Preferred citation: D.J. Priest and J. Stanley. The permanence of papers containing modern high yield pulps. In **Products of Papermaking**, *Trans. of the Xth Fund. Res. Symp. Oxford, 1993*, (C.F. Baker, ed.), pp 1315–1353, FRC, Manchester, 2018. DOI: 10.15376/frc.1993.2.1315.

THE PERMANENCE OF PAPERS CONTAINING MODERN HIGH YIELD PULPS

D J Priest and J Stanley

Department of Paper Science, UMIST,

PO Box 88, Manchester, UK, M60 1QD.

ABSTRACT

Modern high yield pulps, typified by chemithermomechanical pulp (CTMP), are likely to be used increasingly for printing, writing and publication grades where longevity is a major consideration. This paper reports an investigation of the ageing of papers containing CTMP, and sized both with rosin/alum and alkyl ketene dimer (AKD) systems, using paper made specially for the study on a pilot papermaking machine. Emphasis was placed on mechanical properties, in view of the concern of librarians and archivists with the embrittlement of paper due to acid hydrolysis of the cellulose. The results show that use of CTMP has a negligible effect on rates of loss of strength; in a series of papers containing various proportions of CTMP with a bleached softwood sulphate pulp, sized with AKD, the rate of degradation was very similar, and acceptably low. Naturally, the papers containing CTMP are not initially as strong, and will become yellow on exposure to light; in judging whether or not such papers are acceptable for long term use, all these factors need to be considered with respect to particular applications.

INTRODUCTION

Although it has long been recognised that, for various reasons, paper can have a limited useful life (1), the explosive growth in the volume of information on paper throughout the world, coupled with increasing general concern about preserving humanity's heritage, has, in modern times, brought up with fresh emphasis the serious problems facing repositories of paper-based material, especially national libraries and archives. Despite advances in methods of optical and electronic data storage, there is little doubt that the use of paper will remain of great importance for the foreseeable future; it is relatively inexpensive and has the great virtue of needing no auxiliary technology, which can always become obsolete, for reading the printed page. The immense scale and expense of transferring existing printed material on to, say, microfilm or compact disc is often overlooked (2).

At any moment in history, there are two distinct problems; what to do with existing material - including today's newspaper or publication - and what can be done to improve the situation in the future. This paper will be concerned with some of the impacts of modern papermaking and hence mostly with the future, but the importance and urgency of the problem needs to be appreciated in terms of the past. For example, it has been estimated that in the British Library, several million books have deteriorated to an extent which makes them inaccessible to readers, mainly because the paper in them has become too brittle; the United States Library of Congress, reports an even larger number. Since the process of deterioration continues inexorably, day by day, more and more books are reaching a similar condition. The seriousness of this problem has prompted much research into ways of economically treating these books and documents by what are known as mass treatment methods. Approaches include strengthening by polymerising acrylic monomers infiltrated into the pages of books (3), neutralising acidity by exposing books in vacuo to gaseous diethyl zinc (4), and immersing books in inert solvents containing organo-metallic bases (5,6).

Clearly, it is very important that attention should be paid to the nature of the paper being used for information storage today, since it is highly desirable that in the future, books and documents being produced now should not give rise to the same problems.

The causes of the embrittlement of paper with time have been much studied (7,8). Whilst many factors may be contributing, there is general agreement that cellulose chain scission by acid hydrolysis at the β-1,4 link between anhydroglucose units is a major cause of loss of strength (9). Again, there are various possible causes for the acidity (10), but the major one is undoubtedly the extensive use of aluminium sulphate (papermakers' alum) as an adjunct in rosin sizing. This predominance of alum rosin sizing as a cause of deterioration needs emphasising because the notion that different types of acid can lead to widely different effects is not always appreciated by preservationists, who tend to regard any potential source of acid as equally damaging. It follows that the advent of internal sizing methods in which acid conditions are not required has had a considerable impact on the problem of deterioration; papers sized by one of these methods, eg alkyl ketene dimer size, lose their strength in accelerated ageing tests at a much slower rate than comparable papers sized with rosin and alum (11). One consequence is the current interest in producing standard specifications for paper with a long life intended for widespread use in publishing, and the lobbying by preservationists and others to persuade manufacturers of book papers and other communication grades to use neutral or alkaline sizing systems. However, a second relatively modern development which is having an impact on the general situation is the advent of new types of high yield pulp, based on modified mechanical pulping processes and typified by chemithermomechanical (CTMP) pulp (12). These pulps, with their relatively high brightness and acceptable strength, are likely to be used to an increasing extent in the book and general communication grades of paper which are very much the concern of those responsible for depositories in libraries and archives. It is important to realise that archivists and librarians have largely to deal with deposited material comprising whatever paper publishers decide to use; there are very limited areas where highly specialised and expensive archival grades of paper can be employed. This explains why standards directed at general publishing grades need to specify papers which can be used cost effectively. It follows that the possibility of including papers containing CTMP in such standards is a major question.

CTMP, of course, contains a high proportion of lignin. The connection between lignified papers and longevity is not as clear cut as it may seem. The initial problem is to decide which type of property needs to be retained at a high level in stored paper. If an idealised archive is contemplated, in which paper would remain completely unaltered in any respect for an indeterminate period, then it is generally accepted that lignified fibres can in no way meet this ideal, because there is no doubt that exposure to light will cause yellowing; clearly, it is impracticable to consider prolonged storage of printed material in the dark in sealed containers. However, the actual situation is not as clear cut as this and compromise of some sort is required, especially where large collections of books and public archives are concerned. Broadly speaking, properties of interest can be divided into two categories, (a) visual appearance, including colour and especially its variation within, for example, a single page of a book and (b) properties related to the use and handling of the object, which, for paper, means mechanical strength, especially flexibility and toughness. Acid hydrolysis leads principally to loss of extensibility, certainly to a greater extent than loss of modulus or long span tensile strength (13) and so flexibility and toughness are lost and the paper acquires its well known brittle nature.

For CTMP pulps it has to be accepted that exposure to light will cause a degree of yellowing, so in terms of use in books or archives, emphasis needs to be placed on aspects of mechanical strength. The key question then is whether or not papers containing CTMP, when made using neutral or alkaline conditions and synthetic reactive sizes, will retain sufficient strength by comparison with delignified pulps. This question has not been addressed extensively, although some recent work (14,15) has indicated that the use of lignified fibres may not be as detrimental to loss of mechanical properties as was once feared.

The work to be described here provides more detailed information on the problem by means of a series of specifically targetted experiments. Its key features are the use of papers specially made on the pilot paper machine in the Department of Paper Science at UMIST, in order to study the effect of variable amounts of CTMP and to compare similar papers made either with alum rosin sizing under acid conditions or with alkyl ketene dimer sizing under neutral or alkaline conditions.

EXPERIMENTAL WORK

Types of Paper Produced

Two sets of paper were made; one set consisted of two papers both made from a 50:50 blend of CTMP and a bleached kraft sulphate pulp, one alum rosin sized with a clay filler and the other sized with alkyl ketene dimer and containing calcium carbonate, in the other set the proportion of CTMP was varied but the sizing system was the same throughout (a neutral alkaline system with calcium carbonate filler). The two papers for comparing sizing systems were designed to simulate a typical printing/writing grade with about 15% filler; the papers with different amounts of CTMP were made with less filler to simulate what might reasonably be required as an alkaline reserve. Initial properties of the two sets of paper were therefore different, but this in no way affects the outcome of the work. Key details of the composition of the papers are given in Table 1.

<u>A. Set 1 - papers sized either with rosin/alum or alkyl ketene dimer.</u>

Furnish:50% Rockhammar aspen/spruce CTMP (unbeaten)
50% Stora 32 bleached sulphate softwood (beaten to 25-32 °SR).

Sizing materials and fillers were added continuously at the following rates (size to thin stock at the mixing box, filler to thick stock before the refiner):

(a)Rosin size: 0.4% w/w on dry fibre, as a 5% solids solution.
Aluminium sulphate: 1.0% w/w on dry fibre, as a 10% solids solution (of a commerical "iron-free 17% ground" grade).
China clay (grade E) as a 10% solids slurry; ash content of paper found to be 12.9% (ashed at 925 °C).
(b) AKD size: 0.2% w/w solids on dry fibre (2% as received), as a 10% solids dispersion.
Calcium carbonate (Snowcal 60) as a 10% solids slurry, ash content of paper found to be 16.8% (ashed at 575 °C).

<u>B. Set 2 - papers containing varying amounts of CTMP.</u>
Furnish: Rockhammar spruce CTMP, unbeaten.
Stora 32 bleached sulphate softwood, beaten to 25-30 OSR.
Size: AKD (Aquapel C348), 0.2% w/w solids on dry fibre (2% as received), as a 10% solids dispersion.
Filler: Calcium carbonate (Snowcal 60) as a 10% solids slurry.
Ash contents (at 575 °C): 100% CTMP, 5.9%; 75% CTMP, 5.2%; 50% CTMP, 4.5%; 25% CT MP, 4.8%; 100% Stora, 4.8%.

Table 1. Composition of the papers made on the pilot papermaking machine.

Accelerated Ageing

It is now generally accepted (16) that realistic accelerated ageing is best done under humid conditions, and that temperature should not be too high, as long as results can be obtained in a reasonable period of time. As an investigative tool, we were particularly interested in exaggerating degradation, and so we chose to age samples at 90C and 56% rh and to extend the duration of ageing up to 34 days. Also, it should be noted that we were primarily concerned at this stage with internal comparisons and not with external standards.

Assessment of Mechanical Properties

A number of standard tests were performed on samples aged for different periods. Folding endurance was determined on an MIT instrument; an Instron Model 1122 tensile tester equipped with computer control was used to obtain long span tensile index, tensile energy absorption and elongation at break; zero span tensile index was measured on a Pulmac instrument. Scatter of values was usually as expected; a considerable advantage was obtained by using as many as 11 sampling intervals during ageing since the plotted results enabled a good judgement to be made of precision.

RESULTS

Comparing Alum Rosin and Neutral Sized Paper

Since folding endurance has been widely used to study ageing (17) these results are presented first in Figure 1, which shows the geometric mean of machine direction (MD) and cross direction (CD) folding endurance plotted against ageing time. (Geometric mean values have been used in reporting this work unless, as happened occasionally, distinct differences have been found in the form of the dependence of MD and CD properties on

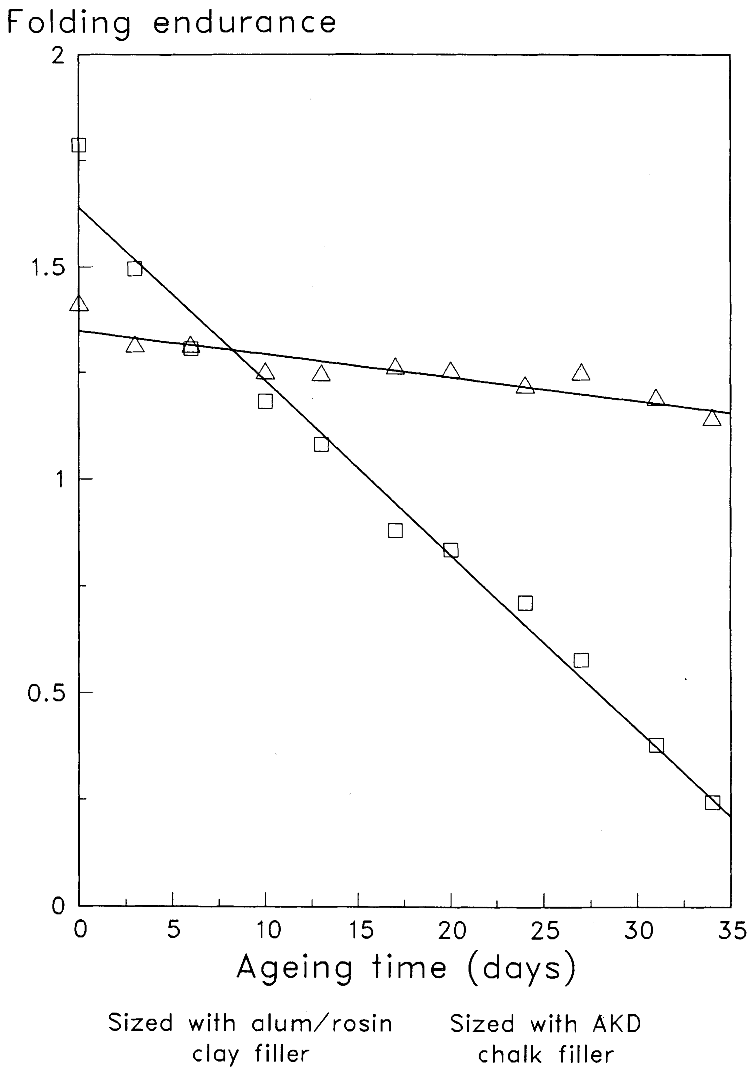

Figure 1. The loss of folding endurance on ageing at 90 OC and 56% rh for paper containing 50% aspen/spruce CTMP, showing the large influence of alum/rosin sizing.

ageing). This is a key result from our work since it illustrates clearly the sharp difference in rate of ageing between paper sized with alum rosin and that made in a neutral alkaline system. It should be noted here that the rosin sized paper contained clay filler, and the AKD sized paper calcium carbonate. This was done since, in production practice, this is very likely to be the preferred option. Calcium carbonate is capable of providing an alkaline reserve (18) to resist acid attack from, say, atmospheric pollution. It is also possible that it plays a part in reducing the rate of strength decrease in accelerated ageing, but a rigorous comparison between clay and carbonate was not made in the context of the experiments presented here on CTMP. Other than the filler type, the fibre furnish and stock preparation were identical for both papers, which were indeed made from a single batch of thick stock. Fillers were added as slurries continuously at the wet end.

Clearly, the presence of 50% CTMP has not caused rapid deterioration of strength in the AKD sized paper, and this aspect can now be explored further in terms of other mechanical properties. A more fundamentally useful property is the tensile strength and Figures 2 and 3 show the long span and zero span tensile indices for each type of paper plotted against ageing time. As expected (19), in the rapidly degrading alum rosin sized paper, the rate of decrease of zero span tensile strength is greater than that of the long span test. This is a consequence of the fact that the major cause of loss of strength is a reduction of fibre strength, caused by acid hydrolytic chain scission of cellulose; by comparison, inter-fibre hydrogen bonds would be less likely to be affected by the presence of acidic hydronium ions. It appears that the presence of 50% CTMP has not perturbed this basic mechanism. In the AKD sized paper (Figure 3) the rate of decline of finite span tensile strength is only slightly less than that in the acid alum/rosin paper. However, the zero span strength declines overall at a much lower rate, although in the initial period of ageing, up to six days, the rate is slightly higher. Even so, after

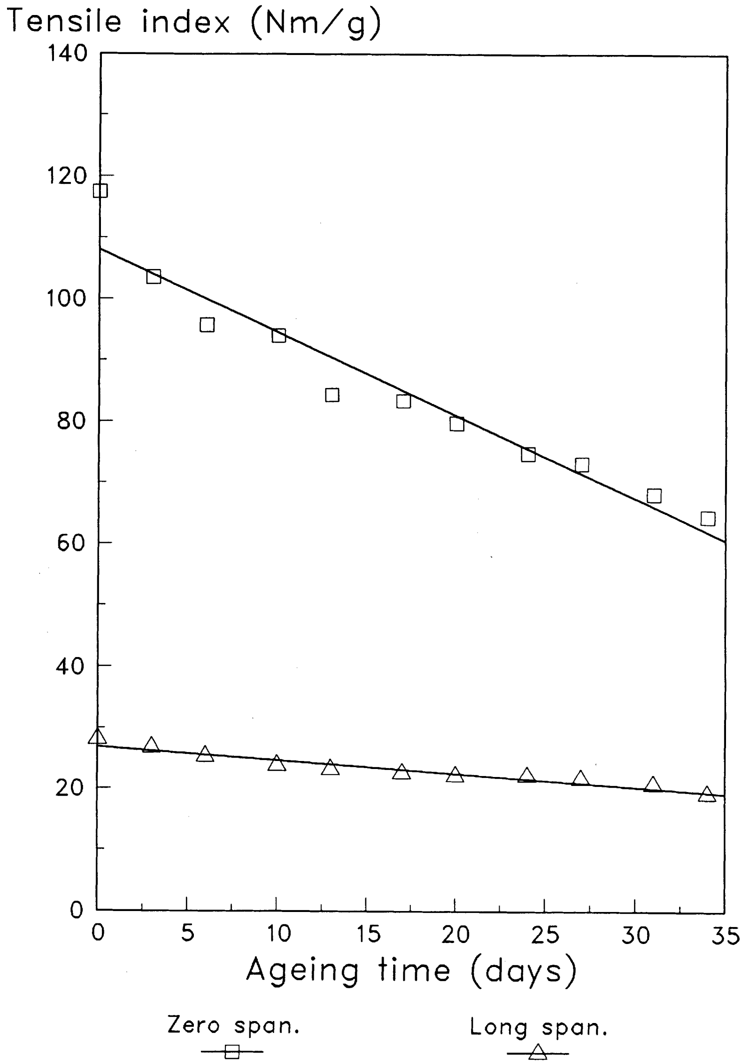

Figure 2. The decline with ageing of zero span and long span tensile index for the paper containing 50 % aspen/spruce CTMP, sized with rosin and alum.

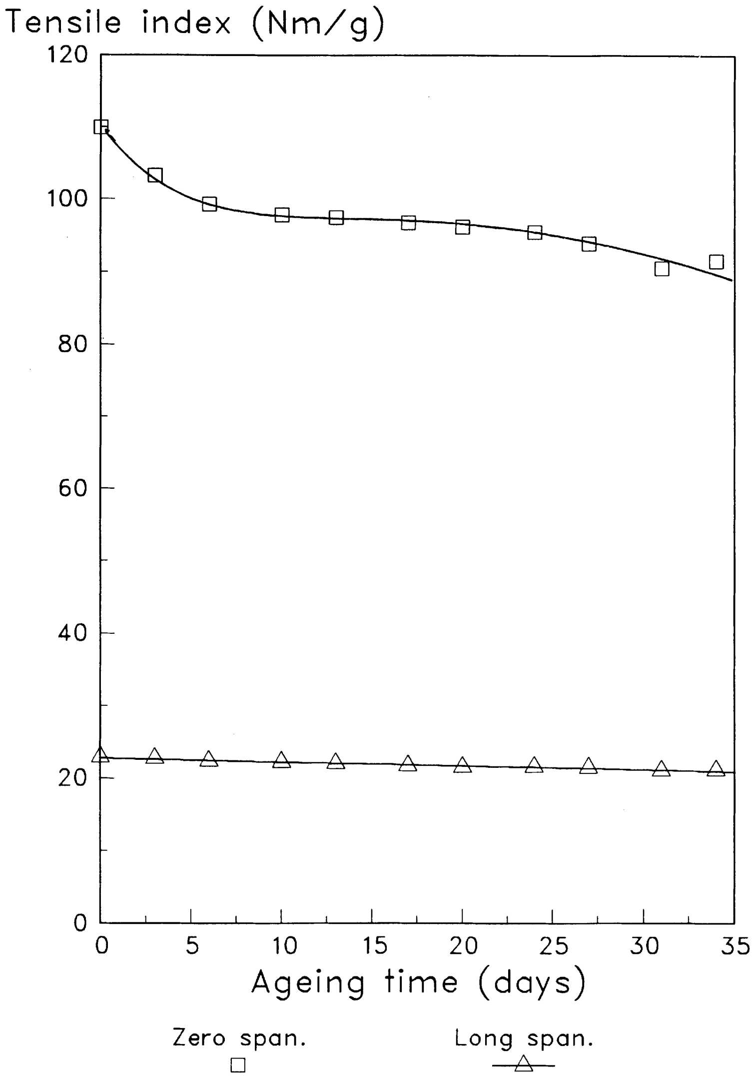

Figure 3. As Figure 2, for the paper containing 50% aspen/spruce CTMP, sized with alkyl ketene dimer.

34 days at 90oC and 56% rh, zero span tensile index is still greater than 90 Nm/g.

Since variations in tensile strength are being observed in particular samples of paper in which the fibre geometry is unlikely to be changing, many of the bonding parameters introduced by Page (20) can be considered to remain unaltered; for example, fibre perimeter and bonded area. Consequently, it is appropriate to use the simplified form of the Page equation, and to plot 1/T against 1/Z (where T is the long span tensile index and Z is the zero span tensile indez) in order to observe any effects there might be on the inclusive bonding factor (b). The result for both types of paper is shown in Figure 4. A clearer picture is obtained for the alum rosin sized paper, since the range of values is greater because degradation is more marked. The good linear correlation (R^2 = 0.964), support the contention that bonding is being unaffected by the degradation. Although the range is smaller in the AKD sized paper, because degradation is less, and the linear correlation is not so strong (R^2 = 0.910), the results suggest that here too the major effect is a loss of fibre strength. In fact, by adjusting the value of 1/b, taking it to be constant, the two lines can be made to virtually superimpose, and this strongly suggests that the mechanism of degradation is the same in both papers. Thus, although AKD and $CaCO_3$ are present, and the paper was made at an apparently neutral pH, it seems that sufficient hydronium ion remains to produce a limited degree of chain scission and loss of fibre strength. This aspect is pursued further below, in connection with the results for papers containing different amounts of CTMP.

Although it is not itself a fundamental easily measurable parameter, brittleness, in more basic terms, implies that a material, on application of stress, will deform only slightly before failure occurs. Hence, it is not surprising that fold endurance, which involves in a rather complex fashion the ability to absorb repeated deformation, is a good indicator of ageing. An

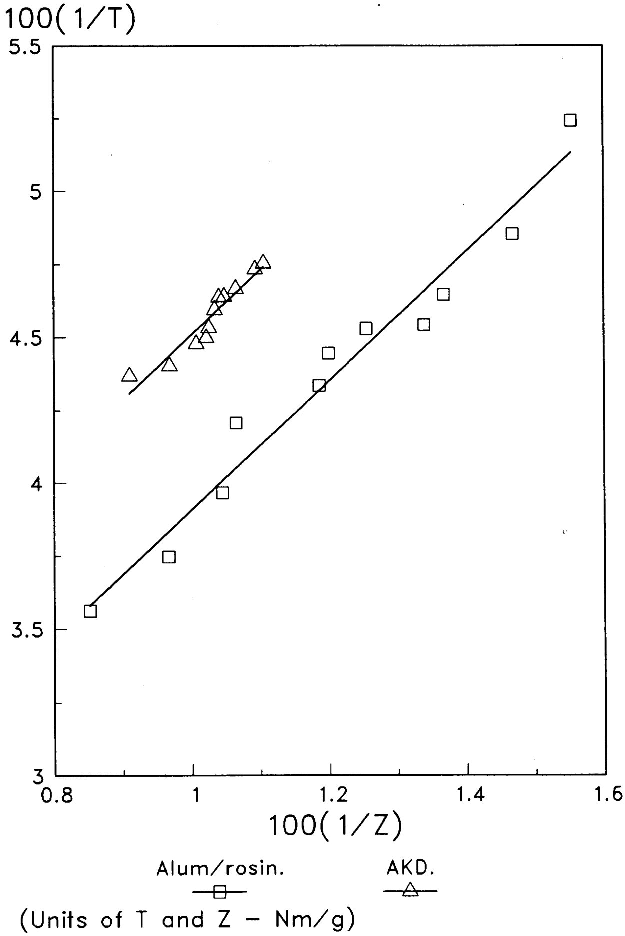

Figure 4. The inverse of long span tensile index plotted against the increase of zero span tensile index for the papers sized with alum/rosin and AKD, indicating the predominance of loss of fibre strength, and suggesting similar mechanisms of degradation in both types of paper.

alternative less complex indicator ought to be the tensile energy absorption (TEA); extensible tough materials show a high TEA. A practical advantage of this parameter is that unlike folding endurance it can be done quickly in a short predictable time, especially on a modern tensile tester fitted with computer control. Figure 5 shows values for TEA as a function of ageing time which clearly demonstrates the difference between acid and neutral papers. For particular samples and ageing conditions, there is often a fairly good relation between fold endurance and tensile energy absorption, and this is illustrated for the rapidly degrading paper in Figure 6. The question of a more general relation between TEA and fold endurance is taken up again later.

Papers Containing Different Proportions of CTMP

The results reported already make it clear that the presence of CTMP is not, in itself, producing any large effect on the rate of ageing. Confirmation of this, and some extra information on the effect of CTMP was obtained from research on a set of five papers in which the proportion of CTMP varied from 0 - 100%. Since the major interest is in the possibility of using CTMP in relatively long life paper, all these test papers were sized in an identical fashion using AKD, and they also contained a small amount of calcium carbonate filler. Thus it is important to realise that the changes observed on ageing are all less than would be seen in a rosin/alum sized paper.

Looking first at folding endurance, Figure 7 shows the relevant data for the geometric mean. It is immediately apparent that the rate of ageing as denoted by the slope of the best fit straight lines, changes very little as CTMP content increases from zero to 100%. There is, of course, a marked change in initial fold endurance. Figure 8 shows the geometric mean folding endurance plotted against CTMP content, for unaged papers and papers aged for 34 days at 90C and 56% rh. The graphs demonstrate very clearly that the CTMP is causing very little

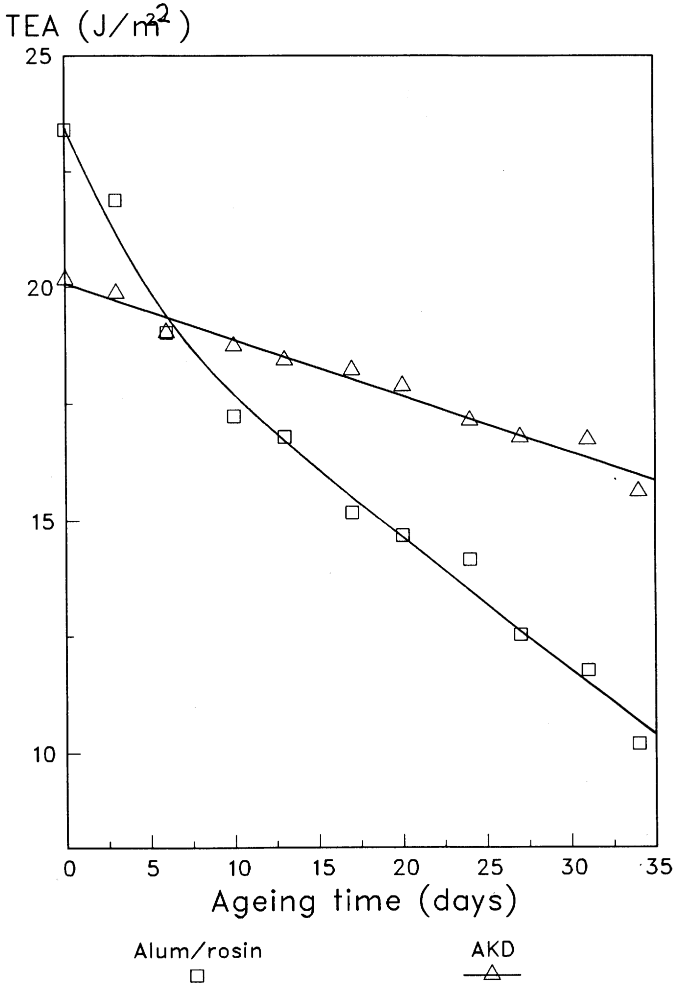

Figure 5. The loss of tensile energy absorption on ageing of papers sized with rosin/alum and AKD.

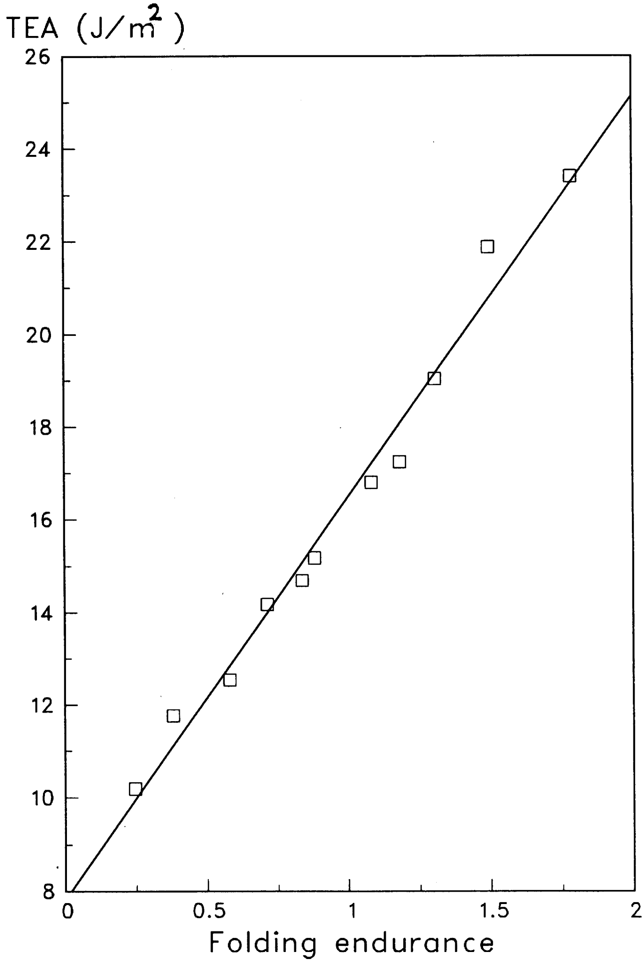

Figure 6. The relationship between TEA and folding endurance on ageing for the paper sized with rosin/alum.

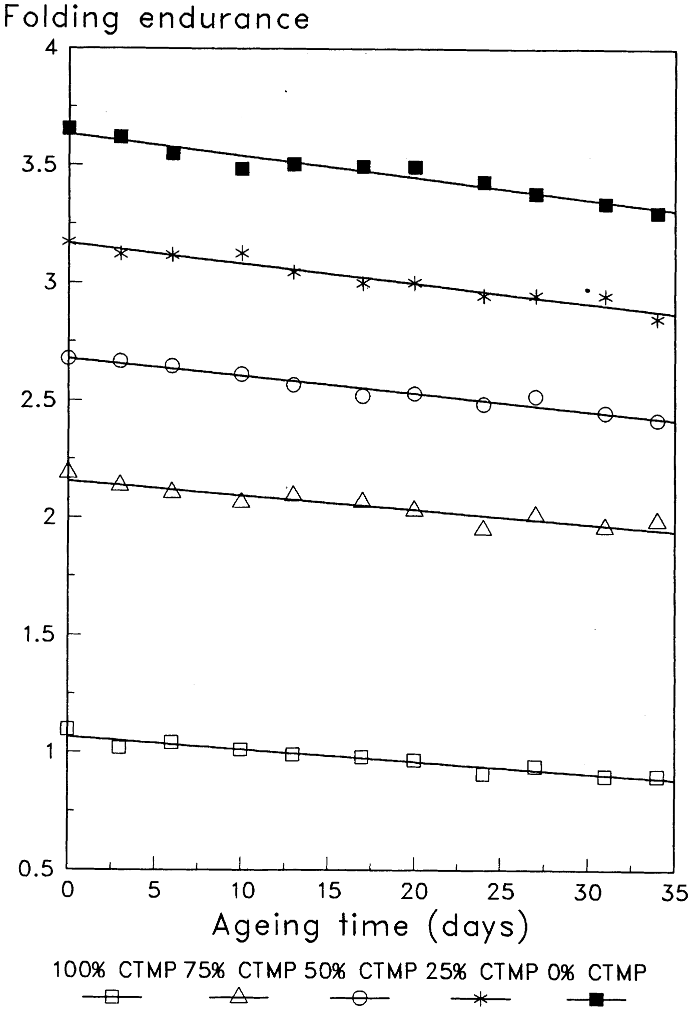

Figure 7. The loss of folding endurance on ageing for the papers containing various proportions of CTMP and sulphate softwood pulp, all sized with AKD.

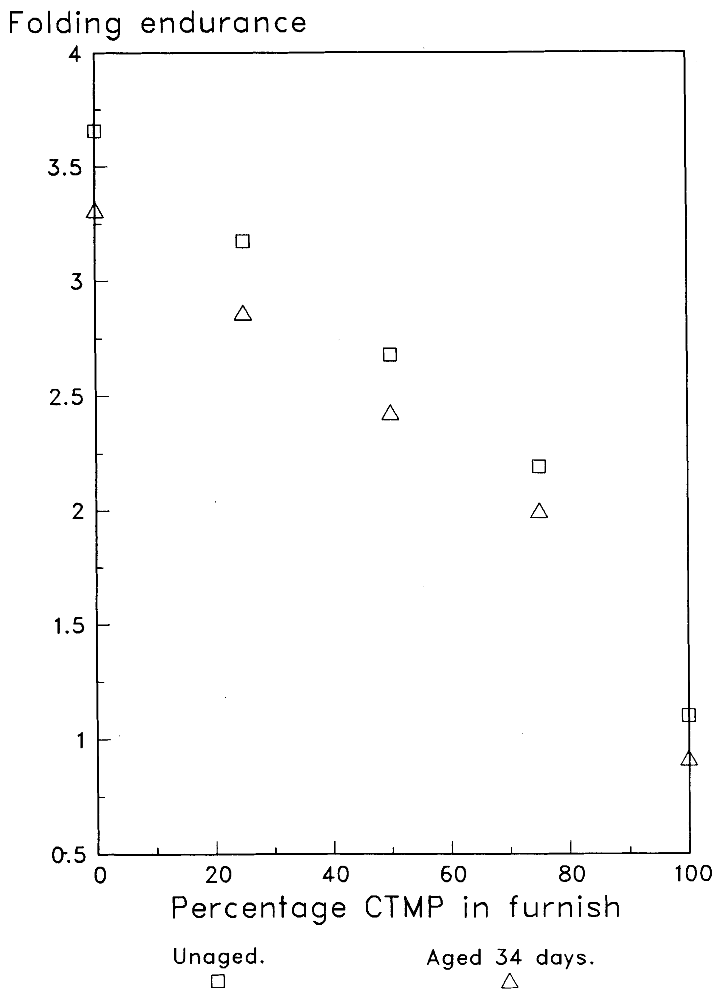

Figure 8. The change of folding endurance with CTMP content for unaged papers, and papers aged for 34 days, showing the small effect of CTMP.

change at all in the observed ageing behaviour. In fact the difference can be shown to decrease slightly as CTMP content increases; Figure 9 is a plot against CTMP content of the difference in fold endurance between unaged and aged papers (34 days).

It is clear, of course, that the durability of the papers containing CTMP is reduced whether or not they are aged. In selecting papers for applications where a long life is required, it is necessary to take into account both the initial durability, in the sense of fitness for purpose, and the rate of loss of strength. However it is important to distinguish between the two aspects of 'durability' and 'permanence'; for example, the initial poor strength of newsprint may have contributed to the poor reputation for permanence attributed to lignified fibres.

Figures 10 and 11 show how the zero span and long span tensile indices decrease on ageing. Once again, the main relevant conclusion is that the CTMP has not caused any sharp change in the rate of loss of strength. In this case it is of some interest to compare the proportionate loss of tensile strength by normalising the values for unaged papers to 100. The corresponding values for 34 days ageing are shown in Table 2.

% CTMP	Zero span tensile index (Nm/g)	Long span tensile index (Nm/g)
0	89	90
25	85	88
50	84	85
75	88	91
100	90	92

Table 2. Proportionate loss of tensile strength after 34 days ageing; unaged values = 100.

These values affirm the relatively small loss of strength occurring

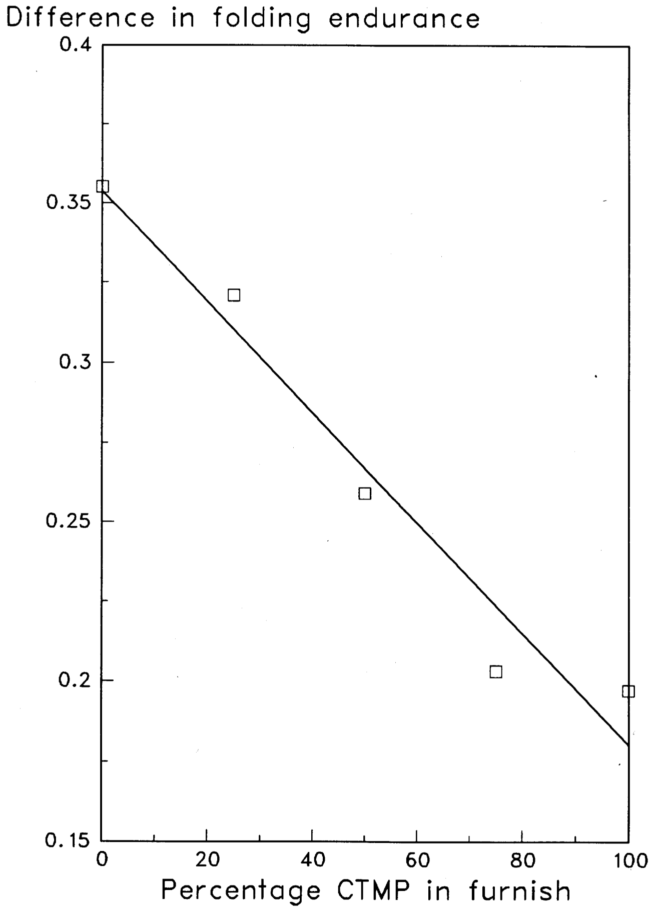

Figure 9. The difference in folding endurance between unaged and aged (34 days) paper as a function of CTMP content, indicating that loss of folding endurance was slightly less in paper containing CTMP.

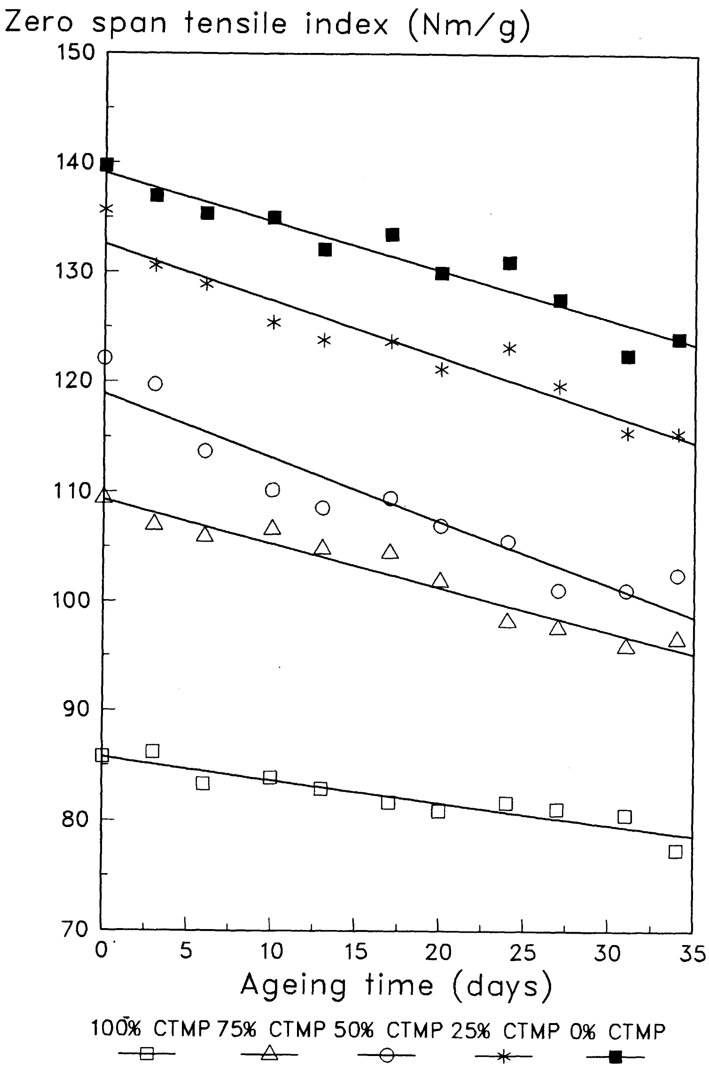

Figure 10. The decline of zero span tensile index with ageing for papers containing various proportions of CTMP.

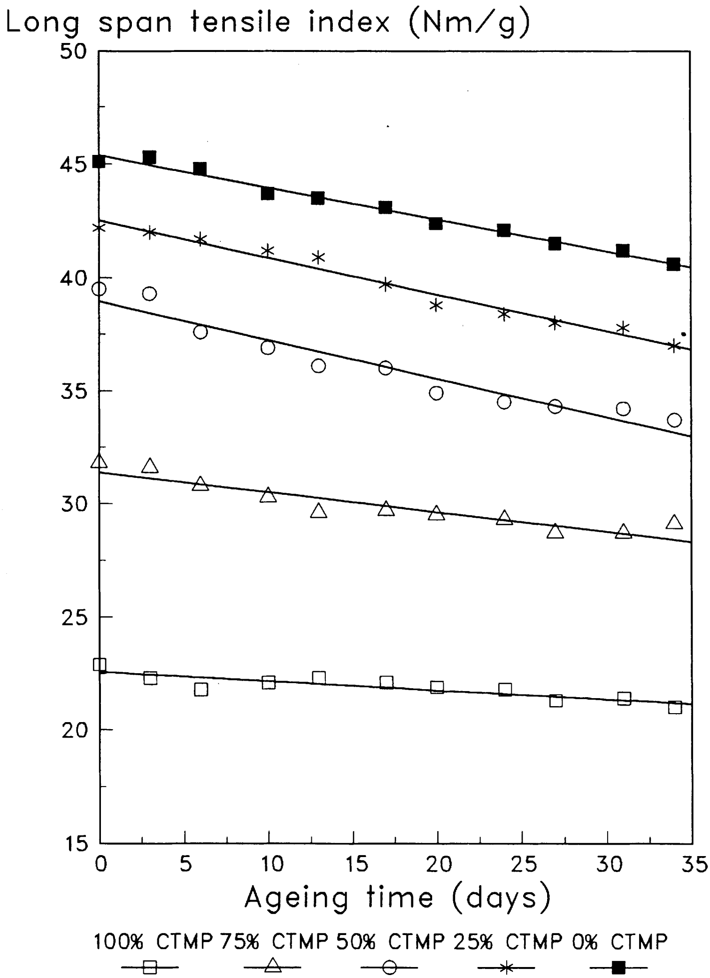

Figure 11. The decline of long span tensile index with ageing for papers containing various proportions of CTMP.

in these AKD sized papers and also indicate that proportionate changes are much the same whether or not CTMP is incorporated. There is a suggestion that the 50:50 blend of CTMP chemical pulp is ageing faster, but the difference between samples is very small. Again, there is a consistent, but only very small, difference between zero span and finite span values; as in alum/rosin sized papers, the zero span decreasing to a greater extent. The small magnitude of the total changes after ageing for 34 days, coupled with the size of the experimental variability (refer especially to Figure 9), does not allow comparison between changes of the fibre strength and bond strength.

The tensile energy absorption values for this set of experiments show some unexpected features, since the paper without CTMP is showing a distinctly more rapid decline in TEA than those containing CTMP, and the form of the decline seems to be different in CD and MD measurements. Figures 12 and 13 show the relevant graphs. The data also shows clearly that most of the effect with respect to TEA is associated with the corresponding changes in elongation at break, shown for comparison in Figures 14 and 15. For samples aged for 34 days, Table 3 summarises proportionate loss in the geometric mean TEA and percentage stretch.

% CTMP	TEA (J/m2) (Geometric mean)	% Stretch (Geometric mean)
0	62	70
25	69	74
50	72	76
75	78	84
100	76	80

Table 3. Proportionate loss of tensile energy absorption and elongation at break (% stretch) after 34 days ageing; unaged values = 100.

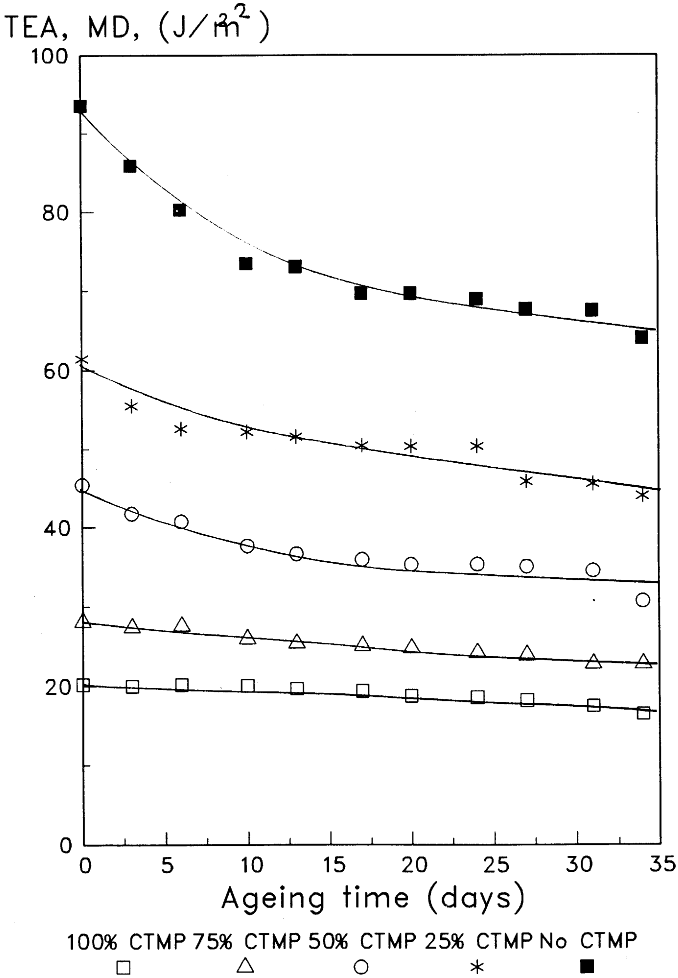

Figure 12. The decline of tensile energy absorption (MD) for papers containing various proportions of CTMP.

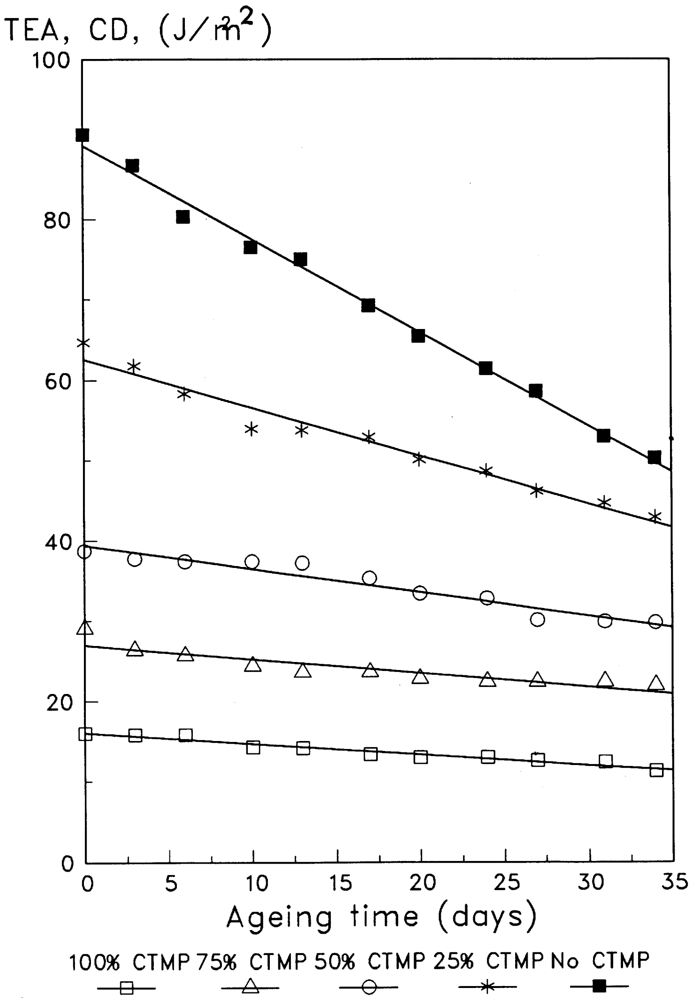

Figure 13. As Figure 12, showing CD TEA values.

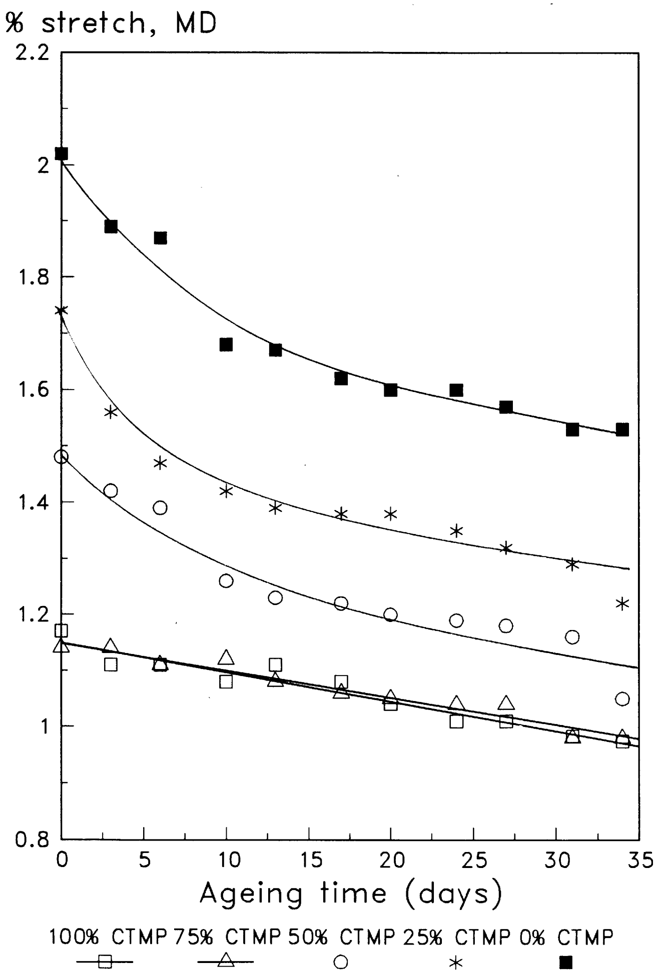

Figure 14. Elongation at break (% stretch) in the MD, plotted against ageing time, for papers containing various proportions of CTMP.

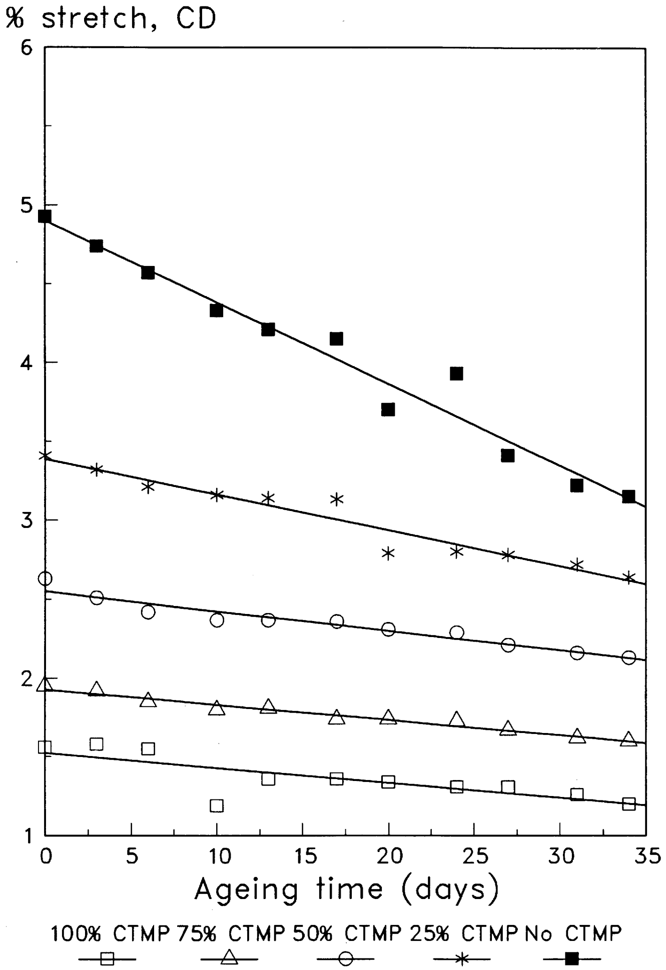

Figure 15. As Figure 14, showing CD values for % stretch.

The results also show that whereas in the CD the TEA and percentage stretch show a steady monotonic decline, in the MD there is an initial decline at about the same rate, followed by a much slower rate of decrease. These differences are clearly associated with the chemical pulp content, since they can be seen to some extent in the samples containing 75% and 50% chemical pulp. It appears that the ageing conditions are having a complex effect on the extensibility of these papers, which is not shown up in either folding endurance or tensile strength. No explanation can be offered for this effect at present, especially since it is clearly first necessary to establish whether or not they are to be found generally in neutral sized chemical pulp paper. Since the effect is absent in CTMP papers, it may be possibly associated in some way with fibre flexibility, and possibly fibre curl.

However, the main point to observe in the context of this work is that it is not the CTMP which is behaving in an unusual manner, and at least for this particular set of papers, retention of TEA and elongation is best for the paper made from 100% CTMP (Table 3).

Relationship between TEA and Folding Endurance

As noted above, with the example shown in Figure 6, good correlations can be obtained between TEA and folding endurance for individual ageing experiments. Although the range of values is much less in the AKD sized samples having different CTMP contents, since these papers show less degradation, a similar correlation can be observed. This is illustrated in Figure 16, for all five AKD sized papers. The individual sample sets can easily be recognised, and the systematic shift from one group of points to another raises the question of a possible single relationship for the whole range of values. In this graph, the folding endurance is shown as number of folds to failure on a logarithmic scale. Conversion of this scale to a linear one, ie a plot of the actual

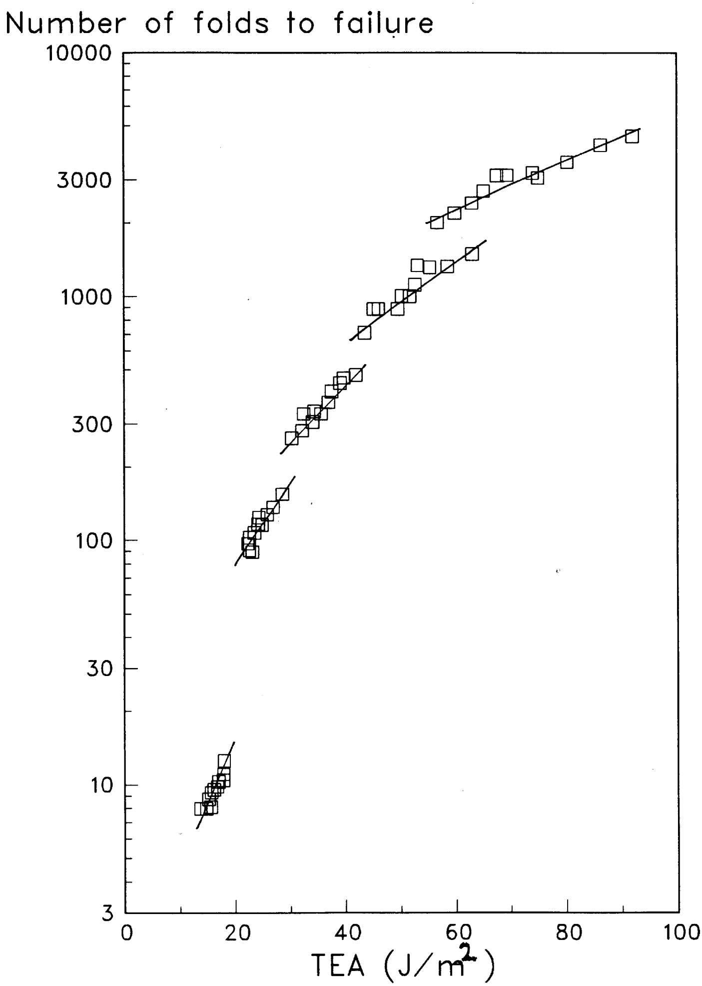

Figure 16. Shows the number of folds to failure, on a logarithmic scale, plotted against the TEA for papers containing various proportions of CTMP. Note the approximate linear relationship for each paper and the systematic change of slope.

number of folds to failure, yields the result shown in Figure 17. This suggests an exponential variation of some kind, and this can be interpreted qualitatively on the basis that, at the lower end, a sample which will not stand even one fold, retains sufficient coherence to require a finite energy input to fracture it. At the upper end, as TEA increases to high values, fold number might be expected to become very large, and it is possible to imagine a very tough sample having by comparison an 'infinite' fold number. On this basis, the values might be expected to fit an equation of the form:

$$x - u = v(1 - \exp(-wy))$$

where x is TEA, y is the number of folds to failure, and u,v and w are constants. The lowest value of TEA observed was 13.7 J/m2, corresponding to a fold number of only 8. Consequently, a value of 10 was chosen for the constant u. A spread sheet (Lotus 123), was then used to obtain values for the constant w, which would give the best rectilinear correlation when plotting (x - u) against 1 - exp(-wy). The result is shown in Figure 18 in which R2 is equal to 0.962. However, the points appear to fall on a slightly S-shaped curve, and re-examination of Figure 17 suggests that, at least for these set of samples, the rate of increase of fold number begins to fall away as TEA increases. A better fit can, in fact, be obtained by using an equation of the form $y = 1/(1 + \exp(-x))$ as indicated by Figure 19 (after again using the spread sheet to optimise the fit). However, any mechanistic significance of this type of curve needs to be explored further using additional data.

Discussion

The major result to emerge from this work is undoubtedly that if CTMP papers are sized with a neutral alkaline system using, say, AKD, and contain an antacid filler, such as calcium carbonate, then, and on the basis of an accelerated ageing test, these

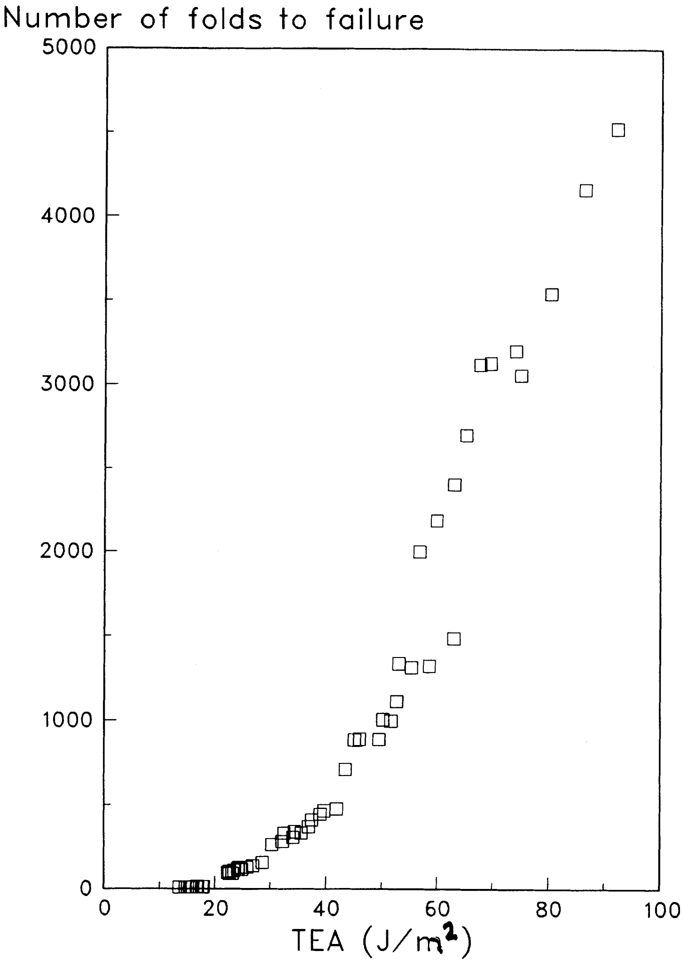

Figure 17. The TEA plotted against the number of folds to failure; note the indication of an overall exponential type relationship.

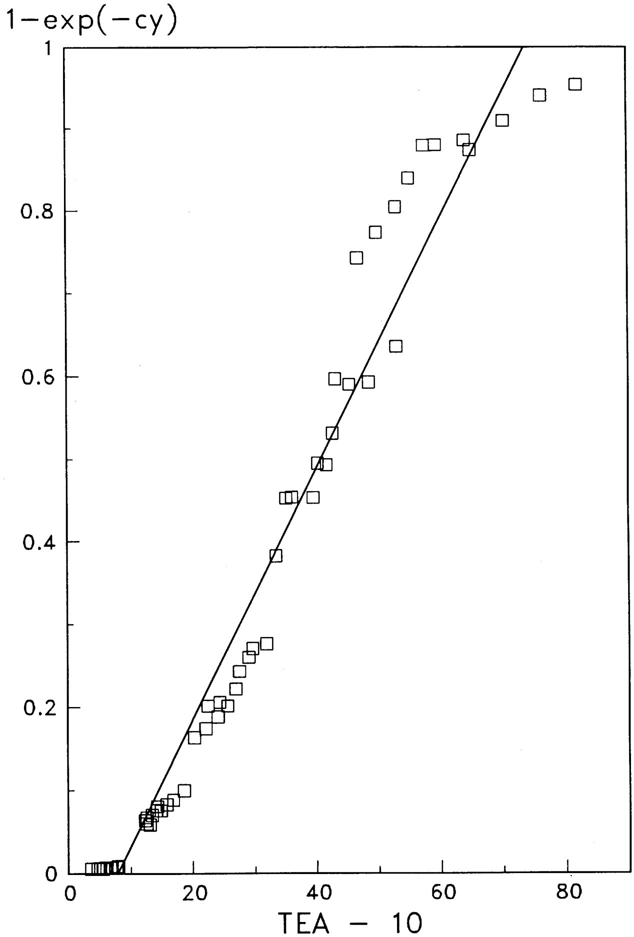

Figure 18. The data of Figure 17 as an exponential plot, showing an imperfect linear correlation.

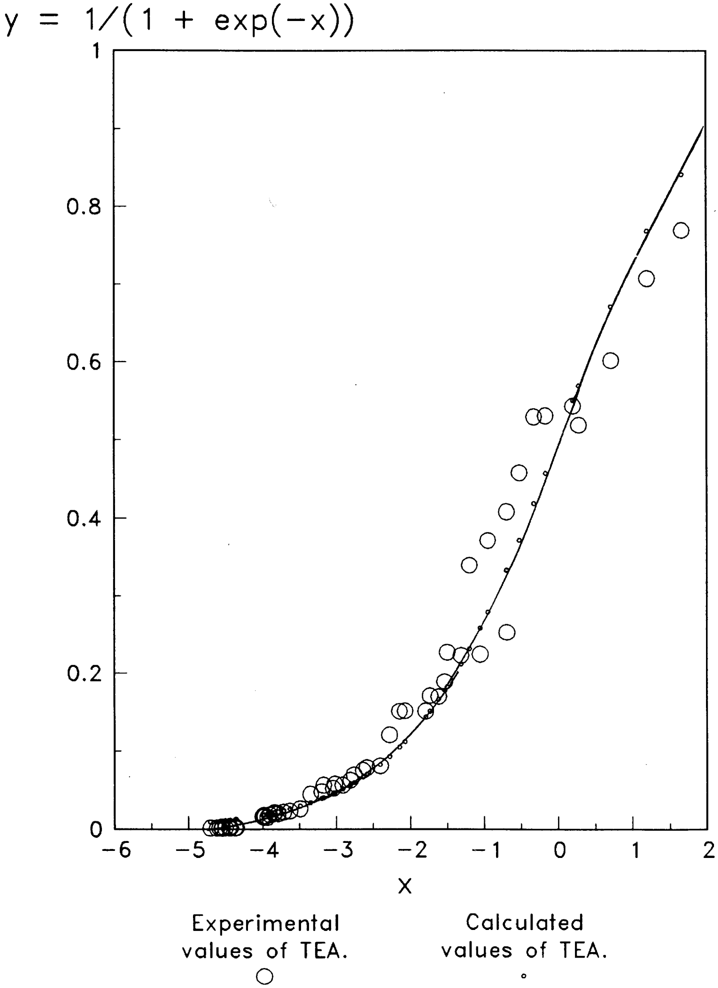

Figure 19. Fitting an expression y = 1/(1 + exp(-x)) to the relationship between TEA and fold number.

papers can retain mechanical strength as well as a wood-free grade. However, as noted above, the CTMP paper will certainly start out with a lower strength and will also become yellow on exposure to light. To illustrate this point, Figure 20 shows how the 100% CTMP AKD sized paper discoloured on exposure to light in a Microscal V light-fastness tester.

Although they lost strength at a much slower rate, the AKD sized papers did show a definite degradation. Some internal evidence from the strength measurement (eg Figure 4 discussed above) suggested that the mechanism was similar to that in the acidic paper. Some additional evidence for this comes from measurement of cold water extract pH of the aged papers, and Figure 21 shows data for all the samples used for the work here, plus three other papers containing CTMP made for other investigations. These results strongly suggest that acidity is the key factor. The source of acid hydrolysis in the neutral alkaline paper is not yet known, but could be connected, for example, with residual carboxylic acid groups introduced by pulping. Clearly, in the present work, using two types of CTMP, the presence of the lignin, of itself, has not produced additional loss of strength on ageing under the conditions employed. Although accelerated ageing procedures have been criticised (21), it seems rather unlikely that under ambient conditions, different mechanisms of lignin degradation would occur to give rapid deterioration. This one-sided treatment of an accelerated ageing test seems reasonable; if a paper does degrade rapidly at high temperatures, there may still be some uncertainty about whether or not similar mechanisms are occurring at ambient temperatures. On the other hand, very slow deterioration at high temperature is highly unlikely, on the basis of chemical reaction mechanisms, to translate into faster degradation under ambient conditions.

With regard to implications for the manufacture of permanent paper for general publishing purposes, and the associated standard specifications, these results clarify considerably the

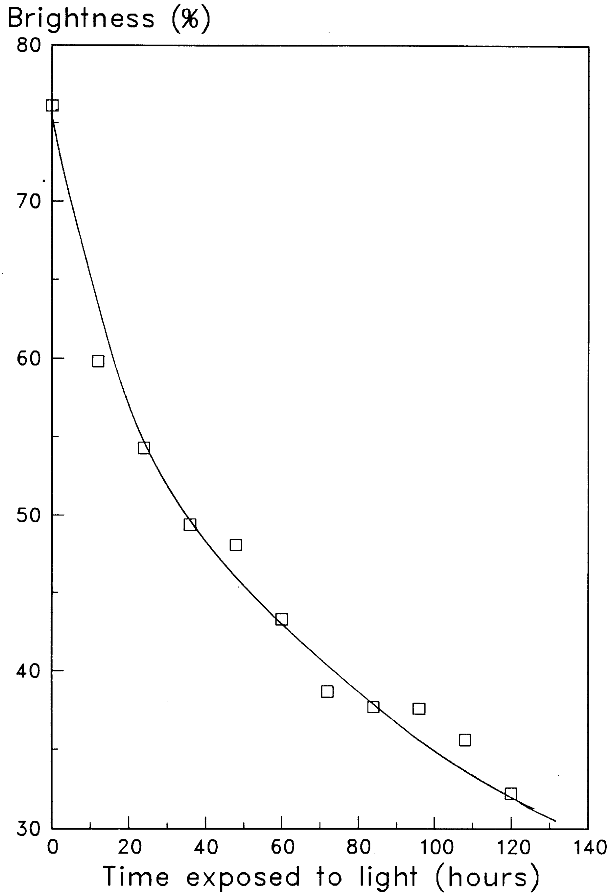

Figure 20. The loss of brightness on exposure to light in a Microscal tester for the paper made from 100% CTMP, sized with AKD.

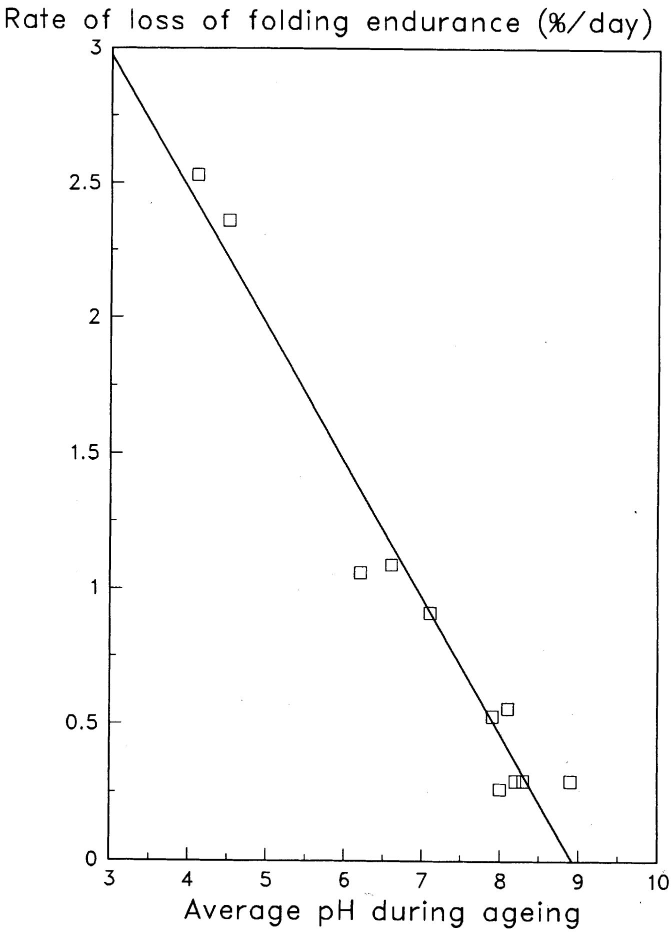

Figure 21. The rate of loss of folding endurance on ageing, plotted against the average cold water extract pH during ageing, indicating the predominance of acid hydrolysis as the degradation mechanism.

position of a modern pulp such as CTMP. Those concerned with such specifications will need to decide the relative importance of initial strength and discoloration. For certain applications, where these effects are not considered to serious, and the economic advantages of a high yield pulp are important, it would be possible to specify grades containing a reasonable proportion of CTMP which did not lose strength at an unacceptable rate.

ACKNOWLEDGMENTS

The authors would like to thank C. H. Johnson Ltd. for financial support through a Bicentennial Student Scholarship, and Prof. Hein Kropholler for useful advice.

REFERENCES

1. Grant, J., "Books and documents: dating, permanence and preservation", Grafton, London 1937.

2. Clements, D.W.G., "Preservation microfilming: a substitution policy in the British Library", Microform review, 17, 1988, 17-22.

3. Burstall, M.L., Butler, C.E. and Mollet, C.C. "Improving the properties of paper by graft copolymerisation", The Paper Conservator, 10, 1986, 95-100.

4. Kelly, G.B., "Mass deacidification with diethyl zinc",Library Scene, 9, 1980, 6-7.

5. Smith, R.D., "Design of a liquified gas mass deacidification system for paper and books", in "Preservation of paper and textiles of historic and artistic value", ed. J. C. Williams, American Chemical Society, Washington, D.C., 1977, 149-158.

6. Wedinger, R., "Preserving our written heritage", Chemistry in Britain, 28, 1992, 898-900.

7. Lyth Hudson, F., "Permanence of paper", in "The fundamental properties of paper related to its uses", Trans. of the symp. held at Cambridge, Sept. 1973, British Paper and Board Industries Federation, pub. Benn, London, 1976, 714-719.

8. Wilson, W.K. and Parks, E.J., "An analysis of the ageing of paper: possible reactions and their effects on measurable properties", Restaurator, 2, 1979, 37-67.

9. Fan, L.T., Gharpuray, M.M. and Lee, Y.-H., "Acid hydrolysis of cellulose", in "Cellulose Hydrolysis", Springer-Verlag, 1987, 121-148.

10. Hey, M., "The washing and aqueous deacidification of paper", The Paper Conservator, 4, 1979, 66-80.

11. Stanley, J., PhD thesis, University of Manchester, 1992.

12. Jackson, M., "CTMP: its manufacture, properties and end uses", Paper Technology, 29, 1989, 18-26.

13. Graminsky, E.E., "The stress-strain behaviour of accelerated and naturally aged papers", TAPPI, 53, 1970, 406-410.

14. Abadie-Maumert, F.A., "Wood containing paper has good ageing stability", PFI Nytt., 4, 1989, 16-17.

15. Johnson, R.W. and Bird, A., "CTMP in fine papers: impact on the permanence of alkaline papers", 1991 Papermakers Conference, TAPPI Press, Atlanta, 1991, 267-273.

16. Graminsky, E.E., Parks E.J. and Toth, E.E. "Effects of moisture and temperature on the accelerated ageing of paper", in "Durability of Macromolecular Materials", ACS Monograph Series 95, American Chemical Society, Washington 1980, 341-355.

17. Cardwell, R., Lyon, L. and Luner, P., "Evaluation of a fold test procedure for ageing studies", TAPPI, 55, 1972, 228-233.

18. ANSI standard Z39.48-1984, "Permanence of paper for printed library materials".

19. Luner, P., "Paper permanence", TAPPI, 52, 1969, 796-805.

20. Page, D.H., "A theory for the tensile strength of paper", TAPPI, 52, 1969, 674-681.

21. Strofer-Hua, E., "Experimental measurement: interpreting extrapolation and prediction by accelerated ageing", Restaurator, 11, 1990, 254-266.

Transcription of Discussion

THE IMPACT OF MODERN PAPERMAKING ON ASPECTS OF PERMANENCE AND PAPER CONSERVATION

D J Priest

Dr P Kolseth, STFI, Sweden

I would like to begin with just a general comment that virtually all references to the optical appearance of paper at this conference make use of the term 'brightness'. I would like to point out that this is a pulp property used to determine the level of bleaching in chemical pulps. I think it is about time that paper physicists realised this and start quoting data as 'Y'-value, whiteness or preferably the spectral reflectance values which are so easily extracted from modern reflectometers. Now I have a specific question. You showed here that neutralized papers with an alkali reserve still show some degradation. If we suppose that this degradation to a great extent involves acid hydrolysis, which is quite reasonable, how do you account for this kind of reaction in an alkaline system?

D Priest

I don't know the answer to your second question, I think it is something that needs to be addressed. You agree with me that it could be an acid hydrolysis mechanism in there somewhere, I guess one has to address what is happening right inside the fibre wall. On your first point, we accept your comment, but you will agree that 'brightness' is often quoted for paper. If you want the colour values we have them. We would be happy to provide you with a whole lot of colour values. I selected brightness for convenience, and to save time.

Dr J Stanley, John Rylands Research Institute, University of Manchester, UK (Co-author of paper)

I would just like to address your question. I think when we are using artificial ageing techniques we see things happening to papers in the oven that cause degradative effects we would not normally see in papers aged under natural conditions, and that there are probably temperature effects causing degradation.

Prof B Lyne, Royal Institute of Technology, Sweden

The origin of the standard of permanence I think was with the National Information Standards Organisation in the USA, NISO, which is basically a group of librarians not papermakers and the standard was corrected initially because they had a very narrow pH range which didn't include modern or some alkaline papers, not standard, but they also included in their standard the exclusion of all papers having a lignin content of a very low value so it really excludes all chemi-mechanical and mechanical pulps. Why this is worth raising is that they are now hoist on their own pretard because there are neutral papers being made lightweight coated which is made under neutral conditions today and that is the paper which is in most of the high volume journals which they would like to be able to declare as being permanent. I believe that they are still reluctant to change the standard and raise that permissible lignin content or simply ignore that as a factor because they feel there isn't enough evidence that mechanical papers do not degrade more quickly than their chemical counterparts. Do you feel we have arrived at a point where there can be a reconsideration of this standard?

D Priest

I think in ISO 9706 what we really thought was that, after all, these standards are reviewed every 5 years. We wanted to get the

Standard up and running. I don't entirely agree that the thing was directed only at library people, there were some paper people on the committee and I think we did our best to meet both types of party but to my view, my last comment merely reflects that. I don't think the user community or the people concerned with where the paper will go have thought seriously enough about just what they want in that sort of paper. I think until that happens it will be hard really to include this lignified pulp. I think another danger is, just following up your comment, that in some countries people have somehow got the idea that this standard is directed at all sorts of publication papers - of course we never intended that. The idea was specifically for paper where somebody wanted it to be permanent. I think that has also given rise to some of the confusion.

Prof E Back, Feedback Consulting E & E Back KB, Sweden
Thank you for some interesting data. I would now like to propose a few additional measurements in order to get a better understanding. That is for the first wet strength because hydrolysis does not produce wet strength - the other one is thickness and swelling and then also to measure hydrolysis itself, eg water extractable material. By doing these things you get a better view about the Weiss(??) mechanisms, the hydrolysis and the Tony Scallan autocrosslinking which I think is present and then it will give additional understanding.

D Priest
Yes, thank you very much for that comment. We have in fact done some work in my group on the effect of aluminium salts on wet strength - I don't want to talk about that here because I haven't got the details with me but thanks very much for the point. I tried to cover that in my talk really by making the point that in terms of the

real effects some aspects are much more important than others - in my view, at least in a practical standard sense. Thank you very much for your suggestions - I am grateful for that.