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A treatment to save historic leathers

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Acid deterioration is a major problem in the conservation of historic leathers. Many different techniques have been used in the past to save these valuable items, and some products have merit in consolidating the structure and possibly improving the appearance. None of these approaches have offered the chance to reliably create an improvement in these articles in terms of leather related performance and the offer of improved longevity.

However, following extensive investigations, a new technique has been developed that provides significant collagen stabilising for these deteriorated leathers and acid-buffering effects, measurable as an increase in shrinkage temperature and a reduction in acidity within these leathers.

Acid deterioration in historic leather, commonly known as red-rot, occurs in vegetable-tanned leathers predominantly manufactured from the mid-nineteenth century onward.¹ This has been observed in a variety of leathers such as bookbinding, gilt leather, screens, wall hangings, upholstery and luggage, where a lower pH (~3.0) and lower hydrothermal stability is shown.^{2,3} Visible changes include a powdery surface and a complete or partial loss of the grain layer.⁴

Many research projects²⁻¹⁶ have been conducted over the years that include various consolidants, and acid and collagen stabilising compounds to find a suitable way to conserve these deteriorated leathers.

Aluminium di (isopropoxide acetoacetate ester chelate), referred to as aluminium alkoxide in this paper, was considered to be most effective as studies^{10, 15, 16} showed that an application

increases both the hydrothermal stability and pH of the aqueous extract. However, this may only provide a short-term stabilisation effect¹⁰ and, therefore, conservation of acid deteriorated historic leather is still a concern.

Accordingly, a study was undertaken to develop a product that will increase the longevity of the acid deteriorated historic leather by delaying the deterioration rate.

The effects of different treatment systems

Samples of acid deteriorated historic leathers as provided by various conservators within Europe were selected based on visual appearance where the surface was powdery and flaking. These were treated with a range of products that were considered appropriate:



1) UNTREATED LEATHERS

The untreated samples exhibited a wide range of Ts (shrinkage temperature) from 42-75°C, with a pH range of 2.5 to pH 3.5. This indicates the variable nature of the acid deterioration of the collagen structure.

2) HYDROXYPROPYL CELLULOSE IN ISOPROPYL ALCOHOL

This is generally sold under the trade name of Cellugel. It is generally used as a surface consolidant⁹ and does not provide a collagen stabilising effect.

3) OXAZOLIDINE II

In this study oxazolidine II was found to be ineffective when applied on its own. Among the three samples trialled a negligible increase in Ts was observed in one sample, with the Ts decreasing in the two other samples. On average there was no change in pH. These findings are shown in *Panel 1*.

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.^{17, 18} At pH 7.4 and pH 4.0 oxazolidine II confers a Ts of 82°C and 72°C respectively with a 5% (w/w) oxazolidine II offer.¹⁹

In this situation the reaction of oxazolidine II was perhaps hindered by the low pH of the acid deteriorated leathers. Along with acidity, the nature of the breakdown products due to deterioration may also affect the reaction.

4) ALUMINIUM ALKOXIDE

The results showed that aluminium alkoxide increased the Ts from an average of 52.6 by 20.7°C. This was coupled with an increased pH from pH 3.0 to pH 4.1, an average of pH 1.1. These changes are shown in *Panel 2*.

A previous study carried out by Calnan¹⁵ also showed that aluminium alkoxide increased the hydrothermal stability of vegetable-tanned leather, and this can be seen as an indication of a collagen stabilising ability.

However, it may also be due to the hydrophobic properties of aluminium alkoxide, as the Ts of collagen increases with a decrease in moisture content in the collagen fibres and leather.^{20, 21} This water repellency and prevention of fibre rehydration – the impart of hydrophobic properties – causes an increase in hydrothermal stability.

Research also carried out by Miles et

Panel 1: Effect of aluminium alkoxide on shrinkage temperature (Ts) and pH of acid deteriorated leather samples

Ts			pH		
Control	Oxazolidine II	Av. increase	Control	Oxazolidine II	Av. increase
52.6 +/- 3.7	49.3 +/- 2.4	negligible	3.0 +/- 0.2	3.0 +/- 0.4	negligible

Values +/- average standard deviations

Panel 2: Effect of oxazolidine II on shrinkage temperature (Ts) and pH of acid deteriorated leather samples

Ts			pH		
Control	Aluminium alkoxide	Av. increase	Control	Oxazolidine II	Av. increase
52.6 +/- 3.6	73.3 +/- 3.8	20.7 +/- 5.8	3.0 +/- 0.2	4.1 +/- 0.1	1.1 +/- 0.3

Values +/- average standard deviations

Panel 3: Effect of aluminium alkoxide + oxazolidine II on shrinkage temperature (Ts) and pH of acid deteriorated leather samples

Ts			pH		
Control	Aluminium alkoxide + Oxazolidine II	Av. increase	Control	Aluminium alkoxide + Oxazolidine II	Av. increase
52.6 +/- 3.8	86 +/- 11.7	33.6 +/- 12.9	2.9 +/- 0.2	4.1 +/- 0.2	1.2 +/- 0.4

Values +/- average standard deviations

al.,²¹ showed that crosslinking agents such as glutaraldehyde and hexamethylene di(isocyanate) stabilise collagen by reducing the distance between collagen molecules through dehydration. It has also been reported that aluminium alkoxide may have a short-term stabilising effect against acid deterioration.^{10, 22}

Metal alkoxides are usually prone to hydrolysis, although chelation with various chelating agents is known to reduce the rate of hydrolysis.^{23, 24, 25} This reduction, however, may not prevent the hydrolysis of alkoxides altogether. Accordingly, the increase in Ts and the hydrophobicity of the acid deteriorated leather following the application of a chelated aluminium alkoxide may not be permanent and hence provide only short-term protection.

5) ALUMINIUM ALKOXIDE AND OXAZOLIDINE II COMBINATION (new formulation)

Treatment with a new formulation of aluminium alkoxide and oxazolidine II increased the Ts by an average of 33.6°C. At the same time the pH was increased from an average of pH 2.9 to pH 4.1, an increase of pH 1.2. These changes are shown in *Panel 3*.

The increase in Ts following the application of this combination could be due to the following reasons:

- Oxazolidine II, as shown in *Panel 1*, did not play a role in increasing the pH of the acid deteriorated historic leather samples. The increase in pH following application of the new formulation is therefore due to the presence of aluminium alkoxide, and this confirms that aluminium alkoxide has acid buffering capacity.
- Aluminium alkoxide increased the pH of the acid deteriorated leathers on average from pH 2.9 to 4.1 as shown in *Panel 3*. This increase may assist oxazolidine II to interact with vegetable-tanned leather resulting in the increase in Ts. 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.
- The acid deteriorated leather samples visually show that treatment with the combination of aluminium alkoxide and oxazolidine II provided a reduced hydrophobicity when compared to treatment with aluminium alkoxide 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.


Panel 4: The average values of shrinkage temperature (Ts) and pH of acid deteriorated leather samples

Following applications of Cellugel, aluminium alkoxide and the new formulation containing aluminium alkoxide and oxazolidine II following 3 weeks and 6 weeks accelerated aging

	Ts			pH		
	Not aged	3 weeks aged	6 weeks aged	Not aged	3 weeks aged	6 weeks aged
Control	53.8 +/-18.4	49.3 +/-18.7	56.9 +/-13.9	2.6 +/-0.4	2.0 +/-0.0	2.1 +/-0.1
Cellugel	55.1 +/-13.4	56.7 +/-6.9	57.1 +/-9.8	2.9 +/-0.4	2.0 +/- 0.0	2.1 +/- 0.0
aluminium alkoxide	72.0 +/-11.7	67.8 +/-4.6	60.4 +/-11.4	3.4 +/-0.1	2.6 +/-0.2	2.6 +/-0.0
aluminium alkoxide and oxazolidine II	81.9 +/-15.6	79.1 +/-6.8	69.8 +/-6.7	4.2 +/-0.4	3.1 +/-0.0	3.1 +/-0.1

The effects of accelerated aging

As these improvements in performance were significant, samples of historic leather after the various treatments were subjected to a 12-week accelerated aging to study the longer term effects.

1) UNTREATED LEATHERS

It was observed that the average Ts of the untreated acid deteriorated leather decreased from 54.2°C to 47.7°C. At the same time, the average pH of the leather reduced from pH 2.6 to pH 2.1.

2) HYDROXYPROPYL CELLULOSE IN ISOPROPYL ALCOHOL

This solution (Cellugel) did not provide any long-term protection. An increase in Ts was observed in one sample only when compared to treated samples before aging. However, the average Ts decreased from 57.5°C to 46.6°C and the average pH decreased from 2.5 to 2.1. These were similar to the values obtained from untreated leather following 12 weeks of accelerated aging.

3) OXAZOLIDINE II

Oxazolidine II was not included within these aging trials. The initial treatment showed that oxazolidine II was ineffective in increasing either the shrinkage temperature or pH when applied on its own.

4) ALUMINIUM ALKOXIDE

Treatment with aluminium alkoxide initially increased the average TS from 54.2°C to 69.7°C, but decreased to 50.0°C following 12 weeks accelerated aging.

5) ALUMINIUM ALKOXIDE AND OXAZOLIDINE II COMBINATION

Aluminium alkoxide and oxazolidine II (as the new formulation) increased the average Ts of the samples from 54.2°C to 76.5°C, which decreased to 58.1°C following 12 weeks of accelerated aging. These leathers showed a higher Ts when compared with all

of the other samples. Both untreated and treated samples showed a similar pH of 2.1-2.3 at the end of the studies.

During this particular study it was observed that the pH of the aqueous extract from the leathers did not always correlate with the degradation of collagen and hydrothermal stability. For example, a number of samples had a pH of 2.8, but the Ts ranged between 41.5°C and 62.3°C. This supports the speculation made by Thomson¹³ and Florian¹¹ that the pH of leather is not the only indicative measurement of deterioration levels: leather with a higher deterioration level may also show pH values higher than 3.0, and this is likely due to the release of free ammonia.¹³

Additional aging trials

Based on the findings from the accelerated aging investigations, it was considered that, to obtain the highest increase in Ts, a pH of around 4 was

required to optimise the reaction between oxazolidine II and vegetable tanned leather (a higher pH may have a de-tanning effect²⁶ as vegetable tanning agents fixes at a lower pH.¹⁹). Accordingly, a trial was carried out using two acid deteriorated leather samples which were treated with Cellugel, aluminium alkoxide, and the new formulation.

The samples treated with the new formulation were allowed to dry, and then a second application made to raise the pH to approximately 4. This was followed by accelerated aging for six weeks, and the average results are given in *Panel 4*.

After application of the new formulation and before aging, the average Ts was 81.9°C with an average pH 4.2. This shows that a pH of approximately 4 assists in obtaining a higher shrinkage temperature. This also indicates that oxazolidine II played a major role in increasing the Ts when acid deteriorated leather samples were treated with the new formulation.

Panel 5: The outline application of the different treatment products

Application of reagents: These were applied to the grain side of the acid deteriorated leathers using the same samples wherever possible. Cotton buds were used until the samples were fully saturated, and the excess reagent was absorbed by the filter paper. The treated samples were dried overnight at room temperature before further analysis. The concentrations of the products used were:

- Cellugel undiluted.
- Aluminium alkoxide (Aluminium (Al) di(isopropoxide) acetoacetate ester chelate (C₁₂H₂₃AlO₅): 9.6% w/w Al diluted to 1.5% w/w Al using white spirit).
- Oxazolidine II (Bicyclic oxazolidine (5-ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane) (C₇H₁₃NO₂), 97% w/v).
- New formulation (aluminium alkoxide and Oxazolidine II combination) undiluted.

Determination of hydrothermal stability: Differential scanning calorimetry (DSC) was used to determine the hydrothermal stability of samples taken from the full structure of the leather pieces. Fully hydrated samples were placed in aluminium crucibles and sealed with an aluminium lid. The temperature was ramped up at 5°C per minute from 0°C to 150°C to determine the onset temperature of the denaturation process.

Determination of pH: The pH of an aqueous extract was based on the British Standard BS1309:197427 method.

Accelerated aging: This was conducted by exposing the samples to a concentration of SO₂ (40 ppm) and NO₂ (20 ppm) at 40°C and 30% relative humidity (RH).



Moreover, after six weeks' aging the leather samples treated with the new formulation showed the highest average shrinkage temperature (69.8°C) when compared to average Ts of the untreated leather (56.9°C), Cellugel (57.1°C) and aluminium alkoxide (60.4°C) samples.

In addition, it should be noted that:

- Only one application of the new formulation product may be needed on thin leathers to raise the pH as required, and it will also depend on the initial pH of the leather subjected to treatment.
- A darkening and firming may occur due to the application.
- The treatment is ineffective where the leather has a heavy surface finish or been treated with leather dressings. In this situation it is likely that the penetration of the formulation through the cross section of the leather is hindered.

Findings from the study

This study was undertaken to develop a product to delay the aging process of acid-deteriorated historic leather. The application of a new formulation consisting of aluminium di(isopropoxide) acetoacetate ester chelate (aluminium alkoxide) and 5-Ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane (oxazolidine II) was found to be effective when compared to other reagents. It was found that:

- An application of aluminium alkoxide and oxazolidine II (as the new formulation) provides significant collagen stabilising and acid-buffering effects, shown as an increase in both pH and Ts.
- To ensure an optimal reaction a pH of approximately 4 is required
- Good penetration of the application is required throughout the leather structure.
- The application may cause an increase in firmness of the leathers and a darkening in colour.
- Long term protection was provided against an acidic environment created artificially using SO₂ and NO₂. ☼

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