THE PRESERVATION OF LEATHER BOOKBINDINGS

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H. J. PLENDERLEITH

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PREFACE

The present communication is designed to take the place of the pamphlet issued by the Trustees entitled *British Museum Leather Dressing for Library Use*, now out of print. As the treatment of leather that has already deteriorated will always remain an important problem for the librarian and book-collector, the essence of the previous communication will be found in its successor; but in bringing the subject up to date it has been found necessary, in the light of modern research, to cover a wider field and deal with the causes and prevention of deterioration of binding leathers.

That this is possible is entirely due to the results of investigations initiated by the British Leather Manufacturers' Association and published as interim reports of a representative Bookbinding Leather Committee. Acknowledgement is due in particular to Mr. R. Faraday Innes, F.R.I.C., of the Research Association. His discoveries in regard to the mechanism and prevention of decay have provided data for the solution of

library problems which have defied interpretation for years. He has established a simple condition under which vegetable tanned leather remains permanently free from chemical decay even when containing sulphuric acid and, what is more, the leading manufacturers are prepared, if invited, to supply leather stamped as guaranteed to comply with this condition. But how long it will take before all bookbinding leather is protected against deterioration as a matter of course will depend on the publicity given to the work, and the present author is glad to take this opportunity of making a contribution towards such a worthy end.

Thanks are due to Mr. Innes for reading the proofs.

H. J. PLENDERLEITH

BRITISH MUSEUM RESEARCH LABORATORY

LIBRARY PROBLEMS: THE SEEMINGLY HAPHAZARD DETERIORATION OF MODERN LEATHERS

The suitability of leather as a medium for bookbinding has been called in question of recent years on account of the surprisingly short life of modern leathers as compared with those of a generation or more ago. The problem is conveniently studied in any long run of leather-bound periodicals where dates can be correlated with bindings. In book covers which are comparable, i.e. where the leather skins are matched as to type of skin, tannage, type of dye-stuff and method of binding and where books can be assumed to have been given the same amount of usage, the date of any one volume is seen to be of little significance as regards its state of preservation. Age may account for physical wear and tear, but bears little relation to the apparent dryness and cracking that result from chemical disintegration. In the Newspaper Library of the British Museum, for example, heavy leather-bound volumes of *The Times* newspaper dated 1846 are still

serviceable; the leather is frayed around the edges and along the hinges (as is only to be expected after 100 years wear) exposing a tough fibrous understructure, but this shows nothing of the powdery decay of many volumes later in the series which are by comparison modern. Another striking illustration is found in the *General Catalogue of Printed Books at the British Museum* ('G.K.I.'). These volumes, bound in straight grain morocco, are subject to heavy use, and we find bindings of over fifty years of age which are badly worn but still serviceable occupying the same shelves as others of about fifteen years of age which already require repair; some have actually had to be rebound. Again, most large libraries can produce examples to illustrate the 'law calf' problem where a run of calf bindings appears suddenly to deteriorate about 1881 and for the next ten years or so the leather is even more than usually rotten, it being customary to tie these volumes up with string in order to prevent the loss of backs and titles. These and similar phenomena are a commonplace to the librarian.

Modern leathers chosen with the greatest

care in consultation with the binders or with the manufacturers yet seem liable to disintegrate in the course of a few years. Confidence has been shaken and now buckram is often chosen for bookbinding instead of leather, the inference being that the manufacture of durable leather for binding purposes is a lost art. Attempts are made to conserve leather bindings by the application of dressings, known to be of value in the saddle and boot and shoe trades and therefore, presumably, good for books; and there is the additional argument for the value of fatty applications to leather in that leather bindings which are often handled appear to last better than those which are not regularly greased. These views, which are very widely held, require modification in the light of recent discovery.

SCIENTIFIC INVESTIGATION: CAUSES AND PREVENTION OF DECAY

Vegetable tanned leather is used for bookbinding and this, exclusively, is the material

to be considered. Deterioration occurs in two forms:

(1) physical wear and tear—the skins of different animals vary in their resistance to abrasion, &c., and

(2) chemical decay which attacks leather whatever the source of the skin.

Chemical decay of bookbindings takes the form of cracking to be noticed in the early stages on the hinges of the book at the top inside (see Plates 1 and 2). As deterioration advances the cracks spread and open; the underlying tissue gradually loses its resiliency and disintegrates to a red or brownish powder, and in a few years the whole of the back of the book may become detached. The edges of the binding are easily abraded with the finger-nail even in the early stages. It is only to be expected that with the advance of chemical decay physical resistance will be impaired and disintegration accelerated.

It has long been known that sulphuric acid is present in badly decayed leather. Gas burners were rightly blamed for much of the damage of a previous age. The atmosphere

of industrial towns was rightly believed to be more liable to cause damage than the purer air of the country, by reason of its much higher content of sulphur gases. Sulphuric acid was regarded as the arch enemy of leather bindings.[1] Leathers were sold and purchased as 'guaranteed free from sulphuric acid'. What was not appreciated, and has only been discovered comparatively recently,[2] is (1) that all vegetable tanned leathers have the property of absorbing sulphur dioxide from the atmosphere—a gradual and cumulative reaction which results in their eventually containing sulphuric acid whether originally present or not, and (2) that even undecayed leather may contain and, indeed, on ageing will certainly contain enough sulphuric acid to cause rotting. It is no safeguard, therefore,

[1] *Report of the Committee of the Society of Arts on Leather for Bookbinding*, George Bell & Sons, 1905.

[2] *The Causes and Prevention of the Decay of Bookbinding Leather*, Interim Reports of the Bookbinding Leather Committee; issued by the Printing Industry Research Association and British Leather Manufacturers' Research Association 1933 and 1936. See also Innes, R. F., *Library Association Record* 1934, p. 393.

much less a solution of the problem, to use only leather which is guaranteed free from sulphuric acid as it will assuredly absorb this acid in time.

These advances in our knowledge of the disintegration of leather bookbindings have been made as a result of an investigation by the British Leather Manufacturers' Research Association carried out by Mr. R. Faraday Innes, F.R.I.C. Having established that old and durable bindings actually contain sulphuric acid, he developed in the laboratory a simple form of chemically treating leather so as to accelerate artificially the decay to which all leathers are subject, namely rotting by oxygen in the presence of sulphuric acid. Old and durable bindings were found to withstand this so-called 'P.I.R.A.' test, but when the same leather was washed in running water before its examination it would no longer withstand the test. Obviously a protective agent had been removed in the washing process, identified as the 'natural water-soluble non-tans'. This observation was confirmed by the discovery that when unprotected leather was treated by soaking it for a time in the aqueous washings it was

then able to withstand the 'P.I.R.A.' accelerated decay test and remained unchanged in appearance.

These observations serve in large measure to explain the apparently haphazard deterioration of bookbinding leathers. The old durable leathers which are still in good condition to-day retain their protective non-tans; but of recent years the desire to attain uniformity of finish has led manufacturers to wash the skins prior to dyeing, the non-tans have been eliminated and thus durability has been sacrificed to appearance. In the case of the early and durable moroccos of 'G.K.I.' already referred to, these were coloured, no doubt, by a staining process and retain their natural protective ingredients, whereas the more recent unsatisfactory bindings were 'drum-dyed' and this immersion process removes natural protection. The law calf problem has perhaps not yet been fully explained, but this much is certain, that about 1881 the vogue for very light calf bindings induced the manufacturers to use strong sulphite bleaching liquors—not necessarily an evil practice, had they made an adequate addition thereafter of a protective

agent, but of course the facts were at that time unknown and unsuspected. The later improvements to be noted about 1890 are probably connected with some rule-of-thumb variation in technique whereby a measure of protection was inadvertently afforded.

It was found that certain salts control the acidity of the leather within narrow limits and the next step was to try the effect of some of these in various dilutions. The results were striking; a very high degree of protection was afforded to the leather, as shown by the P.I.R.A. test. For the protection of leather there would seem to be no special virtue in selecting the natural non-tans, which must vary in composition and effectiveness, in preference to a standard solution of a suitable salt. Using a salt of proved efficiency the protection afforded to leather is likely to be more certain and complete. It was established in the long run that leather is adequately protected when it is treated with a 7 per cent. aqueous solution of potassium lactate (Plate 3). This is all that is required in order to confer durability and ensure that it will survive the P.I.R.A. test

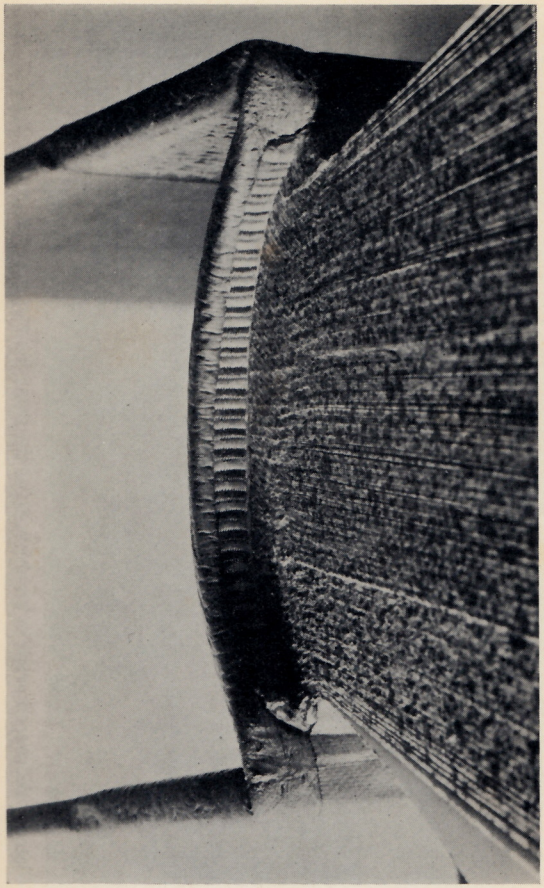

Plate 1 First signs of chemical decay in a recently bound book: cracks in top of hinge, inside

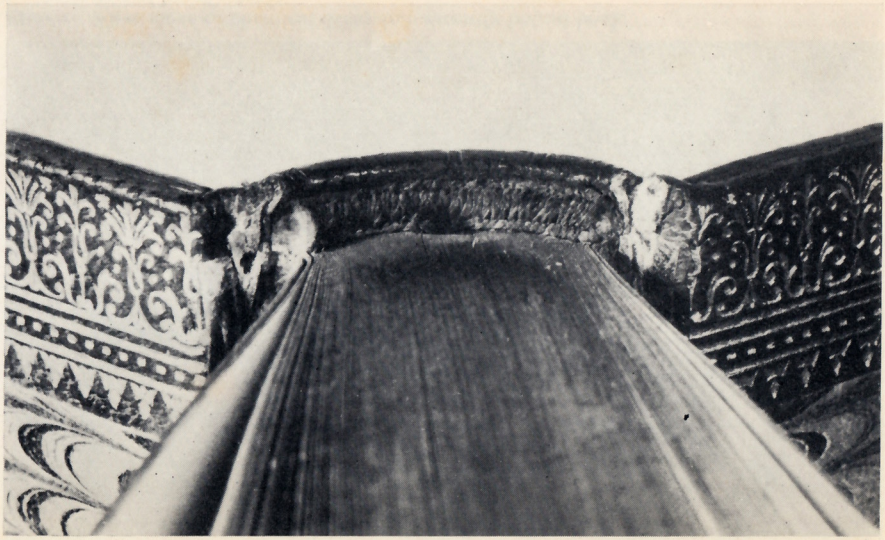

Plate 2 Advanced stage in an old book of the same kind of decay shown in plate 1

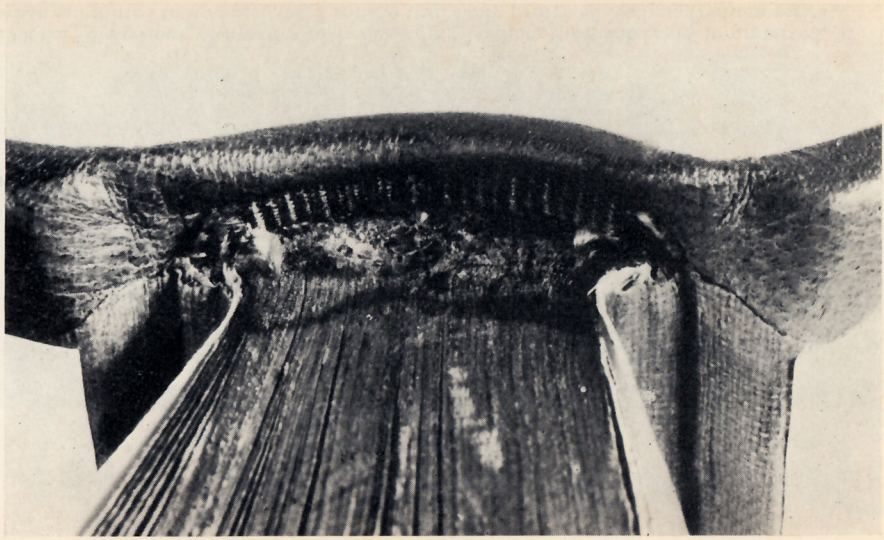

Plate 3 A 'protected' leather strained, but not cracked after ten years.
No indication of deterioration

THE P.I.R.A. TEST FOR DURABLE LEATHER

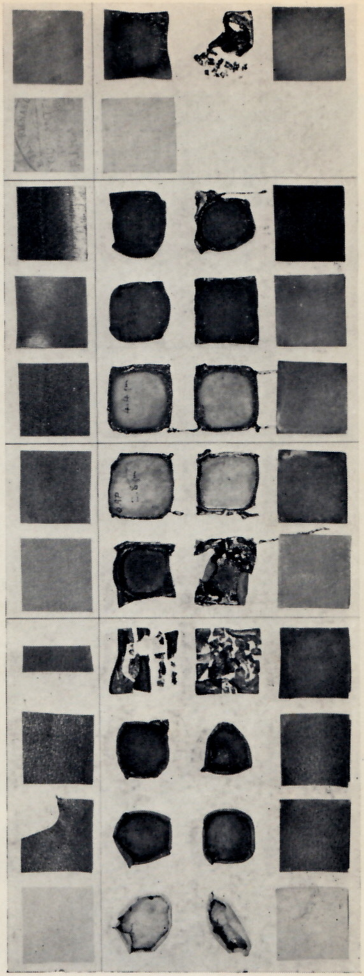

Plate 4 Behaviour of a series of bookbinding leathers, protected and unprotected, when submitted to an accelerated rotting test. Only protected leathers (bottom series and No. 10) survive

unchanged in appearance. Under the same test leathers that are not protected warp, crack, shrink, and many actually become powdery and pinholed in the course of a few days.

In order to study these results the P.I.R.A. test was applied to a series of binding leathers in the British Museum Research Laboratory. Plate 4 shows the results of testing which completely confirm Mr. Innes's findings. A brief description follows.

Eleven different leathers of apparently good quality (shown in the first horizontal line marked Controls) were set aside for comparative purposes. Three samples of each were taken. The P.I.R.A. test was applied to the unwashed series and the result affords information as to the durability of the leather in question. Only No. 10 has survived, completely unscathed. It is a commercially protected leather of the type recommended, and is stamped 'Protected'. No. 11 is a Niger and is obviously superior in durability to any of the others and this is because it retains enough of the natural protective non-tans (which in the native method of manufacture are not completely removed) to afford pro-

tection. Before applying the test to the third row of leathers they were washed, individually, in running water to eliminate any protective agent that might be present; the result of testing these completely unprotected leathers is nearly the same as before only that Niger has now succumbed. The fourth series, before testing, was protected by rubbing each sample with a 7 per cent. aqueous solution of potassium lactate. All leathers now survive the severe conditions of the test which before caused such obvious and complete disintegration, and they are unchanged in appearance. By this simple means impermanent leather is made durable.

Since the original publication of the results (*loc. cit.*), independent corroboration of the protective salt theory has been made by American workers[1] using different methods of artificially hastening and assessing the amount of rotting. For convenience of application and reliability, however, the P.I.R.A. test seems to be adequate and it can easily be carried out within ten days by

[1] Frey and Beebe (*Journal of the American Leather Chemists' Association*, 1934, p. 528, and 1935, p. 459).

anyone even with limited facilities. It has been used both in determining the best salts to use for protective purposes and as a ready means of testing as to whether bookbinding leather is adequately protected. The leading leather manufacturers in this country have now agreed to supply, on demand, leather stamped as 'Guaranteed to resist the P.I.R.A. test'. Only leather so stamped can be relied upon for binding purposes because, as distinct from most other uses to which leather is put, leather bindings are intended to last indefinitely.

THE P.I.R.A. TEST FOR DURABLE LEATHER[1]

A piece of the leather, $2\frac{1}{2}$ inches square and weighing from 2 to 5 gm., is taken and placed on a glass plate and evenly treated on the flesh side with a normal solution of sulphuric acid[2] in the proportion of 1 c.c. of acid per

[1] Second (interim) Report. *loc. cit.*, 1936, Appendix 1.

[2] A normal solution of sulphuric acid is made by dissolving $\frac{1}{2}$ fluid ounce of oil of vitriol in 1 pint of water. The mixing must be carried out

gramme of air-dry leather. This proportion is just enough to damp the leather (moisture content now about 65 per cent.) and to give it when air-dried a sulphuric acid content of 5 per cent. The leather is allowed to dry at ordinary temperature. Hydrogen peroxide (10 volumes strength) is now evenly added on the flesh side by drops in the proportion of 0·6 c.c. per gramme of leather. In the case of very thin leathers (weighing, say, 2 gm. or less) this proportion of hydrogen peroxide is not enough to damp the whole square evenly, and the amount is increased to 1 c.c. per gramme of leather. The damp piece is

with caution. The oil of vitriol should be added drop by drop to the water with thorough shaking. *In no circumstances must the water be added to the oil of vitriol.*

Solutions of hydrogen peroxide are unstable and if stored for any length of time decompose. The peroxide should therefore be purchased in small quantities and used freshly. It should be kept in the dark in a cool room.

Normal sulphuric acid and 10 volumes strength hydrogen peroxide can be purchased from any pharmaceutical chemist at low cost. A fountain-pen filler is a convenient means of applying the liquids to the leather.

allowed to dry by leaving for 24 hours; it is then given five further daily doses of hydrogen peroxide. At the end of the 7 days the piece is inspected and its properties compared with the untreated leather.

Durable leathers are completely unaffected (except for some possible fading of the dyestuff); they are not darkened in any way, are perfectly supple and do not crack on bending. Unsatisfactory leather may crack on bending, may be blackened and gelatinized especially round the edges, and in very bad cases the leather may, in addition, be eaten into holes.[1]

THE TIME TEST

When all is said and done there still remains the one vital test which will decide the matter, the test of time, and in order to provide material for study in this connexion, the British Leather Manufacturers' Research

[1] These results are valid at room temperatures, under conditions of 60-80 per cent. Relative Humidity.

Association in 1932 collected together a series of representative leathers used in bookbinding. These were supplied for the binding of books which were exposed on the shelves of the British Museum Library and the National Library of Wales, Aberystwyth, which has a duplicate set. The idea was to provide material of known composition for a long term test. There were leathers from different animals, of various tannages and protected by certain selected salts. Some of the leathers were degreased, some treated with leather-dressings, &c., and in all such cases control volumes were prepared, bound in untreated leather and placed with the series. The pure atmosphere of Aberystwyth was selected as a contrast to conditions in London. Each library now contains several hundred books in the test series and all bindings are dated.

While it is obviously too soon to draw conclusions, this much can be stated from an unbiased examination of the volumes in London, that in fifteen years or less certain unprotected leathers are already showing initial signs of chemical deterioration (Plate 1) and leathers which are artificially protected

show no sign of deterioration. This is in accordance with anticipation, but the value of the evidence will be enhanced as time passes and the decay becomes more pronounced.

LIMITED USEFULNESS OF LEATHER DRESSINGS

The observation that leather gradually absorbs sulphur dioxide from the atmosphere is based on chemical analysis. It might reasonably be assumed that if means were taken to seal the surface of the leather this noxious gas would be excluded and stability assured. Of the various leather finishes examined by Mr. Innes a certain shellac preparation was found to be most effective in this respect and cellulose was high on the list; and both are in a measure protective as long as the film does not crack, but it would be very difficult to prevent this along the hinges. Aqueous preparations of oils and greases, however, were found to be almost entirely non-effective, and as most dressings come within this category they cannot claim to

afford any protection in the sense of arresting chemical decay. The main claim for leather dressings is that they 'feed' the skin, acting as a lubricant for the fibrous tissue, preventing it from drying up and cracking. Let us examine this claim a little more closely.

Those having the care of books are accustomed to refer to the powdery decay as a 'drying up' whereas leather in such a condition can be shown by analysis to contain its usual quota of water. The phenomenon is one that no grease can prevent. The lubricating effect is entirely unrelated to powdery disintegration. Such things as Turkey Red Oil, Castor or Neats' Foot Oil make leather 'supple', a desirable quality in moving parts of saddlery, belting, &c., and occasional treatment with a little good dressing of suitable quality cannot harm the hinges of a book and will be advantageous. But the treatment thus given is for the lesser evil only, namely wear and tear.

Chemical tests applied to bindings which have been much handled have shown that if the hinges appear in better condition than those of books not frequently consulted, the

appearance of durability is illusory: the backs are found to contain substantially as much sulphuric acid as is normally the case and, as usual, the backs always contain more acid than the sides which are protected from free access of air by the juxtaposition of adjacent books on the shelving. Frequent opening and shutting of a book bound in unprotected leather might be expected in time to cause micro-cracking of the hinges, whereas a book that has not been opened until deterioration is in an advanced stage may well split when the hardened leather is suddenly subjected to flexure through a right angle or more. It is a moot point as to whether a leather dressing would prevent this. Some artificially degreased leather bindings prove to be remarkably sound after thirteen years of neglect! The only conclusion that can be reached at present is that while from the purely physical point of view the application of leather dressing to bookbindings serves a useful purpose in keeping hinges supple and preventing major cracking, it is entirely without influence on the microscopic disintegration of the tissue which determines the life of the leather. The dressing employed in

the British Museum[1] is merely a lanolin lubricant to which has been added enough wax to consolidate superficial powdery decay, and in the latter respect, particularly, it has proved its value, enabling the rebinding of books to be deferred for several years longer than would otherwise be the case.

CHARACTERISTICS OF PROTECTED LEATHER: CLEANING LEATHER BINDINGS WHETHER PROTECTED OR UNPROTECTED

It remains to be considered whether protected leather differs in any way from other leathers as regards working qualities.

[1] *British Museum Leather Dressing*. Obtainable from Messrs. Hopkin & Williams Ltd., Freshwater Road, Chadwell Heath, Essex.

Composition:

Lanolin (anhydrous) . .	7 oz. (avoir.)
Cedarwood oil . . .	1 oz. (fluid)
Beeswax	½ oz. (avoir.)
Hexane (or petroleum ether B.P. 60°-80° C.) .	11 oz. (fluid)

The mixture is inflammable and no naked light must be allowed in the room during application of the dressing and for some time afterwards.

In choosing a protective salt it has to be borne in mind that of those available for use, some might affect the gilt lettering of books; others tend to form a white cloudiness in the leather. Potassium lactate has been advocated as free from criticism in either respect and, when used in the strength recommended, it is actually impossible by mere inspection to tell whether it is present or not. In other words, leather protected by potassium lactate looks and feels quite normal. It is true that an undue excess of lactate would make the leather feel sticky—the salt is hygroscopic—and there might even be a danger of mildewing, but with ordinary care such a state of affairs could not occur.

As regards the maintenance of protected leather the chief consideration is that the protective salt is very soluble in water and if this leather is washed with water (as advocated for cleaning in the *British Museum Leather Dressing* pamphlet, see Preface) the salt will be partially washed out and a measure of protection lost. This may not be immediately serious, but in a large library it is necessary in the interests of hygiene to clean certain bindings, if at rare intervals,

and the cumulative loss of salts on repeated washing could not be ignored. For this reason it is essential to restore protective salts to the leather after washing. It may sometimes be possible to use a soapy solution of 7 per cent. potassium lactate[1] as the cleansing agent, but generally when bindings are so dirty as to require cleaning it is necessary to scrub them with soap and water. Books so treated should be opened and allowed to remain for a day standing on end to dry and then they should be carefully sponged with protective solution. After the lapse of twenty-four hours a little of the British Museum Leather Dressing is rubbed into the surface. Two days later the binding may be polished and the book returned to the shelves.

A bulk supply (10 gal.) of 7 per cent. potassium lactate may be kept in stock and syphoned into Winchester Quart bottles as required. Bindings must obviously be quite

[1] Potassium lactate 50 per cent. (w/w) supplied by British Drug Houses Ltd., Graham Street, City Road, N.1. A 7 per cent. solution (w/v) is prepared by adding 1 vol. of stock solution to 9 vols. of water. Paranitrophenol (0·25%) may be dissolved in the solution as a protection against mould growth.

dry when the protective solution is applied otherwise the final concentration of salt in the leather will be insufficient to afford the requisite degree of protection.

CAN UNPROTECTED LEATHER BINDINGS BE PROTECTED?

It is natural to inquire whether leather-bound volumes which do not already show signs of decay may still be treated with salts in order to prevent deterioration. The answer is that protective treatment may be worth while if the leather is still sound. It can be applied in the washing process. But its efficacy will depend primarily on the state of the leather: it will depend also on the finish of the surface. Where book varnish is present the surface will not be uniformly penetrated and the result will be uncertain. As the varnish is in a measure protective there would be no advantage in attempting to remove it, especially as the use of a solvent for this purpose would be likely to affect the tannage.

When chemical deterioration has once set in, it cannot be cured or even satisfactorily

arrested by belated treatment with lactate. In such cases the best course is to apply the British Museum Leather Dressing, which will soften the tissue and prevent the powdery surface from spreading.

VELLUM BINDINGS

The above remarks on the decay of leather do not apply to vellum, as vellum does not absorb sulphuric acid. It is extraordinarily permanent but is affected by extremes of humidity and dryness, and in order to prevent cockling and embrittlement it must be kept under reasonably equable conditions, preferably within the range 50-60 per cent. Relative Humidity at 60°-70° F.

Regular washing should therefore be dispensed with and, when necessary, this should be restricted to careful cleaning with a damp sponge, drying quickly at room temperature, preferably in a good draught before the window. When applied to vellum, the British Museum Leather Dressing is not absorbed to anything like the same extent as

in the case of leather, and so it should be used sparingly, and the vellum may be polished in the course of a few hours.

SUMMARY

The main cause of the decay of leather is the absence of an ingredient (natural or artificial) which protects the tissue from the action of sulphuric acid which is formed in all leather (in time) by absorption and oxidation of sulphur dioxide, and when this protective ingredient is present vegetable tanned leathers can resist oxidation in presence of sulphuric acid and do not deteriorate. No leather can be relied upon to be durable unless it is so protected. No modern leather should be considered fit for bookbinding which is not stamped by the manufacturers as 'Guaranteed to Resist P.I.R.A. Test'. While leather dressings have little or no influence in preventing leather from rotting, fatty preparations serve a useful purpose in lubricating the tissue and retarding the effects of physical wear and tear. The British

Museum Leather Dressing acts in this manner and also consolidates the frail and powdery surface of leather which is in a state of deterioration. Instructions are given for cleaning bindings and for applying this dressing to leather and to vellum.

1 – Reduce size of volumes –
2 – " thickness of leather
3 – flow : Flow – water
4 – Reduce thinness of leather
words for edges

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