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PERMANENCE OF PAPER

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Synopsis Cellulose has the environmental advantage that it is bio-degradable and that paper made from it is readily recycled by repulping. It is perhaps surprising that cellulose keeps as well as it does and that some books keep for centuries. In spite of much research work, it is impossible to predict the permanence of individual samples really precisely from artificial ageing tests, though the factors to affect ageing are fairly clear. The quality of the furnish has always been known to be important. Acidity has been studied for a long time and the permanence of existing books can be improved, at a cost, by neutralisation. Storage temperature is important, but has been largely ignored, although it could be corrected in many existing libraries.

Review of the subject

THE literature on permanence and durability is now very large indeed; it would not be wise to attempt an extensive review here in addition to those that already exist. I shall refer to some of them. It is my intention to look at the subject in as practical a way as possible and to bring in the point of view of the user of paper. We are concerned here with printers, publishers, librarians and the keepers of archives—and their interests are not all the same. On the technical side, which it is our first duty to consider, there are present in wood cellulose a number of impurities that may react and may interact during either natural or artificial ageing processes. In an excellent review on brightness reversion, covering 155 references, Spinner[1] states in his conclusions, 'Effects of ageing conditions are complicated and not well understood and suggest the need for further clarifying work.' This kind of conclusion from an extensive technical review is almost inevitable, but does not really help the paper user, who might feel that he could reasonably expect more from the mass of work that has been done since Murray first complained about the bad effects of chemicals on the permanence of paper.[2] Neimo[3] has published a review of strength deterioration on ageing and there are numerous useful references in Smith's thesis.[4] Rapson & Spinner's chapter on brightness reversion is also

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relevant.[5] From the practical viewpoint, Wilson & Hebert, who have published experimental results on artificial ageing of a variety of papers, have included a particularly good review, giving a fair summary of the subject.[6]

To define permanence and durability, I quote from Browning & Wink,[7] 'Permanence refers to that property of a material which *resists* changes in any or all of its properties during ageing of a specific type. Durability refers to the degree to which a paper *retains* its qualities under continued usage.' Very similar definitions were given by Gösta Hall[8] as long ago as 1926. Grant devotes part of a chapter to a summary on permanence[9] and lists eight factors, each of which has some effect. The two most important factors listed are the quality of the fibre and acidity. The main change in thought in the last fifteen years since Grant's summary was written is that more emphasis is now placed on acidity and less on the importance of using rag fibre. W. J. Barrow[10] and his co-workers have done much to publicise this view and it appears that librarians, at any rate in U.S.A., have taken the message. The world's largest book, the National Union Catalog, is being printed on a woodpulp paper made to Barrow's specification, but the British Museum General Catalogue of Printed Books, amounting without the supplements to 263 volumes, is printed on a special quality gelatine-sized rag paper. We have tested some volumes of this book for pH value, using a flat glass electrode and the results are given in Table 1. This suggests that a change in specification to a neutral or alkaline paper has been made and one would expect the second supplement to keep much better than the rest of the catalogue.

TABLE 1

Tests for pH value with a flat glass electrode on library copies of the British Museum General Catalogue of Printed Books, from the library of the University of Manchester

Volume	*pH value*
184	4·5
263	4·5
10 year supplement 1956–65, Vol. 25	4·5
5 year supplement 1966–70, Vol. 1	8·1
5 year supplement 1966–70, Vol. 20	8·3

Acidity has actually been considered important for a long time. Herzberg[12] discussed this in 1885, Gösta Hall[8] measured it in his work on ageing and it is worth remembering that, as late as 1926, modern pH value testing methods were not available and he had to titrate free acidity. Herzberg used Congo

Red as an indicator for this. Richter[13] carefully correlated the effect of 200 days' exposure at moderate heat (38° C) with standard oven ageing. Although he was primarily concerned with the importance of good quality fibre, his fold retention figures correlate very well with pH value, apart from one anomalous result. This was obtained with mechanical pulp, but other workers have also obtained unexpected results with mechanical pulp. Evanoff & Kruser[14] have stated that we must change our minds about the poor ageing of coated groundwood sheets or give up the dry oven test.

Ageing tests will be discussed by others in this session, but it is evident from the work of Browning & Wink[7] that, even with the best refinements in the selection of an appropriate atmosphere, prediction from heat ageing of the keeping properties of an individual sample will not be precise.

Acidity in paper normally arises from sizing with rosin and alum or from the addition of alum to gelatine in high quality tub-sized papers. It may also be picked up from the atmosphere, particularly from sulphur dioxide. A paper by Langwell[15] summarises his results on this and it has also been studied by workers in Manchester.[16–18]

The most important contribution to the production of permanent papers in recent years has been the development of methods for sizing under alkaline or neutral conditions.[19] This permits the production of neutral papers or alkaline-sized papers, which will remain at or above a neutral pH value, owing to the presence of calcium carbonate. There appears to be no doubt that papers made according to Barrow's specification will keep well, but his conclusions that acidity is the major factor in causing deterioration have been queried by some others. Dixson & Nelson,[20] for example, tested sixteen papers, some sized with Aquapel, some with rosin and alum. They concluded that acidity or alkalinity of the paper is of secondary importance and that the structure of the sheet appears to be the determining factor.

These statements have been quoted in textbooks.[21] In fact, their results do show that pH value is important in its effect on heat ageing properties. They give detailed tables on sixteen different good quality papers with figures on hot pH value, cold pH value, fold after various ageing times and tearing strength. By interpolating between the figures for 'least squares fold', which had already been corrected statistically, one can readily estimate the number of days ageing at 105° C required to reduce the fold to half. If these figures are arranged in order of decreasing cold pH value, they come out as given in Table 2.

My conclusion from these results would be that there is a good correlation between cold pH value and resistance to heat ageing and that, whereas the best results are likely with Aquapel sizing, it is possible to make a paper with good permanence, using rosin and alum, if the pH value can be kept

reasonably high, say, above 6·5. They have in fact chosen a selection of papers that are mostly high in pH value.

TABLE 2—FOLD DATA FROM DIXSON & NELSON[20]

Sample No.	8	10	7	15	4	16	9	3	2	6	13	11	1	12	5	14
Cold pH value	9·0	9·0	8·8	8·7	8·5	7·0	6·9	6·7	6·5	6·5	6·3	6·1	6·0	5·9	5·6	5·0
Days to half fold	35	31	19	12	14	12	12	11	15	27	16	4	7	11	3	2
Sizing: Rosin or Aquapel	A	A	A	A	A	R	R	A	R	R	R	R	R	R	R	R

Permanence for storage

AT THIS point, it is desirable to think how we can best satisfy the paper users. I suggest that, firstly, we should stop grumbling about the impermanence of paper. One of the great advantages of paper, made from the natural polymer cellulose, is that it is repulpable, bio-degradable and has none of the bad environmental impact of many other man-made artefacts, particularly those made from synthetic polymers. The surprising thing is that we can, by the correct treatment and use of this wonderful material, make sheets that will store information of importance to civilisation for centuries. We shall do pretty well, if we can print on to neutral book paper as specified by Barrow. For really important documents, there has never really been any technical difficulty. Here, we can afford the best quality fibre and a tight specification on acidity. The worst problems are those of the archivist. The samples he wishes to keep may have been printed or written on most unsuitable papers, because their potential importance was not realised at the time. Let us deal with archives first.

Archives and the present stock of excessively acid books in libraries can be made more permanent than they would otherwise be by neutralisation. Many methods, some of them costly, for doing this have been suggested. One of the most attractive is that described by R. D. Smith,[4] who has developed a method for treating whole books with magnesium methoxide dissolved in dichlorodifluoromethane. The operation can be done with one or more shelves of books at a time. These can be held in cramps and immersed under pressure in an autoclave containing the solution. The solvent boils at −30° C at atmospheric pressure. It is easily removed and recovered by distillation and the books (provided no leather binding is present) are not damaged.

Another factor to which archivists and librarians should pay more attention than they do is the storage temperature. From the known fact that ageing can be accelerated by heat, like any other chemical reaction, one can make rough predictions of the effect of heat. Relative humidity is also important. These factors can be connected by equations, but equations do not have the same

impact as tables and I have therefore copied part of Smith's table[22] into Table 3.

TABLE 3

Effective life of paper under varying temperature and relative humidity, related to standard conditions at 25° C and 50 per cent rh from R. D. Smith[22]

Average annual temperature, °C	*Average annual relative humidity, per cent*			
	70	*50*	*30*	*10*
35	0·14	0·19	0·30	0·68
25	0·74	1·00	1·56	3·57
15	2·74	5·81	9·05	20·70

Note—These are theoretical calculations based on an arbitrary standard of 1·00 at 25° C and 50 per cent rh considered to be reasonable conditions for an American library. It is instructive to think of the units as centuries, in which case the extremes in this table are 14 years and 21 centuries.

Smith regards 50 per cent rh and 25° C as typical conditions for a U.S. library and points out that a big improvement in permanence could be produced by a small drop in temperature. He also suggests that this table explains why *any* books over 250 years old are in good condition. They were mostly kept in unheated European libraries at about 10° C and 70 per cent rh in North European countries and have been moved only within the last century or so to U.S.A., where conditions are so much worse.

It has already been suggested that the interest by Barrow and his colleagues in Virginia in the poor keeping quality of books was probably due to the high temperatures in that part of the world.[23]

The present problems of the librarian are similar to those of the archivist in so far as they are caused by poor storage facilities and by poor quality papers made in the past, particularly when these are too acid. Many methods for deacidifying existing stocks have been suggested and all are expensive. They are reviewed by Smith[4] and his own method seems attractive in principle. Books spend most of their time unused on shelves and the evidence in favour of low temperatures for storage is so strong that it seems strange that no effort has been made to keep library stacks at low temperatures, even though reading rooms have to remain comfortable. Owing to a chance opportunity, Edwards & Hudson were able to get a little evidence on the potential usefulness of cold storage by testing a book that had been left in the dry snow of Antarctica from January 1912 until November 1959.[24] The colour and strength were significantly better than those of two secondhand books from the same printing, which had presumably been kept in the United Kingdom.

Interplay of factors

IT REALLY is important for the future of books to use neutral or slightly alkaline papers and Barrow's specifications appear to be essentially sound.

This is recognised by some publishers,[25, 26] but it is realised that it may not be in the immediate financial interests of either printers to use or of paper-makers to make suitable permanent papers. It is encouraging to find that in some parts of the world, particularly in Great Britain, it is possible to make alkaline-sized papers containing whiting as a filler at a satisfactory cost and that mills that have wholly changed over to alkaline sizing do not wish to return to rosin and alum.[27]

I suggest that the time is soon coming when it will be possible to use neutral or alkaline sizing for all book papers without undue increase in cost, possibly with no increase at all.

This will almost certainly introduce some difficulties with specifications. Enough has been written about heat ageing, either dry or moist, to indicate that it is far from precise. The pH value test itself is a useful guide and if done with a flat glass electrode[28] is quick, too. Either extraction methods[29] or the flat electrode will give misleading results with a composite 'sandwich' such as an alkaline coating on an acid base paper.

There is some evidence that similar misleading results might come from pH value determinations on paper containing a calcium carbonate filler after it has been exposed to sulphur dioxide. Edwards[30] found that a paper loaded with calcium carbonate did not take up sulphur dioxide as fast as expected. Singh[31] has found that paper containing calcium carbonate takes up some sulphur dioxide initially, but the rate of uptake slows down to the same level as other papers long before the calcium carbonate is neutralised. This may mean that calcium carbonate, though obviously a highly desirable filler, may not protect the paper from pollution as much as was originally hoped. This matter really requires further elucidation.

The choice of furnish is largely determined by what the user is prepared to pay. Papers will in general go down in permanence according to the furnish used in the order rag, high alpha-cellulose pulp, low alpha-cellulose pulp, groundwood, but in any furnish class insistence on a high pH value and the lowest practicable storage temperature will have the most effect on longevity. There is enough technical knowledge available now to improve the keeping quality of books and records significantly.

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Discussion

Dr J. Grant Thank you, Dr Hudson, for so admirably summarising the recent work on this subject. I have been interested in it for some 40 years.

In my view, the three factors (in order of importance) that determine the permanence of paper are, firstly, the conditions under which it is stored; secondly, the primary raw material of which it is made (that is, the fibre constituents); thirdly, the processing factors, under which I include pH value, sizing and loadings.

Unfortunately, it is impossible to put ageing theories to a strict test. The ageing test now used gives one great confidence and has been in existence for about 40 years. When we are talking about the permanence of paper, we are really talking in terms of 100–500 years and, until the test has been tested on a 500 years' basis, we cannot really know whether it provides true information now; that is the limitation under which we must work for the next few hundred years!

In hand-made paper, you have an almost ideal set of conditions for permanence, because you work with the best quality of rag, it is well cleaned and washed after bleaching and, most important of all, you tub-size it very heavily with gelatine. In my view, this latter operation is of great importance in determining the permanence of paper. Unfortunately, it is seldom a practicable possibility, because one just cannot afford to use hand-made paper for many purposes for which permanent papers are required. I had something to do with the paper for the British Museum Index to which Dr Hudson has referred and, so far as I recall, the low pH values for the earlier pages were because the paper was a heavily tub-sized rag paper. It is the gelatine that produces the low pH value, but that does not mean that the paper is non-permanent. For reasons of cost, there was a switchover to machine-made paper and a higher pH value, which is alkaline and just as effective.

The work of Barrow has without doubt been of inestimable value to makers and users of permanent papers, because it has enabled permanent papers to be produced on a mass production scale instead of having to rely on the hand-made paper process.

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You may be interested to know that the British Standards Institution has two committees dealing with the treatment and storage of paper for the archivist. There will be specifications for the storage and preservation of documents (not for the making of permanent paper), because it is realised that storage is the really important factor rather than the actual composition of the paper. Included in these specifications will be recommendations for the neutralisation of old papers.

It was during the era when gas was first used for heating and lighting that the world lost tremendous value in terms of documents, until it was realised that the sulphur dioxide in the air and the acidity it produced was responsible for the deterioration of paper. We have long since passed through that phase and to my mind permanent paper is a possibility commercially so long as it is properly stored and the materials are selected suitably and properly processed.

Dr J. Marton When we are changing from rosin sizing to alkaline sizing, we change pH value. Aluminium sulphate is eliminated and rosin is substituted. I would like your comments on the relative importance of these factors contributing to the ageing of paper.

Dr F. L. Hudson I think pH value (acidity) is the most important of the three. Rosin itself is unsaturated and we have found in Manchester that rosin tends to increase the amount of sulphur dioxide picked up by paper. In fact, the figures I gave from Dixson & Nelson in Table 2 really showed that, in spite of the use of rosin and alum, paper can still be sized at quite a high pH value and produce a relatively permanent sheet. High class Government papers, as used for printing birth certificates, have for many years been produced at a pH value of 5·5 or higher despite the use of rosin, alum and tub-sizing. The aluminium sulphate itself seems to do no harm, but I just do not know.

Dr E. Graminski We are doing considerable work at the National Bureau of Standards on the permanence of paper. There is one point that has not been mentioned today that we find important—the amount and type of bleaching to which the pulp is subjected. We find that the more a pulp is bleached, the more impermanent it becomes, especially if treated with aluminium sulphate. I presume that there was considerably less bleaching 400 years ago than there is today and papermakers' alum was not yet introduced, which probably contributes to one of the reasons for better permanence of very old papers.

Discussion

Dr Grant The reason for the impermanence of some of the old papers was not that there was less bleaching, but that the bleach residues were not washed out and the residual chlorides formed hydrochloric acid. I am wondering if Dr Graminski really means that the paper is being overbleached or that there are bleach residues resulting from overbleaching to cause the deterioration. Modern methods of multi-stage bleaching with adequate washing, especially at the last stage to give a chloride-free paper, should produce a very stable paper.

Dr Graminski We have found that, as the number of carboxyl groups in the pulp increases, so does the instability. There is a very good relationship between the number of carboxyl groups in a pulp and permanence. The effect is greater when aluminium sulphate is used in preparing the paper. What probably happens is that the aluminium exchanges with the protons of the carboxyl groups. The aluminium then serves as a catalyst to produce cross-linking or an increase in the degree of crystallinity, since we find an increase in wet strength on ageing.

Prof. V. T. Stannett I am not sure that this is entirely relevant, but some months ago I had a call from the Library of Congress because some of their books like those Dr Hudson talked about were decaying more or less rapidly and they asked me whether it would be possible to repair aged paper. We had the idea that by vapour-phased grafting you could do this. We took some very old-looking yellow pages from expendable books from the Library of Congress and treated them with ethyl acrylate in vapour phase and made them reasonably strong and whole again. The idea would be that in the vapour you might be able to repair the whole book, but there are 3 million such books. So there is an aspect, not quite relevant, that one can perhaps repair aged paper, also that those papers might be more permanent after that treatment.

Dr Hudson Dr Graminski and I both attended a conference on this subject in Savannah a year and a half ago. We had then a very interesting paper on the effect of different metal ions on ageing. In my presentation as a whole, I have been deliberately concentrating on the things that have changed or where the emphasis seems to have been changing in the last 12 years. It has not been possible to do justice to the whole subject, which is very important and will obviously occupy research people for a long time.

With some regret, this is my last formal academic appearance, because I retire at midnight of 30th September.

The Chairman We would like to thank you not only for the lecture today, but for your long years of service to this industry.