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Effect of Treatment with Very Dilute Acids on the Wet Tensile Strength and Chemical Properties of Paper

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SUMMARY

Filter paper (α-cellulose content 99·3%) was soaked in very dilute solutions of several mineral and aliphatic dicarboxylic acids and heated for various times at temperatures ranging from 100°C to 140°C. The wet strength of the paper, measured with an Instron tester using a jaw span of 15 cm, was greatly increased by these treatments. The largest increase was by nearly 1000%; this was achieved by heating with oxalic acid at pH 2·7 for 1 h at 140°C. Increases of nearly 750% and 850% were obtained with hydrochloric and sulphuric acids, respectively, under similar conditions. Homologues of oxalic acid, which were too weak to furnish solutions of pH 2·7, caused only small increases in wet strength.

The increases in wet strength have been attributed to the formation of inter-fibre cross-links. A small loss of dry strength was observed and this, together with increases in copper number and fluidity, was taken as evidence that some hydrolytic degradation occurred simultaneously with cross-linking. Short-span breaking-load tests also confirmed this conclusion. The zero-span breaking load, which is a measure of the strength of the fibres rather than of the paper itself, fell markedly as a result of the acid treatments. However, as the span was increased the breaking load of the treated paper levelled out at a finite value whereas that of the untreated paper fell close to zero.

The nature of the cross-links was studied by chemical tests. The effect of chlorous acid and borohydride treatment on the tensile strength of the acid-treated paper showed that a small proportion of the cross-links were hemiacetals. However, the main proportion appeared to be ethers. This was demonstrated by measuring the effects of the acid treatments on the

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proportions of 'available' primary and secondary hydroxyl groups by tosylation followed by iodination.

INTRODUCTION

It has been reported from time to time that the wet strength of paper can be increased significantly by heating with very dilute aqueous solutions of certain salts and acids (Yoshino, 1952; Yoshino *et al.*, 1953, 1954). Various explanations have been given. For example, Yoshino *et al.* (1954) proposed the formation of new inter-fibre hydrogen bonds, but this does not accord with current views on paper structure, which attribute the almost total loss of strength on wetting paper made from pure α-cellulose to the destruction of hydrogen bonds. He also mentioned the possibility that ether cross-links might be formed, but dismissed it. Back and co-authors (Back, 1967, 1973; Back *et al.*, 1967; Back & Stenberg, 1976) did similar work with corrugated board with a view to improving its wet strength and wet stiffness. They obtained the best results when the board was oxidized by periodate before heating. This led them to conclude that hemiacetal cross-links, arising from carbonyl groups either present in the original pulp or introduced by oxidation, were the principal cause of the increases in wet strength. Both Yoshino's and Back's explanations suffer from uncertainty because of the complex nature of the cellulose materials which they used. Their paper and board were made from pulps that had retained considerable quantities of hemicelluloses and lignin and it is impossible to estimate the extent to which these substances contributed to the observed effects. In the present work Whatman No. 1 filter paper (which is practically pure α-cellulose) was used and the reagents with which it was heated were confined to very dilute solutions of a few selected acids. Considerable increases in wet strength were achieved and have been attributed to the formation of covalent (mostly ether) inter-fibre cross-links as a result of chemical tests.

Most of the strength testing has been done on standard strips of paper with a test length of 15 cm, the results being recorded as breaking loads in kilogrammes. A few short-span measurements have also been made.

EXPERIMENTAL

Materials

Except for hand-sheets, which were made from a high α-cellulose pulp beaten to 45°SR, Whatman No. 1 filter paper from a single batch of

46 × 57 cm sheets was used throughout. It had an α-cellulose content (TAPPI-T203, OS-74) of 99·3 ± 0·3%, a basis weight of 88·6 g m^{-2}, a copper number of 0·31 and a cuprammonium fluidity of 7·90.

Analytical grade acids were dissolved in distilled water and diluted either to the required concentration or, with the help of a pH meter, to the required pH level. The solutions were unbuffered.

Acid treatments

For each treatment three sheets of paper (40 × 30 cm) were clipped to glass rods with plastic-coated clips and laid flat in a large photographic dish containing the appropriate acid at room temperature (ca. 20°C). After 1 h, which preliminary tests showed to be adequate for attaining the maximum effect during subsequent heating, the sheets were removed and freed from excess liquid by placing them separately between filter papers and rolling a 200-g glass rod over the sandwich. The sheets were then hung vertically in an air oven previously heated on to the required temperature or, in one set of experiments, in a vacuum oven (0·1 mm Hg). The difference in the effect of the air oven and the vacuum oven was negligible and so its use was abandoned.

Measurements of tensile strength

The breaking loads of 2·54-cm wide strips of paper were measured in the machine direction on an Instron TM-S (table model) at 20°C and 65% r.h. (relative humidity). The test lengths were 15 cm and rate of elongation was kept constant at 5 cm min^{-1}. Each recorded breaking load is a mean of at least six results. For dry measurements the samples were conditioned at 20°C and 65% r.h. for 3 h before testing. For wet measurements the samples were immersed in water at 20°C for 30 min and pressed lightly between sheets of filter paper to remove excess water.

Zero- and short-span wet-strength measurements were made in the machine direction on 1·5-cm wide specimens using a Pulmac Zero-span Tester (Model ZST-15). In this machine the specimen is clamped in jaws, the initial distance between which can be varied from nominally zero to a few millimetres, thus distinguishing it from the Instron in which the jaws are initially a considerable distance apart. The principles and practice of short-span tensile testing have been described by Cowan (1975).

Chemical tests

Copper numbers
These were determined by Braidy's method (see Nevell, 1963).

Fluidities

These were determined in cuprammonium hydroxide by the British Standards Institution method (*B.S. Handbook*, 1974).

Oxidation with chlorous acid

Samples were treated with 0·2 M sodium chlorite in M acetic acid for 72 h at 20°C (see Nevell, 1963) and washed well with cold water. Wet breaking loads were determined before and after oxidation.

Reduction with borohydride

Samples were treated with 0·17 M potassium borohydride for 24 h at room temperature, soaked in 10% acetic acid, and washed well with water (see Nevell, 1963). Wet breaking loads were determined before and after reduction.

Determination of 'available' hydroxyl groups

This was done by tosylation followed by iodination (Honeyman, 1947; Heuser *et al.*, 1950; Lewis *et al.*, 1965). Treatment of a cellulose material with tosyl (i.e. *p*-toluenesulphonyl) chloride under conditions that effect substantially complete substitution of the primary alcohol groups also causes substitution of some of the secondary alcohol groups. Subsequent heating of the derivative with sodium iodide in acetone or acetonylacetone causes the replacement of all the primary, but none of the secondary, tosyl groups with iodine. Thus determination of the iodine and sulphur contents of the final products enables the proportions of primary and secondary alcohol groups that have been tosylated to be calculated.

Three oxalic-acid-treated papers were examined in this way. Each sample (2 g, cut into pieces approximately 5 × 5 mm) was dried for 2 days *in vacuo* over phosphorus pentoxide and immersed in dry pyridine (20 cm^3) overnight. Tosyl chloride (23·5 g) dissolved in dry pyridine (55 cm^3) was then added and the mixture kept for 48 h at 25°C. It was then cooled in an ice-bath and ice-cold 10% aqueous acetone (75 cm^3) was added to destroy the excess of tosyl chloride. After 5 min the mixture was poured into water (600 cm^3) and stirred for 30 min. The tosyl derivative was filtered off and washed with water. It was then extracted first with methanol and then with diethyl ether in a Soxhlet apparatus, and finally dried in a vacuum desiccator over phosphorus pentoxide. The dry tosyl derivative (1 g) was heated with sodium iodide (1 g) in acetonylacetone (100 cm^3) for 7 h at 115–120°C in a flask fitted with an air condenser, and filtered off. It was washed successively with methanol (five 100-cm^3 portions), 0·1 M sodium thiosulphate (four 250 cm^3

portions), and water. Finally, it was extracted with diethyl ether in a Soxhlet apparatus and dried *in vacuo* over phosphorus pentoxide.

Sulphur was determined by the Microanalytical Section of the Chemistry Department, UMIST, by burning the test sample (5–20 mg) and collecting the combustion products in 0·1 M sodium nitrate. This converted the sulphur into sulphate, which was titrated with lead perchlorate using an ion-selective lead electrode.

Iodine was determined by conversion into iodate (Mann & Saunders, 1964). The test sample (0·1 g) was heated with liquid bromine (sufficient to maintain an excess) in 20% potassium acetate in glacial acetic acid for 30 min. After reduction of the excess of bromine to bromide with formic acid, potassium iodide (1 g) and 10% sulphuric acid (10 cm^3) were added and the liberated iodine was titrated with 0·1 M sodium thiosulphate. (The results are given in Table 3.)

RESULTS AND DISCUSSION

Effect of acid treatment on wet breaking load

Most of the work was done with sulphuric, oxalic, and hydrochloric acids. The effect of varying the concentration of sulphuric acid from 0·00075 M to 0·002 M whilst keeping the oven temperature constant at 120°C is illustrated in Fig. 1. A 7·5-fold increase in wet strength was achieved in less than 1 h at concentrations of 0·0015 M and 0·002 M, after which no further increase occurred. With lower concentrations of acid the increase was slower and with distilled water no increase at all was observable. The pH of the 0·002 M sulphuric acid was found to be 2·7. Subsequent experiments with sulphuric, oxalic, and hydrochloric acids were therefore generally done with solutions adjusted to this pH level.

The effect of temperature was studied with the three acids. The results for oxalic acid given in Fig. 2 are typical. Heating for 1 h at 140°C appeared to give the maximum increase in wet breaking load. Table 1 compares the effects of the three acids together with those produced by heating the paper dry, after soaking in distilled water, and after soaking in aqueous oxalic acid at pH 2·2. Thus under the most favorable circumstances, a ten-fold increase in wet strength was achieved. Furthermore, the dry breaking load of the original paper was 6·2 kg, so that the wet strengths of the acid-treated papers shown in Table 1 were from 16% to 24% of the dry strength. This brings them within the definition of a 'wet-strength paper' in the American Pulp and Paper Association's *Dictionary of Paper* (1965).

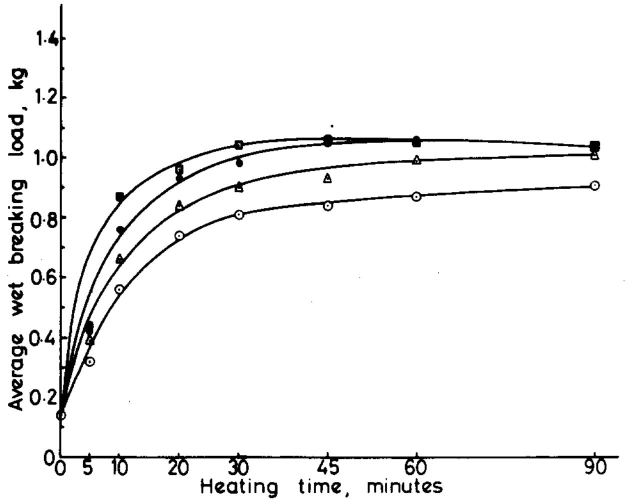

Fig. 1. Effect of concentration of sulphuric acid on wet breaking load of paper heated to 120°C. ○, 0·00075 M; △, 0·001 M; ●, 0·0015 M; □, 0·002 M.

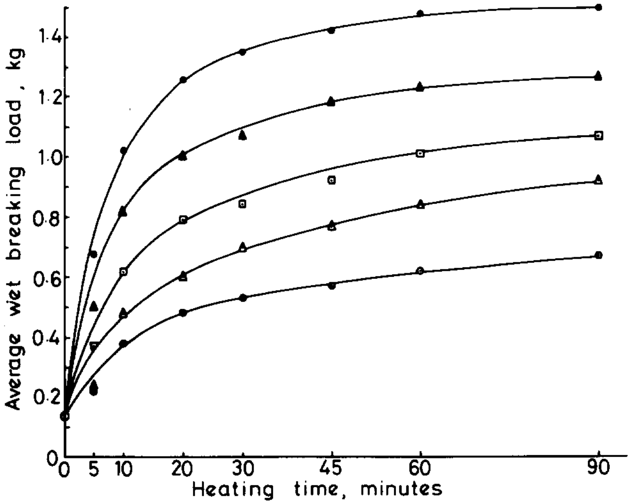

Fig. 2. Effect of temperature on wet breaking load of paper soaked in oxalic acid at pH 2·7 and heated for 1 h. ○, 100°C; △, 110°C; □, 120°C; ▲, 130°C; ●, 140°C.

The reaction responsible for the development of wet strength is clearly accelerated by hydrogen ions, but if the acidity is too high a competing reaction causing loss of strength cancels out some of the increase (see Table 1). That this second reaction is hydrolytic degradation is evident from the increase in fluidity and copper number (Fig. 3)

TABLE 1
Effect on Wet Breaking Load of 2·54-cm Wide Strips of Paper Heated for 1 h at 140°C

Treatment	*Wet breaking load (kg)*
None (original paper)	0·14
Heated dry	0·37
Heated after soaking in water	0·55
Heated after soaking in HCl at pH 2·7	1·18
Heated after soaking in H_2SO_4 at pH 2·7	1·32
Heated after soaking in $(COOH)_2$ at pH 2·7	1·48
Heated after soaking in $(COOH)_2$ at pH 2·2	1·02

and the decrease in dry breaking load (Fig. 4) that accompany the development of wet strength. Hydrolytic degradation causes a loss of intrinsic fibre strength that is reflected in a loss of strength in the paper. However, since the wet strength is virtually zero in the absence of covalent inter-fibre cross-linking, such cross-linking can only improve wet strength, whereas its influence on dry strength is small compared with that of hydrogen bonding.

Effect of dicarboxylic acids

Since oxalic acid seemed to be so effective, a few other dicarboxylic acids were tried in case any evidence of the formation of ester cross-links might be found. None appeared, however, as may be seen from Table 2. It is clear that the very weak glutaric and adipic acids have no greater effect than water itself.

Zero- and short-span wet breaking loads

The combined effect of hydrolytic degradation and inter-fibre cross-linking is nicely illustrated by the variation of wet breaking load with the specimen test length (the span between the jaws of the testing instrument) shown in Fig. 5. Untreated, sulphuric-acid-treated, and oxalic-acid-treated papers were examined at spans increasing from nominally zero to 1·3 mm. Ideally, the zero-span breaking load should correspond to the intrinsic strength of the fibres and the same result should be obtained irrespective of whether the paper is wet or dry. In fact the dry zero-span breaking load of untreated paper was 17·2 kg compared with 14·6 kg wet (1·5-cm wide strips). The small discrepancy is an indication of the virtual

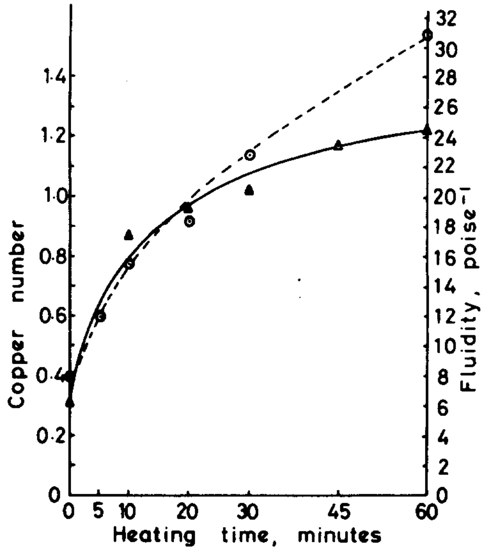

Fig. 3. Effect on fluidity (○) and copper number (△) of heating paper soaked in oxalic acid at pH 2·7 to 140°C.

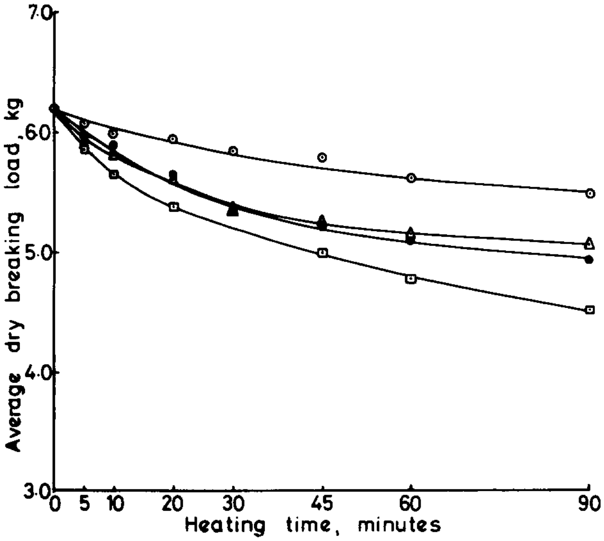

Fig. 4. Effect on dry breaking load of heating paper soaked in water (○) and in hydrochloric acid (△), oxalic acid (●), and sulphuric acid (□), at pH 2·7 to 140°C.

TABLE 2

Effect on Wet Breaking Load of 2·54-cm Wide Strips of Paper Heated for 1 h at 140°C with Various Acids

Acid	*Wet breaking load (kg)*
Water	0·55
Oxalic	1·44
Malonic	0·88
Succinic	0·74
Glutaric	0·56
Adipic	0·58

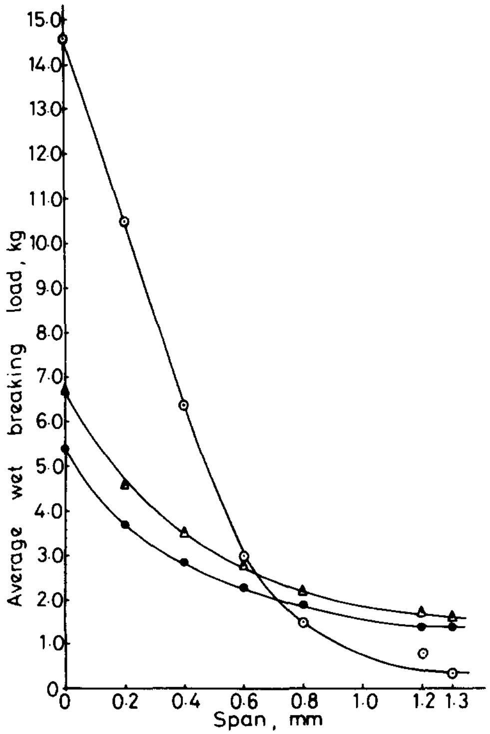

Fig. 5. Effect of varying jaw span on wet breaking load of paper heated for 1 h to 140°C. ○, untreated; △, soaked in oxalic acid at pH 2·7; ●, soaked in sulphuric acid at pH 2·7.

impossibility of achieving a genuine zero span between the jaws of the tester.

Figure 5 shows that the wet breaking load of the untreated paper falls practically to zero as the span approaches 1·3 mm. This is what would be expected, since once the span exceeds the effective fibre length there is nothing to prevent wet paper breaking under stress. The two acid-treated papers have much lower wet zero-span breaking loads because of the depolymerization they have suffered. However, as the span is increased the breaking loads fall much more slowly than that of the original paper and finally become very significantly greater on account of the presence of water-resistant inter-fibre bonds.

Nature of the inter-fibre cross-links

The two most plausible types of cross-link that can be envisaged in the acid-treated papers are the hemiacetals formed from carbonyl and alcohol groups suggested by Back and the ether linkages formed by the elimination of water between two alcohol groups suggested and then rejected by Yoshino.

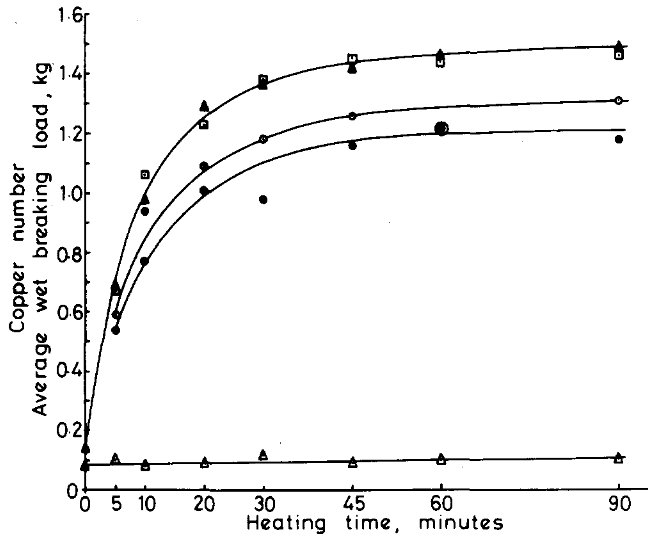

Fig. 6. Effect of chlorous acid and borohydride treatments on wet breaking load of paper soaked in oxalic acid at pH 2·7 and heated to 140°C. ▲, paper treated with water; □, paper treated with sodium borate; ○, paper treated with potassium borohydride; ●, paper treated with chlorous acid; △, copper number of borohydride-treated paper.

The presence of hemiacetal cross-links was tested for by treating a series of papers prepared with oxalic acid (pH 2·7) at 140°C with potassium borohydride and with chlorous acid. Both these reagents would destroy hemiacetal groups by converting the carbonyl part of the group to a primary alcohol and a carboxylic acid, respectively. At the same time the cross-link would be broken and a loss of wet strength would occur. Figure 6 illustrates the results obtained. The top curve gives the wet breaking loads of the papers treated with water and sodium borate (a product of borohydride treatment). Slightly below are the curves for the papers treated with borohydride and chlorous acid. The lowest curve (the copper numbers of the borohydride-treated materials) shows that all reducing power has effectively been removed and that destruction of any hemiacetal cross-links must have been complete. Clearly, a small loss of strength has occurred and this indicates that a few hemiacetal cross-links were present. The bulk of the wet strength was retained, however, and this must be attributed to ether cross-links.

Confirmation of the presence of other cross-linkages has been obtained from the tosylation and iodination experiments described earlier. These experiments gave a primary hydroxyl content of 0·83 (instead of the theoretical 1) group per anhydroglucose unit for the original paper. They also showed that 0·44 secondary alcohol group per anhydroglucose unit was tosylated at the same time. When the paper was heated to 140°C with oxalic acid at pH 2·7 these proportions were progressively reduced to 0·38 and 0·19, respectively, showing that both primary and secondary alcohol groups had been rendered ‘unavailable’ to tosyl chloride. The simplest explanation of this unavailability is the formation of ethers by the elimination of water. The results are shown in Table 3.

TABLE 3

Tosylation and Iodination Experiments on Paper Heated to 140°C with Oxalic Acid at pH 2·7

Time of heating (min)	I_2 *(%)*	*S (%)*	*Primary OH groups per AGU*[b]	*Secondary OH groups per AGU*[b]
0[a]	32·7	4·4	0·83	0·44
30	24·4	2·8	0·48	0·22
45	21·8	2·6	0·40	0·19
60	20·8	2·6	0·38	0·19

[a] Original paper.

[b] Anhydroglucose unit.

Hand sheets

In order to see whether paper with good wet strength could be made by incorporating a small quantity of acid in the stock instead of treating the paper after manufacture, a few hand sheets were made with stock that was 0·001 M with respect to oxalic acid. These hand sheets were heated to 140°C and their wet breaking loads were compared with those of hand sheets made with tap water and with hand sheets made in the usual way and then soaked in 0·001 M oxalic acid and heated. The results are shown in Fig. 7. It is clear that while a considerable improvement in wet strength can be achieved by incorporating acid into the stock it is much less than can be achieved by making the paper first and then heating it with acid.

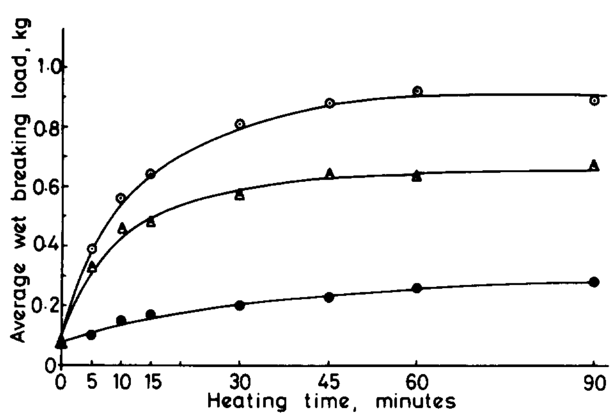

Fig. 7. Wet breaking load of hand sheets heated to 140°C. ●, from pulp only; △, from stock incorporating 0·001 M oxalic acid; ○, from sheets soaked in 0·001 M oxalic acid before heating.

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