DETERIORATION IN LEATHER BOOKBINDINGS – OUR PRESENT STATE OF KNOWLEDGE

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It is not the general policy of the British Library Journal to publish articles on the techniques of librarianship or allied subjects. An exception, however, has been made in favour of this important article by a member of the staff of the British Leather Manufacturers' Research Association, since the library of the British Museum was the scene of part of the long-term storage trial discussed here.

DETERIORATION in leather and the mechanism by which deterioration proceeds has been a subject for investigation by the British Leather Manufacturers' Research Association over a number of years.

Leather is widely used, not only for clothing, upholstery, and bookbinding, but in industry for machinery drive belts, hydraulic seals, etc. and each one of this wide variety of end uses imposes a particular set of conditions which can bring about deterioration in the leather.

Several years ago the Research Association was involved with the study of the mechanism by which leather deteriorated under warm, moist conditions and in contact with the chemical constituents of perspiration: conditions imposed on shoe leather. As a result, tannage with glutaraldehyde provided a leather with improved resistance to perspiration.

The covering of books makes somewhat similar demands on the leather as covering furniture, in that the leather needs to mould well to the shape of the object being covered, and it is required to be durable in the face of atmospheric pollutants for a longer period of time than in any other end use. In addition binding leather needs to be able to retain the impression made by tooling and any surface coating applied to the leather should not hinder adhesion of the gold leaf. This limits the type of surface coating that can be applied to the leather surface, and the degree of protection against pollutants that can be absorbed by the leather.

The mechanism of deterioration has proved a fascinating and challenging subject to the leather chemist, but those concerned with the conservation of bindings are faced with the dilemma of medieval bindings remaining in a good state of preservation alongside twentieth-century bindings in an advanced state of deterioration.

This marked disparity between the performance of early and current bindings was causing concern as early as 1850, when the first investigation began and leather rot was associated with sulphur dioxide present in the atmosphere.



Fig. 1. Deteriorated leather bindings

The improvement in the performance of leather from 1930 onwards was brought about largely through the studies made by Faraday Innes of the B.L.M.R.A. in collaboration with the then library of the British Museum. In 1924 Innes began a series of investigations which extended over 10 years. He confirmed that absorption of sulphur dioxide from the atmosphere accelerated decay and rotted leathers were found to contain as much as $5\cdot 0-8\cdot 0$ per cent sulphuric acid.

He was able to show which tannages gave the most durable leathers and which tannages should be avoided. The salts naturally present in vegetable tanning materials increased durability and this in turn led leather manufacturers to incorporate buffer salts in leather intended to be used for bindings.

By 1935 the evidence obtained from the examination of the breakdown products extracted from rotted leathers indicated that the mechanism of leather rot was an oxidative process accelerated by acidity. It was on this evidence that the P.I.R.A. test was based and used as a test for predicting the durability of leather. Confidence in the test was gained when it distinguished between leathers, the tannage of which held a reputation for either good or poor resistance to deterioration. From that stage leathers were sold bearing a stamp to indicate the leather had passed the P.I.R.A. test and a proportion of leathers are so stamped today.

From these studies a long-term storage trial was set up in 1931 to check on the effect of all the factors that were considered at that time to have a bearing on leather decay. Leathers of various tannages were used to bind books which were held at the British Museum Library in the heavily polluted atmosphere of London and another set at the National Library of Wales in a clean atmosphere. The performance of the leather when inspected in 1950 seemed to be supporting many of the conclusions reached by Innes but by 1970 at the end of the test after 35 years storage some of the conclusions were shown to be incorrect, for example the P.I.R.A. test has been shown to be an unreliable guide as to long-term durability.

There is little to guide the purchaser of a binding leather in his selection of a durable leather. Our present state of knowledge is such that we can advise on the tannages that should be used but as yet we have no confirmatory evidence as to the influence on durability of the type of fat, dye, wetting agent, and synthetic tan all of which can be included in modern leathers. It must be remembered that leather technology is constantly changing and new products can be used to obtain a certain desired character in the leather but their influence as far as long-term durability is concerned is not known, unfortunately, so far, as there is little commercial interest in extremely long periods of durability and as the market is so small.

There is no guarantee of durability in purchasing leather from a particular region of the world, which once held a reputation for durable leather, as tanning materials are now being used that are not indigenous to that country, with the consequence that the performance of the leather may well change.

It is this highly unsatisfactory state of affairs that has prompted the proposal for further studies into deterioration in binding leathers.

It may be helpful at this stage to briefly outline the processes involved with converting raw skin into leather. Comparison of modern methods with those used before 1850 may provide clues as to the reason for the durability of the older leathers.

The main bulk of leather is produced from mammalian skins, from cattle, calves, sheep, and goats. Fig. 2a-d shows the structure of these skins. There is the same basic structure consisting of protein fibres – collagen fibres – held in bundles which interweave in a three-dimensional manner. It is this fibrous weave which gives to leather its particular properties. When leather is stretched or folded the fibres are able to move within the weave to adapt to these strains, which is the reason why leather can be moulded so well over different shapes.

The largest fibre bundles are found in the middle of the skin and these become progressively finer as they approach the outer surface. Towards this outer surface the hairs grow in a distinct layer termed the grain layer and within this layer the fibres are extremely fine.

It is appropriate here to point to the weakening effect of paring down or shaving leather. Fig. 3a shows the full thickness of a goat binding leather. This leather 1.4 mm thick tore at 7.5 kg. In shaving this leather to 0.6 mm thick all the coarse fibre bundles have been removed leaving only the grain layer as shown in fig. 3b. This layer is relatively weak tearing at 1.2 kg. The thickness had been reduced by half but the strength by five-sixths.

In young animals the skin is thinner and the constituent fibres smaller in dimension, but the ratio of grain layer to full thickness is the same as in more mature animals – compare fig. 2a and b. Consequently a thinner leather retaining its full thickness is likely to be stronger than a thicker leather shaved down to the required thickness.



Fig. 2. Vertical sections through leather to illustrate the fibre structure in : (a) cattle $\times 20$; (b) calf \times 37; (c) goat \times 37; (d) hair sheep \times 37; (e) pig \times 37

Fig. 3b. Area that had been pared to 0.6 mm thick, 1.2 kg tear load (\times 40)

Fig. 3a. Full thickness goat binding leather $(\times 39)$, 1.4 mm thick, 7.5 kg tear load

The collagen fibres consist of molecules very much longer than they are thick and these molecules lie side by side and overlapping one another. An analogy can be drawn between a textile yarn and a collagen fibre. In a textile yarn the individual fibres of a yarn are arranged parallel to one another and overlap. To prevent the individual fibres of a yarn from slipping over one another when the yarn is stretched the manufacturer imparts a twist. In the collagen fibre the individual molecules are held together by chemical bonds. In the raw skin a limited number of bonds exist, sufficient to hold the fibre in a stable form at room temperature but insufficiently strong to prevent the fibre from shrinking when the temperature rises above $60 \,^\circ C$.

Tanning materials introduce a greater number of stable bonds by chemical linkage with the protein as shown in fig. 4 so as to prevent the protein being broken down by microorganisms and to impart to the leather the properties required by the user.

The increase in stability by this chemical bonding with the tanning material is shown by the higher temperature that can be reached before the fibre shrinks.

However, the raw skin has to pass through a series of cleansing and purifying stages before it is tanned. Firstly the hair and the epidermis covering the outer surface have to be removed to expose the fine surface that gives leather its pleasing appearance. The cavities left in the surface after the removal of the hair are arranged in distinct pattern

Fig. 4. Diagram illustrating the structure of the collagen molecule, and the intra- and intermolecular crosslinks

which is characteristic of each animal type as shown in fig. 5a-e and which can be used for identification purposes.

Before 1850 the hairs and epidermis were either loosened by bacterial action (sweating) or immersing the skins for as long as 2-3 weeks in a suspension of lime. This was sufficient time for the skin to become thoroughly impregnated with particles of lime. After 1850 sodium sulphide became available and its rapid destructive effect on hair has allowed the liming process today to be shortened to a few hours. Apart from removal of hair and epidermis, the lime extracts soluble proteins and other ground substance from the skin, in order to provide clear channels through which the tan can readily penetrate.

In the production of vellums and parchments the skins are held in lime for much longer periods before they are dried stretched out on frames. This material retains considerable quantities of lime throughout its structure as evidenced by its opacity.

Before the skins pass into the tan liquor the alkalinity of the lime liquor needs to be reduced. Before about 1850 this was carried out by weak organic acid such as butyric, acetic, and lactic produced by fermentation of natural tannin infusions. Such acids reach an insufficiently low pH to displace all the calcium from the skin and it is likely that leathers produced at this time would retain quantities of the calcium salts of these acids, valuable with regards to durability because of their buffering action to acid atmospheres. It would be of interest to analyse aged leathers with regards to this specific feature.

At the present time the alkalinity of the skin is reduced firstly with ammonium salts and in many cases further by a sulphuric acid-brine mixture which ensures a sufficiently low pH to displace virtually all the calcium from the skin.

Fig. 5. Surface of leathers showing hair follicle pattern of: (a) cattle; (b) calf; (c) glazed goat; (d) hair sheep; (e) pig (all $\times 11$)

At this stage the skins are immersed in the tan liquor. A wide variety of tanning materials are available for use. Before 1850 alum or extracts from plants and trees known collectively as vegetable tans were used, or even a combination of the two.

Alum tawing which consists of applying alum and salt to the skin is not recognized as a true tannage in that the salts and alum can be washed out of the skin and there is little chemical bonding with the protein as shown by the low shrinkage temperature of this type of leather. The durability of this leather may be in part due to its high salt content.

Vegetable tans differ considerably depending on the tree or plant from which it was extracted, or indeed whether the bark, leaves, or seed pod was used. However, these tans can be classified broadly into two main groups – hydrolysable tannins – so named because they can be hydrolysed by enzymes or acid, to give initially a sugar and phenolic residue and – condensed tannins – based on heterocyclic phenolics which resist such biological breakdown and are converted into more insoluble compounds by acids. The reputation of leathers from different world regions depended on the tanning material obtained from indigenous plants and trees. For example leather produced in Nigeria would have been tanned with extracts from the pods of *Acacia arabica*. This is a tannin mainly of the hydrolysable type.

Sumac widely used in the Mediterranean area and N. Africa is entirely of the hydrolysable type. Various tanning materials are used in India and these can be of either chemical type or a combination of the two. Mimosa, a popular tanning material widely used today, is of the condensed type.

Tan extracts and blends are distributed extensively over the world and today no one particular area can be considered as using exclusively any one particular type of vegetable tanning material.

Vegetable tan extracts contain both tannins and non tans. The latter consist of sugars, salts of various organic acids, and low molecular weight phenols. These salts act as buffer salts and hence the leather content of non tans is of importance with regard to its long-term durability.

After 1850 mineral tanning salts based on chromium sulphate became available. Chromium salts are widely used today and these form co-ordination compounds with the skin protein to form a leather with a shrinkage temperature of 100 °C or above. Today there is the possibility that binding leathers will be tanned firstly with a vegetable tan and then retanned with a mineral salt. Retannage with aluminium sulphate or chloride has produced a more durable leather than retannage with chrome. The mechanism of this is not understood but recent work has indicated that close control of the molar ratio of aluminium and phenolic hydroxyl is important for optimum effect.

The addition of buffer salts such as potassium citrate or lactate should not be added to any leather without knowledge of the tannage given. For example buffer salts will react with chromium removing them from their combination with the skin protein. Consequently these salts should not be indiscriminately applied to chrome tanned, or to leather retanned with chromium. A simple test to check the presence of chromium is to burn a piece of the leather until it glows red. If a green coloured ash forms, chromium salts are present.

Each tanning material imparts different characteristics to the leather. Vegetable tans fill the leather, that is excess tanning material fills the spaces between the fibres and so holds the fibres to the shape to which it has been moulded. This is one reason why vegetable tanned leathers tool well – fig. 6a.

Mineral tannages leave little excess tanning material between the fibres. The leathers have a lower relative density and tend to be springy, failing to hold any impression by the tooling iron – fig. 6b.

Fig. 6. Vertical sections through the tooled region of a binding leather: (a) vegetable tanned leather, some heat damage below the tooled surface, $\times 38$; (b) chrome tanned leather, little retention of tooling, no heat damage, $\times 38$

At the end of the tannage a lubricant has to be applied before the leather is dried in order to maintain the flexibility of the leather. Earlier processes will have used natural fat and greases and natural emulsifiers found in materials such as egg yolk and brains. At the present time fish and animal oils are used but to achieve an emulsion, part of the fat will have been sulphated. Such fats contain no free acid, but no information is available as to their influence, if any, on the long-term durability of the leather. Apart from imparting a soft handle to the leather it is an advantage to have grease in the outer surface layer of the leather, as it has been shown to retard the absorption of sulphur dioxide.

Dyes are generally applied to the leather surface of vegetable tanned leather by padding or spraying. In this way the protective salts – the non tans – are not washed from the leather. Finally, to prevent easy soiling of the grain surface a light casein finish can be applied: this has no adverse effect on the adhesion of gold leaf, as can other finishes such as acrylic resins normally used on leather intended for shoe manufacture.

It is appropriate at this stage to review the performance of the variously tanned leathers which were included in the long-term storage trial which extended over 35 years.

Skins that contained no tanning material at all, that is vellum, parchments, and acetone dehydrated skin showed no sign of deterioration at the end of the storage period nor had

they accumulated significant amounts of sulphuric acid. Chromium tanned leathers were equally resistant.

Of the vegetable tanned leathers those tanned with Sumac showed little decay. Leathers tanned with hydrolysable type of tannins were more resistant than those tanned with condensed tannins. The latter had generally reached an advanced stage of deterioration after 20 years storage in the polluted atmosphere of London. The generally better performance of untanned and chrome tanned material indicates that some vegetable tans play a definite and positive role in the degradation process.

Mechanism of Deterioration

The mechanism by which deterioration proceeds is not fully known although the influence of certain factors has been well established.

For example it is well established that sulphur dioxide in the atmosphere contributes towards leather rot. Sulphur dioxide oxidizes to sulphur trioxide, providing a source of sulphuric acid. The catalytic role of metal contaminants of the leather in the oxidation of sulphur dioxide is open to question since workers at Harwell have shown that sulphur dioxide once it is absorbed on a surface will be oxidized to trioxide within two weeks in the absence of metals. Consequently the beneficial effect of applying sodium pyrophosphate to the leather is also open to question. The benefit, originally demonstrated by the P.I.R.A. test, may well have been derived from the buffering action of the salt rather than its sequestering action on the metal contaminants.

Deterioration appears to depend on acid conditions within the leather. At the end of the long-term storage trial the sound leathers were at a pH greater than $2\cdot 8$ and rotted leathers at a pH of $2\cdot 5$ or below.

Consequently it is essential that a binding leather should at the outset have a pH above 3.5. The inclusion of buffer salts will serve to maintain this pH level. The long-term storage trial clearly demonstrated the protective action obtained by adding buffer salts such as potassium citrate or lactate to vegetable tanned leather.

Hydrolytic breakdown of the peptide linkage in the collagen molecule occurs in the following way:

The rate of hydrolytic degradation is highly dependent on pH as shown by the graph in fig. 7. Below pH 3.0 the rate of degradation rapidly increases. It is also dependent on the relative humidity – fig. 7. However, at the low relative humidity of 60 per cent or less generally found in libraries, hydrolytic degradation is slow.

There is another mechanism by which the peptide linkages in the collagen molecule can be attacked – this by oxidation which occurs in the following manner:

The breakdown products extracted from the rotted leathers of the long-term storage trial point to this being the main mechanism of deterioration.

Although absorption of sulphur dioxide from the atmosphere and the acidity of the leather has been shown to be related to deterioration in binding leathers, other pullutants may well be essential to the mechanism of breakdown but they have never been studied in any depth.

Sulphur dioxide and oxides of nitrogen form the greatest proportion of atmospheric pollutants, but in the presence of sunlight, oxides of nitrogen and hydrocarbon react to form new products such as ozone, nitrogen dioxide, and peroxyacetyl nitrate all of which could be involved in the oxidative degradation of the protein.

The P.I.R.A. test as developed by Innes aimed at bringing about oxidative degradation in the leather, by applying acid and then peroxide to the leather. Unfortunately at the completion of the long-term storage trial the P.I.R.A. test has been shown to be an unreliable guide as to the durability of leather, certainly over a period of 35 years or more.

At the present time there is no reliable accelerated laboratory test by which the durability of binding leather can be evaluated. A form of gas chamber test would seem to be the most promising but test conditions have not been standardized.

It is highly unsatisfactory that at the present time the information available on which advice can be given relating to the production or purchase of durable binding leather must be highly qualified.

The most appropriate immediate action would seem to be that binding leathers should carry information concerning the tanning materials used in its preparation to serve as a guide to the purchaser.

However, far more work needs to be done and for this reason a new research programme has been prepared. It consists of three parts:

1. Shorter-Term Projects.

These projects have the aim of obtaining information, which though limited, can be of practical value in a relatively short period of time of one to two years. These are to be:

- (a) the modification of mineral tanned leathers with a view to imparting those properties required by bookbinders
- (b) methods of conservation
- (c) accelerated laboratory tests
- (d) bookbinding practices.
- 2. Longer-Term Project the mechanism of deterioration.

3. Confirmatory Project - a further long-term storage trial.

The work of the B.L.M.R.A. is supported financially by the leather manufacturers of the U.K. but the market for quality bookbinding material is too small to justify the expenditure of research funds to the extent to which this programme requires. For this reason the programme has been presented to organizations interested in obtaining and using a durable binding leather, such as the National Libraries of Europe, N. America, and Australia. They have been invited to participate on a multiclient basis in order to finance this research programme. Copyright of British Library Journal is the property of British Library Board 96. The copyright in an individual article may be maintained by the author in certain cases. Content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.