THE CHEMISTRY OF PAPER DETERIORATION

by

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A C K N O W L E D G E M E N T S

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GUIDE TO THE READER

This report is presented in two separate parts.

Part 1 deals with the investigations carried out by the Author.

In Part 2 a review of the literature concerning the deterioration of paper is given. An Appendix covering the terminology used in Parts 1 and 2 of the report is included at the end of Part 2.

CONTENTS

PART 1

THE CHEMISTRY OF

PAPER DETERIORATION

SYNOPSIS

The relationships between a number of aging factors and physical and chemical indicators of deterioration of paper and the fundamental mechanism of paper deterioration were investigated.

It was found that

(i) chemical parameters of aging, more specifically average degree of polymerization and solubility in 1 per cent hot alkali were the most sensitive indicators of aging;

(ii) amongst the strength properties internal tearing- and folding strength were the most sensitive indicators of aging;

(iii) increases in aging temperature introduced the greatest changes in strength, and in chemical properties such as average degree of polymerization, alkaline solubility and copper number;

(iv) decreases in strength appeared to correlate positively with acid content of the paper, but chemical parameters indicated that the least deterioration takes place at the neutral point;

(v) the paper samples did not absorb sulphur dioxide and did not deteriorate as a result of the presence of sulphur dioxide in the aging atmosphere, and

(vi) hydrolysis of the polysaccharides was the only mechanism of paper deterioration under the conditions of this work.

SINOPSIS

Die verwantskappe tussen 'n aantal verouderingsfaktore en fisiese en chemiese indikatore van papierbederf en die fundamentele meganisme van papierbederf is ondersoek.

Dit is gevind dat :

(i) chemiese parameters van veroudering, meer spesifiek die gemiddelde graad van polimerisasie en die oplosbaarheid in een persent warm alkali die sensitiefste indikatore van veroudering was;

(ii) interne skeursterkte en vousterkte die sensitiefste indikatore van veroudering onder die sterkte eienskappe was;

(iii) toenames in verouderingstemperatuur die grootste veranderinge in sterkte en in chemiese eienskappe soos gemiddelde graad van polimerisasie, alkali oplosbaarheid en kopergetal teweeggebring het;

(iv) verlaging van sterkte oënskynlik positief gekorreleer is met die suurinhoud van die papier maar chemiese parameters het aangedui dat die minste bederf intree by die neutrale punt;

(v) die papiermonsters nie swaweldioksied geabsorbeer het en nie bederf het as gevolg van die teenwoordigheid van swaweldioksied in die verouderingsatmosfeer nie, en

(vi) hidrolise van die polisakkariede die enigste meganisme van papierbederf was onder die toestande van hierdie ondersoek.

1. INTRODUCTION

The impermanence of paper was recognized more than half a century ago. It has become of increasing importance to archivists, librarians and scientists and a quantitative understanding of the causes and mechanism of deterioration of paper has become imperative.
A study of literature (see Part 2) indicated qualitatively which factors are responsible for deterioration of paper but possible interactions between these factors have been overlooked. Consequently very little exact knowledge exists on paper deterioration.

The changes in paper resulting from natural aging may only become measurable after a few decades and therefore resource must be made to accelerated aging intended to introduce measurable physical and chemical changes in paper in a relatively short period. Ideally these changes should be identical with those occurring during natural aging. It will require many years to quantitatively correlate natural with artificial aging. In the meantime predictions of paper permanence based on accelerated aging tests will be inaccurate and can serve only as a very rough guide. The correlation of artificial with natural aging is complicated by the fact that the latter can vary considerably depending on prevailing conditions.

The ultimate aim of this work is to determine quantitatively the contribution of a number of aging factors to deterioration of paper. This information is essential in order to be able to manufacture more permanent paper in future and also to lay down criteria for the preservation of documents in storage. This is a vast task which could only be simplified by means of a foundation experiment.

This report covers the foundation experiment of which the object was to :

(i) indicate the most sensitive parameters of aging;

(ii) establish relationships between a number of factors contributing to the deterioration of paper on the one hand and the degree of deterioration as indicated by physical and chemical changes on the other hand, so that unnecessary experimentation in the continuation of the work will be obviated;

(iii) elucidate the fundamental mechanism of paper deterioration, and

(iv) examine the possibility of extrapolation of the results obtained to conditions which would approach those to which paper is exposed during natural aging.

2. EXPERIMENTAL PROCEDURE

a. Aging factors

The study was designed to establish the influence on paper deterioration of eight factors namely :

(i) temperature (T),

(ii) relative humidity (RH),

(iii) oxygen content of the aging atmosphere (O_2),

(iv) sulphur dioxide content of the aging atmosphere (SO_2),

(v) aging period (P),

(vi) acid content of the paper (A),

(vii) rozin sizing content of the paper (R), and

(viii) lignin content of the paper (L).

The above mentioned eight factors were varied one at a time in five steps while the other seven factors were kept constant. The experimental plan indicating

the variation of aging factors is given in Table 1*.

b. Test material

The raw material for preparation of test sheets consisted of commercially produced pine sulphate pulp beaten to a wetness of 20° Schopper-Riegler. Test sheets at a basis weight of 60 g/m^2 were prepared according to the requirements of the plan given in Table 1. The sample for each experiment consisted of 25 sheets, randomly selected from a common batch made beforehand.

The strength of the test sheets varies because of differences in their chemical composition with the result that their strength values after aging are not directly comparable with each other. Comparison, therefore, has to be based on the percentage change in properties. In order to be able to determine the percentage change it was necessary to determine the properties of aged samples as well as unaged reference samples. Enough sheets were therefore prepared so that reference samples each consisting of 25 sheets were available for experiments 1 and 22 to 33 (see Table 1).

The acid content of the sheets was adjusted to the desired levels by the use of either aluminium sulphate or calcium carbonate. Various chemical compositions of the pulp were obtained by bleaching with calcium hypochlorite and chlorine dioxide to different levels of lignin content and by extraction of one of the bleached pulps to a high alpha cellulose content with 17.5 per cent sodium hydroxide.

c. Aging and testing

The samples were aged according to the plan given in Table 1 using a cabinet** in which temperature and RH can

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* Tables are at the end of this report.

** Manufactured by Vötsch Ltd., W. Germany.

be varied as required.

From Table 1 it will be noticed that the samples for groups 1 to 5 were chemically identical, i.e. they contained :

(i) 10 m.eq. acid/1000g,

(ii) no sizing, and

(iii) 3.5 per cent lignin.

These samples were aged under different conditions - the temperature, RH, oxygen and sulphur dioxide contents of the aging atmosphere and the period of aging being varied.

The samples for groups 6 to 8 were prepared with different acid, size and lignin contents, but they were aged under identical conditions of temperature (50°C), RH (25 per cent), oxygen content (20 per cent) and sulphur dioxide content (nil) of the aging atmosphere, all for a period of 10 days.

Two further samples (prepared according to the requirements of group 1 (see Table 1) were severely aged by exposing them to 100°C for 30 days, in the one case at zero per cent RH and in the other at 55 per cent RH.

Various levels of oxygen content of the aging atmosphere were obtained by appropriate manipulation of a steady stream of either oxygen or nitrogen entering the aging cabinet. The percentage oxygen present in the atmosphere was determined by absorption of the oxygen in alkaline pyrogallol solution in an Orsat apparatus. Aging of the paper samples in a sulphurous atmosphere was conducted in a 150 litre sealed polythene container inside the cabinet. Sulphur dioxide was bled into this container from the outside of the

cabinet while the air in the cabinet at the desired temperature and RH was pumped into the container at a rate of 20 litres per minute. The sulphurous atmosphere from this container was vented to the atmosphere. The sulphur dioxide content of the aging atmosphere was determined by titration of the sulphuric acid resulting from absorption in hydrogen peroxide of the sulphur dioxide present in a known volume of air.

In order to avoid the effect of hysteresis, the aged paper samples were desiccated over silica gel at room temperature before conditioning at 50 ± 2 per cent RH and $23\pm1^{\circ}C$. The samples were then tested for the following strength properties :

(i) Tearing strength - 9 replicates, APPITA method P400m-62;

(ii) Folding strength - 30 replicates, TAPPI method T423m-50;

(iii) Bursting strength - 12 replicates, TAPPI method T403m-53;

(iv) Tensile strength - 12 replicates, TAPPI method T404m-49;

(v) Edge tearing strength - 12 replicates, Bekk's method;

(vi) Zero-span tensile strength - 12 replicates, TAPPI method T231sm-60.

In addition to the above, the following chemical determinations were carried out on selected aged samples and corresponding reference samples :

(i) Average and fractionated degree of polymerization (DP) of the cellulose, Jayme's method[56,57]* and TAPPI method T238su-63 respectively;

(ii) Copper number, Hägglund method;

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* References in alphabetical order at the end of this report

(iii) Solubility in one per cent hot caustic soda, i.e. hot alkaline solubility, TAPPI method T212m-54;

(iv) pH; TAPPI method T435m-52, cold extraction;

(v) Carbonyl groups, sodium borohydride reduction[31];

(vi) Carboxyl groups, TAPPI method T237su-63;

(vii) Water soluble sugars, paper chromatography;

(viii) Infrared absorption spectra.

3. RESULTS

The average strength values of identical samples aged under various ambient conditions (see Table 1, groups 1 to 5) are listed in Table 2, while those of samples which differed in chemical composition but were aged under identical ambient conditions (see Table 1, groups 6 to 8) are listed in Table 3 which also contains the strength values of the corresponding unaged reference samples.

The results of the chemical determinations on samples of groups 1 to 5 (see Table 1) are listed in Table 4 while those of samples of groups 6 to 8 (see Table 1) and the corresponding unaged reference samples, are listed in Table 5.

Strength properties and chemical analyses of the samples aged at 100°C are listed in Table 6 together with those of an unaged reference sample and a sample aged at 90°C and 25 per cent RH for 10 days. Table 7 contains fractionated DP values of an unaged and of the two samples aged at 100°C.

4. ANALYSIS OF RESULTS

The results obtained were subjected to regression analysis and linear relationships between each strength property and the various aging factors were established

The straight line relationships, given as equations of the type $y = a + bx$ where y is the dependent variable (strength) and x the independent variable (aging factor) for identical samples aged under various ambient conditions (see Table 1, groups 1 to 5) are listed in Table 8. The correlation coefficients, r, of the equations listed in Table 8, and the significance level, L, at which these relationships show significant correlation are listed in Table 9.

Since the initial strength values of the samples for groups 6 to 8 (see Tables 1 and 3) were different as a result of the differences in chemical composition, relationships could not be established directly. The strength values listed in Table 3 were therefore expressed as percentages of the unaged strength (see Table 10) and from these the percentage reduction in strength as a result of aging was calculated. Relationships between the percentage reduction in strength and aging factors were then established. These linear relationships are listed in Table 11.

The correlation coefficients, r, of the equations listed in Table 11 and the significance level, L, at which these relationships show significant correlation are listed in Table 12.

5. DISCUSSION OF RESULTS

a. Paper strength

(1) Correlation between paper strength and aging factors

(a) Aging temperature

As can be seen from Table 9 the influence of temperature on tearing-, folding- and zero-span tensile strength was significant at the 0.01 probability level while that on edge tearing

strength was significant at the 0.05 level. Its influence on bursting strength was significant only at the 0.10 level, while breaking length was not significantly influenced at the 0.10 level.

The correlation coefficients for the relationships between aging temperature (in the range 50 to 90°C) and all the properties examined were negative indicating that an increase in aging temperature results in a decrease in strength.

The linear regressions between aging temperature and tearing-, zero-span-, tensile- and folding strength are illustrated in Figures 1, 2 and 3 for the range 50 to 90°C. The values plotted in these three figures each represent the average of the number of replicate determinations indicated in section 2.b.

Although these relationships are valid for the range of 50 to 90°C, it is of importance to know the influence of temperature at lower levels. Aging at natural temperatures would require many years to furnish an answer to this question. The alternative is therefore to extrapolate the values obtained to natural temperature levels.

Examination of Figures 1 to 3 indicates that extrapolation of the linear regressions to lower temperatures gives the impression that the original paper strength (indicated by the reference value in these figures) can be exceeded, which is of course impossible. Examination of the values plotted in Figures 1 and 3 which show the relationships between aging temperature and tearing strength and folding strength respectively, indicate that these values will be better fitted by a curve.

According to the theory of reaction rates the influence of temperature on a large number of chemical reactions is described by an exponential function, such that the plot of log k, the reaction constant, against 1/T (where T is the absolute temperature) is a straight line[46], and further, that plotting of k against 1/T on a linear scale would indicate that a certain minimum value of k would be approached assymptotically as the reaction temperature decreases. It is therefore reasonable to assume that the amount of aging that would take place in paper at $0^{\circ}C$ (273 degrees on the absolute scale) would be negligibly small. In other words, when aged at this temperature, the paper would retain its original strength, namely that of the reference sample.

Assuming that the strength decreases were caused by some type of chemical reaction (as will be seen later), it was considered permissible to fit exponential functions of the types

$$y = ae^{bx} \quad \text{----------} \quad (1)$$

$$y = ax^{b} \quad \text{----------} \quad (2)$$

$$y = ab^{x} \quad \text{----------} \quad (3)$$

to the experimental observations and the assumed values at $0^{\circ}C$, expressing the temperature in degrees Kelvin ($^{\circ}K$) instead of $^{\circ}C$, in order to avoid dealing with log o.

The above functions, when rewritten in log form, become linear and are respectively as follows :

$$\log y = \log a + bx \log e \quad \text{--------} \quad (4)$$

$$\log y = \log a + b \log x \quad \text{---------} \quad (5)$$

$$\log y = \log a + x \log b \quad \text{---------} \quad (6)$$

The corresponding linear regressions of tearing strength on aging temperature based on equations

4, 5 and 6 were respectively

$$\log y = 2.859 - 0.0056x \quad \text{--------} \quad (7)$$

with $r = -0.76$;

$$\log y = 6.293 - 1.680 \log x \quad \text{----} \quad (8)$$

with $r = -0.73$, and

$$\log y = 2.856 - 0.0024x \quad \text{--------} \quad (9)$$

with $r = -0.76$

Reverted to the original form, equations 7, 8 and 9 respectively become

$$y = 722.8e^{-0.0129x} \quad \text{----------} \quad (10)$$

$$y = 196.3 \times 10^{4} x^{-1.680} \quad \text{---------} \quad (11)$$

and $$y = (717.8)(1.006^{x}) \quad \text{----------} \quad (12)$$

Fitting the three functions in equations 4, 5 and 6 to the observations for zero-span tensile strength, the following regressions were respectively obtained :

$$\log y = 1.502 - 0.004x \quad \text{---------} \quad (13)$$

with $r = -0.86$;

$$\log y = 4.146 - 1.270 \log x \quad \text{---} \quad (14)$$

with $r = -0.89$, and

$$\log y = 1.500 - 0.0017x \quad \text{--------} \quad (15)$$

with $r = -0.86$.

Similarly, for folding strength :

$$\log y = 4.534 - 0.014x \quad \text{---------} \quad (16)$$

with $r = -0.73$;

$$\log y = 13.07 - 4.176 \log x \quad \text{----} \quad (17)$$

with $r = -0.71$, and

$$\log y = 4.535 - 0.006x \quad \text{---------} \quad (18)$$

with $r = -0.72$.

The correlation coefficients for the transformed exponential functions are significant at the 0.05 level if the assumed value at $0^{o}C$ is

classed as an observation. The hypothesis that the influence of temperature on the aging of paper over a wider range than that investigated can be described by an exponential function is therefore supported.

It must be realized, however, that although the above is true for many chemical reactions the hypothesis is still based on an assumption as far as paper is concerned and the suggested exponential relationships cannot be proved for years to come. However, it is suggested that the above mentioned functions can be used in the meantime to predict the aging behaviour of paper at low temperature.

(b) Percentage relative humidity

The influence of percentage relative humidity (RH) of the aging atmosphere on the aging of paper was insignificant at the 0.10 level under the conditions of this work except for edge tearing strength which showed a significant decrease at the 0.10 level on increasing the RH.

It is suggested that the influence of RH under conditions which would result in greater changes, e.g. at higher aging temperatures, would be more significant.

(c) Oxygen content of the aging atmosphere

The influence of oxygen content of the aging atmosphere (between 1 and 92 per cent) was found to be insignificant at the 0.10 level under the conditions applied in this work.

(d) Sulphur dioxide content of the aging atmosphere

The presence of sulphur dioxide between nil and 315 mg/m^3 in the aging atmosphere had an insigni-

ficant influence at the 0.10 level on all the strength properties tested. It is likely that increased aging periods and RH's may increase the influence of sulphur dioxide.

(e) Period of aging

The influence of period of aging up to 10 days under the conditions of this work was significant at the 0.01 level in the case of tearing and at the 0.10 level for zero-span tensile strength.

The influence on the other strength properties was insignificant at the 0.10 level. It appears therefore that most of the strength properties examined were rather insensitive to the aging conditions applied in this work.

(2) Correlation between chemical characteristics of paper and strength reduction upon aging

(a) Acid content of paper

The influence of acid content of the paper samples on the percentage decrease in strength was found to be positive and significant at the 0.01 level for bursting and folding strength (see Table 12). It was significant on tearing strength at the 0.10 level and insignificant at the same level on the other properties tested.

The linear regressions of the percentage reduction in bursting and folding strength on acid content (significant at the 0.01 level) are shown in Figure 4.

Figure 4 suggests that sheets having a negative acid content, actually increased in bursting and folding strength after aging. Both these properties

are primarily dependent on interfibre hydrogen bonding for their development. However, the same phenomenon was shown by tearing strength (significant at the 0.10 level) which is negatively influenced by increased fibre bonding and is more dependent on fibre strength, which in turn is related to intra-fibre bonding. It would therefore appear that inter- and intra-fibre hydrogen bonds were either strengthened or increased in number by the aging treatment applied. This anomaly has not yet been reported and will have to be reconsidered after further experimentation.

Nevertheless, it appears safe to conclude that the aging rate of paper judged from strength values, is positively influenced by increasing acid content which is in accordance with findings reported in literature.

(b) Sizing content of paper

From Table 12 it appears that the influence of sizing content on folding strength was significant at the 0.05 level and significant at the 0.10 level for breaking length. The influence of sizing content on all the other strength properties investigated was insignificant at the 0.10 level. Sizing content correlated negatively with the percentage decrease in folding strength and breaking length on aging (see Table 12).

In reports in literature "acid and rozin sizing" have always been grouped together as one factor contributing towards deterioration of paper probably because rozin sizing has up to now been used in conjunction with aluminium sulphate. Rozin sizing is dependent on the availability of

aluminium ions for its bonding to the fibres and consequently it has never previously been attempted to determine the individual contribution of these two factors to the deterioration of paper. It is therefore also not a foregone conclusion that rozin sizing does contribute towards paper deterioration. The present work indicates that the opposite may be true.

(c) Purity of the fibres

In this part of the investigation the purity of the fibres was expressed indirectly by means of the percentage residual lignin. The lignin content had a significant influence at the 0.05 level on the decreases in tearing strength and breaking length while its influence on the other strength properties tested was insignificant at the 0.10 level. The correlations between lignin content and the decreases in the above mentioned two properties were positive.

b. Chemical changes

(1) Chemical structure of paper components

Aging of paper manifests itself by decreases in its physical strength. However, decreases in paper strength are only convenient parameters of aging and explain little about its basic causes. Changes in paper strength upon aging are therefore secondary to certain basic chemical and structural changes in the cellulose and hemicellulose of which paper mainly consists.

In order that these changes may be understood, it is necessary to give a short chemical background of the structure of cellulose and hemicellulose.

Cellulose in wood is associated with a variety of

different substances such as non-cellulosic carbohydrates (e.g. hemicellulose) and non-carbohydrates such as lignin, mineral matter and resins. For the manufacture of fine paper grades the cellulose is separated from the other wood components by pulping and bleaching operations. The ultimate product is obtained in the form of fibres* which consist mainly of cellulose but also contain some non-cellulosic polysaccharides. Cellulose is a linear polysaccharide of a sufficiently high DP to be insoluble in water or dilute alkali and acids at room temperature. It contains only anhydroglucose units linked together with 1, 4-beta-glucosidic bonds and possesses a well-ordered structure[30,93] as illustrated in Figure 5[34] showing the linkage between anhydroglucose units. The molecular chain length or DP of the cellulose is the number of anhydroglucose units in these chains. However, the chains vary widely in length within a given cellulose sample. In general, the greater the DP of the constituent cellulose molecules, the stronger are the fibres and the pulp[34,93]. For general purposes the average chain length is determined but because of the polymolecular nature of cellulose, information on the chain length distribution can be useful. The average DP of commercial pulp is as low as 600 to 1500 probably as a result of degradation during pulping but the DP of undegraded cotton cellulose can be as high as 6000 to 8000[34]. Values of 140 to 200 are reported for beta cellulose and 10 to 140 for gamma cellulose[34].

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* In general, pine pulp fibres (also used in this investigation) are approximately 3 mm long and 40 micron wide while the cell walls are roughly 3 micron thick whereas the cellulose molecules themselves are 500 to 1000 Å long[34]. Their width is considered to be about 9 Å and the thickness 4.7 Å.

Hemicelluloses which are the principal non-cellulosic polysaccharides present in wood are soluble in dilute aqueous alkali and are hydrolyzed by warm dilute acids into simple pentose and hexose sugars. The average DP of the hemicellulose is about 155[34] with a molecular weight of about 20,000.

The chemical structure of the hemicelluloses has not been finally elucidated. Whereas cellulose yields only glucose upon hydrolysis, hemicelluloses hydrolyze to a variety of saccharide units such as glucose, mannose, galactose, xylose, arabinose and glucuronic acid and its methylated derivatives[34]. (See Figure 5). Hemicelluloses in hardwoods consist mainly of xylose units whereas in softwood hemicellulose, mannose is the most important monomer.

(2) Changes in average DP as an indicator of paper deterioration

(a) General

As outlined above cellulose molecules consist of linear chains of anhydroglucose units and the molecular size may be expressed as the number of these units in the chain, namely the DP.

Methods for determining molecular weights of cellulose can be divided into three main groups[31], namely :

(i) methods based on hydrodynamic analyses e.g. viscosity, sedimentation velocity and diffusion;

(ii) methods based on thermodynamic analyses e.g. osmotic pressure, equilibrium ultra-centrifuging and light scattering, and

(iii) other measurements such as analysis of end groups.

Viscosity measurement found the widest application and was also used in this investigation employing cadoxen[56,57], a solution of cadmium oxide in ethylene diamine, as solvent for the cellulose.

The intrinsic viscosity of a solution of a polymer has been related to the size of the solute molecule but it is not yet feasible to determine molecular weight directly from viscosity measurements[31]. It is determined by an indirect method based on the Staudinger equation[31] which relates intrinsic viscosity to molecular weight as follows :

$$[n] = K_m M \quad \text{---------- (19)}$$

where $[n]$ is the intrinsic viscosity,
K_m is a constant depending on the nature of the polymer and the solvent and is determined by an independent method such as osmotic pressure, light scattering or sedimentation in the ultracentrifuge, and
M is the molecular weight.

Equation (19) may be expressed in terms of DP as follows :

$$[n] = K_{dp}.DP \text{ or } DP = K[n] \quad \text{--------- (20)}$$

where $K = 1/K_{dp} = 75$

and the intrinsic viscosity

$$[n] = \left(\frac{N_{sp}}{C}\right)\left(\frac{1}{1 + kN_{sp}}\right)$$

N_{sp}, the specific viscosity is given by

$(N - N_o)/N_o = n_r - 1$

where n_r is the viscosity of the solution relative to that of the solvent. C is the concentration measured in g per 100 ml of solution and k is a constant which is 0.35 in the case of cellulose nitrate[31] and 0.15 in the case of cellulose[56,57].

(b) **Discussion**

As indicated previously, the average DP is an indicator of the number of anhydroglucose units in the cellulose molecule. In addition, it was also indicated that generally fibre and paper strength increases with increasing DP. This is further illustrated in Figure 6 which shows the linear relationship between tearing strength and average DP, for the conditions of this work. Likewise the DP correlated well with other strength properties e.g.

(i) Burst factor = 28.89 + 0.0075x ------- (21)
r = 0.95;

(ii) Folding strength = -246 + 0.75x ------ (22)
r = 0.93;

(iii) Edge tearing strength = 4.9 + 0.0009x (23)
r = 0.93, and

(iv) Zero-span tensile strength = 3.98+0.006x (24)
r = 0.95

where x = DP

The correlation coefficients, r, for the relationships between DP on the one hand and tearing strength, burst factor, folding-, edge tearing- and zero-span tensile strength on the other hand, were all significant at the 0.01 level.

As shown in Figure 7, DP correlates linearly and negatively with aging temperature within the range 50 to 90^{o}C, the correlation coefficient, r, for this relationship being significant at the 0.01 level.

For reasons discussed previously, the transformed exponential functions (equations 4, 5 and 6)

were fitted to the observations, again expressing aging temperature as ^{o}K and assuming that no aging would occur at $273^{o}K$. The following linear regression equations were obtained :

$$\text{Log } y = 4.0028 - 0.0075x \quad \text{---------} \quad (25)$$

with $r = -0.88$;

$$\text{Log } y = 8.76 - 2.317 \log x \quad \text{-------} \quad (26)$$

with $r = -0.86$, and

$$\text{Log } y = 4.003 - 0.0033x \quad \text{----------} \quad (27)$$

with $r = -0.88$.

The correlation coefficients for these relationships were significant at the 0.05 level, thus again supporting the validity of these exponential functions in describing the influence of temperature over a wide range on paper aging.

Decreases in DP are caused by hydrolysis but can also be caused by severe oxidation. The only source of oxidation in the present case was atmospheric oxygen and it seems unlikely that this could have had any significant effect. Alternatively, decreases in DP can be caused by shortwave radiation (photolysis) or microbiological action both of which were excluded in this work.

Hydrolysis can take place in acid as well as in alkaline medium[93]; the rate of hydrolysis increasing both with increasing acidity and alkalinity[93] with a minimum at the neutral point. Acid hydrolysis can proceed at appreciable rates even below $100^{o}C$ while the rate of alkaline hydrolysis is much lower[93].

It appears probable that acid hydrolysis was the main contributor to decreases in DP in the present case; its rate having been increased by

the increase in temperature.

An increase in the percentage relative humidity of the aging atmosphere from 0 to 75 per cent, did not show any relationship with DP under the conditions of this experiment (see Table 4). However, it appeared (Table 4, Exp. no. 9) that aging at 95 per cent RH produced a sharp decrease in DP as compared to aging at lower RH's. It is therefore possible that percentage RH of the aging atmosphere could have an effect on hydrolysis of the cellulose in paper and this part of the investigation will have to be extended to include more drastic aging conditions e.g. longer periods or higher temperatures.

Oxygen content of the aging atmosphere (between 1 and 92 per cent) had no influence on the aging of paper as indicated by the DP. (Table 7).

Sulphur dioxide had no influence on DP even at the high concentration of 315 mg/m^3 which is about 10,000 times higher than that present in industrial atmospheres. In actual fact sulphur dioxide was not absorbed at all by the paper as shown by its constant pH values and by the fact that its sulphate content did not increase. Likewise no sulphites were present.

The period of aging was probably too short to allow absorption of measurable quantities of sulphur dioxide. The absorption of sulphur dioxide may also have been retarded by the low relative humidity used, namely 25 per cent, and by the high temperature used, namely $50^{o}C$.

Although the decreases in DP as a result of increasing the aging period from 1 to 10 days were small, the correlation coefficient, r, for this relationship was significant at the 0.05 level, indicating that the DP is an extremely sensitive measure of degree of aging of paper (see Figure 8). It will be of importance to ascertain whether this relationship stays linear for longer periods of aging.

The influence of acid content of the paper samples on the percentage reduction of the DP resulting from aging is illustrated in Figure 9. The percentage reduction in DP on aging decreases sharply with decreasing acid content until a zero acid content is reached whereafter the reduction of DP progressively increases again. Although the reductions illustrated in Figure 9 are relatively small they conform to the theory of hydrolysis of cellulose[93].

If this finding is correct, it casts some doubt on reports in literature that paper buffered to a pH of 8.6 to 9.0, e.g. with calcium carbonate, is the most stable. The buffer in such paper is claimed to neutralize acids formed in the paper by catalytic oxidation of sulphur dioxide. The same purpose, however, can be achieved by using chelating agents to inactivate the metal catalysts normally present in paper, and thereby preventing oxidation of sulphur dioxide and consequently the formation of sulphuric acid.

The influence of size content and of lignin content of the paper sheets on the reduction in DP was insignificant at the 0.10 level.

It is evident from the values listed in Table 5 for experiments 30 to 33 that the purification treatments resulted in pulps with lower average DP's compared to that of the unpurified samples. It is generally believed[107] that paper prepared from a low DP pulp is more liable to deteriorate than paper from high DP pulps. The fact that the percentage reduction in DP for the above mentioned 4 experiments was generally higher than those obtained from the experiments in groups 6 and 7 (see Table 5) may be an indication that this belief is valid. However, other factors, e.g. purity of the fibres and sizing of the paper samples were also introduced and consequently the influence of DP on deterioration of paper needs further clarification.

(3) Changes in alkaline solubility as an indicator of paper deterioration

(a) General

Cellulose is insoluble in alkaline solutions; this being the principle applied in alkaline pulping procedures. Substances such as lignin and low molecular weight non-cellulosic substances are dissolved from wood resulting in a pulp mass consisting mainly of cellulose fibres. A high percentage of the hemicelluloses in wood are also dissolved by virtue of their low DP and the presence of carboxyl groups.

Hydrolysis and oxidation of cellulose leads to the formation of products soluble in alkali owing to a reduction in DP and introduction of carbonyl and/or carboxyl groups which enhance solubility in alkaline solutions.

Alkaline solubility methods find general application in the evaluation of cellulose preparations. The tests are empirical since the substances dissolved can vary widely in chemical composition, but it can be indicative of deterioration.

(b) Discussion

A linear relationship between alkaline solubility and aging temperature within the range 50 to 90°C is illustrated in Figure 10. The correlation coefficient, r, is significant at the 0.05 level.

However, examination of the values shown suggest the possibility that the influence of temperature on alkaline solubility within the range investigated may be better described by a curvilinear relationship. For reasons described previously the transformed exponential functions described earlier were fitted to the observations and an assumed value of zero deterioration at 273°K. The following linear regression equations were obtained :

$$\text{Log } y = -1.504 + 0.015x \quad \text{----------} \quad (28)$$

with $r = 0.90$;

$$\text{Log } y = 4.67 - 11.103 \log x \quad \text{------} \quad (29)$$

with $r = 0.88$, and

$$\text{Log } y = -1.503 + 0.0066x \quad \text{---------} \quad (30)$$

with $r = 0.90$.

The correlation coefficients, r, are significant at the 0.05 level and suggest that the assumption (see section 5.a.(1)(a)) made led to a relationship which may be a true approximation of aging at lower temperatures.

However, it is not possible at this stage to state whether the increased alkaline solubility was caused solely by decreases in DP (which were significant as already shown), and by concomitant aldehyde groups or whether ketonic carbonyl groups which formed as a result of oxidation of the polysaccharides contributed to the increased solubility in alkali.

Contrary to the fact that the percentage relative humidity (between 0 and 95 per cent) of the aging atmosphere did not influence the strength properties of the paper samples or the DP of the cellulose it correlated well with the alkaline solubility of the pulp as illustrated in Figure 11. The correlation coefficient, r, for this relationship is significant at the 0.05 level. The fact that a relationship does exist between alkaline solubility and RH, suggests that alkaline solubility of the pulp may be even more sensitive than DP as an indicator of aging.

Oxygen and sulphur dioxide content of the aging atmosphere did not influence the alkaline solubility under the conditions of this experiment.

On increasing the aging period from one to 10 days, the alkaline solubility increased from 3.0 to 3.6 per cent as illustrated in Figure 12. Although the increase was much smaller than that obtained by increasing the aging temperature from 50 to 90^{o}C the correlation coefficient, r, was significant at the 0.05 level.

It would be of importance to ascertain the shape of the curves correlating alkaline solubility with extended periods of aging since the rate of

aging will probably change with increasing aging period.

The relationship between percentage increase in alkaline solubility of paper as a result of aging and acid content of the paper is shown in Figure 13. This relationship is similar to that between DP and acid content.

Contrary to the above mentioned findings the decreases in strength values of paper because of aging showed a linear correlation with acid content and no minima occurred at the neutral point. It therefore appears that DP and alkaline solubility are more sensitive indicators of aging than strength values in general.

The relationship between sizing content (x) and percentage increase in alkaline solubility on aging (y) is given by the equation $y = 16.15 - 0.39x$ and is illustrated in Figure 14. The correlation coefficient, r, is significant at the 0.10 level. This substantiates the previous finding that sizing itself actually stabilizes paper.

From a comparison of the reference samples in group 8 (see Table 5) it appears that purification of the pulp resulted in a slight increase in percentage alkaline solubility probably because of the decreased DP that resulted from the purification treatments.

The relationship between the percentage increase in alkaline solubility on aging and the lignin content of the paper samples is illustrated in Figure 15. The correlation coefficient, r, for

this relationship was significant at the 0.05 level.

(4) Influence of aging on the pH of paper

The pH of paper was, without exception, insensitive as an indicator of aging.

(5) Influence of aging on the copper number of paper

(a) General

The reducing nature of cellulose is caused by the presence of carbonyl groups. For the greater part these groups are probably aldehydic end-groups[34] arising from hydrolysis of the polysaccharide chains. For this reason hydrolysis of cellulose increases its reducing power by shortening the chain length and increasing the number of aldehydic end-groups.

The determination of reducing properties of polysaccharides is based on oxidation, reduction or the formation of derivatives. In the present case the damage done to the polysaccharides on aging has been assessed by oxidation of carbonyl groups to carboxyl groups utilizing cupric (Cu^{2+}) ions according to the Hägglund method.

Oxidation with Cu^{2+}-ions takes place in alkaline medium and the reaction may be expressed as $R\text{-}CHO + 2\ Cu^{2+} + 2H_2O \longrightarrow R\text{-}COOH + Cu_2O + 4H^+$. From the amount of Cu^{2+}-ions reduced, the copper number, defined as the number of grams of copper reduced from the Cu^{2+} to the Cu^{+} state by 100 g of dry paper is calculated. The reaction between Cu^{2+} and carbonyl groups is nonstoichiometric[31] and therefore gives only relative values for the reducing capacity of polysaccharides. Nevertheless,

these values have been widely applied in the evaluation of cellulose.

(b) Copper number as an indicator of paper deterioration

The numerical change in copper number i.e. from 0.74 in unaged paper to 1.51 in paper aged at 90°C for 10 days (Group 1, Table 4) was small. However, the correlation coefficient, r, for the relationship between copper number and aging temperature (see Figure 16) was significant at the 0.01 level. It is accurate and easy to determine and may therefore serve as a useful indicator of the relative increase in carbonyl content of paper on aging.

c. Mechanism of paper deterioration

(1) General

In an attempt to obtain further indications and evidence as regards the mechanism of paper aging, two further samples (prepared according to Group 1, Table 1) were severely aged by exposing them to 100°C for 30 days, in the one case at zero RH and in the other at 55 per cent RH. These two samples, together with other selected samples were used for the following determinations according to the methods mentioned in section 2.c.

(i) Physical strength.
(ii) Infrared absorption spectra.
(iii) Water soluble sugars.
(iv) Average DP.
(v) Fractionated DP.
(vi) Carbonyl groups.
(vii) Carboxyl groups.

The values obtained from the four samples (A to D) and details about aging are listed in Tables 6 and 7. Infrared absorption spectra are illustrated in

Figures 17 and 18.

(2) Paper strength

It is evident from Table 6 that the strength of samples C and D decreased to a very low level, that of sample D being the lowest. Samples C and D were aged under identical conditions except that sample D was aged in a humid atmosphere. It therefore appears that the moisture in the aging atmosphere can be an important factor contributing towards aging.

(3) Infrared absorption spectra

Infrared absorption spectra in the frequency range 4,000 to 200 cm^{-1} (2.5 to 50 micron) of samples A to D were determined on a Beckman double beam infrared spectrometer IR 12 employing the potassium bromide disc technique.

Preparation of samples entails intimate mixing of dry, finely milled paper samples with analar grade dry potassium bromide (2 mg paper to 250 mg KBr) and pressing of the mixture under vacuum (1 mm Hg) in a die at 50 ton/in^2 for 1 min.

The spectra of samples A, B and C were identical and are illustrated in Figure 17. The spectrum of sample D (Figure 18) shows incipient changes in the carbonyl stretching band at approximately 1710 cm^{-1}. Normally the carbonyl stretching vibrations of various carbonyl groups absorb in the region 1900 to 1600 cm^{-1}. More specifically[82], ketonic carbonyls absorb at 1715 cm^{-1}, aldehydic carbonyls at 1725 cm^{-1}, acid monomers at 1760 cm^{-1}, acid dimers at 1710 cm^{-1} and esters at 1735 cm^{-1}. The presence of intra-molecular hydrogen bonds may cause absorption bands to shift to lower frequency with a certain amount depending on the

H-bond strength[82,122]. This could have happened in the present case and it is therefore impossible to state with certainty to which type of carbonyl groups this absorption is due. It appears likely that the absorption noticed is due to aldehydic carbonyls resulting from breakdown of the cellulose chains as reflected by the low DP (see Table 6).

The intensity of the carbonyl stretching band at 1710 cm^{-1} (Figure 18) is very low. Considering that this sample showed large changes with respect to strength and average DP (see Table 9) it must be concluded that infrared spectroscopy is too insensitive to study changes resulting from aging of paper and further investigation by means of this technique was therefore abandoned.

(4) Soluble sugars

Samples A to D were extracted overnight with cold water, filtered and the filtrates concentrated to about ½ ml by evaporation at 40°C under reduced pressure. The solution obtained was applied to Whatman no. 1 chromatographic paper and the components were separated using Whaley's solvent (butanol 300 parts, water 240 parts, pyridine 200 parts, acetic acid 60 parts, all by volume). The chromatograms were developed with p-anisidine hydrochloride[37] and with silver nitrate[50]. The latter solution was the most sensitive.

The chromatograms of sample A were negative, that of sample B showed only traces of oligosaccharides while those of samples C and D showed the presence of large amounts of oligosaccharides which appeared as streaks on the paper. It is therefore evident that depolymerization of the cellulose in paper as a result of aging, is not a "peeling" reaction in which sugar units

are stripped off the ends of cellulose chains. The chains are probably shortened at random and may be attacked in any spot. The fact that sample A contained no oligosaccharides while sample B showed the presence of traces only, indicates that deterioration must progress to an advanced stage like that of samples C and D before part of it becomes water soluble.

In order to obtain more information about the origin of the oligosaccharides, the concentrates of samples C and D were hydrolyzed in acid medium and the chromatograms were repeated in the same manner. The best separation was obtained after 36 hours.

In both cases (see Figure 19) xylose, glucose, arabinose and glucuronic acid were identified, with the highest concentration in sample D. Figure 19 is a reproduction of one of the paper chromatograms developed with silver nitrate. The hydrolysates of samples C and D were applied in different amounts - the applications on the left of the figure being double that of the applications near the centre. Spectrophotometric determination of these elementary sugars according to ASTM D 1915-61T revealed that these sugars were present in the approximate ratio of 3:2:1:0.5 respectively.

The xylose and arabinose originated from the hemicelluloses present in the paper. Glucuronic acid is a normal constituent of hemicelluloses but can also be obtained from cellulose by severe hydrolysis followed by oxidation. Non-cellulosic glucose is common in wood but glucose can also be obtained through hydrolysis of cellulose. However, since the average DP of cellulose is about 10 to 20 times higher than that of hemicellulose, the cellulose must be degraded to a greater extent than the hemicellulose before it would become water soluble.

It is therefore likely that practically all the elementary sugars found after hydrolysis of the extracts originated from the hemicelluloses present in the paper. This finding, however, does not exclude the fact that the cellulose itself was severely degraded as evidenced by the low average DP values of samples C and D. (See Table 6).

(5) Chain length fractionation

In order to obtain information on the relative stability of various chain length fractions of the polysaccharides, paper samples A, C and D were nitrated, dissolved in acetone/water, fractionally precipitated and the DP of each fraction determined viscometrically (see Tappi method T238su-63). The values obtained are listed in Table 7. The weighted average DP of each fraction (W) was also calculated. It is evident that the sum total of the weighted average DP's (see W in Table 7) agreed well with the average values obtained by the cadoxen method (listed in Table 6). Recovery of the cellulose nitrate was satisfactory, between 100 and 102 per cent being recovered (see Table 7).

Figure 20 illustrates the chain length distribution of the unaged sample A, which had an average DP of 1168. The DP of the cellulose in this sample is distributed between 750 and 2,000 with a maximum between 1,300 and 1,400. It further appears that the DP of the cellulose in this sample did not extend far below 750 since the next fraction appeared at an average DP of 266. The region 300 to 700 DP was very weakly represented and probably indicates the transition between high DP cellulose and low DP hemicelluloses.

Examination of Figure 21 and Table 7 indicates that the chain length of sample C extended from 50 to

760 while that of sample D extended from 16 to 245. The apparent transition between the cellulose and hemicellulose fractions occurred at 190 and 120 DP respectively. However, it is not possible to state whether these low DP fractions contained degraded cellulose. It also appears irrelevant to know whether degraded cellulose contributed to these fractions since the progressive decrease in the chain length of the most important constituent of paper, namely cellulose, is evident. This is further illustrated in Figure 22 (based on Table 7) which shows the relationships between weighted average DP and the cumulative percentage by weight of the polysaccharides. The pronounced decrease in the weighted average DP upon aging is very clear. It appears that if aging is extended far enough, practically only elementary sugar units will remain with complete destruction of the fibre structure and paper strength.

(6) Carbonyl groups

In order to further the knowledge about the mechanism of paper aging it is important to know whether oxidation of the polysaccharides took place in addition to hydrolysis.

Carbonyl groups in cellulose can form as a result of

(i) hydrolysis which will result in aldehyde end-groups;

(ii) mild oxidation which can cause formation of ketone groups in the cellulose ring positions 2 and 3;

(iii) more severe oxidation which can cause ring cission between C_2 and C_3 resulting in aldehyde groups, and

(iv) even more severe oxidation which can result in formation of carboxyl groups.

The most satisfactory method to distinguish between aldehydic and ketonic carbonyl groups appears to be selective oxidation of aldehyde groups with chlorous acid[31]. The carbonyl groups remaining are claimed to be ketones only. Reduction with sodium borohydride ($NaBH_4$) on the other hand reduces both aldehyde and ketone groups[31].

Consequently representative finely divided portions of samples A, C and D were oxidized with chlorous acid and the carbonyl content of oxidized and unoxidized portions was determined by reduction with alkaline $NaBH_4$.[31] The results obtained are listed in Table 6.

Examination of Table 6 shows that the amount of ketonic groups stayed constant while aldehydic groups increased with increasing severity of aging. If the above reasoning, namely that oxidation would result in formation of ketone groups is correct, it can be stated with confidence that oxidation did not take place under the conditions of this experiment.

(7) Carboxyl groups

Carboxylic groups were determined according to Tappi method T237su-63. In this method the cation exchange capacity of the cellulose is utilized as follows :

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

The amount of carboxylic groups obtained are listed in Table 6. If oxidation had taken place during aging an increase in carboxylic content should have been observed. The fact that the amount of carboxylic groups remained constant, is a further confirmation that oxidation did not occur even with severe aging.

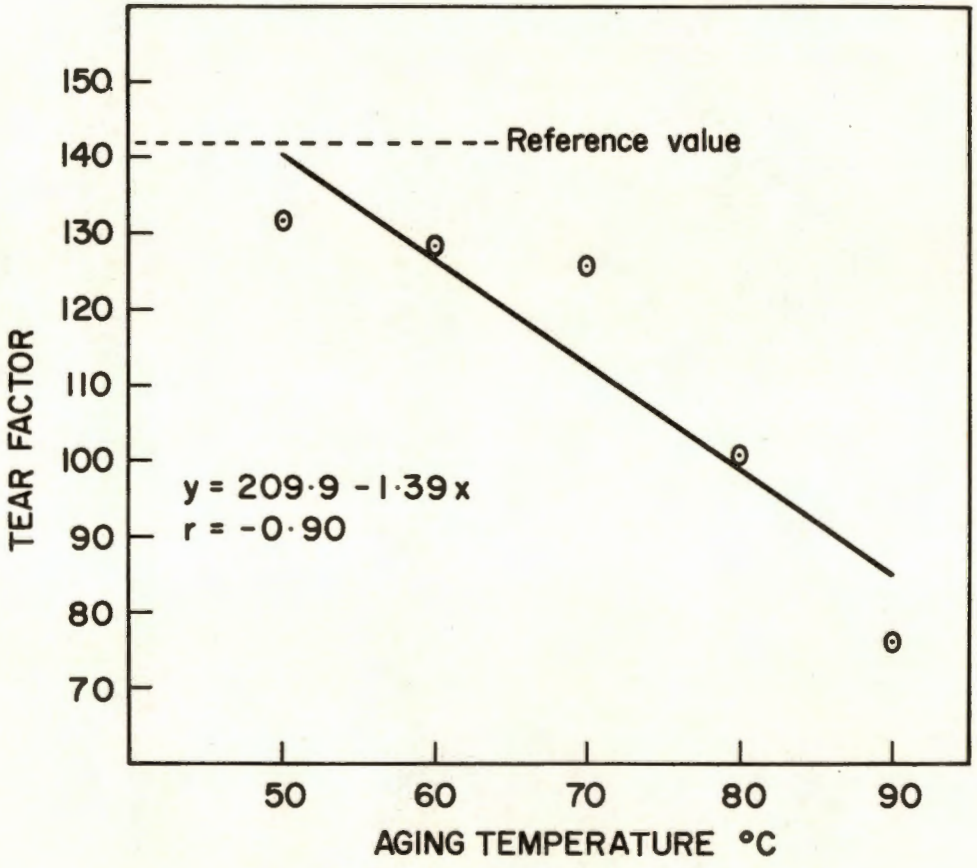


FIGURE 1

Regression of tearing strength on aging temperature

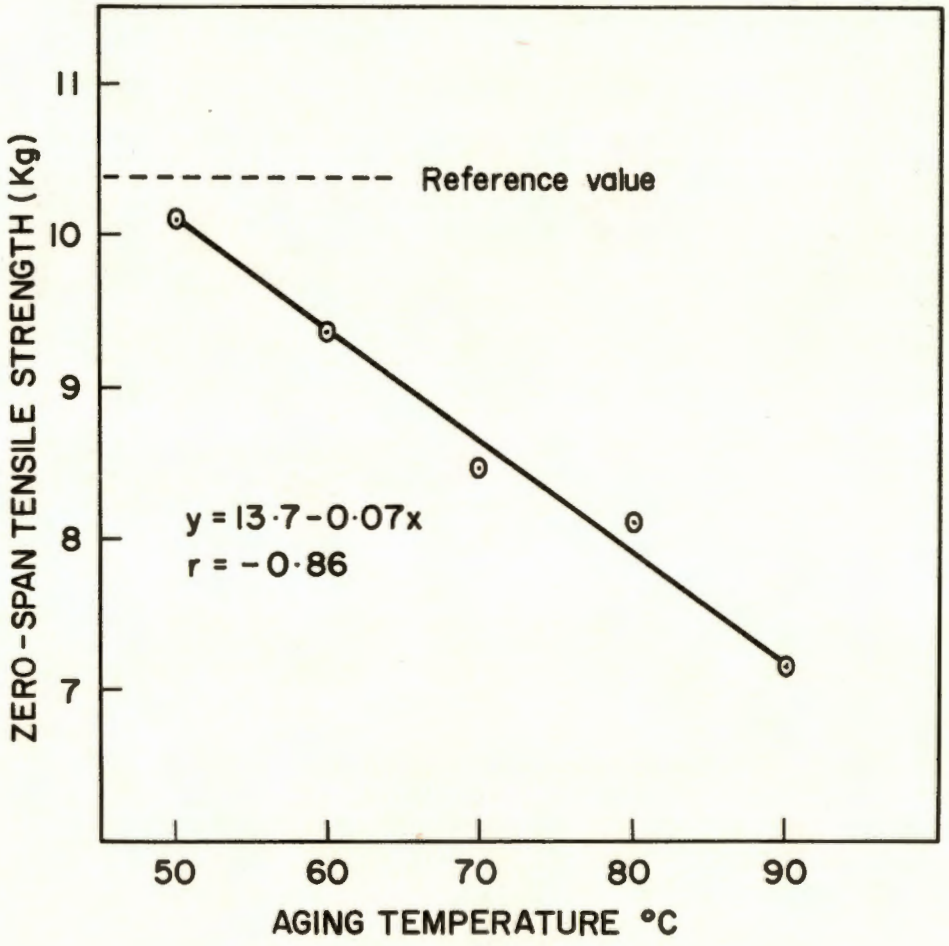


FIGURE 2

Regression of zero-span tensile strength on aging temperature

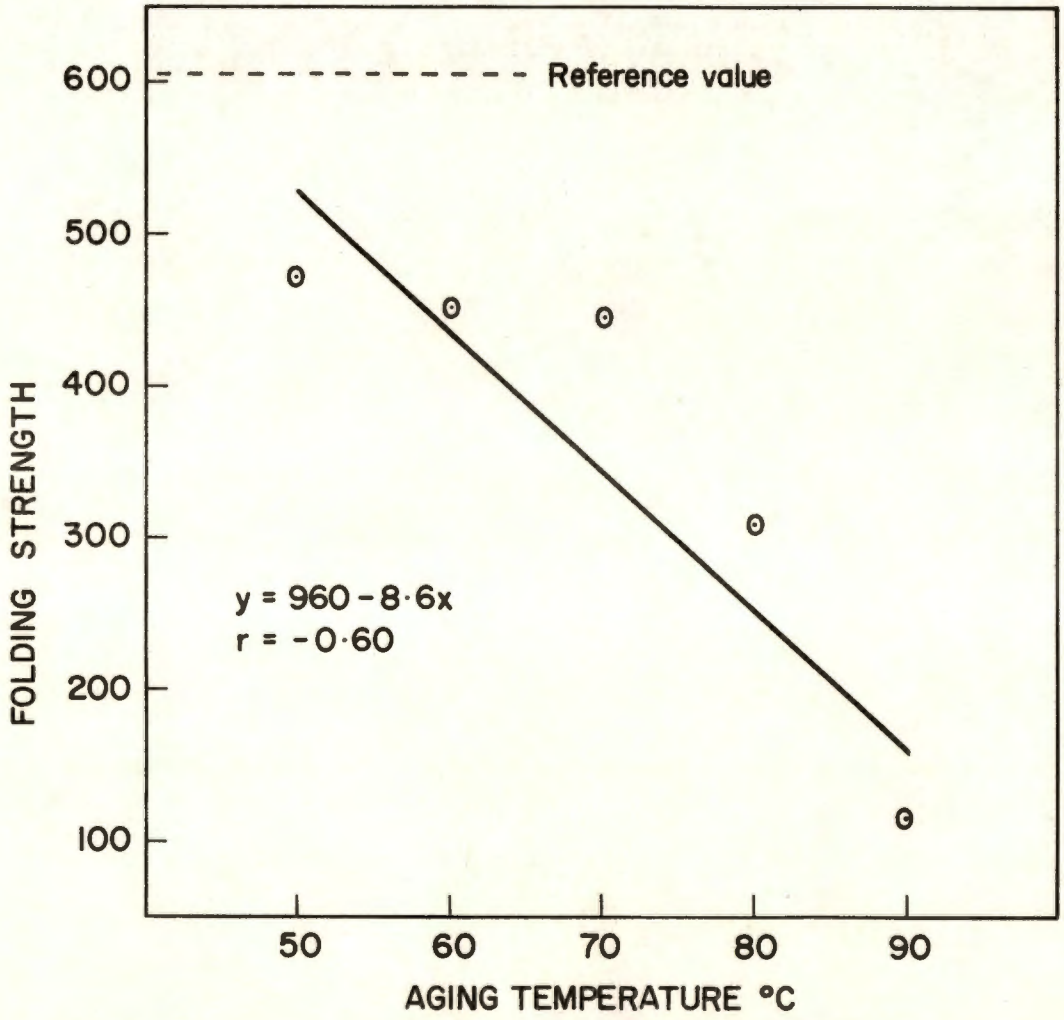


FIGURE 3

Regression of folding strength on aging temperature

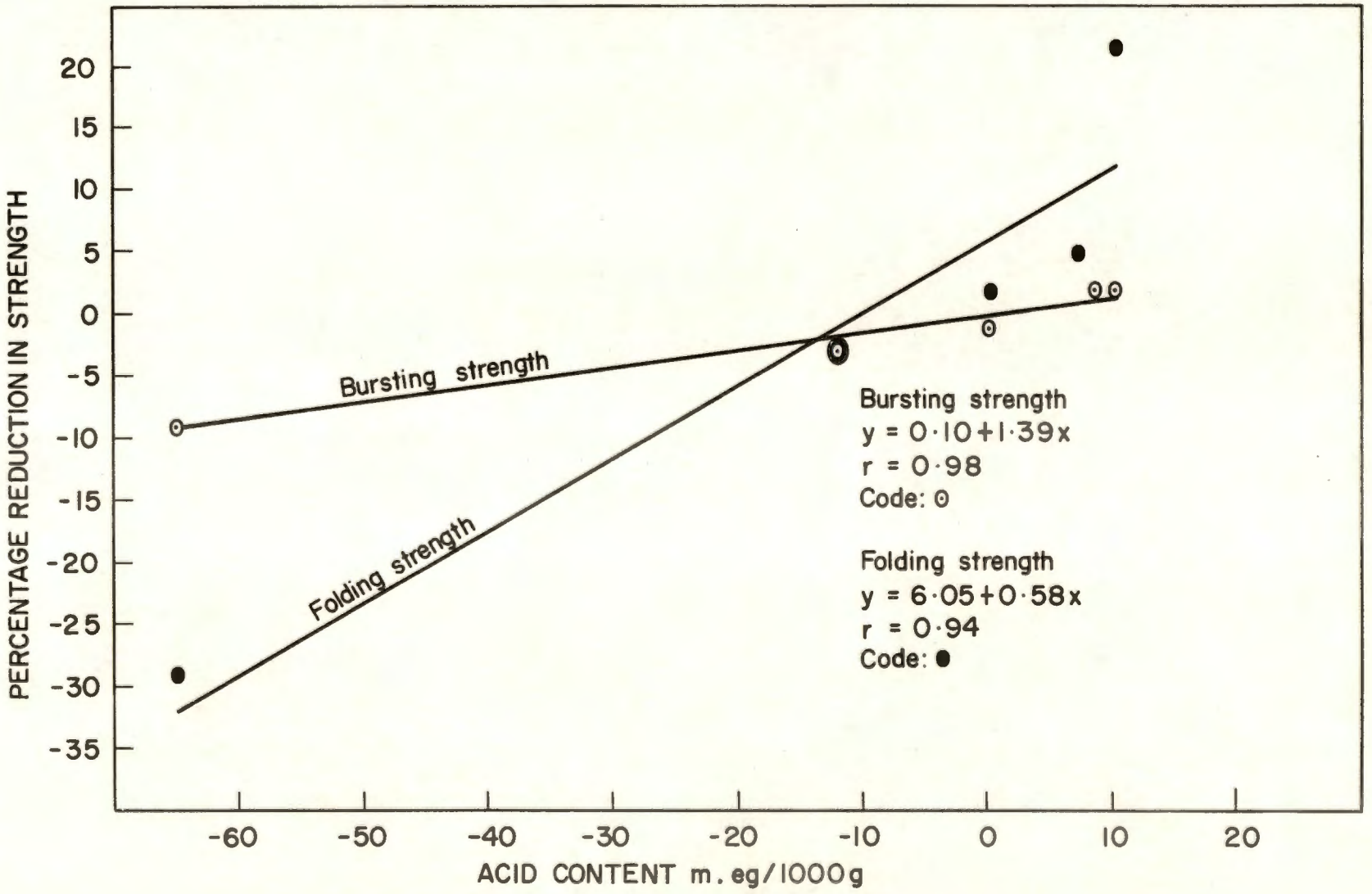
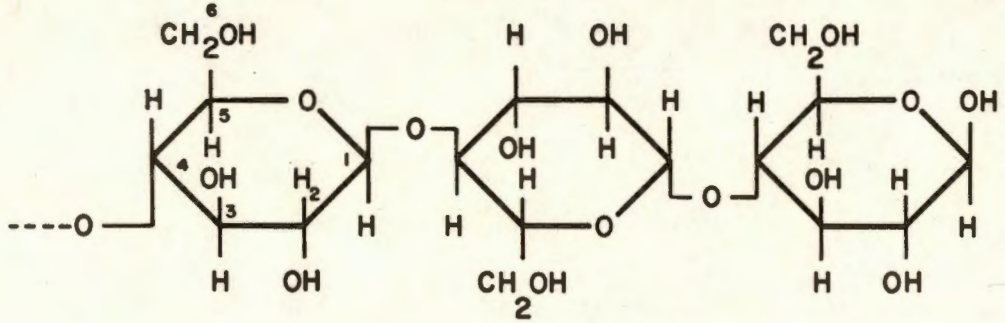
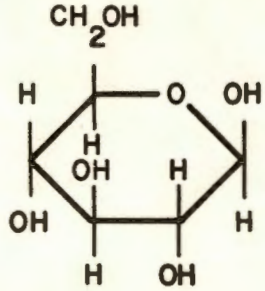


FIGURE 4

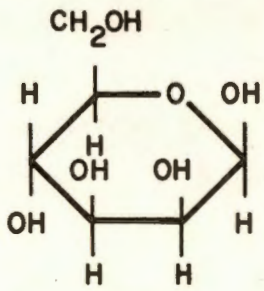
Regressions of percentage reduction on aging of (a) bursting strength and (b) folding strength on acid content of paper



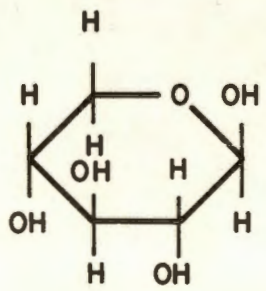
CELLULOSE



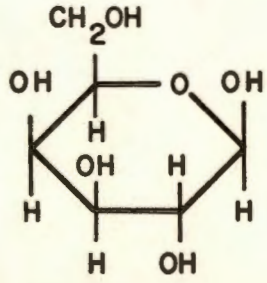
GLUCOSE



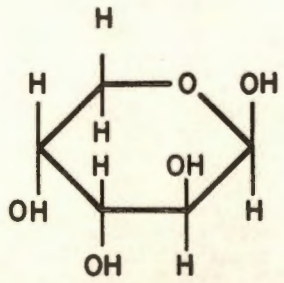
MANNOSE



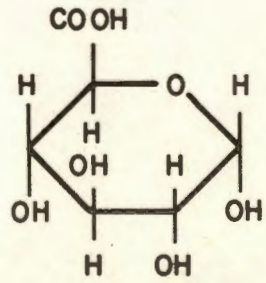
XYLOSE



GALACTOSE



ARABINOSE



GLUCURONIC ACID

FIGURE 5

Chemical structure of cellulose and of carbohydrate monomers

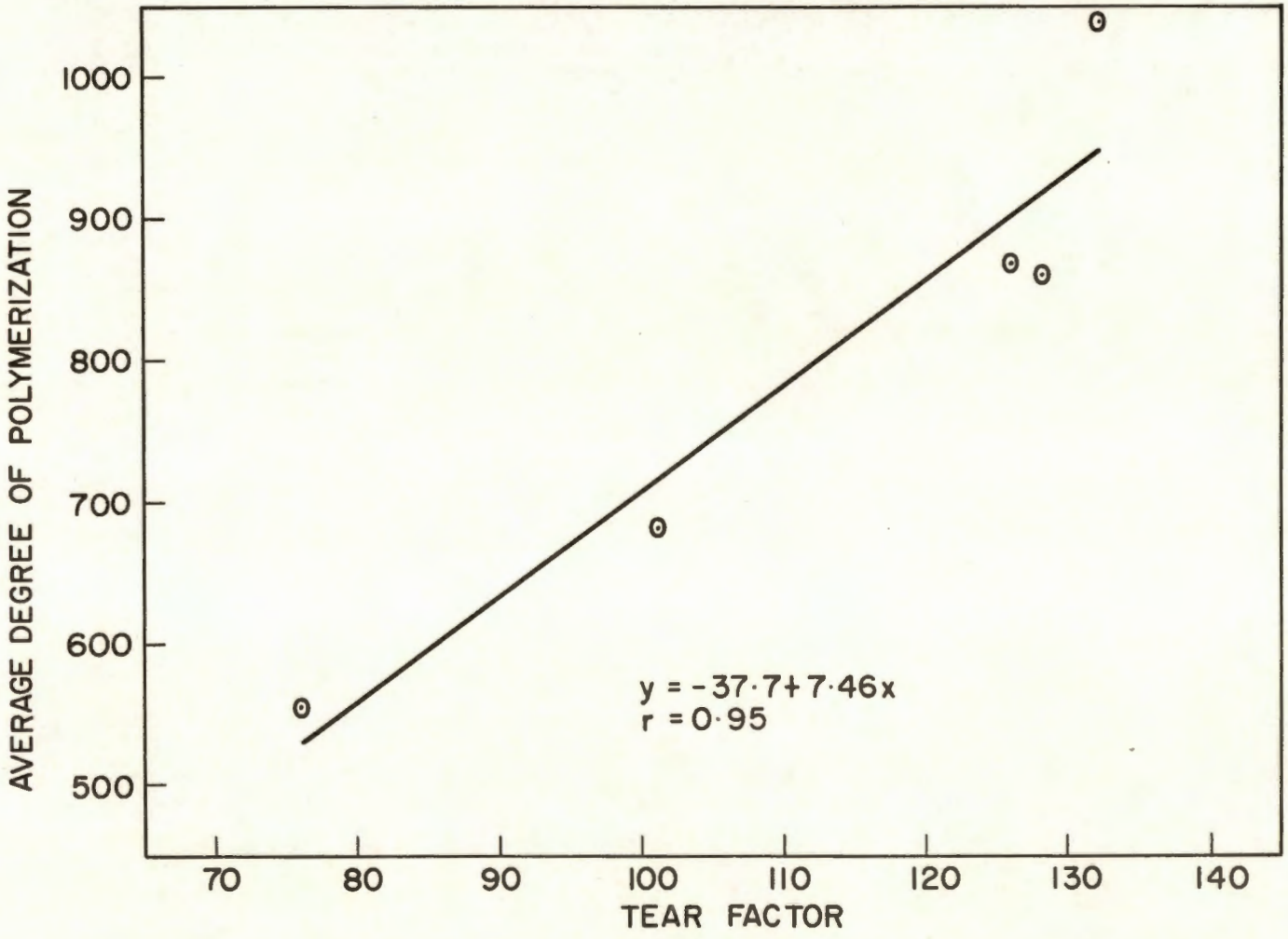


FIGURE 6

Regression of average degree of polymerization on tearing strength

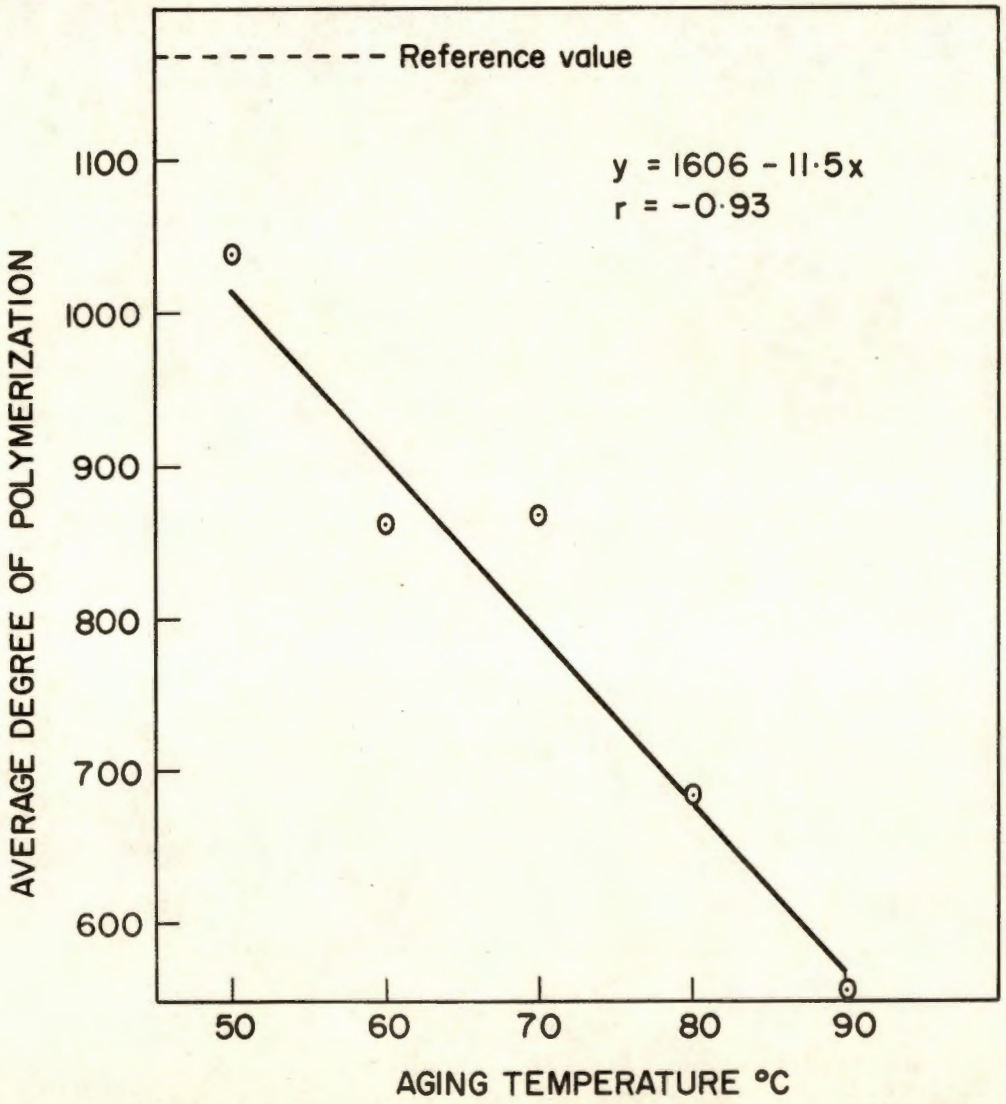


FIGURE 7

Regression of average degree of polymerization on aging temperature

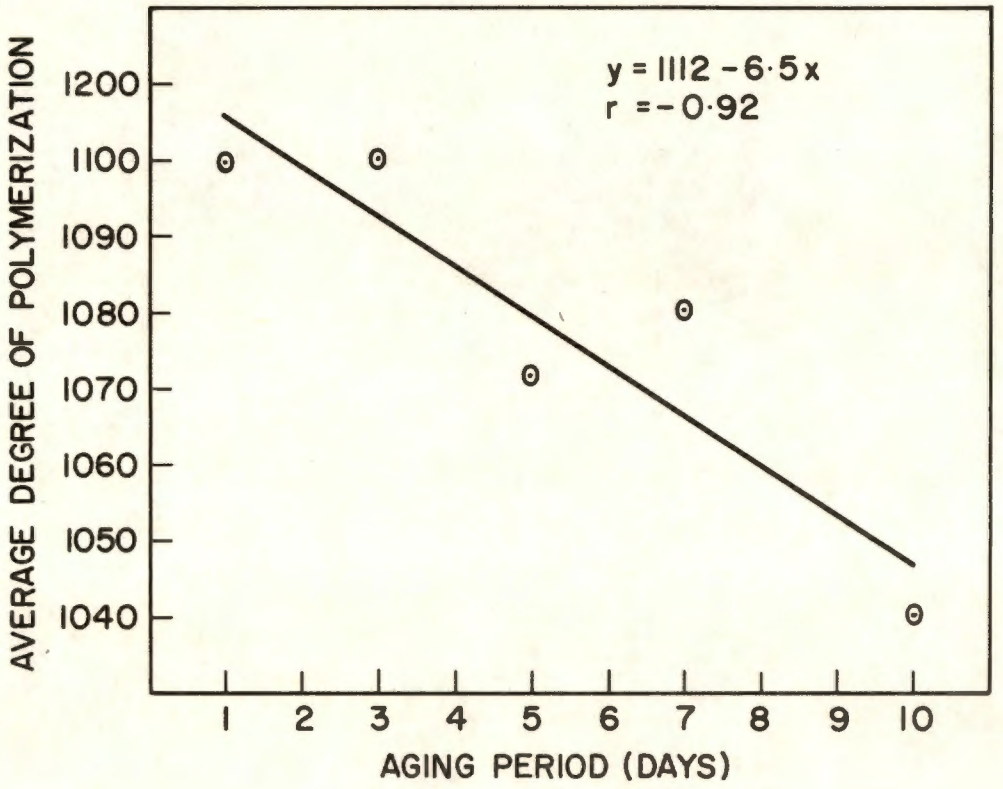


FIGURE 8

Regression of average degree of polymerization on aging period

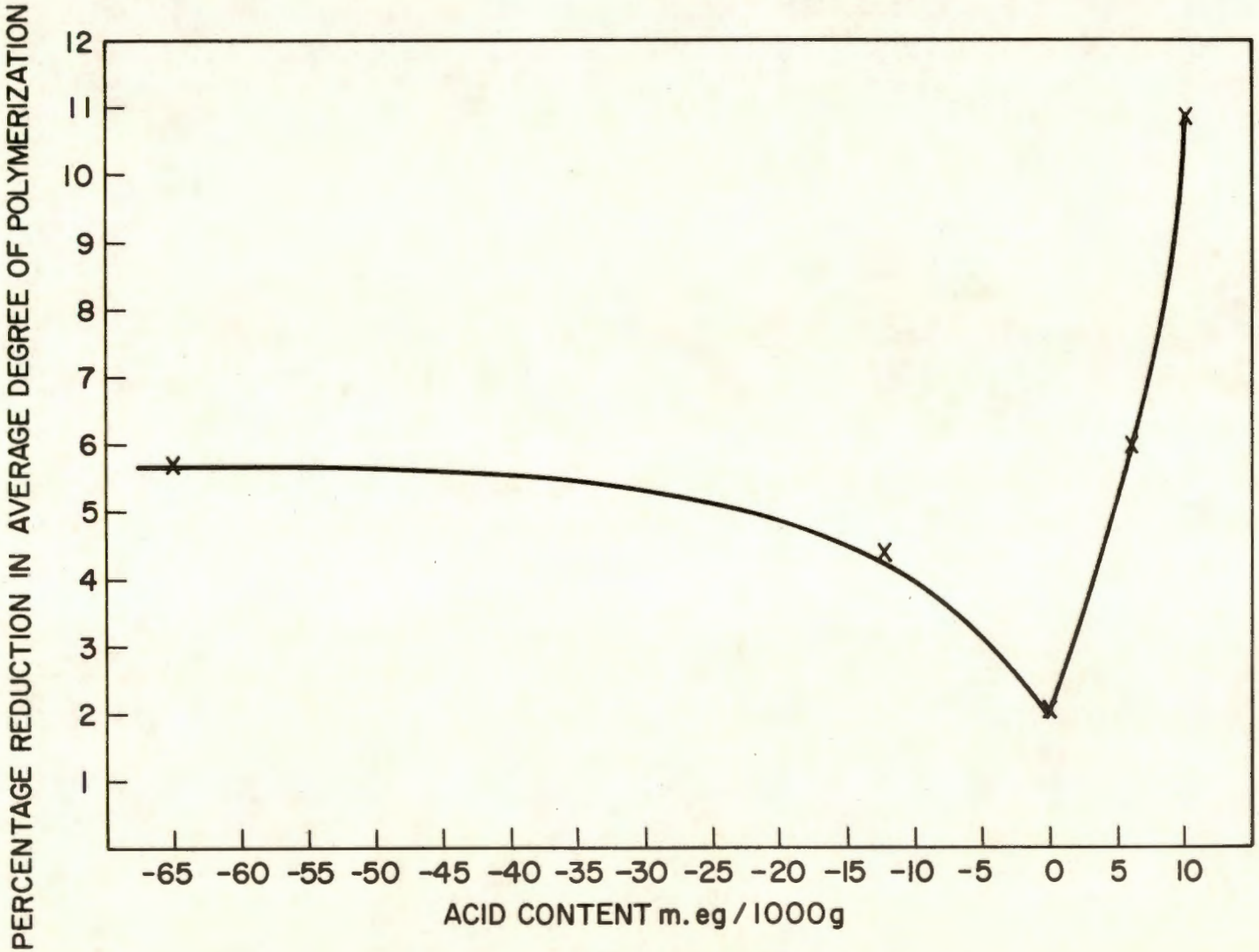


FIGURE 9

Relationship between percentage reduction in average degree of polymerization and acid content of paper

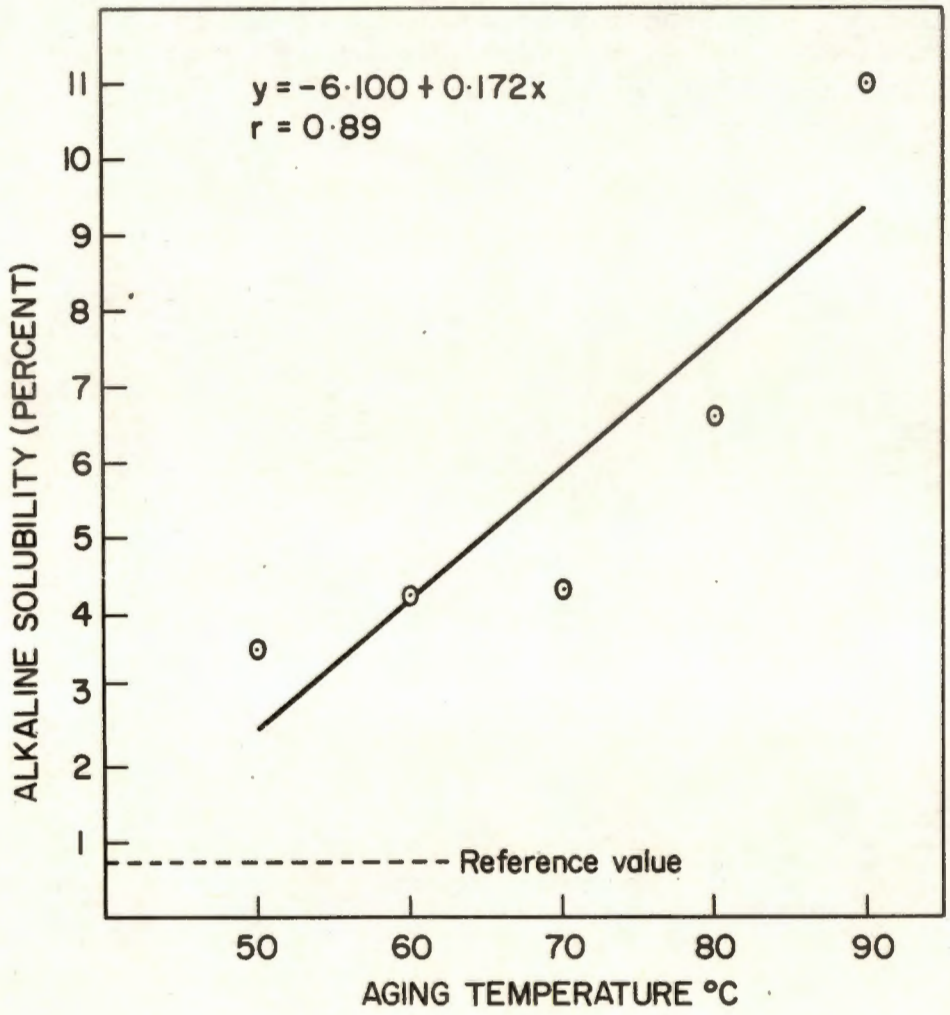


FIGURE 10

Regression of alkaline solubility on aging temperature

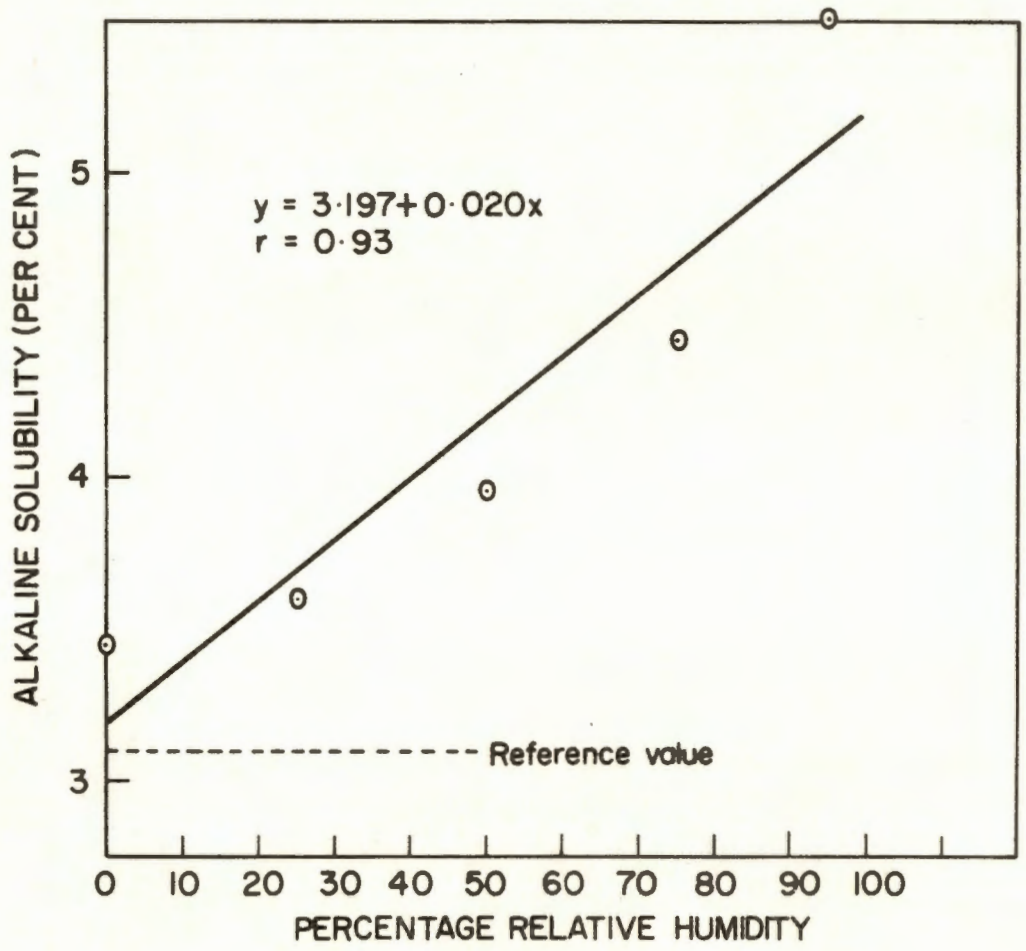


FIGURE II

Regression of alkaline solubility on percentage relative humidity of the aging atmosphere

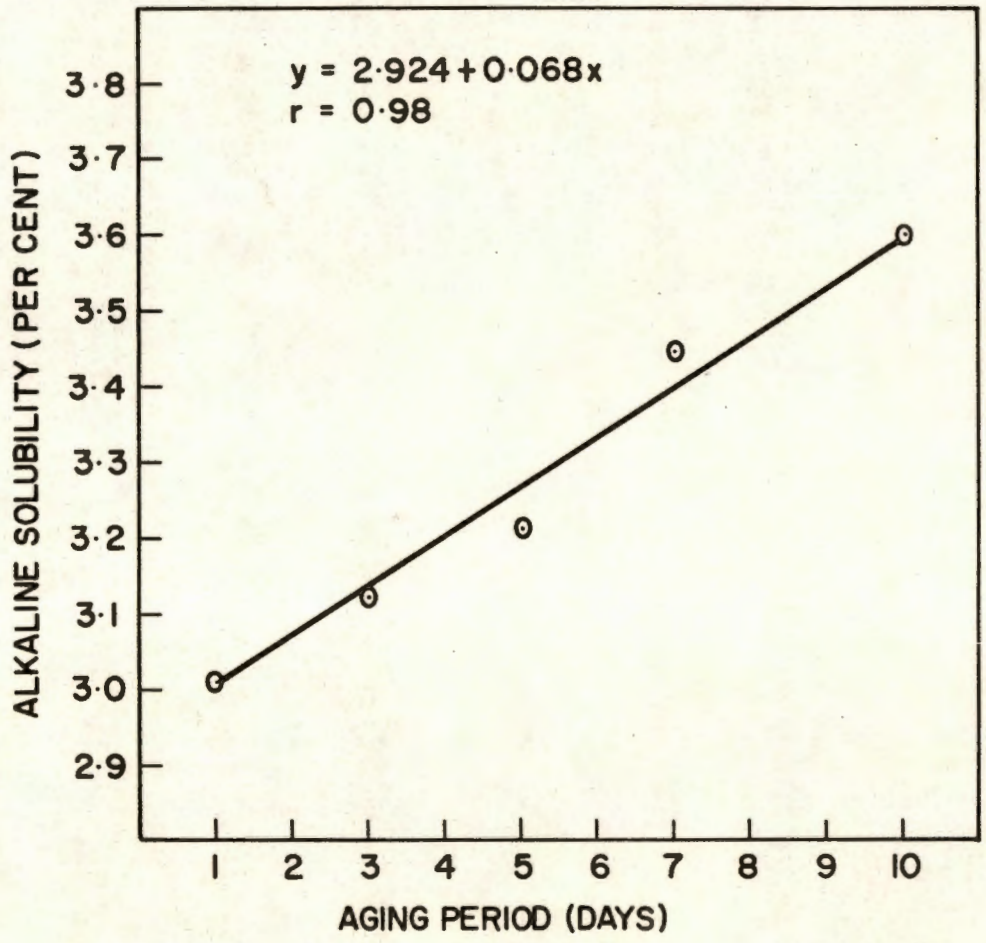


FIGURE 12

Regression of alkaline solubility on aging period

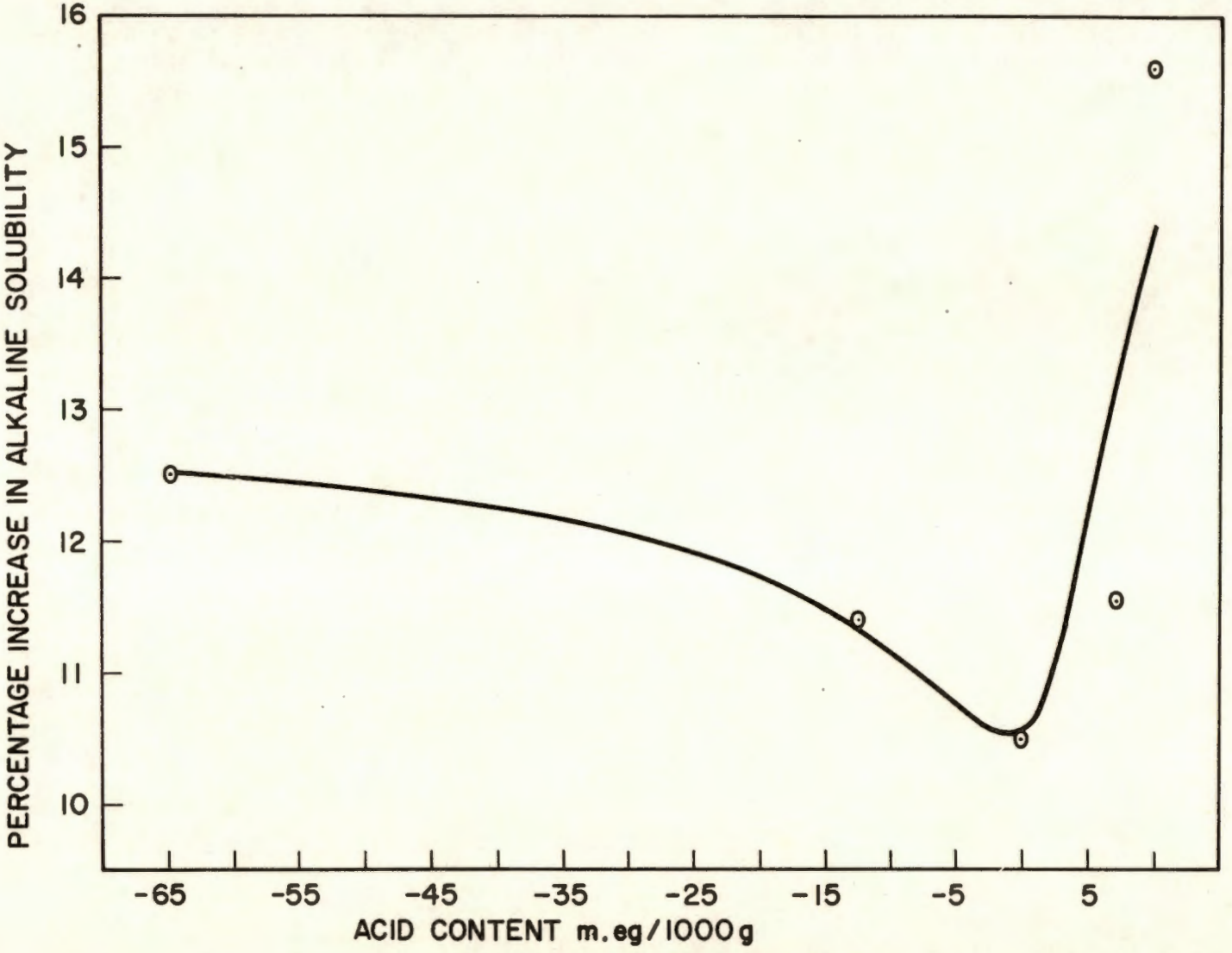


FIGURE 13

Relationship between percentage increase in alkaline solubility and acid content of paper

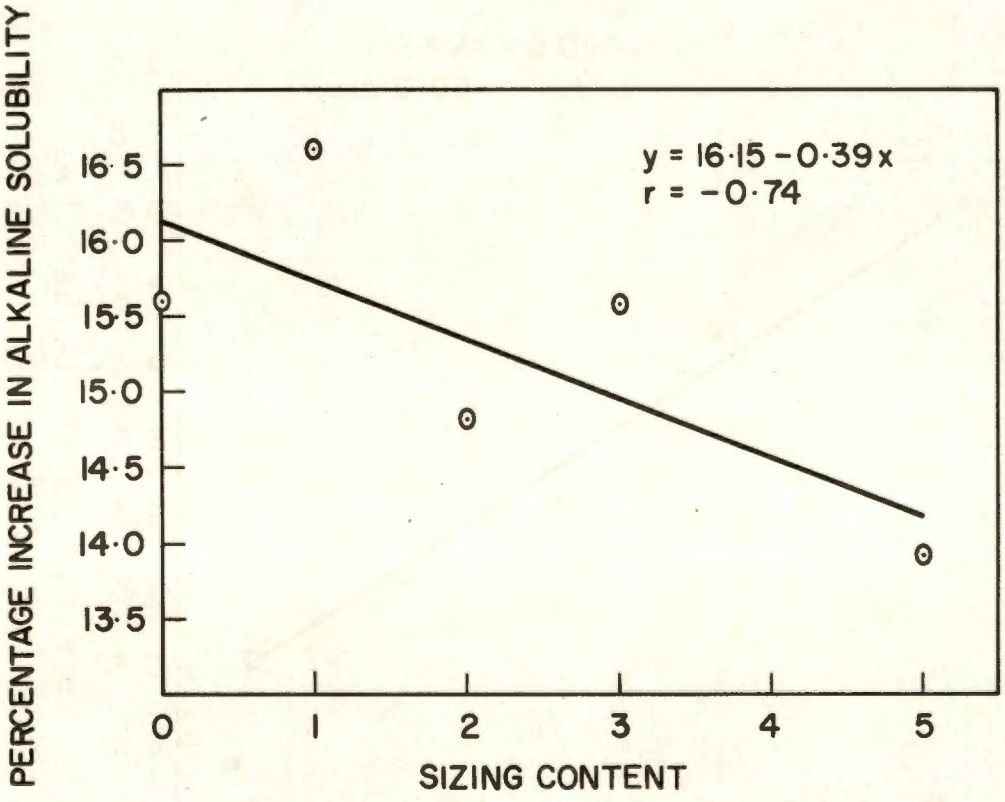


FIGURE 14

Regression of percentage increase in alkaline solubility on sizing content

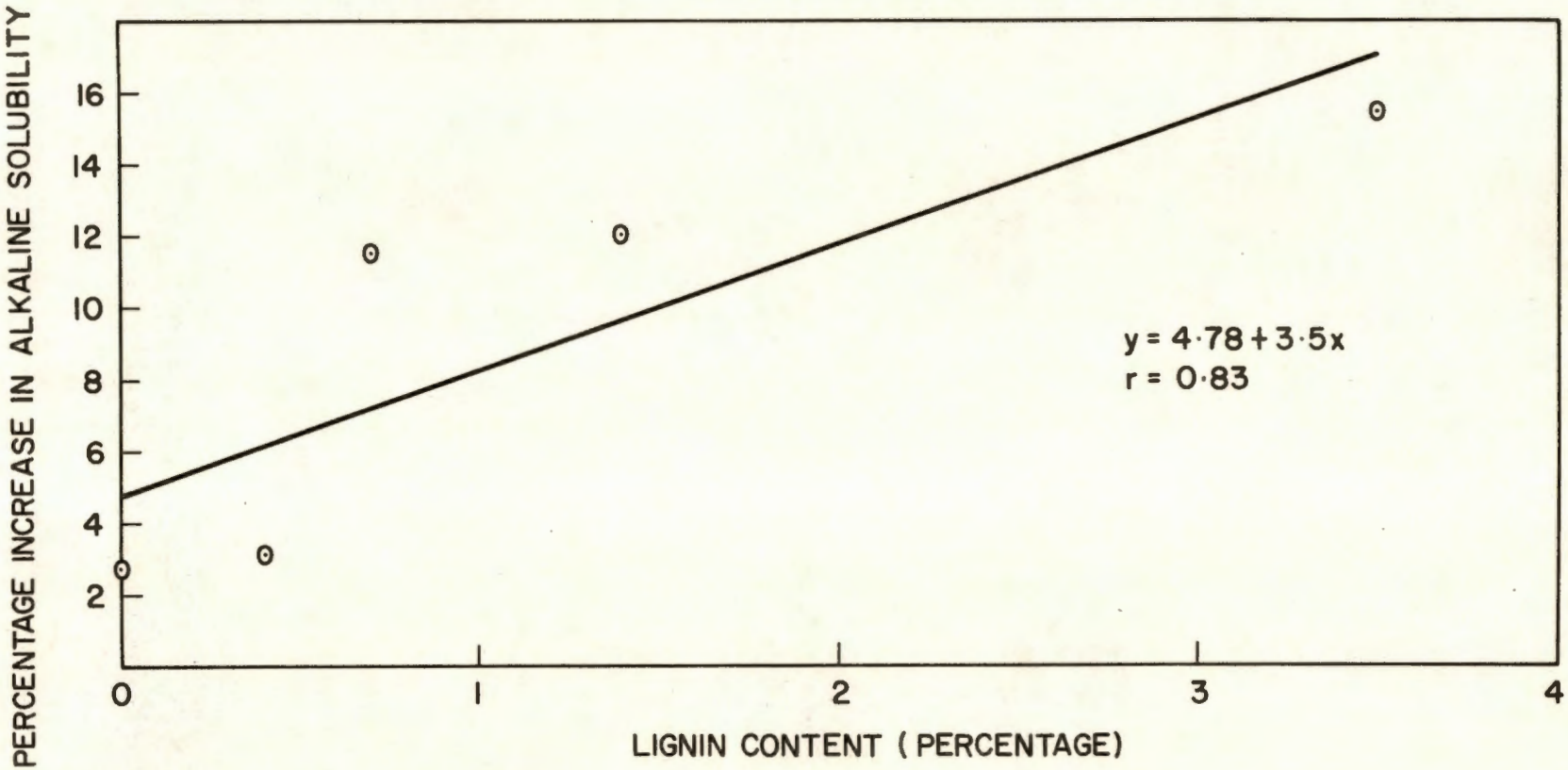


FIGURE 15

Regression of percentage increase in alkaline solubility on lignin content of paper

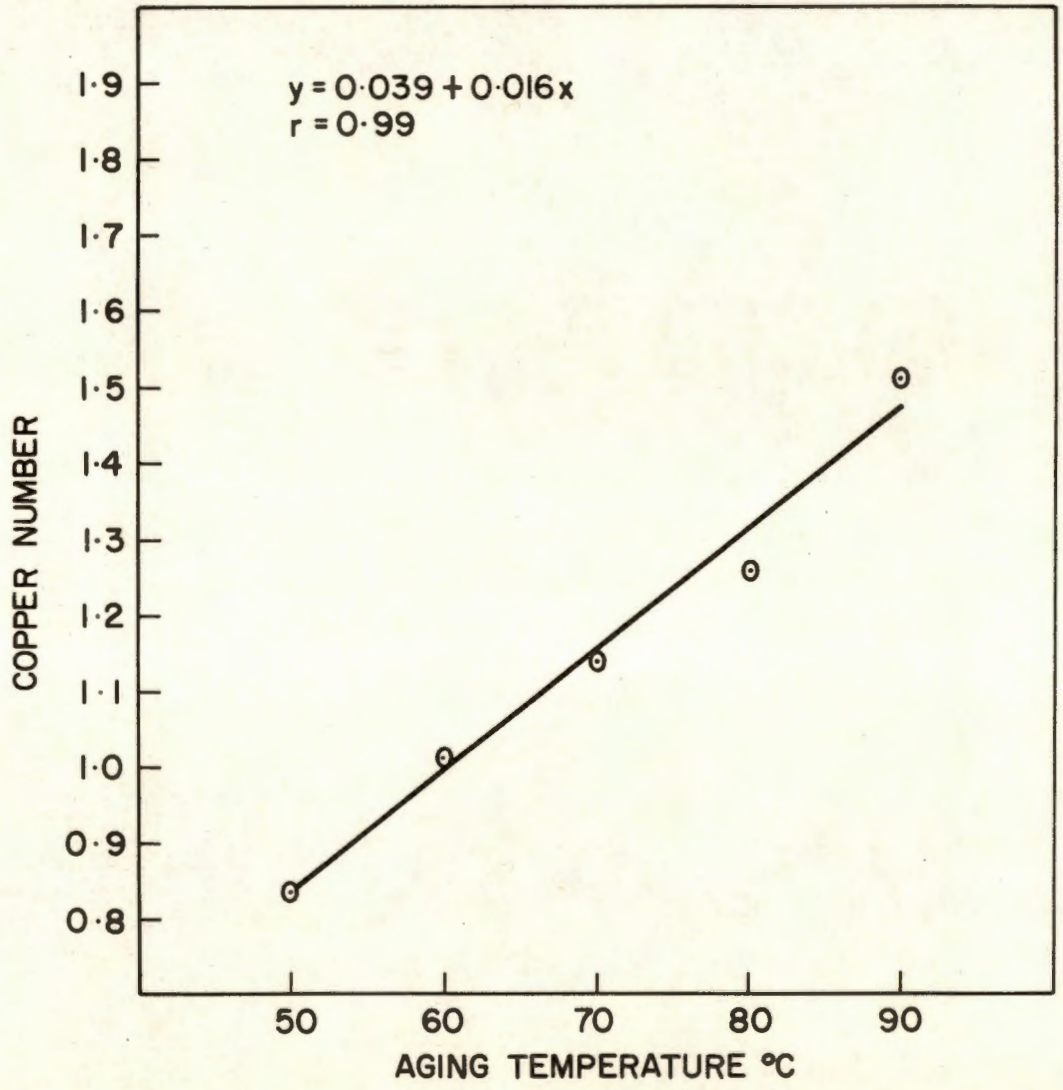


FIGURE 16

Regression of copper number on aging temperature

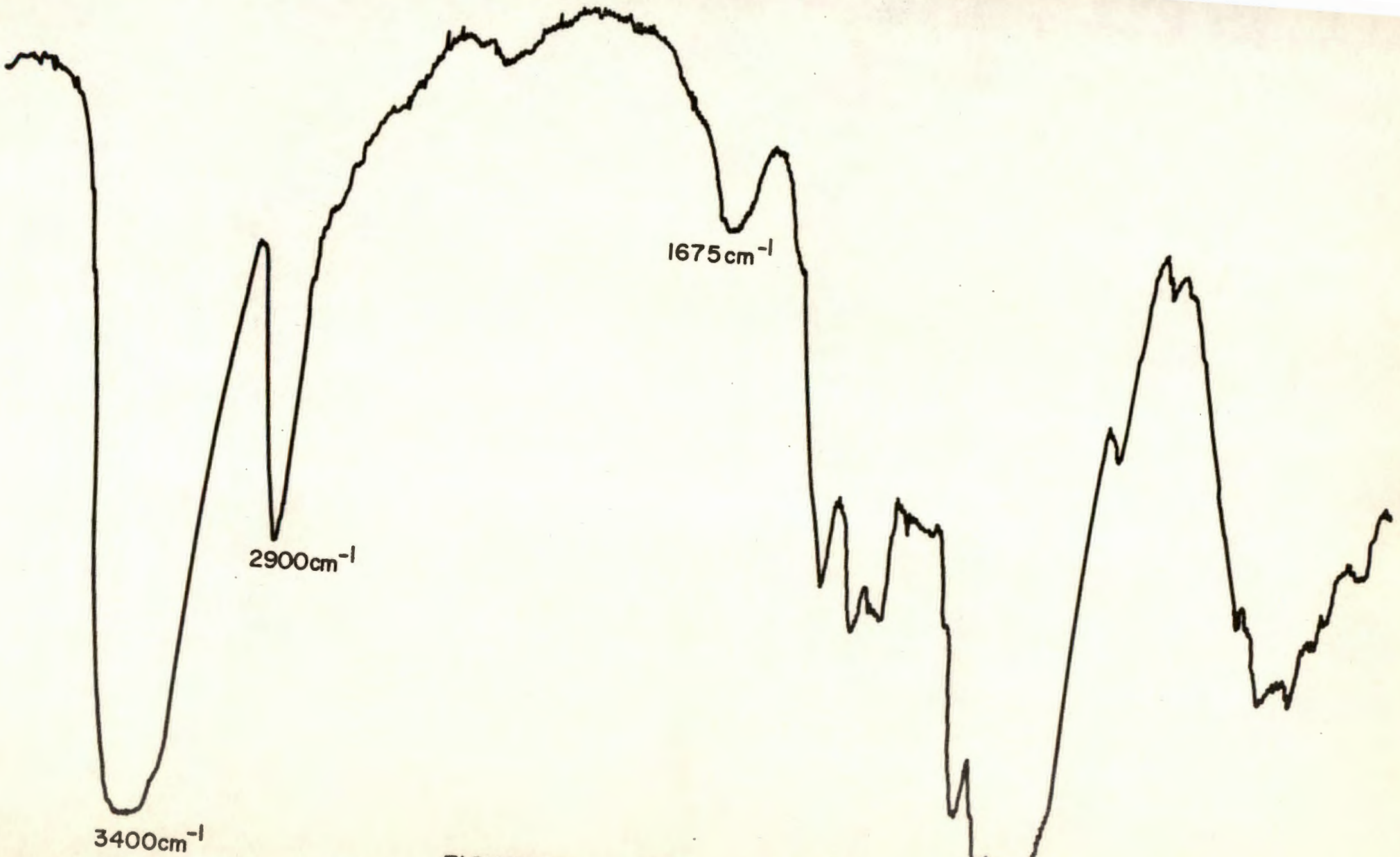


FIGURE 17

Infrared absorbtion spectrum representing samples A, B and C

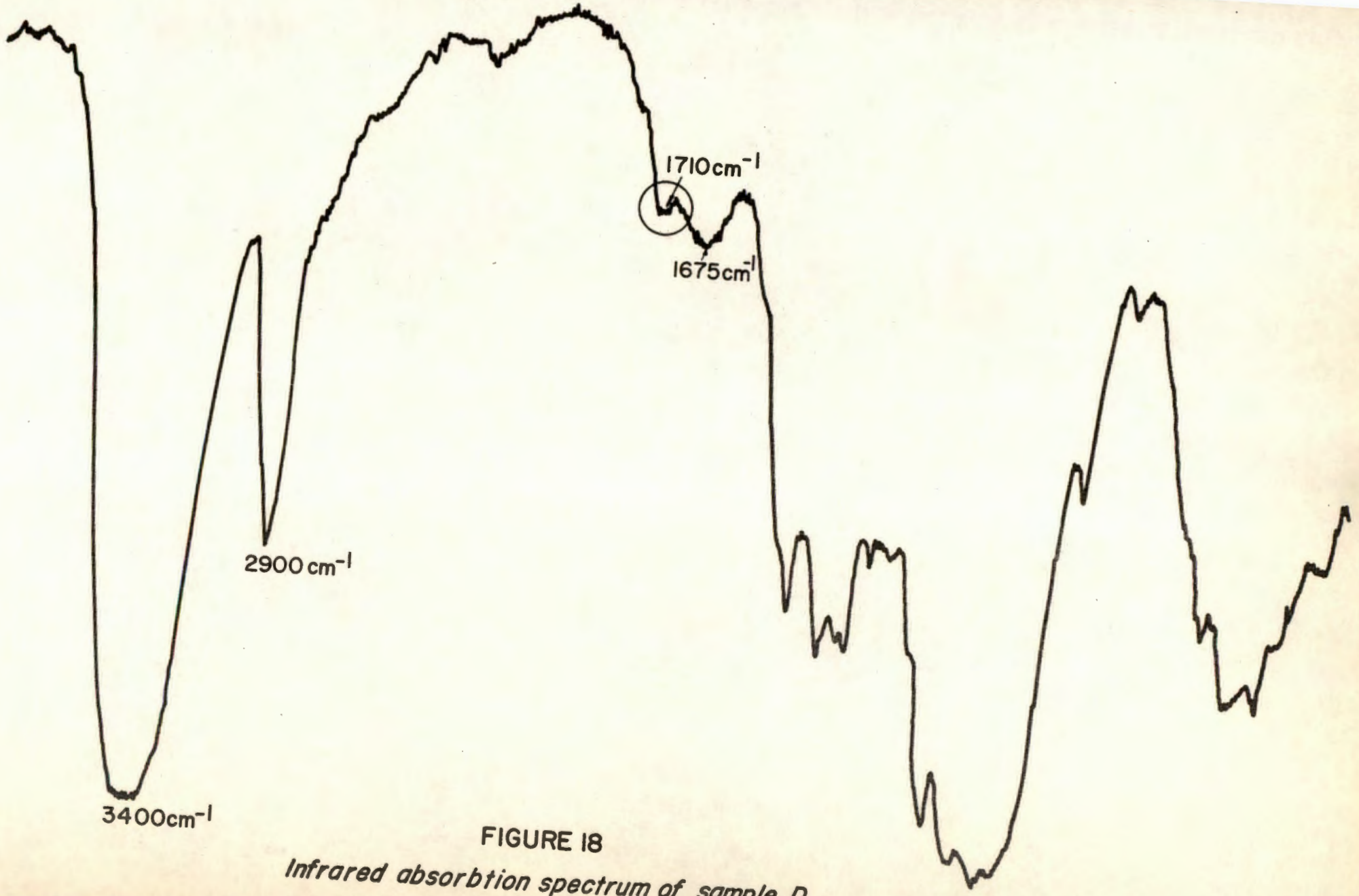


FIGURE 18

Infrared absorbtion spectrum of sample D

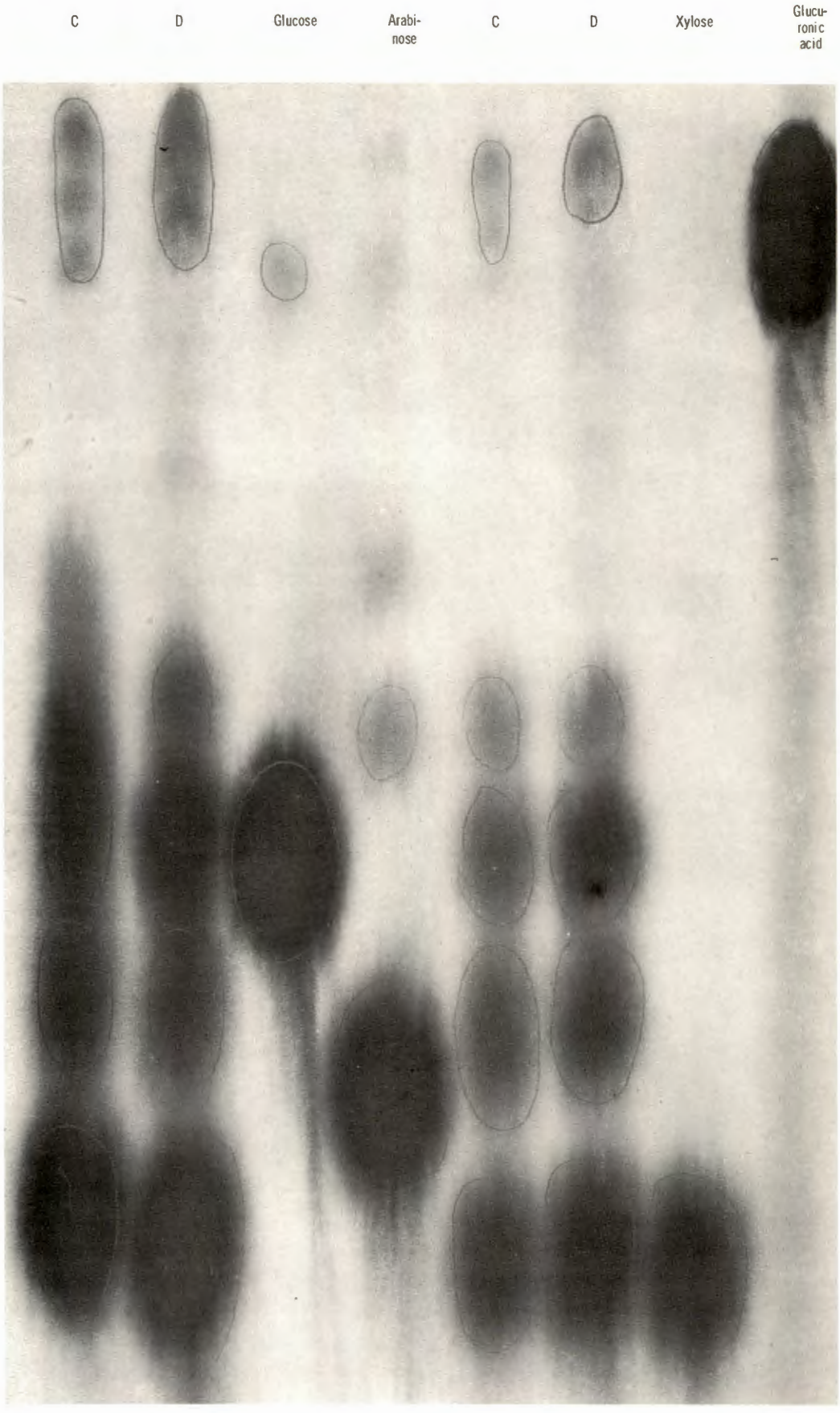


FIGURE 19

Paper chromatogram showing the presence of glucose, arabinose, xylose and glucuronic acid in the hydrolysates of samples C and D.

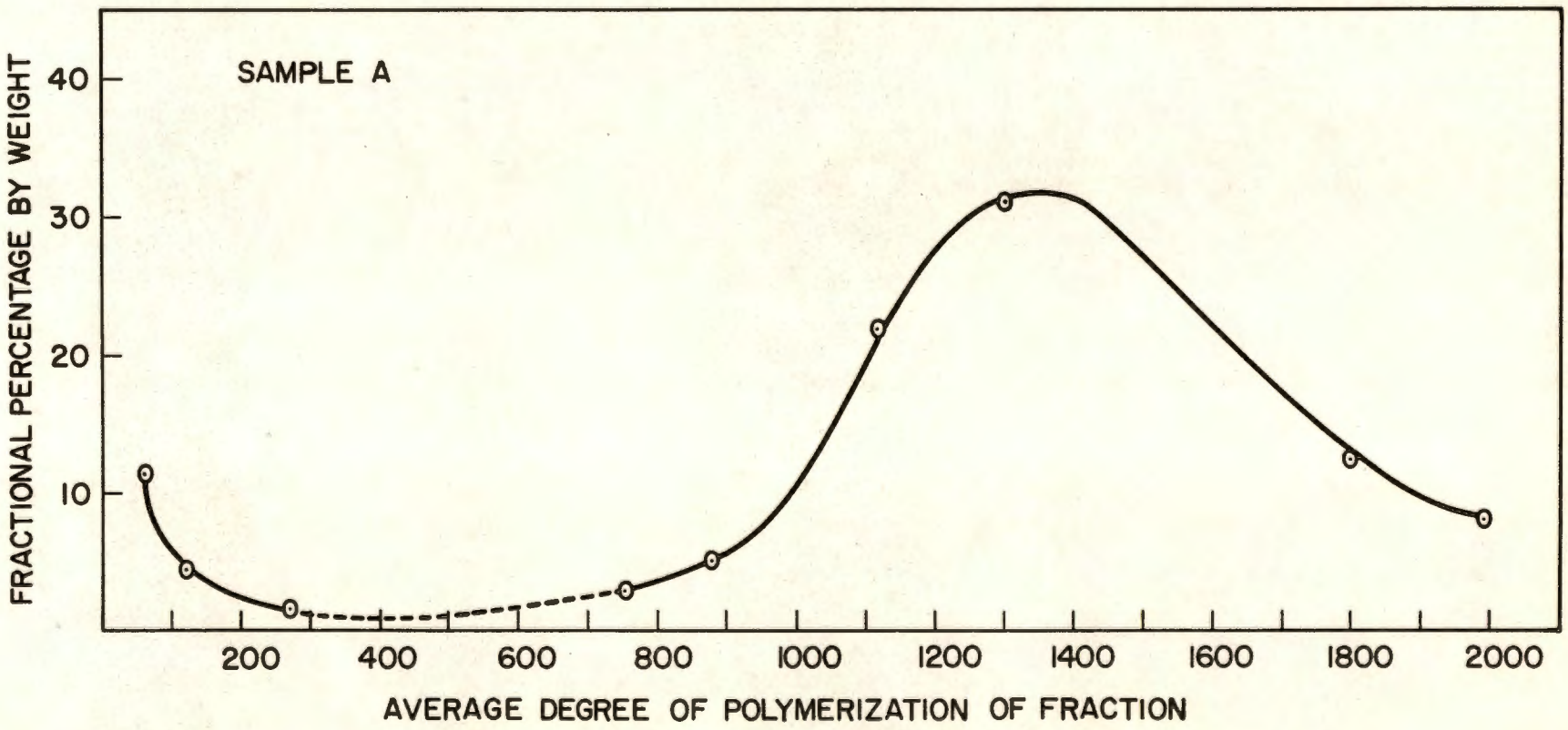


FIGURE 20

Chain length distribution of unaged paper Sample A

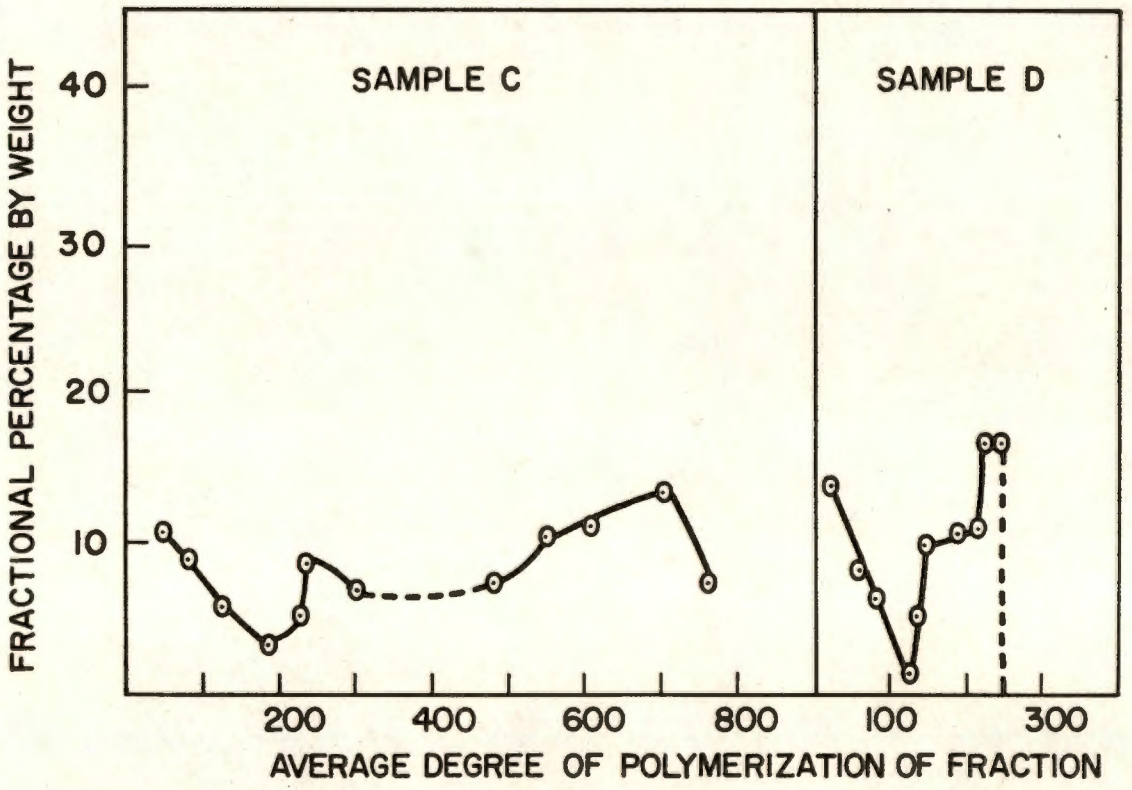


FIGURE 21

Chain length distribution of aged paper samples C and D

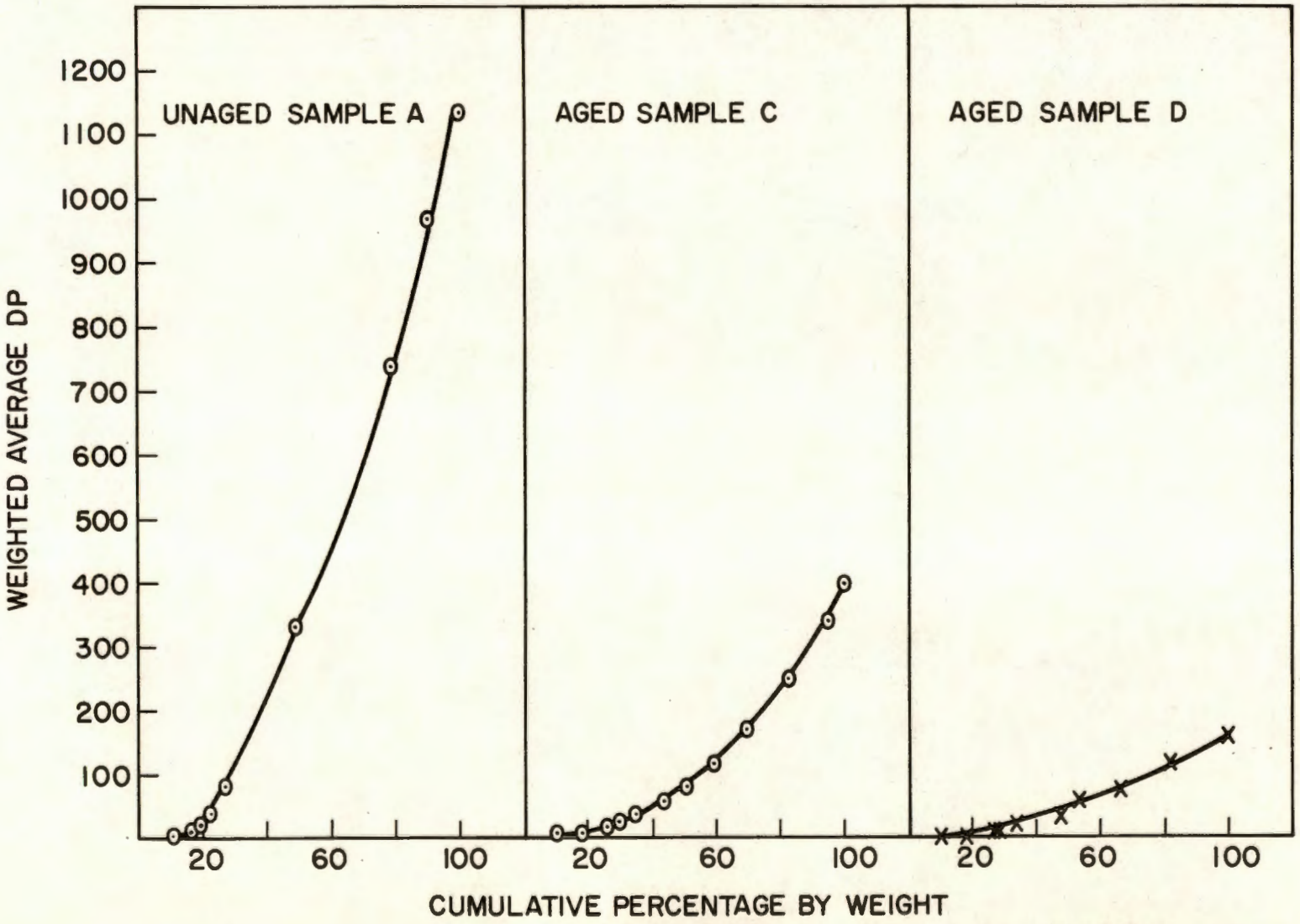


FIGURE 22

Relationship between weighted average DP and cumulative percentage by weight of the polysaccharides in unaged and aged paper samples

TABLE 1

Experimental plan for preparation and aging of samples

	Exp. No.	T	RH	O_2	SO_2	P	A	R	L
	1	50	25	20	0	10	10	0	3.5
Group 1 Variation in temperature (T^oC)	2	60	"	"	"	"	"	"	"
	3	70	"	"	"	"	"	"	"
	4	80	"	"	"	"	"	"	"
	5	90	"	"	"	"	"	"	"
Group 2 Variation in RH (%)	6	50	0	"	"	"	"	"	"
	7	"	50	"	"	"	"	"	"
	8	"	75	"	"	"	"	"	"
	9	"	95	"	"	"	"	"	"
Group 3 Variation in oxygen content (O_2%)	10	"	25	1	"	"	"	"	"
	11	"	"	50	"	"	"	"	"
	12	"	"	75	"	"	"	"	"
	13	"	"	92	"	"	"	"	"
Group 4 Variation in sulphur dioxide (SO_2 mg/m^3)	14	"	"	20	23	"	"	"	"
	15	"	"	"	42	"	"	"	"
	16	"	"	"	103	"	"	"	"
	17	"	"	"	315	"	"	"	"
Group 5 Variation in aging period (P days)	18	"	"	"	0	1	"	"	"
	19	"	"	"	"	3	"	"	"
	20	"	"	"	"	5	"	"	"
	21	"	"	"	"	7	"	"	"
Group 6 Variation in acid content (A m.eq./1000 g)	22	"	"	"	"	10	7	"	"
	23	"	"	"	"	"	0	"	"
	24	"	"	"	"	"	-12	"	"
	25	"	"	"	"	"	-65	"	"
Group 7 Variation in rosin sizing content (R%)	26	"	"	"	"	"	10	1	"
	27	"	"	"	"	"	"	2	"
	28	"	"	"	"	"	"	3	"
	29	"	"	"	"	"	"	5	"
Group 8 Variation in lignin content (L%)	30	"	"	"	"	"	"	0	1.4
	31	"	"	"	"	"	"	"	0.7
	32	"	"	"	"	"	"	"	0.4
	33	"	"	"	"	"	"	"	0

* Exp. No. 1 is common to all groups.

TABLE 2

Average strength values of identical samples aged under various ambient conditions

	Exp. No.	Tear factor	Breaking length (Km)	Burst factor	Folding strength	Edge tearing strength (Kg)	Zero-span tensile strength (Kg)
	Reference	142	6.02	37.2	604	6.0	10.38
Group 1 Influence of temperature	1	132	5.71	36.6	470	5.8	10.12
	2	128	5.52	35.8	449	5.7	9.38
	3	126	5.70	34.9	445	5.7	8.45
	4	101	5.82	34.5	306	5.6	8.08
	5	76	5.54	32.7	111	5.3	7.13
Group 2 Influence of percentage relative humidity	6	132	5.68	38.1	490	5.8	8.51
	1	132	5.71	36.6	470	5.8	10.12
	7	128	5.54	35.4	576	5.5	8.97
	8	127	5.37	36.2	576	5.2	9.60
	9	128	5.70	42.8	648	5.2	9.26
Group 3 Influence of oxygen	10	130	5.28	34.1	481	5.8	10.22
	1	132	5.71	36.6	470	5.8	10.12
	11	134	5.79	39.5	400	6.0	10.33
	12	133	5.59	36.0	567	5.6	10.58
	13	132	5.62	37.6	465	5.8	10.29
Group 4 Influence of sulphur dioxide	1	132	5.71	36.6	470	5.8	10.12
	14	126	5.65	36.6	464	6.0	9.63
	15	128	5.36	34.2	403	5.7	9.83
	16	121	5.41	35.7	353	5.6	9.70
	17	121	5.22	36.0	320	5.4	9.82
Group 5 Influence of aging period	18	139	5.58	37.0	492	6.0	10.66
	19	142	6.08	38.8	487	5.7	9.71
	20	132	6.08	39.0	541	6.0	9.50
	21	136	5.84	38.1	503	6.0	9.11
	1	132	5.71	36.6	470	5.8	10.12

TABLE 3

Average strength values of samples which differed in chemical composition and were aged under identical ambient conditions.

	Exp. No.	Tear factor	Breaking length(Km)	Burst factor	Folding strength	Edge tearing strength(Kg)	Zero-span tensile strength(Kg)
Group 6 Influence of acid content	1 Ref*	142	6.02	37.2	604	6.0	10.38
	1 Aged	132	4.90	36.6	470	5.8	10.12
	22 Ref	125	3.19	16.3	20	3.2	8.65
	22 Aged	130	3.07	15.9	19	3.3	8.54
	23 Ref	120	6.46	41.0	569	6.2	10.55
	23 Aged	121	6.30	41.4	559	6.3	11.19
	24 Ref	133	5.32	35.7	433	2.2	8.95
	24 Aged	137	5.90	36.6	446	2.6	9.38
	25 Ref	90	2.04	9.9	44	5.8	10.74
	25 Aged	97	2.19	10.8	57	6.0	10.23
Group 7 Influence of sizing content	1 Ref	142	6.02	37.2	604	6.0	10.38
	1 Aged	132	5.71	36.6	470	5.8	10.12
	26 Ref	122	5.66	35.0	483	5.9	9.28
	26 Aged	122	5.50	34.4	487	6.1	8.95
	27 Ref	133	5.18	30.6	294	5.6	9.62
	27 Aged	145	5.03	30.7	275	5.6	9.89
	28 Ref	138	5.28	30.6	368	5.4	9.75
	28 Aged	130	5.33	31.9	348	5.4	9.76
	29 Ref	151	5.76	36.5	470	6.3	10.75
	29 Aged	142	5.68	31.8	554	6.3	10.06
Group 8 Influence of lignin content	1 Ref	142	6.02	37.2	604	6.0	10.38
	1 Aged	132	5.71	36.6	470	5.8	10.12
	30 Ref	107	5.99	46.3	446	6.2	9.87
	30 Aged	102	5.95	45.8	448	6.5	9.89
	31 Ref	104	6.20	49.3	526	6.7	9.67
	31 Aged	105	6.22	47.8	519	7.0	8.86
	32 Ref	108	5.84	41.2	591	6.2	8.22
	32 Aged	107	5.68	38.9	498	6.3	8.72
	33 Ref	62	1.07	5.1	9.0	1.2	4.43
	33 Aged	64	1.10	4.8	8.6	1.0	3.39

* Unaged samples.

TABLE 4

Chemical analyses of identical samples aged under various ambient conditions

	Exp. No.	Average degree of polymerization	Alkaline solubility %	Copper number (g/100g)	pH
Group 1 Influence of temperature	1	1040	3.60	0.84	4.5
	2	861	4.25	1.01	4.6
	3	868	4.30	1.14	4.5
	4	683	6.60	1.26	4.6
	5	555	11.00	1.51	4.5
Group 2 Influence of percentage relative humidity	6	1008	3.45	ND	4.6
	1	1040	3.60	"	4.5
	7	1018	3.95	"	4.6
	8	1024	4.46	"	4.6
	9	841	5.50	"	4.6
Group 3 Influence of oxygen	10	1083	3.30	ND	4.5
	1	1040	3.60	"	4.5
	13	1073	3.25	"	4.6
Group 4 Influence of sulphur dioxide	1	1040	3.60	ND	4.5
	14	1122	4.22	"	4.5
	15	950	4.45	"	4.5
	16	996	4.28	"	4.5
	17	1108	4.45	"	4.6
Group 5 Influence of aging period	18	1100	3.01	ND	4.6
	19	1100	3.12	"	4.6
	20	1072	3.21	"	4.6
	21	1080	3.45	"	4.6
	1	1040	3.60	"	4.5

Note: ND denotes "Not done".

Table 5

Chemical analyses of samples which differed in chemical composition and were aged under identical ambient conditions

	Exp. No.	Degree of polymerization		Alkaline solubility		pH
		Average values	Percentage* of reference	Average values	Percentage** of reference	
Group 6 Influence of acid content	1 Ref	1168	89.1(10.9)	3.11	115.6(15.6)	4.6
	1 Aged	1040		3.60		4.5
	22 Ref	1137	94.0(6.0)	3.09	111.6(11.6)	5.0
	22 Aged	1068		3.42		4.9
	23 Ref	1180	98.0(2.0)	2.65	110.5(10.5)	7.2
	23 Aged	1158		2.78		7.1
	24 Ref	1150	95.6(4.4)	3.60	111.4(11.4)	8.7
	24 Aged	1101		4.10		8.1
	25 Ref	1112	94.2(5.8)	3.42	112.5(12.5)	9.0
	25 Aged	1050		4.27		9.0
Group 7 Influence of sizing content	1 Ref	1168	89.1(10.9)	3.11	115.6(15.6)	4.6
	1 Aged	1040		3.60		4.5
	26 Ref	1077	99.0(1.0)	2.88	116.6(16.6)	4.5
	26 Aged	1047		3.35		4.4
	27 Ref	1057	96.6(3.6)	3.02	114.8(14.8)	4.5
	27 Aged	1020		3.46		4.5
	28 Ref	1098	90.4(9.6)	3.48	115.6(15.6)	4.5
	28 Aged	993		4.02		4.5
	29 Ref	1015	94.4(5.6)	3.12	113.9(13.9)	4.5
	29 Aged	957		3.55		4.5
Group 8 Influence of lignin content	1 Ref	1168	89.1(10.9)	3.11	115.6(15.6)	4.6
	1 Aged	1040		3.60		4.5
	30 Ref	630	92.0(8.0)	3.26	112.0(12.0)	4.3
	30 Aged	580		3.65		4.4
	31 Ref	666	87.0(13.0)	3.51	111.6(11.6)	4.4
	31 Aged	580		3.92		4.4
	32 Ref	607	90.1(9.9)	4.00	103.0(3.0)	4.4
	32 Aged	547		4.12		4.4
	33 Ref	762	87.4(12.6)	4.18	102.7(2.7)	4.6
	33 Aged	665		4.30		4.6

*Values in brackets denote percentage reduction on aging.

** Values in brackets denote percentage increase on aging.

TABLE 6

Strength properties and chemical analyses of an unaged and three severely aged paper samples

Sample	Method of aging	Tear factor	Folding strength	Zero-span tensile strength (Kg)	Edge tearing strength (Kg)	Breaking length (Km)	Average DP	Alkaline solubility (%)	Aldehyde* groups	Ketone* groups	Carboxyl* groups
A	Unaged	142	604	10.38	6.0	6.02	1168	3.11	3.78	3.04	5.28
B	90°C, 25% RH, 10 days	76	111	7.13	5.3	5.54	555	11.00	4.97	2.93	5.37
C	100°C, zero % RH, 30 days	31	9	4.48	4.3	4.44	373	13.40	7.91	3.10	5.23
D	100°C, 55% RH, 30 days	17	1	2.77	1.5	1.25	153	18.20	10.95	3.05	5.39

* Expressed as m. moles/100g

TABLE 7

Fractionated DP values of samples A, C and D

Sample	Fraction (% by weight	Cumulative %	DP of Fraction	Weighted average DP of fraction (W)	Cumulative weighted average DP (ΣW)
A	11.50	11.5	64	7	7
	4.47	16.0	121	5	12
	1.81	17.8	266	5	17
	3.20	21.0	751	24	41
	5.09	26.1	881	45	86
	22.06	48.2	1121	248	334
	31.12	79.3	1300	404	738
	12.54	91.8	1842	231	969
	8.20	100.0	1992	163	1132
C	10.82	10.8	50	5	5
	9.26	20.2	80	7	12
	6.34	26.5	124	8	20
	3.74	30.3	186	7	27
	5.28	35.5	228	12	39
	8.86	44.4	232	21	60
	6.88	51.3	300	21	81
	7.42	58.7	481	36	117
	10.00	68.7	550	55	172
	12.30	81.0	610	75	247
	13.50	94.5	700	94	341
	7.50	102.0	760	60	401
D	14.22	14.2	16	2	2
	8.50	22.7	61	5	7
	6.50	29.2	80	5	12
	1.37	30.6	121	2	14
	5.33	36.1	125	7	21
	9.86	46.0	153	15	36
	10.78	56.7	195	21	57
	11.10	67.8	215	24	81
	16.80	84.6	232	39	120
	17.06	101.6	245	42	162

Note Samples were aged as indicated in Table 6.

TABLE 8

Relationships of the type $y = a + bx^*$ between strength properties of identical samples aged under various ambient conditions (Groups 1 to 5)

y \ x	Temperature (°C)	RH (%)	Oxygen content (%)	Sulphur dioxide content (mg/m^3)	Aging period (days)
Tear factor	y = 209.9 - 1.39x	y = 130.8 - 0.04x	y = 131.4 + 0.02x	y = 128.6 - 0.03x	y = 140.5 - 0.85x
Breaking length (Km)	y = 5.70 + 0.0005x	y = 5.67 - 0.0014x	y = 5.49 + 0.002x	y = 5.60 - 0.001x	y = 5.87 - 0.002x
Burst factor	y = 41.1 - 0.09x	y = 36.10 + 0.04x	y = 35.46 + 0.03x	y = 35.80 - 0.001x	y = 38.35 - 0.009x
Folding strength	y = 959.9 - 8.62x	y = 466.3 + 1.75x	y = 462.0 + 0.30x	y = 445.6 - 0.45x	y = 507.2 - 1.66x
Edge tearing strength (Kg)	y = 6.40 - 0.01x	y = 5.88 - 0.008x	y = 5.84 - 0.001x	y = 5.85 - 0.001x	y = 5.94 - 0.008x
Zero-span tensile strength(Kg)	y = 13.7 - 0.07x	y = 9.08 + 0.004x	y = 10.17 + 0.003x	y = 9.84 - 0.002x	y = 10.15 - 0.06x

*
y represents the specific strength property
x " " " aging factor
a and b are constants

TABLE 9

Correlation coefficients, r, and significance levels, L, for the relationship given in Table 8 between strength properties and aging factors.

Strength property \ Aging factor	Temperature		RH		Oxygen content		Sulphur dioxide content		Aging period	
	r	L	r	L	r	L	r	L	r	L
Tear Factor	-0.90	SSS	-0.09	I	0.08	I	-0.51	I	-0.40	SSS
Breaking length	-0.01	I	-0.09	I	-0.17	I	-0.33	I	-0.01	I
Burst factor	-0.23	S	0.21	I	0.18	I	-0.001	I	-0.06	I
Folding strength	-0.60	SSS	0.27	I	0.05	I	-0.29	I	-0.02	I
Edge tearing strength	-0.29	SS	-0.46	S	-0.06	I	-0.36	I	-0.06	I
Zero-span tensile strength	-0.86	SSS	0.15	I	0.16	I	-0.04	I	-0.22	S

Note: SSS indicates a significant influence at the 0.01 probability level (or 99 per cent confidence level) of the aging factor x (in the equation $y = a + bx$) on the strength property y.

SS indicates a significant influence of x on y at the 0.05 probability level.

S indicates a significant influence of x on y at the 0.10 probability level.

I indicates an insignificant influence of x on y at the 0.10 probability level.

TABLE 10

Average strength values* of samples which differed in chemical composition and were aged under identical ambient conditions.

	Exp.No.	Tear factor	Breaking length(Km)	Burst factor	Folding strength	Edge tearing strength(Kg)	Zero-span tensile strength(Kg)
Group 6	1	93 (7)	81 (19)	98 (2)	78 (22)	97 (3)	98 (2)
Influence of	22	104 (-4)	96 (4)	98 (2)	95 (5)	103 (-3)	99 (1)
acid con-	23	101 (-1)	97 (3)	101 (-1)	98 (2)	101 (-1)	106 (-6)
tent	24	103 (-3)	111 (-11)	103 (-3)	103 (-3)	118 (-18)	105 (-5)
	25	108 (-8)	107 (-7)	109 (-9)	129 (-29)	104 (-4)	95 (5)
Group 7	1	93 (7)	95 (5)	98 (2)	78 (22)	97 (3)	98 (2)
Influence	26	100 (0)	97 (3)	98 (2)	101 (-1)	103 (-3)	97 (3)
of sizing	27	109 (-9)	97 (3)	100 (0)	94 (6)	100 (0)	102 (-2)
content	28	94 (6)	101 (-1)	104 (-4)	95 (5)	100 (0)	100 (0)
	29	94 (6)	99 (1)	87 (13)	118 (-18)	100 (0)	94 (6)
Group 8	1	93 (7)	95 (5)	98 (2)	78 (22)	97 (3)	98 (2)
Influence	30	95 (5)	99 (1)	99 (1)	100 (0)	105 (-5)	100 (0)
of lignin	31	101 (-1)	100 (0)	97 (3)	98 (2)	105 (-5)	92 (8)
content	32	99 (1)	97 (3)	94 (6)	84 (16)	101 (-1)	106 (-6)
	33	103 (-3)	103 (-3)	94 (6)	96 (4)	83 (17)	77 (23)

*Expressed as percentages of the unaged strength.
Values in brackets denote the percentage reduction in strength on aging.

TABLE 11

Relationships of the type $y = a + bx$* between strength properties of samples which differed in chemical composition and were aged under identical ambient conditions (Groups 6 to 8)

y \ x	Acid content m.eq./1000g	Sizing content %	Lignin content %
Tear factor	y = -0.40 + 0.12x	y = 0.78 + 0.49x	y = -1.31 + 2.48x
Breaking length (Km)	y = 4.29 + 0.24x	y = 4.02 - 0.81x	y = -1.02 + 1.71x
Burst factor	y = 0.10 + 0.14x	y = - 1.43 + 1.77x	y = 4.76 - 1.04x
Folding strength	y = 6.05 + 0.58x	y = 17.27 - 6.41x	y = 3.59 + 4.23x
Edge tearing strength (Kg)	y = 3.69 + 0.05x	y = - 0.49 + 0.13x	y = 1.20 - 0.16x
Zero-span tensile strength (Kg)	y = - 1.29 - 0.06x	y = 0.63 + 0.59x	y = 9.06 - 2.86x

* y represents the specific strength property
x " " " aging factor
a and b are constants

TABLE 12

Correlation coefficients, r, and significance levels, L, of the relationships given in Table 11 between percentage reduction in strength and aging factors

Strength property \ Aging factor	Acid content		Sizing content		Lignin content	
	r	L	r	L	r	L
Tear factor	0.70	S	0.14	I	0.92	SS
Breaking length	0.63	I	-0.69	S	0.80	SS
Burst factor	0.98	SSS	0.54	I	-0.67	I
Folding strength	0.94	SSS	-0.85	SS	0.59	I
Edge tearing strength	0.18	I	0.08	I	-0.04	I
Zero-span tensile strength	-0.41	I	0.32	I	-0.35	I

Note: SSS indicates a significant influence at the 0.01 probability level of the aging factor, x, on the strength property, Y, in the equation $y = a + bx$.
SS indicates a significant influence of x on y at the 0.05 probability level.
S indicates a significant influence of x on y at the 0.10 probability level.
I indicates an insignificant influence of x on y at the 0.10 probability level.

PART 2

REVIEW OF LITERATURE

1. INTRODUCTORY REMARKS ON THE MANUFACTURE OF PULP AND PAPER

a. General

In South Africa pulp is manufactured from wood and bagasse by different processes depending on its end-use as shown below :

Raw Material	Process	End-use	Percentage
Wood	Sulphate	Fine paper and packaging paper grades	45
Wood	Mechanical	Newsprint	30
Wood	Cold soda	Packaging paper grades	15
Bagasse	Cold soda	Packaging paper grades	10

Since the problem of longevity applies mainly to fine paper, further discussion in this section will be restricted to sulphate pulp which is the principal type used locally for these grades of paper.

The fibrous raw material consists of various pine (long fibre), eucalyptus and wattle (short fibre) species. The long and short fibre species are kept separate throughout all the intermediate stages of processing until their pulps are ultimately blended in the papermaking stage to impart the desired strength and surface properties to the paper grades manufactured.

b. Delignification of wood

The object of pulping is to set the fibres free from the lignin matrix in wood.

Wood is received at the mill in debarked log form. The logs are mechanically reduced to chips which are approximately 1 in long x 1 in wide x ⅛in thick and

digested in autoclaves with a mixture of sodium sulphide and sodium hydroxide under the following conditions :

Active alkali charge	: 17-19 per cent on oven-dry wood basis
Sulphidity	: 17-22 per cent
Liquor-to-wood ratio	: 3.5/1 ml/g
Temperature	: 170°C
Period	: 1.5 to 2 hours

The above conditions are a compromise between economical and technical considerations; economy in the use of steam and chemicals is achieved, delignification of the wood proceeds at a satisfactory rate and selectivity of reaction is achieved to a large extent. The yield of the unbleached pulp is approximately 45 per cent by weight of oven-dry wood and contains about 85 to 90 per cent alpha cellulose, 2 to 4 per cent lignin and small amounts of non-cellulosic polysaccharides consisting mainly of hemicellulose.

c. Bleaching of pulp

Purification of the unbleached pulp is carried out in a series of bleaching stages in which the lignin and part of the non-cellulosic polysaccharides are removed. Bleaching of sulphate pulp for production of fine writing and printing paper is conventionally carried out in six carefully controlled stages, as follows :

Stage	Treatment with	Approx. amount (per cent) *	Stock concentration (per cent)	Temperature °C	Period (hours)
1	Cl_2	5	3	25	0.5
2	NaOH	3	10	60	0.5
3	$Ca(OCl)_2$	2	6	40	2
4	ClO_2	0.8	10	65	3
5	NaOH	1.5	10	65	0.5
6	ClO_2	0.5	10	65-70	2

* Based on oven-dry pulp weight.

The final brightness of the pulp is approximately 85 per cent GE.

d. Beating of pulp

Bonding in paper results from inter-fibre hydrogen bonding. A prerequisite for these bonds to form is that the fibres must be in intimate contact with each other and therefore have to be conformable. In order to enhance softness and thus conformability of the fibres, the pulp is subjected to mechanical action between metal surfaces commonly called beating or refining, which results in defibrilation, softening and swelling of the fibres until a given degree of wetness has been reached.

e. Papermaking

Prior to papermaking the beaten stock is sized and filling materials are added. The mixture then flows onto a fine moving wire mesh screen at a stock concentration of approximately 0.1 per cent. Draining of the water leaves a fibrous mat on the screen. This mat is couched, pressed and dried by means of steamheated rollers and finally emerges from the machine as an endless sheet of paper. The hydrogen bonds between fibres are formed during the drying stage.

2. NATURAL AGING OF PAPER

a. Measurement of degree of deterioration

The impermanence of paper is a problem recognized as long ago as the end of the 19th century. It is a problem that has become of increasing importance to archivists, librarians and scientists. The magnitude of the problem is indicated by the fact that if no preventive measures are taken, most library books printed in the first half of the 20th century, will be in an unusable, brittle condition early in the next century.[24] Undoubtedly this argument also applies to most of the documents prepared from standard modern paper.

Visual examination gives some indication of the embrittlement that occurs in paper as a result of storing it for a long period, but comparative data can only be obtained from scientific tests.

Deterioration of paper as a result of aging can be detected and determined by numerous physical and chemical tests. The most important physical tests are folding strength, internal tearing strength, tensile strength, bursting strength, edge tearing strength and fibre strength while the most important chemical tests are pH, reducing capacity, viscosity, average degree of polymerization, hot water solubility, solubility in 1 per cent sodium hydroxide, and alpha cellulose content.

The stresses involved when paper is handled, appear to be mainly those of bending and tearing. It is therefore not surprising that most investigators[25,39,87,112,113,121,122] agree that folding strength is the most sensitive parameter for comparing the aging characteristics of different papers. In order to increase the sensitivity of this test, the majority of investi-

gators modified the Tappi standard method and used a ½ Kg tension on the paper sample instead of 1 Kg as prescribed.

According to some investigators[25,39,42,47,115,116,125] the tear test ranks lower than the folding strength test for measuring aging characteristics of paper.

Like plastics and glass paper is a notch-sensitive material, i.e. the force required to continue a tear in these materials is significantly less than the force required to start it. The tear test as ordinarily performed on paper measures the internal tearing strength, in other words the force required to continue an already existing tear. This test is valuable in the case of packaging paper grades, but in the case of writing and printing paper grades it appears more important to measure the edge tearing resistance. However, in the literature, there are no reports referring to this test regarding aging of paper.

The tensile and bursting strengths depend primarily on the degree of fibre bonding. Although these tests give an indication of aging of paper, they are less sensitive than folding strength and tearing strength.[25,39,90,116,124,125] Determination of rupture energy is normally carried out only on packaging paper grades and it has not been considered as an indicator of aging of paper.

It is likely that the primary chemical attack on paper would be on the most important component namely cellulose. One would therefore expect to find decreases in viscosity, degree of polymerization of the cellulose, alpha-cellulose content and pH and increases in alkaline

solubility, water solubility and copper number of the paper. This view is amply supported in literature [42, 47, 90, 124] but it has also been found that values obtained for the above phenomena can be inconsistent.[25,116]

The only criticism against the use of chemical methods for measurement of aging of paper is that except for pH measurement, they are rather laborious compared to physical tests.

The fundamental mechanism of deterioration of paper with time is probably of a chemical nature and the physical manifestations of paper aging such as decreases in paper strength are apparently secondary phenomena. Therefore, the use of chemical parameters to measure and compare aging characteristics of paper is of prime importance and probably essential.

b. Acid degradation

(1) Influence of acid

Most investigators seem to agree that acidity is an important cause of paper deteriorating with age.[19,21, 22,25,51,67,68,98,110,120] The importance of the contribution of acid to the deterioration of paper is illustrated by the fact that paper made from chemical wood pulp fibres at a pH of 5.0 lost half of its original strength within 5 to 8 years, indicating a useful lifespan of not more than 50 years, while paper made at a pH of 9.5 was claimed to retain 95 per cent of its original strength after 25 years of aging.[109] The latter claim is based on the assumption that artificial aging of paper at 100°C for 72 hours is equivalent to 25 years "natural" aging.[5,8,117,124] It was also found[19] that papers manufactured at pH's

of 5.2 and 4.5, all other factors being identical, and aged at 100°C for 72 hours, will respectively retain 58 and 14 per cent of their original strengths when aged under the same conditions as mentioned above.

The presence of acids in the paper probably results in acid hydrolysis and consequently in depolymerization of the cellulose* in paper but it appears that this aspect of paper deterioration has hitherto received little attention.

(2) Source of acid

Paper is sized almost universally with sodium rozinate at a pH of approximately 5.0 in the presence of trivalent aluminium ions; the latter two factors being essential for satisfactory operation. The low pH is obtained by addition of aluminium sulphate which hydrolyzes to form, amongst others, free sulphuric acid. Most investigators[6,9,23,27,90,120,126] agree that this free acid is the real cause of impermanence in modern paper. However, many investigators report on the effect of "alum and rozin sizing" without distinguishing between the individual contribution of each factor. Some investigators[39,66,89] at an earlier stage even negated any influence of acid from this source. Nevertheless, it stands to reason that cellulose would hydrolyze in the presence of strong acids, the rate of hydrolysis being determined amongst others by the concentration of the acid present and also by the temperature and available moisture. It appears

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* Strictly speaking this term should read "polysaccharides" but since cellulose is the main component of the polysaccharides, the term cellulose is used throughout this report.

reasonable to believe that pH's in paper as high as 5 will still be destructive over prolonged periods.

Another important source of acid in paper is the sulphur dioxide present in the atmosphere. Sulphur dioxide is claimed to be absorbed by the paper where its oxidation to sulphur trioxide is catalysed by traces of metallic impurities, mostly ferric ions.[52,53,65,66,69] These ions are introduced into the paper as impurities present in the fibrous raw materials and in the chemicals used in modern papermaking or are dissolved from the machinery. The sulphur trioxide so formed, dissolves in the 5 to 10 per cent moisture normally present in the paper to form sulphuric acid. Owing to the use of coal as a fuel, contamination of the atmosphere by sulphurous fumes is widespread and many investigators[14,51,53,55,65,66,69,72,120,] claimed this to be the primary cause of chemical deterioration in paper. The concentration of sulphur dioxide in industrial atmospheres can be as high as 0.5 PPM. As long ago as 1953 it was estimated[69] that the equivalent of five million tons of sulphuric acid is liberated into the atmosphere of Great Britain each year. The average annual concentration of sulphur dioxide measured in the centre of Pretoria over the past five years was 30 micrograms per cubic metre[62] corresponding to approximately 0.03 PPM.

The influence of industrial atmospheres is further borne out by the fact that books in city libraries were found to have a higher acid content than books in rural libraries[7,109]; presumably owing to the higher sulphur dioxide content of city atmospheres. Books stored in contaminated atmospheres for approximately 20 years contained 0.8 per cent more sulphate at the edges than at the centres of the pages, indicating the

absorption of sulphurous constituents from the atmosphere at the edges.[69,71] Apparently many papers absorb up to 0.2 per cent sulphate during the first year of storage and less thereafter, but it is claimed that there are wide variations in the tendency of different papers to absorb sulphur dioxide.[96]

It appears logical to assume that absorption of sulphurous fumes and their subsequent oxidation to sulphur trioxide in the paper should be deleterious. However, no publication could be traced in which the claims regarding the ill effects of sulphurous atmospheres have been substantiated by controlled tests revealing their influence on either the strength of paper or on the cellulose in the paper. Assuming that these degradative influences of sulphurous gases are real, their removal from the atmosphere[61] or deactivation of catalysts in the paper[65,66,72] by the use of chelating agents appears desirable.

(3) Migration of impurities

It has been noticed that the sulphuric acid present in iron gall inks[7,20] and sulphates and chlorides present in writing inks[18] migrate to adjoining sheets. Many compounds, including residuals from the paper-making process and non-cellulosic compounds from the fibres migrate from one paper to another over an extended period of time.[18] Fibre boards prepared from acidic pulp and used for mounting documents ultimately crumble away, but what is of vital concern is the chemical injury to the document as a result of migration of acid from the board to the document. The folders and mounting boards for archival documents should therefore be free from harmful impurities.[17,86,99] Undesirable results may also be expected if documents are filed in contact with newspaper clippings,

photocopies, cellulose nitrate film, paper clips made from ferrous metals and rubber bands.[18]

c. Influence of relative humidity and temperature

(1) Direct effect on some strength properties

Folding strength is greatly affected by changes in relative humidity (RH) and can increase by as much as 10 per cent for each 1 per cent increase in RH.[36] The increase in folding strength is especially sharp at RH's above 60 to 65 per cent. Weaker papers such as printing paper prepared from mechanical pulp tend to achieve a maximum at approximately 60 per cent RH. Folding strength shows a marked decrease with increasing temperature at a constant RH.[36]

Tearing strength is directly proportional to RH.[36,41] The total change in tearing strength over the RH range of 20 to 90 per cent, is about 50 per cent.[36] Temperature has no appreciable effect on tearing strength.[36]

Tensile strength decreases with increasing RH's, with the rate of change increasing progressively as the RH rises.[36] The average total change in tensile strength over the range 20 to 90 per cent RH is approximately 55 per cent. A 15°F increase in temperature reduces the tensile strength by approximately 5 per cent.[36]

A high moisture content is associated with high RH's and low temperatures.[36] The equilibrium moisture content of paper is subject to hysteresis.

Since the properties of paper are significantly influenced by moisture, it is imperative to condition paper samples by a standard method prior to testing.

(2) Effect of RH on the deterioration of paper

Apart from qualitative indications that :

(i) RH's in excess of 65 per cent may result in the growth of fungi;[4,14,121]

(ii) a variable RH effects dimensional changes in paper with resulting stresses and strains which may have a degrading effect,[3,19,104] and that

(iii) low RH's are associated with temporary embrittlement of paper,[36]

nothing appears to be known quantitatively about the influence of RH on the deterioration of paper. For this reason there is no unanimity about the ideal RH for paper storage purposes, anything from 30 to 68 per cent being recommended.[3,14,33,63,85,88,99,104,106,113,121]

It is generally agreed[44,59,80,100,111,124] that the aging rate of paper during artificial aging increases with increasing RH. Although it remains to be proved, it is logical to assume that the same principle is at least partly applicable to natural aging of paper. Molds and fungi[4,14,121] can be one of the primary causes of paper deterioration in tropical climates but this type of deterioration is easily controlled,[15, 29,32,58,70,73,85,121] and will not be dealt with further.

(3) Effect of temperature on the deterioration of paper

Many investigators[3,14,59,60,63,66,85,99,106,113,121] consider a temperature of approximately 20°C as "ideal" for storing paper. It appears, however, that the only consideration behind these recommendations was the comfort of the working personnel and not the longevity of the paper.

It is known that the deterioration of organic materials is retarded by storage at low temperatures.

It is also known that an increase in temperature accelerates reaction rates. Applied to paper, these facts were borne out by the fact that books found in the antarctic[54] showed little deterioration compared with copies of the same books stored in libraries in temperate climates. It was also claimed[19,48] that for a drop in temperature of 20°C the deterioration rate of paper is decreased approximately by 7.5 times. If this were true, the amount of deterioration taking place in 25 years at 20°C would require approximately 10,000 years at -40°C.

However, whether freezing of documents would be practicable and whether repeated freezing and defrosting affects paper strength adversely, remains to be investigated.

d. Effect of fibrous components on the deterioration of paper

A number of investigators[33,42,55,69,90,97,106,109,110] claim that highly purified fibres containing practically only alpha cellulose will guarantee permanence in paper. However, this claim cannot account for the permanence of papyrus which contains a large proportion of supposedly impermanent low-polymer celluloses and hemicelluloses. On the other hand, the impermanence of paper containing impure mechanical pulp is well known.

Other investigators[98,109] again could not correlate aging of paper with alpha cellulose content. The contribution of alpha cellulose content to the aging rate of paper is therefore not clear.

The fact that books made from rag paper five hundred years ago still exist in an almost undeteriorated condition[35,109] gave rise to the belief that only pure rag paper has a high degree of permanence[89] and some results were furnished[90,98,124] to indicate the appa-

rently greater chemical stability of rag fibres (which have a high alpha cellulose content) compared to sulphite wood pulp fibres, all other conditions being equal.

Nevertheless, it now appears that paper produced from wood pulp exhibits a degree of permanence comparable with that of paper made from rag pulp[25,42,109] all conditions being equal. Provided these two types of paper have equal original strength, they should last for the same period[9,75,76,106,109,110].

Rag content in itself is therefore not a guarantee of permanence and may only be preferred to wood pulp because of its higher initial strength, which under similar conditions, ensures a longer usable life than that of paper made from wood pulp.

e. Effect of light on the deterioration of paper

The injurious effect of artificial and natural light on paper is well known.[85,91,92,112,123] It was reported[1] that irradiation of paper with ultra-violet light in the presence of oxygen :

(i) destroys and volatilizes part of the cellulose;
(ii) causes yellowing of the paper;
(iii) decreases the alpha cellulose content, and
(iv) rapidly decreases the strength of the paper.

The decomposition continues even if the documents are subsequently stored in the dark.[75] The post-radiation effect can be arrested by storing documents in the dark in an atmosphere of an inert gas such as nitrogen or helium.[75]

Documents on permanent exhibition therefore need protection against the harmful effects of short wavelength light.[85] Since documents are normally stored in the dark or at least not in direct sunlight, this

factor will not be considered further.

f. Effect of oxygen on the deterioration of paper

Most investigators claim that oxygen plays an almost negligible role in the aging of paper at temperatures ranging from room temperature to well above 100°C[2,13,14,41,79] but there are investigators[42,84] who differ from the above view. Although variations in relative humidity and temperature in the latter two investigations[42,84] cause uncertainties, it stands to reason that cellulose can react with atmospheric oxygen under certain conditions. In addition, oxygen may be consumed in the formation of sulphur trioxide as outlined earlier. The contribution of oxygen to deterioration of paper can therefore not be dismissed.

g. Yellowing of paper

Apart from loss in strength, aging of paper and pulp is also accompanied by yellowing. Whereas practically all kinds of chemical attack on paper are conducive to a loss in strength, this is not universally true with respect to yellowing.

Light, heat, humidity and oxygen[40,49,90] as well as certain fungi[43] contribute to yellowing but yellowing cannot be completely avoided if these factors are eliminated. Peroxide formation has been related to yellowing[78] and it was also found[49,64] that aging at high humidities results in higher contents of peroxide.

It has been suggested that yellowing of paper can be the result of :

(i) recoloration of bleached lignin residues;[75,90]

(ii) yellowing of sub-gamma celluloses and certain hemicelluloses;[90,100,114]

(iii) changes in colour of resinous extractives,[28,44,90] or

(iv) coloration of sizing agents.[90]

Although the cause of yellowing of paper is still largely a matter of speculation, there are certain points of general agreement. The tendency of pulp to yellow[29,45] depends on the number of carbonyl groups in the cellulose chains and on their position in the chain. It is claimed that aldehydic carbonyl groups in the end units of molecular chains do not affect the yellowing of pulp[103] although their presence is shown by an increase in copper number but that carbonyl groups in other positions contribute significantly to the yellowing tendency.[100] It has also been found that cations exert a significant influence on the yellowing tendency[102,119] in the order

$$Na^{+} > Al^{3+} > Mn^{2+} > H^{+} > Cd^{2+}.$$

The formation of carbonyl groups is largely dependent on the pH of hypochlorite bleaching;[74,118] the action of which is most drastic at pH's between 5 and 7 and becomes increasingly mild at increasing or decreasing pH's.

From the above it is clear that although the influence of various factors on yellowing has been recognized, the mechanism of yellowing is not fully understood yet.

3. ARTIFICIAL AGING OF PAPER

a. Requirements

The only completely satisfactory way of determining the life expectancy of paper would be to observe its deterioration in the environment of storage or usage until the point of collapse is reached. While this approach may be feasible for materials with a short lifespan, it is hardly likely to be so in the case of ordinary paper which has a lifespan that extends over a number of decades. This indicates the necessity of

instituting an artificial aging test.

The ideal environment for a test of this nature is one that brings about an increase in the rate of deterioration of the material without affecting the nature of the deterioration. Further it should be possible to measure the amount of deterioration that has taken place in a given time and to correlate this deterioration with the life expectancy of paper during natural aging.

b. Heat aging

The fundamental assumption underlying the acceleration of aging by heat is that by exposing paper to an elevated temperature the process of deterioration is speeded up and results in measurable changes within a short period.

A large number of artificial aging tests ranging from low to high temperature in different atmospheres at RH's ranging from 0 to 100 per cent, some of them combined with ultra-violet light irradiation or variation in the amount of oxygen or acidic gases in the aging environment, have been tried.[12,42,65,69,83,109] It seems, however, that the final choice of an artificial aging test must be influenced by practical considerations.

It has been found that aging for 72 hours at 100°C is equivalent to approximately 22 years of "natural" aging.[5,8,124] This investigation, however, permitted only qualitative conclusions to be drawn since the testing of paper at the time of the investigation had not progressed far enough to permit proper control of variables. In addition, the term "natural" aging was not qualified - it stands to reason that "natural" aging in temperate climates will not be comparable to

"natural" aging in tropical climates. Similar criticism applies to another independent investigation[115] where it was concluded that aging for 72 hours at 100°C corresponds to "natural aging" for 28 years with confidence limits of 17 and 48 years. Subsequent work on the aging of paper[5,8,16,108,124] was based on the theory that heat aging at 100°C simulates natural aging and that aging at this temperature for 72 hours is equivalent to approximately 25 years of natural aging. This assumption was further extended to aging at 100°C for 24 and 48 days[7,116] which is assumed to be equivalent to approximately 200 and 400 years of natural aging respectively. Whether these assumptions are right or wrong, is of no real consequence. It is both encouraging and significant that a correlation has been found to exist between heat and natural aging. It is immaterial to what period of natural aging a certain method of heat aging is equivalent since it will be possible to compare the permanence of different grades of paper and to estimate their expected lifespan on a common basis.

Nevertheless, it appears that more work should be directed at correlating natural with artificial aging, regarding both chemical and physical changes.

An important factor in artificial aging appears to be the amount of moisture present in the aging atmosphere.[37,41,64,80,90,95,100] It has been found that the aging rate of paper at a constant elevated temperature increases linearly with increasing relative humidities above 25 per cent.[111] Although this is so, it is claimed that aging in the presence of moisture does not differ from dry heat aging as far as the respective gradings of the pulp tested are concerned[44] and therefore dry heat aging of paper is preferable to

humid aging owing to its practicability.[94] The amount of moisture present in the atmosphere is nevertheless a factor that can affect the correlation between "natural" and artificial aging significantly and its influence should therefore be known quantitatively.

c. Aging with sulphur dioxide

It has been claimed that the worst chemical deterioration in paper is caused by the action of sulphur dioxide[65,69,109] and therefore an artificial aging test has been proposed based on the amount of sulphate that accumulates in paper after storage in an atmosphere containing 0.5 per cent sulphur dioxide at a relative humidity of 100 per cent for a period of 7 days.[69] An increased content of sulphate in the paper is claimed to indicate its liability to deteriorate on aging. This proposed test has, however, not been widely approved of.

d. Aging with ultra-violet light

The use of ultra-violet light to study the aging characteristics of paper has not received much attention, presumably because the presence of ultra-violet light in repository buildings is an easily controllable abnormality.

Severe degradation of cellulose starts in the vicinity of 2500Å and increases with decreasing wavelength.[26,77,81,101] The chemical changes evidenced when paper is exposed to direct sunlight are increases in copper number and decreases in the degree of polymerization of the cellulose and alpha cellulose content.

4. CONCLUSIONS

(i) The usable life of modern paper is limited. This condition presents grave problems especially to Archives and libraries all over

the world.

(ii) Deterioration of paper is caused by a number of factors. The most important of these appear to be acid content, sizing materials, original chemical composition, types of fibrous raw materials, climate and impurities in the atmosphere and paper.

(iii) The information gained from literature is valuable, but it appears that most investigators treated the subject qualitatively and overlooked the fact that deterioration of paper is probably the result of the interaction of a number of variables.

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APPENDIX I

TERMINOLOGY[10*]

Active alkali : The sum of the caustic soda and half of the sodium sulphide in sulphate pulping liquor, i.e. ($NaOH + \frac{1}{2}Na_2S$) expressed as Na_2O.

Alpha cellulose : That portion of a pulp or other cellulosic material that resists solution in 17.5 per cent NaOH under specified conditions.

Appita : Australian Pulp and Paper Industry Technical Association.

Bagasse : The crushed stalks of sugar cane after the sugar has been extracted.

Basis weight : The weight of paper in grams per square meter.

Beater : A machine consisting of a tub and containing a heavy roll revolving against a bedplate. A pulp suspension in water circulates through the beater between the roll and bedplate where the fibres are fibrilated and softened.

Beating : Refining of pulp carried out in a beater.

Beta cellulose : That portion of pulp or other cellulosic material that dissolves in 17.5 per cent NaOH under specified conditions but which is reprecipitated on neutralization of the alkaline solution.

Brightness : The percentage reflectivity of a sheet of pulp or paper for blue light measured under standard conditions on an instrument designed and calibrated for the purpose.

Bursting strength : A measure of the ability of a sheet to resist rupture when pressure is applied to one of its sides by a specified instrument under specified conditions.

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* Most of these definitions have been taken over partly or wholly from the Dictionary of Paper.

Cellulose : The main solid constituent of woody plants. Chemically it is a linear polysaccharide consisting of anhydroglucose units joined at the 1 and 4 positions.

Chemical pulp : A general term used to indicate pulp prepared entirely by chemical purification of the raw material.

Cold soda pulp : A semi-chemical pulp generally produced from hardwoods by treatment with sodium hydroxide at temperatures below the boiling point of the solution followed by mechanical defibration.

Copper number : The number of grams of copper reduced from the cupric to the cuprous state by 100 grams oven-dry pulp or paper under specified conditions.

Couch : A term referring to dewatering and picking off of the wet paper web from the wire on which it was formed by a felt covered roll.

Edge tearing strength : The resistance offered by paper to the onset of tearing at the edge of a sheet.

Fibrilation : A term indicating loosening of threadlike elements from fibres during beating or refining.

Filling material : A non-fibrous material e.g. clay added to the fibre furnish of paper to enhance certain properties such as opacity of the paper.

Folding strength : The number of folds under specified conditions in a specified instrument which a specimen will withstand before failure.

Gamma cellulose : That portion of a pulp or other cellulosic material that remains in solution after neutralization of the alkaline solution obtained under the conditions imposed in the alpha cellulose test.

G.E. brightness : A standard of brightness adopted by the paper industry and named after the manufacturer who made the original specified instrument.

Hemicellulose : Non cellulosic polysaccharides occurring in practically all vegetable fibres and yielding simple pentose and hexose sugars, uronic acid and acetic acid when hydrolyzed in acid medium.

Hysteresis : The term refers to the difference in value of a property depending on whether a given value is approached from a high or a low level e.g. a paper sheet conditioned at 50 per cent relative humidity (RH) will have a higher moisture content when conditioned from a higher than from a lower RH.

Internal tearing strength : The force required to continue a tear in paper under specified conditions and measured in a specified instrument.

Lignin : The non-carbohydrate portion of plant material left as residue on hydrolysis with strong acid after removal of extractives. It is an amorphous material of high molecular weight and predominantly aromatic in character. It consists of phenylpropane units and contains the major portion of the methoxyl groups present in plant material.

Mechanical wood pulp : Pulp prepared entirely by mechanical "defibration" of wood either by refining of wood chips or by grinding of logs.

Permanence : The term, as applied to paper, refers to chemical stability and the retention of desired handling properties over prolonged periods as opposed to "durability" which refers to resistance to mechanical wear and tear.

Pulp : The fibrous mass obtained by reducing cellulosic materials to fibres by mechanical and/or chemical means.

Pulping liquor : The solution of chemicals used to soften and/or partly delignify wood or other cellulosic materials in semi-chemical or chemical pulping operations.

Rag paper : A term describing paper containing cellulose fibres derived from cotton or flax.

Refining : A term describing mechanical action on pulp (in a water suspension) to fibrilate and soften the fibres (cf. beating).

Schopper-Riegler : See "wetness".

Semi-chemical pulp : A pulp produced by a mild chemical treatment of the raw material followed by mechanical defibration.

Sizing : Any material used internally or on the surface of paper to increase the resistance of the paper against penetration by water and which transforms the surface to such a state that it can be written on. Ink "feathers" on unsized paper such as newsprint grades and blotting paper.

Stock concentration : The amount of pulp present in a pulp-water suspension expressed as a percentage of the total weight, e.g. "10 per cent stock concentration" indicates that 100 weight units of the pulp suspension contain 10 units of pulp.

Sulphate pulp : Chemical pulp produced by pulping wood with a mixture of sodium hydroxide and sodium sulphide. The latter is obtained from reduction of sodium sulphate.

Sulphidity : The ratio between the sodium sulphide and the total alkali present in sulphate cooking liquor expressed as a percentage. It is common practice in the sulphate pulping industry to express the concentration of pulping chemicals as g/l Na_2O.

Sulphite pulp : Chemical pulp produced by pulping wood with a mixture of sulphite and sulphurous acid. The base can be calcium, magnesium, sodium or ammonium.

Tappi : Technical Association of the Pulp and Paper Industry (American).

Test sheets : Laboratory sheets prepared batchwise in a specified manner from a suspension of fibres in water with or without the addition of sizing, filling or colouring agents and used for testing purposes.

Tensile strength : The force, parallel with the plane of the paper required to produce failure in a sample of specified dimensions under specified conditions.

Viscosity : The property of cellulose pulp or other polymer which is expressed by the viscosity of a solution of the material in a suitable solvent under specified conditions.

Wetness : A measure of the rate with which water drains from a stock suspension through a wire mesh screen under specified conditions and is expressed as degrees Schopper-Riegler, named after the instrument used.

Web : The sheet of paper coming from the paper machine in its full width or from a roll of paper in any converting operation.

Zero-span tensile strength : The tensile strength of a sheet of fibrous material, measured with special jaws under specified conditions at an apparent initial span of zero. It is an indication of the strength of the fibres of which the sample is composed as opposed to the ordinary tensile strength test which measures mainly bonding strength between fibres.