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THERMOMECHANICAL STABILITY OF PULP AND PAPER

P. LUNER, Empire State Paper Research Institute, State University of New York College of Environmental Science and Forestry, Syracuse and R. D. CARDWELL, New Zealand Forest Products Ltd., Auckland

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Synopsis The thermal stability of papermaking pulps under conditions of accelerated ageing was examined. Degradation was found to be extremely complex and influenced both by the technical processes of papermaking and by the experimental methods used. At moderate temperatures as used for accelerated ageing, the folding endurance test was a sensitive measure of degradation. Methods of reducing the variability of the test were considered and a new technique capable of handling widely different results was developed and evaluated.

Several papermaking pulps were artificially aged and the resultant loss of strength attributed to the interaction between a gradual fibre strength reduction and a rapid increase in interfibre bonding. Excessive initial interfibre bonding decreased handsheet stability. Softwood sulphite and kraft pulps were more stable than a birch kraft pulp, but the behaviour of sulphite pulps varied greatly. The presence of lignin or of high hemicellulose content was not of itself sufficient to cause rapid ageing.

Introduction

RECENTLY, attention has been focused on the fact that modern writing papers and books tend to have a much shorter life expectancy than books manufactured 100 years ago.[1–3] The increased use of wood fibres, the use of chemical additives, especially those promoting increased acidity, as well as environmental conditions, have been given to account for these results. In view of these findings and because of the importance and necessity of preserving books and documents in the best possible state, investigation of the factors governing the stability and durability of paper has increased greatly.[4–6]

Considerable changes have occurred in the last few decades in pulp processing, especially in bleaching. Pulps produced by the newer bleaching sequences can therefore be expected to perform differently on ageing than pulps produced in the past. Today, in addition to the well-established kraft and sulphite

Under the chairmanship of Dr H. G. Higgins pulps, pulps retaining more carbohydrates and lignin are gaining importance for a variety of uses, including writing and printing papers. Very little information exists on their permanence properties and little can be said at this time therefore on the role of lignin and hemicelluloses in paper permanence.

The objectives of this paper are to highlight several considerations involved in the study of paper permanence. This includes a brief discussion of conditions for accelerated ageing studies and for fold testing of aged samples. In addition, the relationship of chemical composition and sheet characteristics to paper permanence will be explored and results applied to commercial papers. Finally, the thermal stabilities of a wide range of papermaking pulps will be compared and discussed in relation to the fibre and sheet mechanical properties of the pulps.

TESTING FOR PAPER PERMANENCE

Temperature and humidity

EXTENSIVE work has shown that polymers, including cellulose, may degrade thermally by a number of different mechanisms, depending on reaction temperature and the nature of the atmosphere. Thus, cellulose in a vacuum degrades by means of a random mechanism between 250° and 300° C, the degree of polymerisation dropping sharply because of scission of glucoside links. At lower temperatures, water, carbon monoxide and carbon dioxide are involved, indicating that a non-random stripping of the molecule takes place. Major[7] studied the effect of oxygen and nitrogen on the thermal degradation of cellulose and found that in all cases degradation was much greater in an oxygen atmosphere, with oxygen acting as a non-specific oxidant. Other studies indicate that metal impurities contribute to cellulose degradation.[8]

Moisture accelerates the ageing of paper[9, 10] considerably, but the rate at which this increase occurs varies, depending on the type of pulp. The presence of moisture leads to hydrolysis of glucosidic linkages in cellulose and hemicellulose, probably also accelerates the reactions of impurities (trace metal and extractives) with cellulose.

Establishing the upper temperature limit for accelerated ageing is important, since the degradation most likely involves pyrolytic fragmentation at elevated temperatures. The lower the temperature, the closer the process approaches natural ageing, but ageing below 60° C is too slow to be useful for experimental work. Based on data from existing studies, ageing temperatures should be between 60° and 100° C and the humidity level such that a normal amount of moisture (3–8 per cent) is retained by the samples at ageing temperatures.

Even under these carefully controlled environmental conditions, the mechanisms of natural ageing and accelerated ageing may be different. While the importance of moisture in accelerating the loss in permanence has been recognised,[4–6] it is rather surprising that both the ASTM and TAPPI tests for paper permanence involve only dry heat.

Type of strength test

THE choice of mechanical tests used to evaluate paper permanence depends to a great extent on the purpose of the paper. Thus, if the use of the paper clearly involves tensile strength, then the burst and breaking length tests would be appropriate. In paper permanence studies, the mechanical test most closely corresponding to use is the folding endurance of paper. Usually, however, several mechanical properties of paper are determined, as a clear understanding of the relationship between the use requirements of the product and any single test is not yet available. Since natural ageing of papers usually occurs with some moisture in the sheet, accelerated ageing tests should also include moisture.

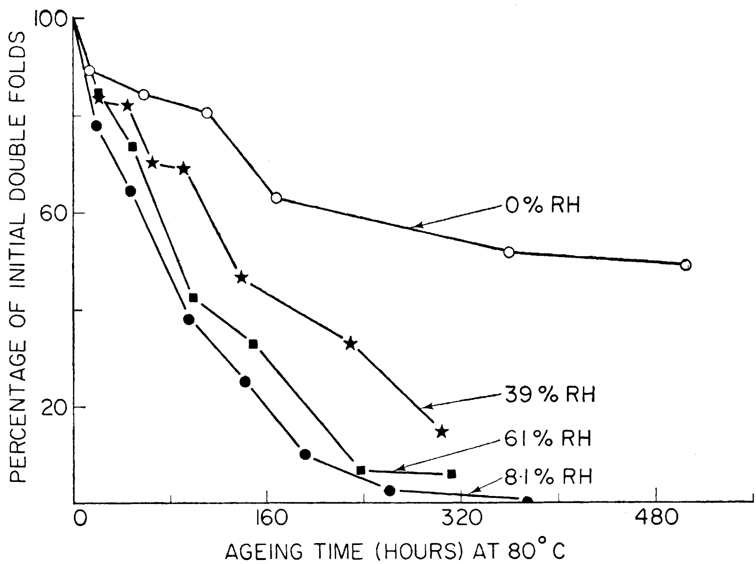

Fig. 1—Effect of humidity on folding endurance (bond paper aged at 80° C)

For the above reasons, the effect of ageing on several mechanical properties of three commercial papers was determined at 80° C and at three different humidity levels. The effect of humidity was similar for all strength tests examined—tensile, tear, work-to-rupture and MIT fold, with the folding test displaying the greatest sensitivity. Fig. 1 & 2 show the results for the folding test. It is seen that humidity accelerates the loss in folding endurance considerably, with the effect diminishing as a higher humidity level is reached. The absolute values for the folding endurance of three papers shown in Fig. 2 illustrate the differences between papers and the range of folding values encountered on ageing.

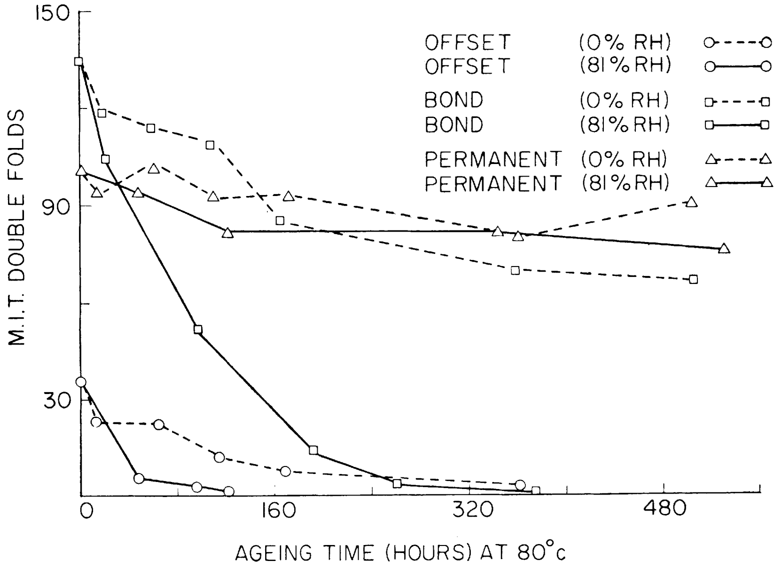

Fig. 2—MIT double folds plotted against time of ageing at 80° C

Because of the greater sensitivity of the folding test to ageing and its close relationship to performance, it qualifies as the test of choice for permanence studies. Nevertheless, some important questions regarding the folding endurance test remain to be resolved. One is the strong dependence of the folding value on the load. Thus, the folding values of weaker papers are compared with stronger papers at the same tensile load. This raises the question as to the basis of comparison. Furthermore, on ageing, very low folding values are encountered and the significance of these low values may be questioned. Finally, the experimental variation in folding values is well known[11–13] and must be considered in any investigation involving permanence. Some of these topics were therefore considered of sufficient importance to investigate further and are summarised in the following section.

A folding test procedure for ageing studies

WITH relatively weak papers, a lower load than prescribed in the TAPPI standard method may have merit; using higher loads than 1 kg for very strong paper would certainly decrease the testing time. Special methods of utilising the folding test include determining the load required for a sample to fail at a given number of folds or determining the number of double folds at a load that is a given percentage of the breaking load of the sample.[14] It is frequently difficult to decide in advance which variation of the folding test would be most useful and a study was undertaken to develop a folding test procedure that could simultaneously apply to several of these methods and would be applicable to aged as well as unaged papers. The results of this study were reported previously[15] and only the highlights will be recalled.

To reduce the experimental error in the MIT folding test, several modifications and precautions were taken. These include deadweight setting of the load, reduction of frictional effects of the plunger, as well as reducing the heat built up at the jaw sites. The paper strips were mounted in the instrument in a vertical position with the felt side of the sample always against the fixed jaws. The folding test was always started in the same direction. The sample-to-sample variation was reduced considerably when these procedures were followed.

Several studies[14, 16, 17] have examined the relationship between load and folding endurance. In one form, the natural log of fold against the load fitted the exponential equation—

$$\ln F = mL + b \qquad (1)$$

where F = folding endurance, double folds
L = load on testing machine, kg
m, b = equation parameters

Others[18, 19] have found a ln fold against ln load relationship to be more valid. This equation takes the following or some related power function form—

$$\ln F = m \cdot \ln L + \ln A \qquad (2)$$

where m, F and L are as in equation (*1*) and $\ln A$ is an equation parameter corresponding to b. Both these equations were tested, using data selected from the literature as well as data generated in our own laboratory, using commercial pulps in the unaged and aged condition. The load/fold relationship was established by testing 5 samples at 4 different test loads. In all, 30 sets of data were evaluated and no statistically significant difference was found between the two equations. Fig. 3 shows the fold/load relationship according to equation (*2*) for 6 samples representative of 23 unaged and 7 aged pulps.

The universal applicability of this linearising procedure makes it practicable to obtain folding results at loads other than those tested. For example, if high load values were used to test aged papers, very low and unreliable folding data would be obtained. On the other hand, using very low load values suitable for the aged paper would lead to excessively high folding values when testing the unaged samples. Thus, by using the fold/load relationship, folding values can be obtained at loads otherwise impracticable or unreliable. Other methods of using this relationship have been previously mentioned. Table 1 gives some statistical data using these procedures and compares them with results obtained from the literature in the conventional manner. It is seen that little precision is lost by following this testing procedure.

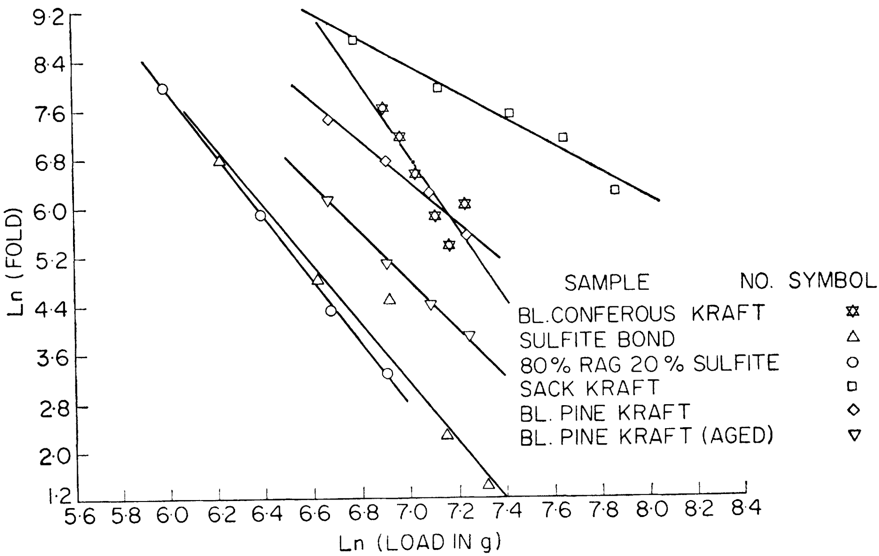

Fig. 3—Graph of ln fold against ln load for various samples

TABLE 1—THE PRECISION OF COMPUTED FOLDING ENDURANCE VALUES
(*Standard deviation as percentage of computed mean*)

Sample source	*Average*	*Minimum*	*Maximum*
Last 14 samples of Table 1 (computed fold at 1 kg)	28·6	16·7	49·3
Last 14 samples of Table 1 (computed fold at 0·5 kg)	76·9	36·5	123·0
Last 14 samples of Table 1 (computed fold at 20 per cent of the breaking load)	43·4	17·8	88·4
Comparative values from the literature			
B.P. & B.M.A. Test Method S-1[21]	45·0	19·0	82·0
Köhler, S.[18]	25·9	13·1	50·9
Wink, Ward & Swenson[20]	32·4	18·9	60·8
Kronstad, W.[16]	39·4	19·8	94·9

PREDICTION OF PAPER PERMANENCE

AN ACCELERATED ageing test increases the intensity of deterioration so that the deterioration of paper corresponding to normal conditions for extended times is obtained in a relatively short time. For paper permanence studies, elevated temperatures with or without the presence of moisture have been used to accelerate the intensity of deterioration. The Arrhenius equation in logarithmic form—

$$\log k = \log A - \frac{E}{2{\cdot}303RT} \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where k = specific rate constant
A = frequency factor (usually treated as a constant)
E = activation energy, kcal/mole
R = gas constant
T = absolute temperature, °K

has then been used to describe the temperature dependence of the reaction rate. For paper, in most instances, the rate constant refers to a mechanical property of paper. For this equation to be used in predicting the rate of ageing, a number of conditions have to be fulfilled. The rate plot must be linear and the activation energy independent of temperature, so that a graph of log k against $1/T$ yields straight lines. Once E is obtained, the rate constant k can be evaluated at any other temperature. Fairly extensive data on activation energies[4, 5, 22] for paper strongly suggest that an E value for each paper is necessary in order to predict its permanence with any accuracy.

There are several difficulties inherent in the use of the Arrhenius-type equations that are not readily apparent. Graphs of log k against $1/T$ have been found to be fairly linear and, from these results, it has been inferred that the mechanism of permanence loss does not change throughout the temperature range and time intervals employed. It should be recognised, however, that the mode of failure of paper may change on accelerated heating and natural ageing. This may easily be recognised by examining the ruptured areas microscopically. All papers, when extensively aged, fail by fibre failure during folding; in unaged or slightly aged papers, bond failure also occurs. Indeed, the non-linear relationship often encountered between the logarithm of the folding value and ageing time may reflect this difference in failure mode.

In view of the existence of different modes of failure, it would not be surprising if the activation energy should vary with temperature. In most instances, however, this is not the case, most likely caused by the fact that other reactions occur simultaneously. Cross-linking, dehydration, hydrolysis and oxidation are a few of such reactions that may be occurring. The resulting activation energy is then the average of several simultaneous competing reactions that involve chemical as well as physical processes and predictions based on activation energies for papers are uncertain. Another shortcoming of the Arrhenius relationship for predictiong paper permanence is the accuracy necessary in determining k and, hence, E. The large inherent variability in the folding endurance test, as well as the frequent necessity for empirically linearising the rate data, makes it difficult to obtain activation energies with the precision required to calculate rate constants that can be used for predicting permanence with any great degree of reliability. Table 2 gives one such example.[4]

TABLE 2—ESTIMATION OF PERMANENCE OF PAPERS AT 20° C[4]

Sample	*By extrapolation of Arrhenius plot*	*Range* 95 per cent confidence limits	*Range* 50 per cent confidence limits
Estimated time in reach one half original folding endurance, years			
A–2	714	196–2 606	523–975
C–2	2 159	79–58 910	975–4 791
F–2	1 529	97–24 173	788–2 972
H	452	83–2 486	301–681
Estimated time to reach a specific absorption coefficient of 60 cm²/g, years			
A–2	835	357–1 951	681–1 024
C–2	709	171–2 937	502–998
F–2	179	113–285	160–201
H	314	125–788	251–391

Some of the shortcomings in the utility of the Arrhenius equation to predict folding endurance may be circumvented by the use of a prerupture mechanical property of the paper such as Young's modulus. In this case, paper or fibre failure is not involved; consequently, the effect of temperature on the mechanical property (Young's modulus) is more closely related to chemical transformations for which the Arrhenius equation applies. It remains, then, to correlate the more complex mechanical tests such as folding endurance with prerupture behaviour. Little or no data exist in this area of paper testing. Until more information is available on the reactions and failure mechanism occurring in paper as a result of ageing, only the relative stabilities (in terms of folding endurance) at a given temperature can be assessed with ease. Rankings in stability obtained at elevated temperature should be extrapolated to room temperature with extreme care and conclusions should be based on other supporting evidence.

FIBRE CHEMISTRY

A NUMBER of studies[25–27] have shown that loss of paper permanence correlates with a decrease in paper pH value. It seems reasonable to believe that one chemical reaction leading to loss in paper permanence is acid hydrolysis. Thus, a knowledge of the relative rates of hydrolysis. of the hemicelluloses is of interest. Results from the heterogeneous acid hydrolysis of hemicelluloses in pulp show that the hemicelluloses hydrolyse at a much greater rate than does cellulose.[28, 29] This process is catalysed by the organic acids produced by the cleavage of acetyl and methoxyl groups from the hemicelluloses. When the differences in accessibility are taken into account, the differences in rates of hydrolysis become even more marked. Pulps containing hemicelluloses, then, may lead to more rapid ageing. In addition, their breakdown is likely to make the sheet more acidic and contribute to the premature breakdown of the more resistant carbohydrates.

TABLE 3—ACIDIC GROUPS IN SPRUCE AND BIRCH SULPHITE PULPS[32]

Yield, per cent	Total lignin, percentage of pulp	Carbohydrates, percentage of neutral polysaccharides			Accessible groups, meq/100 g pulps		
		Glucan	Mannan	Xylan	Total acidic groups	Sulphonic acid groups	Carboxyl groups
			Spruce				
75·7	19·2	77·2	16·8	6·0	33·96	28·59	5·37
67·7	13·8	78·4	16·6	5·0	27·14	21·86	5·28
63·3	8·6	78·5	15·7	5·8	20·33	15·44	4·89
60·6	5·9	79·2	14·9	5·9	15·35	10·94	4·41
			Birch				
83·8	19·5	68·7	1·9	29·4	20·11	10·13	9·98
69·0	15·1	73·1	3·9	23·0	17·98	10·39	7·59
55·8	6·7	80·6	2·1	17·3	10·99	5·39	5·60
53·4	4·0	83·4	2·0	14·6	8·41	3·10	5·31
50·1	2·2	84·2	2·1	13·7	6·40	1·74	4·66

While pulping processes retaining hemicelluloses introduce acidic groups, the bleaching process may also introduce acidic groups (that is, carboxyl groups), as well as aldehydic or ketonic groups, depending on where the oxidative attack occurs. The amount of such groups may range 0·005–0·0010 groups per glucose unit (Rydholm, p. 965[23]). The profound effect of the oxidised groups on colour formation during accelerated ageing has been amply demonstrated,[30, 31] but these studies have not examined the relationship between functional groups and the mechanical properties of paper after ageing. Indeed, the data suggest that the mechanical properties, although adversely affected by oxidised groups, do not follow the relationships established between colour reversion and functional groups.

In bleached and unbleached pulps, sulphonic and carboxylic acids from the lignin may be present together with the native aldonic and uronic acids. In addition to these strong and moderately weak acids, phenolic groups may be found in the unbleached pulps. A quantitative analysis of some of these groups for a number of pulps are shown in Table 3.[32] Other evidence, summarised in Fig. 4 & 5, shows that chlorine either in the lignin[33] or extractives[34] is released as hydrogen chloride under accelerated ageing conditions, causing colour reversion. Under these conditions, a loss in the mechanical properties of the pulp is very likely.

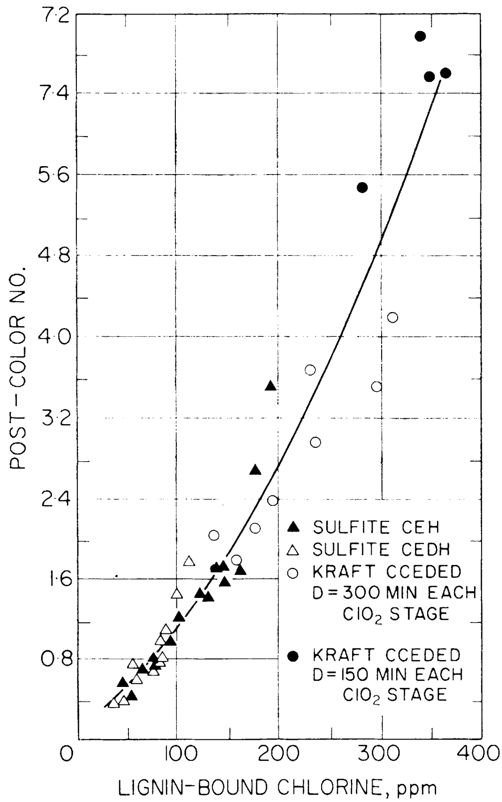

Fig. 4—Graph of post-colour number against lignin-bound chlorine (wet heat reversion)[33]

These results clearly show that pulp processing introduces acidic and potential acidic groups, even in purified pulps and cotton. In converting pulps into permanent grade papers, it is important to keep these groups under control so that the best methods for their neutralisation may be used.

Although acidic groups in pulps are of potential detriment to paper permanence, other studies have shown that such groups are of considerable value in several papermaking operations.[35] Careful consideration must therefore be given to the question of where in the papermaking operation and how these acidic groups should be neutralised or eliminated.

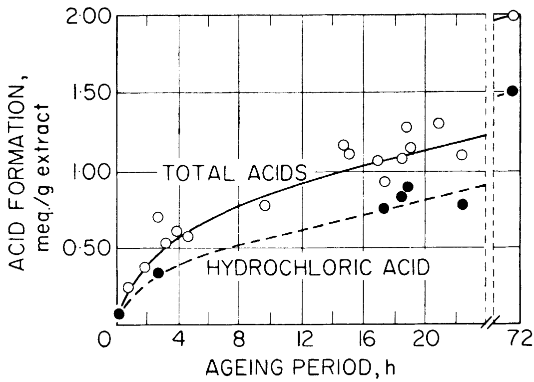

Fig. 5—Acid formation during heat treatment (120° C) of ethanol-benzene extract from bleached birch kraft pulp[34]

SHEET CHARACTERISTICS AND THERMAL STABILITY

Structural considerations

Theoretical and experimental studies by Van den Akker,[36] Corte & Kallmes[37] and Page[38] have shown that the mechanical properties of paper may be described by considering the fibres in a sheet of paper as randomly distributed and highly bonded. These mathematical relationships between fibre strength and sheet strength have proved to be of great utility in understanding the mechanism of paper failure. Indeed, Page[38] has discussed the effects of ageing in terms of fibre and sheet strength. In spite of these advances, little theoretical connection exists between fibre and sheet properties and folding endurance, thus the effect of ageing on folding endurance can be interpreted only on an empirical basis.

Dry strength

To EXPLORE the effect of fibre dimensions and interfibre bonding on ageing, handsheets were prepared from three different fibre fractions. The extent of interfibre bonding was varied by beating to several freeness levels. Three different southern pine kraft pulp samples were used—one sample consisting of 68 per cent springwood and 32 per cent summerwood fibres (called springwood), one unfractionated sample consisting of 52 per cent springwood and 48 per cent summerwood fibres (called wholewood) and one sample consisting of 26 per cent springwood and 74 per cent summerwood fibres (called summerwood). All the samples also contained a small percentage (about 5 per cent) of hardwood fibres, since they were derived from a commercial pulp. The sheets were then aged at 80° C and 81 per cent rh.

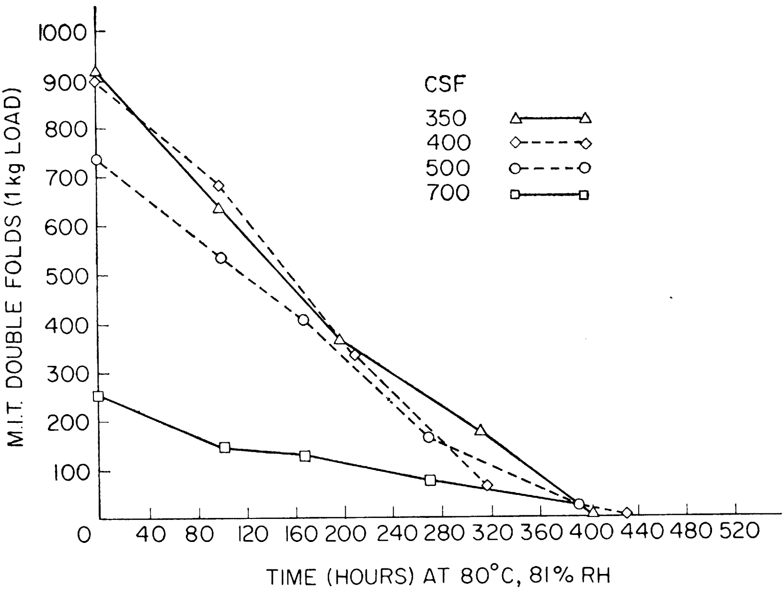

Fig. 6—Effect of freeness on fold loss with ageing at 80° C and 81 per cent rh (southern pine kraft)

The effect of beating on folding endurance after ageing is shown in Fig. 6 & 7. The results for the whole pulp as well as the two fractions show that beating increases the rate of loss in folding endurance. At a fixed freeness level, the springwood fraction decreases in fold more rapidly on ageing than does the summerwood fraction. This is in contrast to the tensile strength changes as shown in Fig. 8. Fig. 9 shows that the single fibre strength of both fractions decreases only moderately on ageing.

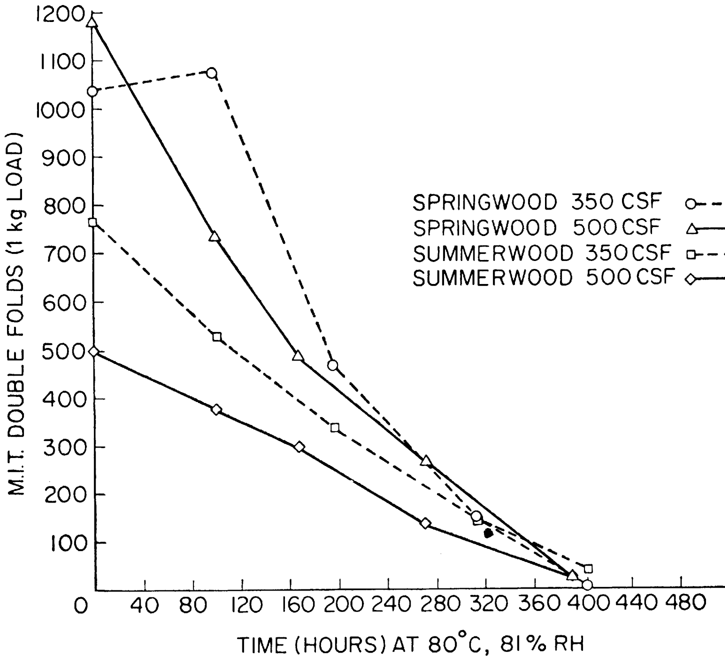

Fig. 7—Graph of MIT double folds against ageing time at 80° C and 81 per cent rh

These results lead to the conclusion that folding endurance is very strongly influenced by the extent of interfibre bonding. In the unaged sheets, greater interfibre bonding leads to higher folding values; on ageing (that is, exposure to heat and humidity for extended times), a greater interfibre bonding results in a loss in folding endurance. These effects are consistent with the idea that a chemical cross-linking reaction occurs throughout the fibre network on ageing.(39) As the extent of interfibre bonding is increased, either as a result of greater fibre collapse (springwood against summerwood) or of beating, the cross-linking reaction is enhanced, leading to brittleness and low folding endurance values. These results show that it is entirely possible that ageing of papers made from an initially superior pulp may make them inferior to aged papers made from pulps of initially poorer properties.

Wet strength

When papers or pulps are treated in an accelerated ageing test, the scattering coefficients do not vary significantly.(40) This suggests that the bonded area has not changed greatly during ageing. On the other hand, when paper is heated,(39, 41) the wet strength increases up to 40 per cent of the dry strength—

that is, the bond strength is increased on ageing. This again is not reflected in the scattering coefficient measurements. The new linkages formed during ageing are detrimental to some of the sheet properties, especially folding endurance. To explore this further, the changes in wet strength on accelerated ageing were determined for handsheets and commercial papers. The mechanical properties of these papers were reported earlier.

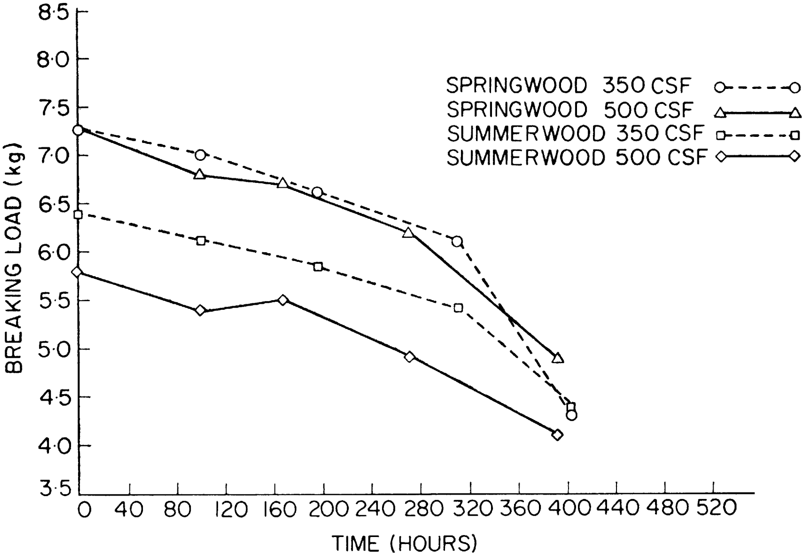

Fig. 8—Graph of dry breaking load against ageing time at 80° C and 81 per cent rh

Fig. 10 shows the increase in wet strength on the ageing of handsheets made from the summerwood and springwood fractions. The latter show higher initial wet strengths than do the former; the wet breaking load increases with ageing time and there is a tendency for the curves to diverge.

Fig. 11 shows the changes in wet strength on the ageing of three commercial papers at 0 per cent and 81 per cent rh, both at 80° C. Except for the permanent paper at 0 per cent rh, wet strength increases initially and then decreases, especially for papers aged at higher humidities. It is clear that the variations in wet strength of commercial papers are less systematic than those of the handsheets. This is a reflection of the greater complexity of the reactions taking place in commercial papers. For instance, an inverse relationship exists between loss in folding and wet strength (Fig. 7 & 10) for the pulp handsheets, whereas such a relationship is not readily apparent for the commercial papers. Further studies along these lines may lead to a better understanding of the factors responsible for paper deterioration and eventually to the manufacture of more permanent papers.

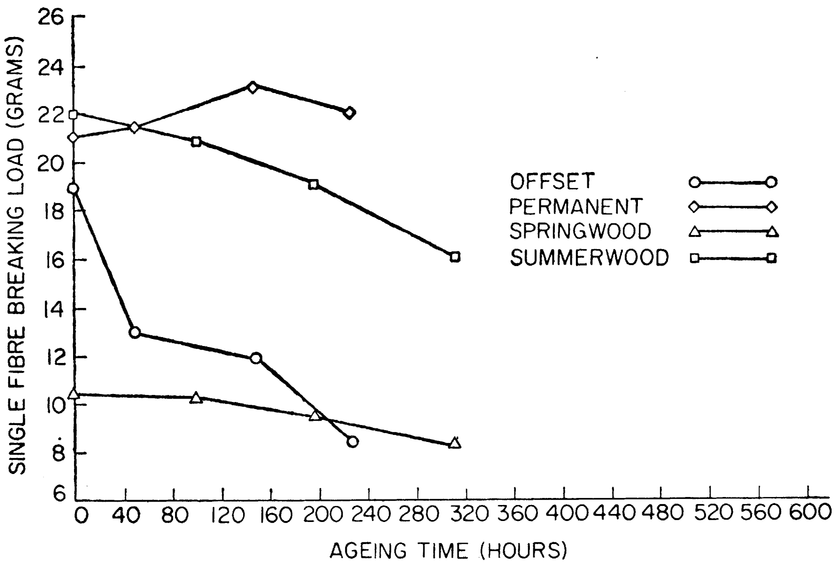

Fig. 9—Graph of single fibre strength against ageing time at 80° C and 81 per cent rh

ACCELERATED AGEING OF PAPERMAKING PULPS

THE foregoing considerations have shown that the degradation of paper is extremely complex. Each of the steps in the manufacture of paper from the procurement of the raw materials, processing into pulp, addition of chemicals to make a more useful product and the final storage conditions affects the useful lifetime of the paper.

It is clear, then, that in order to make meaningful and systematic comparisons on low temperature thermal stability or permanence, the systems to be studied must be simplified. Only when the characteristics of the basic papermaking pulps have been examined and the actions and interactions of the various additives essential to the papermaking process evaluated can valid conclusions be drawn about what factors are responsible for the deterioration of physical properties under accelerated ageing conditions. For these reasons, a series of experiments were undertaken aimed at classifying a wide variety of commercial pulps in terms of their ability to yield thermally stable paper. Information was sought concerning the mechanism of paper degradation, in terms of fibre and bond strength. To this end, zero span tests (fibre strength) and wet strength (bonding) were determined before and after ageing.

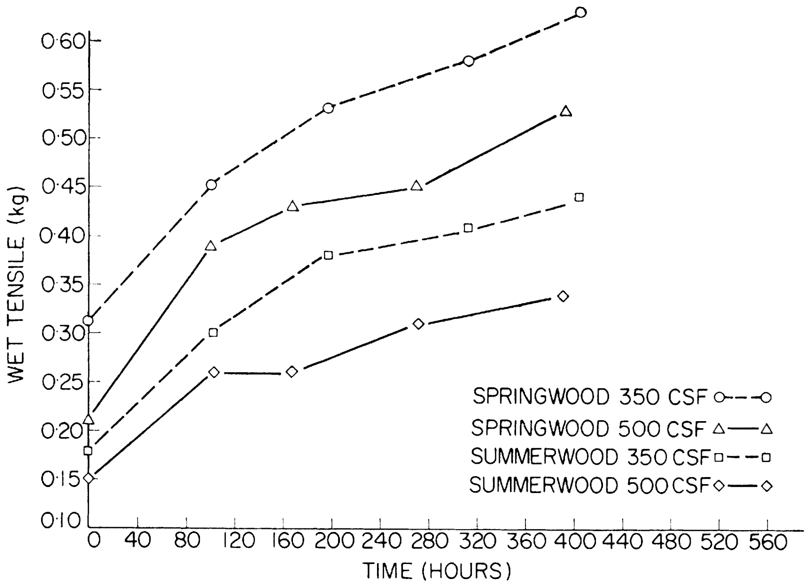

Fig. 10—Effect of ageing at 80° C and 81 per cent rh on the wet breaking load

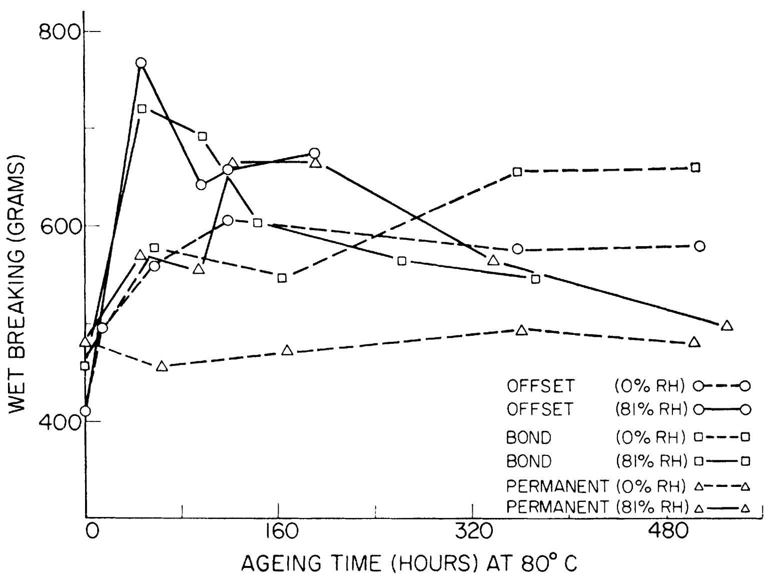

Fig. 11—Graph of wet breaking load against ageing time

It was previously noted that even the extremely time-consuming process of ageing at a number of different temperatures and humidities with the objective of extrapolation to room temperature does not necessarily lead to very accurate predictions of stability.[4, 5] Consequently, accelerated ageing at a single temperature was chosen as the method to determine the relative permanency of the pulps considered, even though crossover effects at lower temperatures are possible and any order of permanence established will be exactly valid only for the ageing temperature used. Nevertheless, gross differences in pulp stabilities can be determined and an indication of the relative ranking obtained from the changes in physical properties.

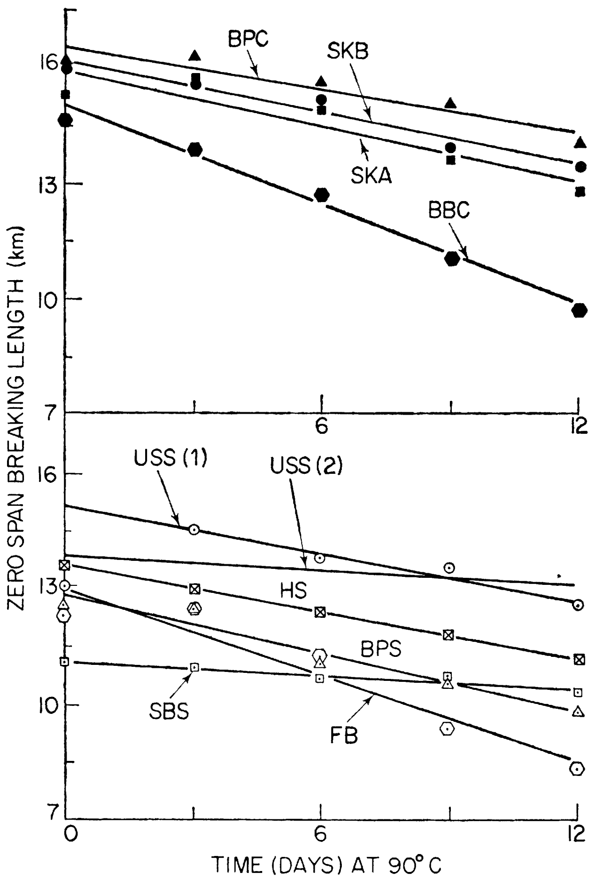

Fig. 12—Zero span breaking length (km) as a function of ageing time

Methods

THE pulps used are listed in Table 4. They were beaten to 400 ml CSF before handsheets were prepared and aged at 90° C and 73·5 per cent rh. Linear plotting methods were found to give the best fit for the data of this study and computed regression lines are shown in the figures that follow. It should be pointed out that log-linear plotting also provided good fitting in some cases, but not so consistently.

TABLE 4—IDENTIFICATION OF PAPERMAKING PULPS

Type of pulp	*Identifying code*
Scandinavian bleached birch kraft	BBC
Scandinavian bleached pine kraft	BPC
Scandinavian bleached pine sulphite	BPS
Bleached mixed hardwood neutral sulphite semi-chemical	FB
Unbleached mixed hardwood sulphite	HS
Scandinavian unbleached semi-chemical birch sulphite	SBS
Scandinavian bleached pine kraft (pressed at 30 lb/in^2 instead of standard 50 lb/in^2)	SKA
Scandinavian bleached pine kraft as above (pressed at 300 lb/in^2 instead of standard 50 lb/in^2)	SKB
Unbleached mixed softwood sulphite	USS

Whenever possible, the results from kraft pulps were plotted in the upper section of the two-section figures and the results from sulphite pulps were plotted in the lower section. In some cases, the wide diversity of results would have led to unsatisfactory graphs if this natural subdivision of pulps had been used. In such cases, the two sections of the figure were given different y axis scales and the test results were plotted in the section having an appropriate scale.

Grammage and specific volume

AN AVERAGE 1·2 per cent grammage loss occurred during ageing, which may be attributable to a loss of bound water. In addition to these losses, measured calipers also decreased slightly during ageing so that the total effect on specific volume was small.

Tensile and related properties

ZERO span breaking length and 10 cm span breaking length were calculated; the results are plotted in Fig. 12 & 13, respectively. Fig. 12 shows that for sample USS, a moderate increase in zero span breaking length resulted from the initial ageing period. This unexplained increase was not apparent in other samples, which showed little or no initial increase in zero span. A least squares regression, including the initial value, gave a poor fit (USS 2 in Fig. 12); when the initial value was excluded, an excellent fit for the remaining data points was obtained (USS 1).

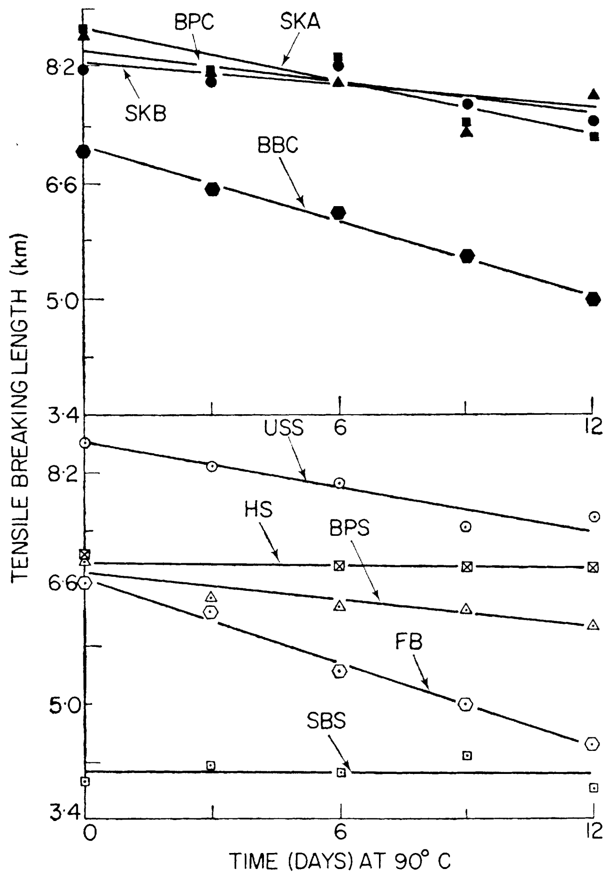

Fig. 13—Tensile breaking length (km) as a function of ageing time

Previous work [39, 41] indicated that wet breaking length may be a sensitive measure of interfibre bond strength, since test strips show no significant fibre failure under wet conditions. Calculated wet breaking lengths are plotted in Fig. 14. All the pulps exhibited substantial increases in wet breaking length, which were often as much as three or more times the initial values.

Zero span and standard breaking length results, respectively, both show the initial and continued superiority of the softwood krafts over the hardwood kraft. The sulphite pulps exhibited wide differences. Pulp SBS (unbleached semi-chemical birch sulphite), although it had the lowest initial strength properties of all the pulps studied, showed little loss of either zero span or breaking length, whereas an initially stronger hardwood sulphite HS also showed little loss of breaking length, but a more obvious loss of zero span breaking length. At the other extreme, pulp FB (bleached semi-chemical neutral sulphite) exhibited severe losses of both zero span and standard breaking length. Pulp USS, unbleached spruce sulphite, showed both initial strength and rate of strength loss similar to those of the bleached softwood krafts.

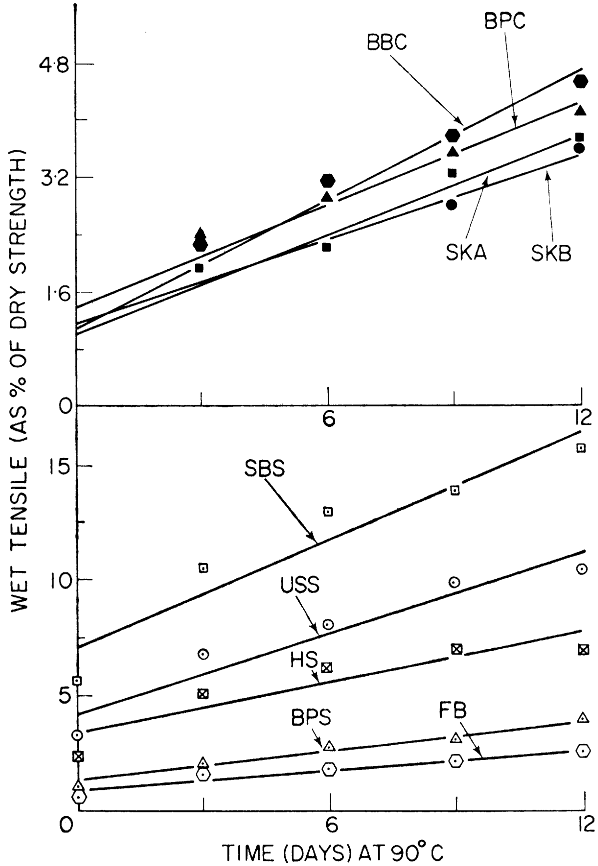

Fig. 14—Wet tensile strength (as percentage of dry tensile strength (km) as a function of ageing time

Kraft pulp sheets tended to have lower initial wet strength than did sulphite pulps, although pulp FB was an obvious exception. Pulp BPS (bleached pine sulphite) also showed similarities to the kraft group of pulps. These increases in wet breaking length were related to the initial values such that the higher the initial wet strength, the greater the rate of increase. This is immediately apparent from the lower graph of Fig. 14.

Interfibre bonding is a function of both bonded area and bond strength. Specific scattering coefficient determinations had indicated that the bonded area was essentially unchanged as handsheets were aged, thus the increase in wet tensile breaking length suggests a corresponding increase in bond strength per unit bonded area. It follows therefore that more and/or stronger bonds are formed on ageing. The rate of formation of such bonds with ageing depended upon the wet breaking length of the unaged handsheet, which is related to the original bond strength.

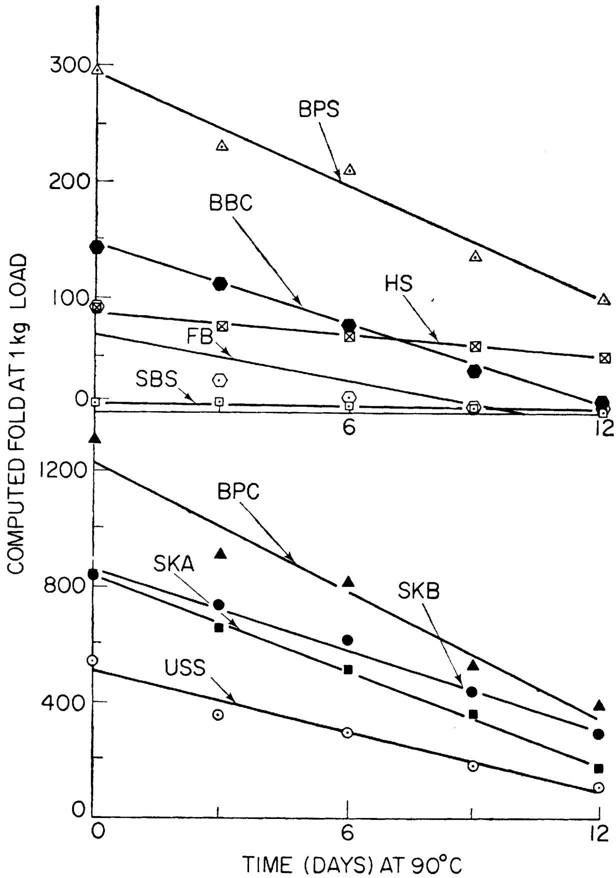

Fig. 15—Computed folding endurance at 1 kg load as a function of ageing time

Folding endurance

THE effects of accelerated ageing on folding endurance at 1 kg load and load to give 300 folds are plotted in Fig. 15 & 16. The spread of computed folding values at 1 kg load is very wide and the technique of determining the load value required to cause failure at 300 folds enables all the pulps to be plotted to the same scale[42] (Fig. 16).

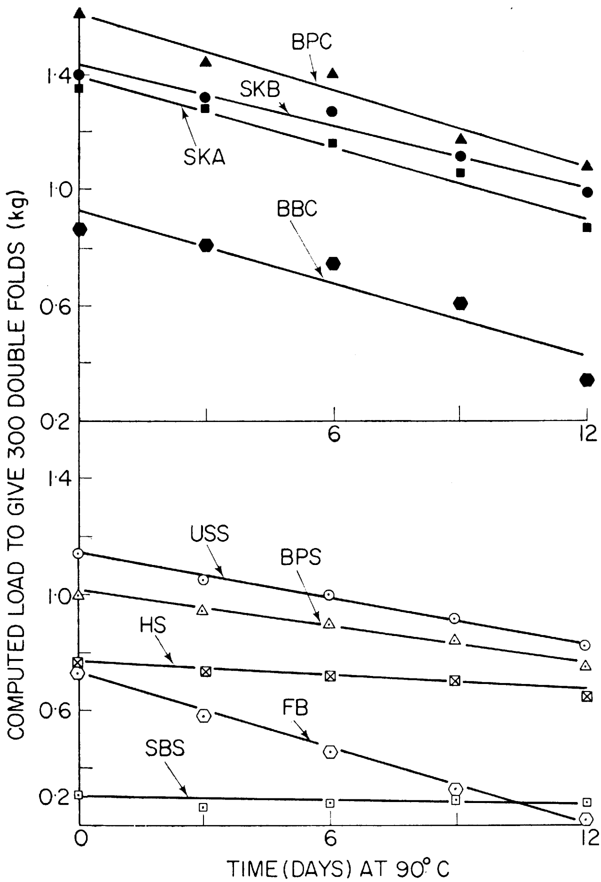

Fig. 16—Computed load (kg) to give 300 folds as a function of ageing time

Softwood kraft pulps had higher initial folding endurance values than do softwood sulphite pulps, but the rate of loss and folding strength during accelerated ageing was greater. The hardwood kraft and NSSC pulps BBC and FB had low initial strength combined with a high rate of loss during ageing, whereas the remarkable stability of the hardwood sulphite pulps

SBS and HS is apparent. Particularly in the case of SBS, however, the very low initial folding strength would make this pulp of limited usefulness in the grades of paper for which stability to ageing is important. There was only a slight difference in folding endurance retention between the differently wet pressed pulps SKA and SKB and little difference in the initial values.

Ranking of pulps for stability

THERE are several ways of treating strength property against ageing time data to rank stability. If a strength property decreases with ageing time, then the magnitude of the slope of property loss curves could be used as a criterion for stability. Yet, if two pulps have similar slopes, but different intercepts (that is, initial values), this method tends to rank the pulp having the higher intercept lower. It would also be possible for a pulp exhibiting inferior stability with respect to slope or rate of decrease to maintain higher absolute strength values at all ageing times within its useful life as a result of a much higher initial value. Another possible ranking method would be to use the time taken to reach an arbitrary minimum value as an index of stability.

TABLE 5—SLOPE OF PROPERTY CHANGE WITH AGEING TIME
(Expressed as a percentage of the intercept value)

Sample	Mechanical property					
	Load to give 300 folds	*Folds at 1 kg load*	*Zero span breaking length*	*Tensile breaking length*	*Wet tensile breaking length**	*Tensile energy absorption*
BBC	4·53	7·86	2·81	2·43	27·4	5·83
BPC	2·74	6·02	1·09	0·92	17·0	2·32
BPS	1·98	5·49	1·93	0·87	15·6	2·55
FB	5·94	9·81	2·82	2·85	16·9	6·25
HS	1·00	3·42	1·46	0·09	10·8	0·21
SBS	0·68	3·45	0·54	0·03	11·0	1·68
SKA	2·90	6·51	1·50	1·41	22·5	3·11
SKB	2·46	5·34	1·37	0·64	16·8	2·23
USS	2·32	6·82	1·32	1·16	14·1	2·77

* Expressed as a percentage of the dry tensile breaking length

The method chosen here was to accept the commonly used slope value method, but to express this slope as a fraction of the initial intercept in an attempt to compensate for the effects considered above. Since a small slope, but a large intercept is desirable, pulps having lower fractional or percentage values would be ranked higher. These percentage values and the resultant rankings are given in Tables 5 & 6, respectively. It is recognised that situations could arise in which this method could also be criticised, but as yet no single index is entirely satisfactory.

TABLE 6—ORDER OF RANKING WITH RESPECT TO SLOPE*

Sample	Total rank	*Individual mechanical property ranks*					
		Load to give 300 folds	*Folds at 1 kg load*	*Zero span breaking length*	*Tensile breaking length*	*Wet tensile breaking length*	*Tensile energy absorption*
BBC	8	8	8	8	8	9	8
BPC	5	6	5	2	5	7	4
BPS	5	3	4	7	4	4	5
FB	9	9	9	9	9	6	9
HS	2	2	1	5	2	1	1
SBS	1	1	2	1	1	2	2
SKA	7	7	6	6	7	8	7
SKB	3	5	3	4	3	5	3
USS	4	4	7	3	6	3	6

* Expressed as a percentage of intercept

The difference in ranking between the differently wet pressed pulps SKA and SKB was unexpected and apparently anomalous. Other tests (unpublished results) relating bonding to permanence showed that decreased bonding reduced initial strength properties, but also reduced the rate of strength loss on ageing. In the case of these pulps, the reverse appeared to be true.

A comparison of the rankings for individual tests with the total ranking based on all the tests[6] shows that reasonably consistent rankings are obtained. If deviations of rankings for individual tests from those of total ranking are taken to indicate the accuracy or utility of an individual test method, then the three most accurate predictive tests are breaking length, TEA and load to give 300 folds. Folds at 1 kg load and zero span breaking length give rankings less consistent with the total rankings, whereas wet breaking length is the least accurate indicator of the total rankings. These results are not too surprising. Tensile breaking length, TEA and folding tests depend on both fibre strength and interfibre bonding. Zero span breaking length and wet breaking length, on the other hand,depend essentially on fibre strength or bond strength, respectively and are less influenced by interaction between these two parameters.

Correlation of individual parameters

THE correspondence between any two of the corrected rates of loss (slope/intercept) of physical properties—that is, any two of columns 2–7 in Table 5—can be most appropriately examined by calculation of correlation coefficients. Such coefficients for each pair of rate values of all nine pulps are given in Table 7. The values obtained ranged 0·604–0·974. A correlation coefficient of 0·604 indicates that 36 per cent of the variation in one parameter can be accounted for by variation of the other parameter. The corresponding value for a correlation coefficient of 0·974 is 95 per cent. Table 7 indicates that the slope/intercept values for the three tests—load to give 300 folds, breaking length and TEA—are highly correlated (0·947–0·974), whereas the slope/intercept values for wet breaking length are poorly correlated with these three indices (0·644–0·699).

TABLE 7—CORRELATION COEFFICIENTS BETWEEN RATES OF LOSS FOR VARIOUS PAIRS OF MECHANICAL PROPERTIES

Mechanical property	*Folds at 1 kg load*	*Zero span breaking length*	*Tensile breaking length*	*Wet tensile breaking length*	*Tensile energy absorption*	*Specific absorption coefficient*
Load to give 300 folds	0·963	0·847	0·974	0·644	0·947	0·817
Folds at 1 kg load		0·786	0·971	0·604	0·929	0·715
Zero span breaking length			0·872	0·612	0·827	0·816
Tensile breaking length				0·699	0·971	0·803
Wet tensile breaking length					0·696	0·834
Tensile energy absorption						0·832

These results again show that wet breaking length is responding to other structural changes in the pulps than those that influence folding, tensile and TEA tests.

Somewhat similar correlations were reached in another study.[43] In addition, that study showed poor correlation between changes in papers aged at 90° C, 76 per cent rh and at 105° C under dry conditions. A relatively poor correlation between specific absorption coefficient and physical tests was also found, together with a very poor correlation between the pH values of cold or hot water extracts and physical properties. Wet tensile tests were excluded.

Bergman & Rennel[44] studied the relationship between the strength of individual fibres and the strength properties of paper by examining handsheets that incorporated varying proportions of fibres weakened by hydrolysis. The parallel of this situation with that of accelerated ageing is apparent. For both sulphite and kraft pulps, the breaking length, work to rupture and strain at failure decreased with the proportion of weakened pulp added. Folding endurance was evaluated only for the kraft pulp, but was found to decrease much more rapidly than the other strength properties. A 10 per cent decrease in fibre strength brought about a 30 per cent decrease in folding endurance.

The loss of folding strength closely follows that of loss of fibre strength, but this situation is not fully representative of accelerated ageing, since there is no contribution to sheet strength as a result of increased interfibre bonding.

It was seen earlier that a good correlation exists between loss of folding strength and breaking length and to a lesser extent between loss of folding strength and zero span breaking length, which is a measure of fibre strength. The results of the mechanical tests clearly indicate that the physical property changes occurring in pulps subjected to accelerated ageing are caused by a gradual reduction of fibre strength, combined with a rapid increase in interfibre bonding. These two interacting and competitive phenomena help explain the variety of ageing curves obtained, dependent upon the sample, sample treatment and test procedures. The increased bonding combined with a weight loss, predominantly as a result of dehydration, indicates that water molecule 'bridges' firmly held between the cellulose molecules have been released, allowing the formation of more or stronger hydrogen bonds within the existing bonded areas or that intermolecular hemi-acetal or ether linkages have been formed as suggested by Back.[45] Such phenomena would, of course, be expected to occur within the fibre as well as between fibres. This may account for the apparent increase in crystalline order during ageing (unpublished results) and increase in wet strength along with a greater dimensional stability in ageing.

Most studies on ageing show that some anomalous behaviour exists such as an increase in strength on ageing in some cases. Such results may be due to chemical and distributional differences of cell wall components, which further modify the effects of physical and structural differences that exist between pulps. In particular, with semi-chemical pulps in which substantial amounts of lignin and hemicelluloses are retained, such factors may be paramount. This study has shown that large differences can exist between semi-chemical papermaking pulps and confirms similar findings in a more comprehensive earlier study,[46] which, since it was based on commercial papers, also included the effects of sizing and filler additives.

DIMENSIONAL STABILITY

So FAR, the changes occurring to the mechanical properties on ageing have been emphasised, but it is instructive to examine other phenomena not directly related to tensile properties and evaluate what additional information can

TABLE 8—DIMENSIONAL STABILITY—RELATIVE LENGTH CHANGES AT DIFFERENT ATMOSPHERIC CONDITIONS

	Relative humidity, per cent					
Type of material	*86·5*	*65·5*	*49·0*	*46·3*	*38·0*	*27·0*
Permanent paper	0	12·0	20·4	22·4	26·4	NT
Permanent paper (aged)	0	8·4	14·4	16·4	20·0	NT
100 per cent rag paper	0	12·3	19·0	21·2	24·9	32·4
100 per cent rag paper (aged)	0	11·4	17·6	19·8	23·0	29·7
Bond paper (NSSC)	0	9·0	13·7	15·4	17·8	23·5
Bond paper NSSC (aged)	0	7·8	11·7	13·1	15·3	19·8
Bleached pine kraft handsheets (A)	0	26·0	40·5	44·8	51·7	64·0
Bleached pine kraft handsheets (A) (aged)*	0	21·0	33·4	37·0	42·8	53·1
Bleached pine kraft handsheets (B)	0	24·0	38·4	42·2	49·0	61·2
Bleached pine kraft handsheets (B) (aged)*	0	23·3	37·0	40·8	47·1	58·7

Notes—Values in the table are cumulative relative length decreases of the form $\Delta l/l \times 10^4$ (aged) indicates samples were aged at 90° C and 73·5 per cent rh for 12 days, except * indicates 10 days ageing only
NT means not tested at this level
Each value shown is the mean of 5 tests

be gained on the ageing process of paper. The dimensional stability of paper, both in printed and unprinted form, is of technical importance and its change on ageing is frequently of direct interest to the manufacturer and converter. With this in mind, the effect of ageing on the dimensional stability of three commercial papers and two pulp samples was determined (Table 8). A number of features can be discerned. Most outstandingly, the dimensional stability of the commercial papers and handsheets increases on ageing. Among the commercial papers, the permanent paper increased in stability to the greatest extent. The kraft handsheets containing no papermaking additives were almost twice as sensitive to humidity-induced length changes as were the commercial papers. Bleached pine kraft (A) increased in stability on ageing much more than the other sample (B). These increases in dimensional stability on ageing are indicative of a more tightly bonded structure that resulted from the formation of additional chemical linkages during the ageing process. It reinforces the utility of the wet tensile strength as an index of cross-linking, which can now be directly linked to dimensional stability. A quantitative assessment of this relationship would be useful.

CONCLUSION AND PROSPECTS

A FOLDING test procedure suitable for use in ageing studies is described. It is based on the existence of a linear correlation between the logarithm of the test load and of the folding endurance. This relation permits the conversion of folding endurance values at one load level to another. In this way, folding endurance values can be obtained at loads otherwise impracticable or unreliable with no increase in the number of test samples now prescribed at a single load.

The ageing behaviour of a variety of commercial papermaking pulps were subjected to environmental ageing conditions and the mechanical properties evaluated.

Loss of mechanical properties during accelerated ageing is a result of two competitive structural effects, one being a slow loss of fibre strength and the other a marked increase in interfibre and intrafibre bonding.

The interpretation of ageing behaviour in terms of pulp characteristics is complex, but a number of generalisations are possible. A high lignin content does not necessarily lead to poor ageing behaviour, since unbleached pulps can have superior permanence to bleached pulps. The effect of bleaching on the residual lignin appears to be important. Sulphite pulps are capable of producing more permanent handsheets than do kraft pulps in spite of their lower initial strength. Pine kraft pulps are more stable than a birch kraft pulp. The ageing behaviour of hardwood pulps is extremely variable, ranging from very good for a weak, but stable semi-chemical birch sulphite pulp to very poor for a strong, but unstable bleached birch kraft pulp.

The most permanent paper will thus not necessarily result from making the strongest sheet. Extensive interfibre bonding as a result of beating decreases stability. Indications are that the most useful permanent papers will be produced from pulps with high fibre strength and with initial fibre bonding not excessive in terms of the requirements of a paper's final use.

The most promising approach to a greater understanding of paper permanence is to interpret the changes that occur on ageing in terms of paper structure. Even though this involves a knowledge of bond strength and bonded area, these properties need not be evaluated in absolute terms for studies for which only changes such as in paper ageing are of interest. Thus, measurements of zero span tensile strength and breaking length may give an index of bonding. The increase in wet tensile strength and dimensional stability on ageing shows that cross-linking reactions are occurring during ageing and this aspect should be incorporated into any theory of paper ageing and permanence. Thus, the increase in wet strength and loss in folding endurance merits further study and interpretation.

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Contribution No. 78 from the Empire State Paper Research Institute, State University of New York College of Environmental Science and Forestry, Syracuse, New York 13210

Transcription of Discussion

Discussion

Dr D. A. I. Goring I would like to ask Prof. Luner to finish his last point.

Prof. P. Luner My last point was that, in the thermo-treatment and in the various other physical treatments, many competing reactions occur simultaneously and all these methods are non-specific. If we want to do something about paper permanence or the modification of cellulose, we have to look at a process that is a little more specific than any of those listed. For instance, if we can cross-link cellulose in a specific way, perhaps we could produce some interesting modification of fibres and paper. Unfortunately, these methods have not so far lent themselves to any specific developments.

Mr P. Howarth I was very interested to see the effect of coating on the ageing properties measured by Prof. Luner. Of course, the word coating covers a multitude of processes and formulations. Have you investigated the effect of different processes and formulations or intend to do so?

Prof. Luner With both the coatings in the magazine paper and in the offset grade of the paper, the sheets seem to be nominally the same. They are both supercalendered, but I was not in the mill when it was done. It might have been done under quite different conditions.

In discussion of the coating formula with one of the manufacturers, when we did get a beneficial effect on calendering, I asked for the formulation. The reply was that a conventional starch/kaolin mixture was employed. I said, 'Nothing else?' He said, 'Well, we have one per cent calcium carbonate in it.' Of course, other coatings might have different effects, but again it is the coating interaction with the physical process of supercalendering that is probably the important thing.

Dr N. G. M. Tuck One thing that really surprised me is the correlation between the MIT folding test and the tensile energy absorption. I was of your opinion that the MIT folding test is unscientific and the tensile

Under the chairmanship of Dr H. G. Higgins absorption energy is very scientific. I am rather surprised: maybe the two are correlated, because both are highly variable in a single test.

Prof. Luner I am sorry to give you that impression. The correlation is the ranking in instability, not the test itself.

The folding endurance test is complicated in itself, involving bending, pulling and tension, which is partially involved in the tensile energy absorption.

Dr E. Graminski I believe you had performed ageing in an atmosphere with controlled humidity. A question that crosses my mind and is constantly arising in our work at the National Bureau of Standards is what should the conditions be in an ageing test. For example, one of your illustrations shows an increase in wet strength with laboratory ageing followed by a decrease in wet strength. The decrease in wet strength also decreases during the same interval. How many of the reactions occurring in an accelerated ageing test also occur in natural ageing? One way to avoid hydrolysis is by doing the ageing, as has been done for years, in a dry atmosphere. What is important here is to determine what the conditions of an accelerated ageing test should be, because the data obtained can mislead many, if the conditions are such that they produce unrealistic changes in the paper.

Prof. Luner The question of ageing conditions is a perennial one and we just have to make some intelligent guesses what to use. What guides me is that, if you age at room temperature, moisture is present in the sheet. To accelerate the ageing, you raise the temperature, but you also need moisture in it, but not to have more moisture than at room temperature and humidity conditions.

Even in a dry test, if you look at the heating of the cellulose under dry conditions, there is no doubt that hydrolysis occurs without the presence of water. The rates might be different, but it is still perceived.

Dr J. D. Peel You showed a graph (not in the paper) on the effect of coating and calendering on ageing. Is not the effect in calendering simply that the folding endurance value is much lower to start with?

Prof. Luner Naturally, the higher you are, the faster the decrease. That is why the problem of permanence is intimately tied to durability and it is difficult to separate the two. That is why I think it is always better to start at a higher value even though the instability may be greater