tear to the leather objects as well as physical contortion due to changes in relative humidity contributes to the deterioration of leather objects (Thomson 2006).
- Chemical deterioration, hydrolysis and oxidation, cause breakdown to collagen structure. Both oxidation and hydrolysis are responsible for the deterioration of historic leather (Haines 1977), however, the dominant reaction is often driven by the environmental conditions (Thomson 2006). Oxidation of metal ions due to atmospheric oxygen may also contribute to the deterioration of historic leather. It has been speculated that most of the severe deterioration in leather is caused by acid hydrolysis and therefore the hydrolysis reaction is considered to be the primary cause of acid-deterioration in historic leather (Thomson 2006).

## 3 – Acid-deterioration in historic leather

As acid deterioration in historic leather is predominantly observed in leather manufactured from the 19th-Century onwards; it has been linked to the changes in leather making process as well as environmental impact during that period.

### 3.1. Changes in leather making process

The changes in technology during the 19th-Century have affected the quality of leather production. The demand for leather during that period was increased due to population growth, increase in literacy rate and mechanisation of printing process. Therefore to meet the demand strong infusion of tanning agents were used (Hulme *et al*. 1905) to achieve rapid tanning as opposed to traditional tanning, where hides/skins were first treated with a low astringent tanning bath, gradually increasing the strength of tannin liquor and the process used to take a year (Thomson 2000).

To meet the demand, leathers were also imported from other regions, such as Asia including the Indian sub-continent, Africa, Australia and New Zealand. The materials were often variable and therefore in order to achieve uniformity the vegetable tanning agents were stripped using alkali followed by retanning. This processes may had an impact on the strength of the manufactured leather (Hulme 1905; Thomas *et al*., 1983; Cockerll 1900).

Alternative tanning agents such as larch, mimosa, gambier, myrabolans, hemlock, mangrove instead of traditionally used tanning agent such as sumac leaves, oak bark and nutgalls were used (Thomson 2000; Thomas *et al*. 1983). It has been found that leather tanned with condensed (catechol) tannins is more susceptible to acid-deterioration than the leather tanned with hydrolysable (pyrogallol) tannins (Larsen 1995; Thomas *et al*. 1983). The presence of a higher amount of non-tannins in hydrolysable tannins may provide the leather with some degree of protection against acid-deterioration (Thomas *et al*. 1983).

Additionally, use of acid during making processes was also increased due to introduction of synthetic dyestuff and shaving machines. Synthetic dyestuff, mainly derived from textile industry, required fixing to the leather by reducing pH (Thomas *et al*. 1983; Cockerell 1900). Iron sparks produced by the shaving machine often left blue or black stains on the leather which were generally removed using acids (Thomas *et al*. 1983). Acids and bleaching agents were also used to obtain an even and brighter shade of colour (Calnan, and Haines (eds.) 1992; Cockerell 1900; Hulme 1905; Thomas *et al*. 1983). The increase in the application of acid may have accelerated the acid-hydrolysis causing rapid deterioration to the historic leather.

3.2. Environmental impact:

The rapid industrialisation during the 19th century and use of coal gas were considered as major contributors to the environmental pollutants such as sulfur dioxide ($SO_2$) and nitrogen dioxide ($NO_2$) (Haines 1980). These environmental pollutants convert to acid in the presence of water when absorbed by vegetable-tanned leather as shown below (Haines 1980).

$$SO_2 \rightarrow \text{sulphur trioxide } (SO_3) \rightarrow \text{sulfuric acid } (H_2SO_4).$$

The formation of a hydronium ion ($H_3O^+$) in an acidic environment may cause acid-hydrolysis of the collagen molecule. Atmospheric $NO_2$ can act as free radicals, enhancing oxidation and hence deterioration of historic leathers (Thomson 2006).

## 4 – Treatment for acid-deteriorated historic leather

Various products have been investigated to treat acid-deterioration in historic leather and few examples are given below;

4.1. Consolidants

These products do not usually have any stabilisation property and are usually applied as a surface treatment to protect historic leather. Consolidants such as Pliantex® or Plexisol®, a polyacrylate resin-based product and was introduced by Waterer (1972) (Waterer 1972 a and b). However, the application of such a product is limited due to the limited availability as well as due to the use of organic solvents, such as 1,1,1-trichloroethane and toluene, as diluents. 1,1,1-trichloroethane is hazardous in nature and toluene has potential health impacts to humans. Polymethyl acrylate, an acrylate polymer was investigated by Phillips (1984). The application of the polymer has not been investigated further perhaps due to the similar reasons as Pliantex®/ Plexisol®.

Currently, the most commonly used consolidant is Klucel G® or Cellugel®, a hydroxypropyl cellulose-based product with isopropyl alcohol (IPA) is used as a diluent. A disadvantage of using IPA it may cause damage to the historic leather by solubilising oils and tannins present in leather (Kite and Thomson 2006).

### 4.2. Buffers

Aqueous-based buffer salts, such as sodium citrate, potassium tartrate and lactate have been used to buffer the acidity (European Commission 1996). A disadvantage of using aqueous-based buffer is, deteriorated leathers darken and harden in contact with water due to the movement of salts and water soluble tannins within the leather (Cains and Swifts 1988; Kite and Thomson, 2006; Thomson, 2006). Therefore, imidazole in IPA has been introduced to buffer the acidity (Van Soest *et al*. 1984). Although, buffers, both aqueous and solvent-based, can reduce acidity of acid-deteriorated historic leather, they do not have collagen stabilising properties and therefore unable to provide long-term protection against acid-deterioration (Calnan, 1989).

A study carried out by van Soest *et al*. (1984) showed that ammonia vapour has acid buffering properties and was recommended for leathers with pH < 3. Similar to the aqueous and solvent-based buffer, ammonia also has no collagen stabilising effect. It reduces the acidity by reacting with the acids present within the leather, forming ammonium salts. However, the ammonium salts produced could break down over time producing free ammonia and acids (Jackman 1982). Therefore, similar to the buffers, ammonia may also provide a short-term protection against acid-deterioration (Calnan 1989).

### 4.3. Aluminium di(isopropoxide) acetoacetate ester chelate (referred to as aluminium alkoxide in this study)

Application of aluminium alkoxide to treat acid-deterioration in historic leather was introduced by Calnan (1989). Studies (Calnan 1989; European Commission 1994 and 1996) showed that aluminium alkoxide has collagen stabilising ability and acid buffering properties as it increases hydrothermal stability and pH of acid-deteriorated leather. However, further research also showed that aluminium alkoxide may only provide a short-term stabilisation effect (European Commission, 1996).

Conservation of acid-deteriorated leather therefore is still a concern due to the limited treatment options. This study showed a new formulation consisting of aluminium alkoxide and oxazolidine II has the potential to treat acid-deterioration in historic leather as the product showed both collagen stabilising and acid-buffering properties.

## 5 – Materials and Methods

### 5.1. Materials and Reagents

I. Mimosa-Tanned Leather: Goat skins (Lacto Ltd., UK) were tanned using mimosa extract (Mimosa ME, Mimosa Extract Company Ltd., South Africa) (Lama *et al*. 2011).

II. Acid-Deteriorated Leather: Samples were supplied by various conservators and organisations. The acid-deteriorated historic leather samples were selected based on the visual observation, such as flaky and powdery surface with acrid smell. The pH of these acid-deteriorated historic leathers was within 2.5-3.5.

III. White Spirit: In this study white spirit was used as a diluent. As a non-polar organic solvent, white spirit reduces the probability of solubilising polar components, such as salts and water-soluble tannins in leather. White spirit is considered as a safer solvent option (when used correctly) and has been used in the cleaning of historic leathers (Kite and Thomson, 2006).

IV. Aluminium Alkoxide: Aluminium (Al) di(isopropoxide) acetoacetate ester chelate, 9.6% w/w Al (chemical formula: $C_{12}H_{23}AlO_5$) (Alfa-Aesar, UK) was diluted to 1.5% w/w Al using white spirits.

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

VI. New Formulation: The new formulation consists of aluminium alkoxide and oxazolidine II. The exact formulation cannot be published due to commercial sensitivity.

VII. Cellugel®: Cellugel® (Preservation Solutions, USA) was applied directly to the experimental leather samples without any dilution.

5.2. Methods

I. Application of reagents on Leather Samples: Cellugel®, oxazolidine II, aluminium alkoxide and the new formulation were applied to acid-deteriorated historic leather samples using cotton buds or brush and dried overnight at room temperature before conducting further experiments and analysis. The untreated corresponding acid- deteriorated historic leather samples were used as references.

II. Determination of Thermal Stability: 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 (Chahine 2000; Covington 2009). Differential scanning calorimetry (DSC) (DSC822e, Mettler-Toledo, Switzerland) was used to determine the hydrothermal stability. The samples for thermal analysis were cut into small pieces, soaked in deionised water overnight at 20±2°C to ensure the samples were fully hydrated. The excess water was removed from the samples using Whatman No.1 filter paper prior to analysis.

Samples, 5-10mg (Cucos *et al.* 2014), 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 $T_S$.

III. Determination of pH: The pH of an aqueous extract was determined based on the British Standard BS1309:1974 method. Leather samples, 0.25±0.002g, 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±2°C. The following day the pH of the aqueous extract was then measured using a standard pH meter.

IV. Artificial Ageing: Accelerated ageing was carried out based on the experiments conducted during the STEP leather project (European Commission 1994) and Environment leather projects (European Commission 1996) as well as internal experimental trials carried out within the Leather Conservation Centre (2005). The test was used to estimate the longevity of the studied leather samples. However, the authors would like to stress that the accelerated ageing will not strictly reflect real life scenarios, as historic leather objects are usually not exposed to such acidic conditions and storage of conditions of historic leather artefacts are often variable.

Artificial ageing was carried out by exposing the new mimosa tanned leather and acid-deteriorated historic leather to an acidic environment for 6 to 12 weeks. The acidic environment was created by using 40-80ppm $SO_2$ and 20-40ppm $NO_2$ at 40°C and 30% relative humidity. Figure 2 shows the ageing chamber that was used for artificial ageing trial.

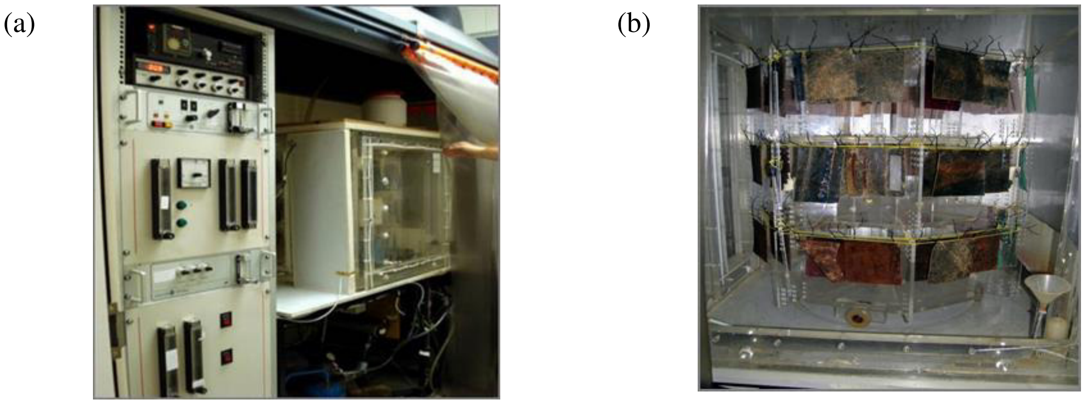

Figure 2: Ageing chamber that was used for the study, a: control panel and b. sample chamber (courtesy of The Leather Conservation Centre, Northampton, UK).

## 6 – Results and Discussion

Vegetable tannins are commonly 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 leathers tanned with hydrolysable tannins (Larsen 1995). Therefore in this study, mimosa (a condensed tannin) was used to tan the leather samples as a standard. Leathers fully tanned with condensed tannins generally exhibit a $T_S$ value of 80-85°C (Covington 2009). Samples of acid-deteriorated historic leather, analysed for the purpose of this research, exhibited a wide range of $T_S$ from 37 to 78°C, indicating the variable and unpredictable nature of the acid-deterioration process of historic leathers. However, some acid-deteriorated historic leather samples analysed in this study also showed undetectable $T_S$. Thermographs of such leathers did not show transition peaks and therefore it was not possible to measure the onset values for these leathers. This is likely to be an indication of high levels of deterioration. Treatment of such leather may not improve its condition due to loss of collagen structure, and therefore were not included in this study.

Figures 3 and 4 show a comparison between the DSC thermographs of a new mimosa tanned leather and acid-deteriorated historic leather samples. The figure shows that the thermographs of new mimosa-tanned leather contain a sharp and compact peak whereas the thermographs of the acid-deteriorated historic leather samples show variable peaks, often shallow and wide as opposed to new leather.

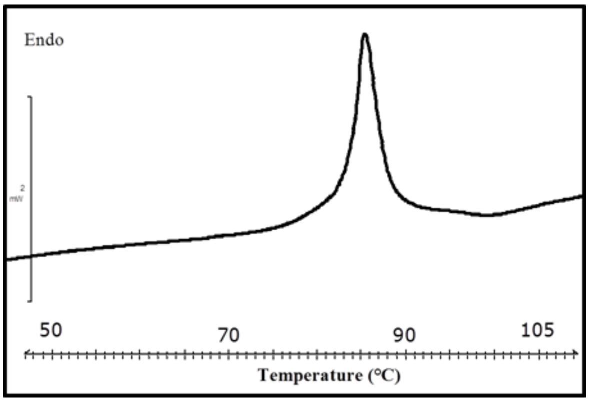

Figure 3: Example of a DSC (Differential Scanning Calorimetry) thermograph of a new-mimosa tanned leather.

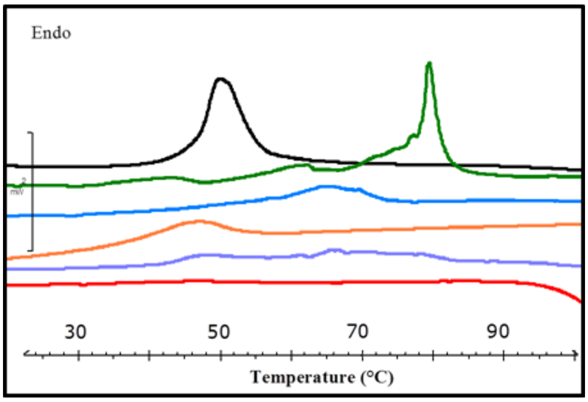

Figure 4: Example of DSC (Differential Scanning Calorimetry) thermographs of acid-deteriorated historic leather samples.

Additionally, the supplied samples were varied in thickness, tanning types, processing and storage conditions as well as treatments that were applied to the leathers. Historic leather and leather objects were often found to be extremely fragile. Due to variable nature of the materials it was extremely difficult to obtain leather samples with uniform properties to conduct the study. There is a possibility that during the treatment some tannins may be removed causing damage to the leather. Supplied leathers may often attach to other materials such as textile, paper and metal, as well as other reagents such as glue may have applied. Therefore, it is also important to consider that any treatments applied to leather should not have any detrimental impact on the materials attached to the leathers.

The study carried out by Lama *et al.* (2015) together with speculation made by Thomson (2006) and Florian (2006) indicated that pH of aqueous extract of the leathers does not always represent or correlate with the degradation of collagen and corresponding hydrothermal stability. In fact, acid-deteriorated historic leather with a higher deterioration level may show a pH >3 (Lama *et al*. 2015; Thomson 2006). This is thought to be due to the hydrolysis of collagenic amino acids releasing free ammonia ($NH_3$) (Thomson, 2006). Nevertheless, pH of aqueous extract can be a useful indication of the acidity of acid-deteriorated historic leather.

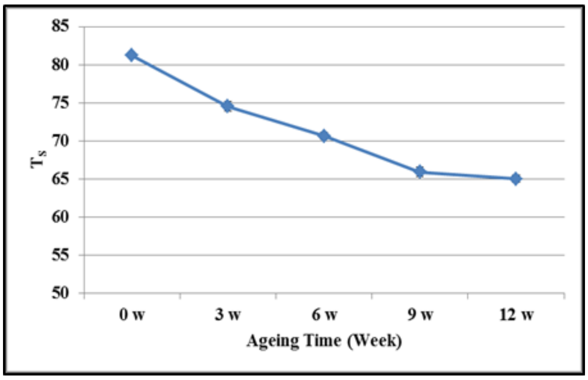

Figure 5: Changes in shrinkage temperature (TS) during 12 weeks artificial ageing of new mimosa-tanned leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity (n=2).

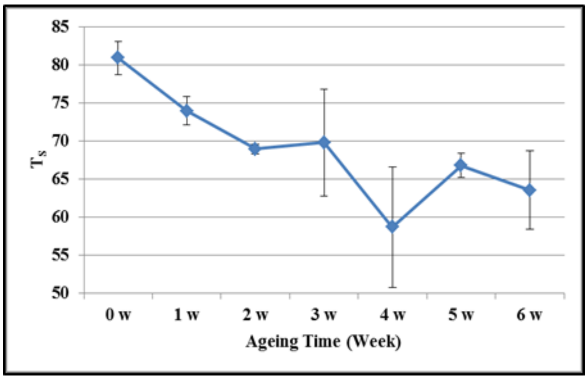

Figure 6: Changes in shrinkage temperature (TS) during 6 weeks artificial ageing of new mimosa-tanned leather subjected to 80ppm $SO_2$ and 40ppm $NO_2$ at 40°C and 30% relative humidity (n=2).

Figures 5 and 6 show the changes in $T_S$ following 12 weeks ageing at lower $SO_2$ and $NO_2$, concentrations and 6 weeks ageing at higher $SO_2$ and $NO_2$ concentrations respectively. The average $T_S$ after 12 weeks ageing at high acid gas concentration was 65.0±0.5°C, which was similar to the average $T_S$ (63.5±5.2°C) following a 6-weeks ageing at lower concentration of $SO_2$ and $NO_2$. However, the results obtained indicated that a gradual change in $T_S$ occurred during the 12 weeks. Therefore the final trial to determine the longevity of the treatment was measured using 12 weeks ageing at 40ppm $SO_2$ and 20ppm $NO_2$.

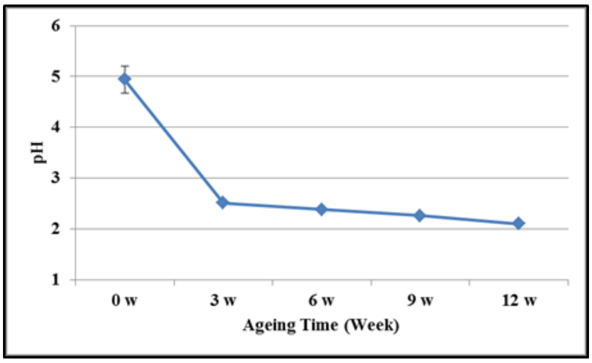

Figure 7: Changes in pH during 12 weeks artificial ageing of new mimosa-tanned leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity.

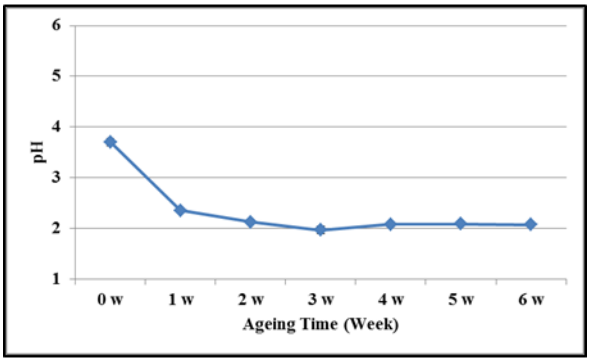

Figure 8: Changes in pH during 6 weeks artificial ageing of new mimosa-tanned leather subjected to 80ppm $SO_2$ and 40ppm $NO_2$ at 40°C and 30% relative humidity.

Figures 7 and 8 show the change in pH during the 12 weeks and 6 weeks artificial ageing respectively. A steep decrease in pH was observed during the initial period of ageing. The pH of aqueous extract was 2.1 following 6 and 12 weeks ageing at a lower and higher $SO_2$ and $NO_2$ gas concentrations.

Oxazolidine II was found to be ineffective for increasing both $T_S$ and pH of acid-deteriorated historic leather (Lama *et al.* 2011 and 2015). Table 1 also shows that aluminium alkoxide increased both $T_S$ and pH of acid-deteriorated historic leather samples when compared to the corresponding untreated samples.

Although, aluminium alkoxide increased both $T_S$ and pH of acid deteriorated historic leather, it is known to have a sort-term effect against acid-deterioration. Studies carried out by Lama *et al.* (2015) demonstrated that the application of aluminium alkoxide increased the hydrophobicity of acid-deteriorated historic leather. Therefore, an increase in hydrothermal stability following the application of the aluminium alkoxide could be due in part to its hydrophobic nature. Hydrothermal stability is found to increase with the decrease in moisture content (Miles *et al.* 2005). Metal alkoxides are susceptible to hydrolysis and chelation can reduce the rate of hydrolysis (Arslan 2010), reflecting the increasing stability of chelated metal alkoxides. However, the process of chelation may not prevent the hydrolysis of alkoxides completely; hence they may provide short-term protection only.

Table 1: Effect on shrinkage ($T_S$) and pH of acid-deteriorated historic leather samples following application of oxazolidine II, aluminium alkoxide (1.5% w/w Al) and the new formulation consisting of aluminium alkoxide and oxazolidine II. An untreated corresponding sample was used as control (Total sample number; n=2) (Lama *et al.* 2011).

| **Sample name** | **$T_S$ (°C)** | **Δ $T_S$** | **pH** | **Δ pH** |
|---|---|---|---|---|
| **Control** | 53.3±4.9 | 0 | 2.9±0.3 | 0.0 |
| **Oxazolidine II** | 50.5±1.5 | -2.8±6.3 | 2.9±0.5 | 0.0 |
| **Aluminium alkoxide** | 75.1±2.9 | 17.2±7.7 | 4.1±0.1 | 1.2±0.4 |
| **LCC formulation** | 79.5±4.8 | 26.2±0.0 | 4.2±0.2 | 4.3±0.6 |

A combination of aluminium alkoxide and oxazolidine II also increased $T_S$ and pH of acid-deteriorated historic leather. Artificial ageing of the treated acid-deteriorated historic leather samples was carried out in order to determine the longevity of the treated leather samples. Untreated corresponding samples were used as a reference sample to compare the changes in $T_S$ and pH during the artificial ageing.

Figure 9 shows an anomaly observed when the $T_S$ of the 6-weeks aged acid-deteriorated leather samples was determined, where the $T_S$ of all the other samples appears to be similar. However, for the remaining samples the highest $T_S$ was shown by the leather samples treated with the new formulation (aluminium alkoxide + oxazolidine II) even after 12 weeks of ageing. Figure 10 shows all the samples (both treated and untreated) exhibit similar trends, when the pH decreased to 3 or below within the first 3 weeks of artificial ageing.

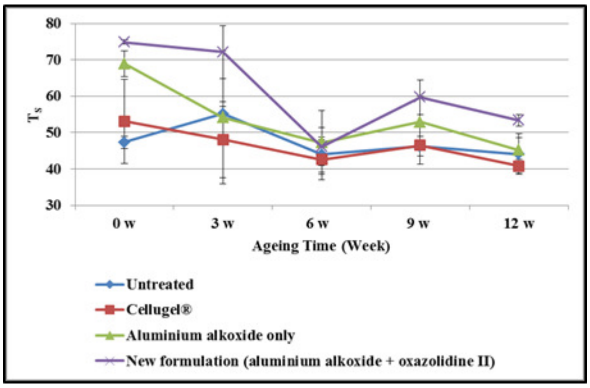

Figure 9: Changes in shrinkage temperature (TS) during 12 weeks artificial ageing of acid-deteriorated historic leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity (n=2)*.

*results shown here were obtained from Lama *et.al.*, 2015

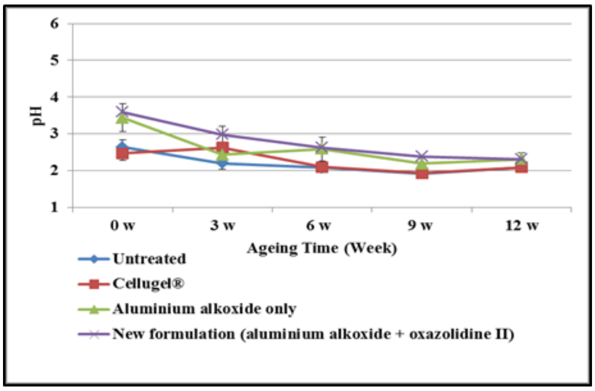

Figure 10: Changes in pH during 12 weeks artificial ageing of artificial ageing of acid-deteriorated historic leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity (n=2)*.

Studies carried out by Lama *et al.* (2015) also showed that if the pH of the acid-deteriorated leather samples is increased to approximately 4.0 a higher increase in $T_S$ and pH stability was observed when compared to the samples with a pH lower than 4.0. Results are shown in Figures 11 and 12. This shows that aluminium alkoxide present in the formulation increased the pH of the acid-deteriorated historic leather, assisting oxazolidine II to interact with vegetable-tanned leather providing a higher buffering and collagen stabilising effect.

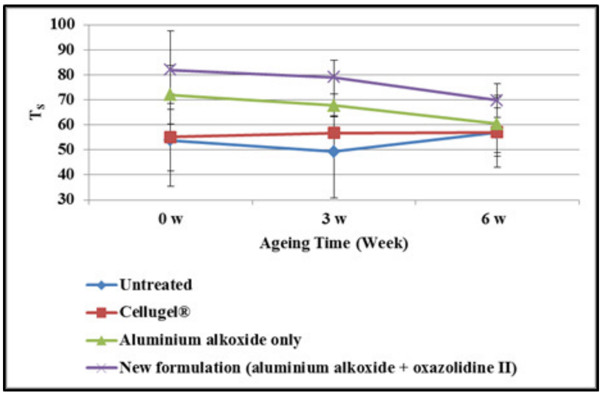

Figure 11: Changes in shrinkage temperature ($T_S$) during 6 weeks artificial ageing of acid-deteriorated historic leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity (n=2) (Lama *et.al.*, 2015).

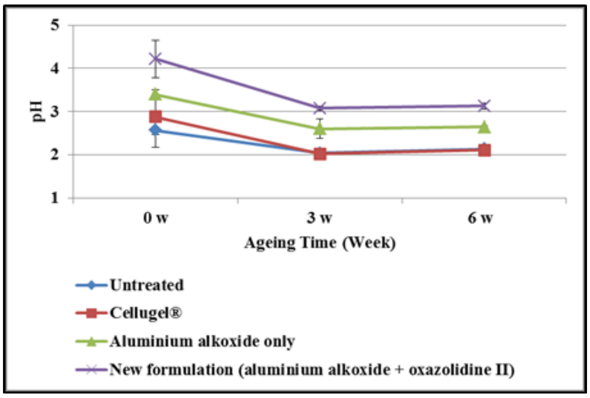

Figure 12: Changes in pH during 6 weeks artificial ageing of artificial ageing of acid-deteriorated historic leather subjected to 40ppm $SO_2$ and 20ppm $NO_2$ at 40°C and 30% relative humidity (n=2) (Lama et.al., 2015).

## 7 – Conclusion

The formulation shows potential to provide acid-deteriorated leather samples with long term protection and therefore may be used as a treatment option for acid-deterioration in leather.

## 8 – Acknowledgement

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