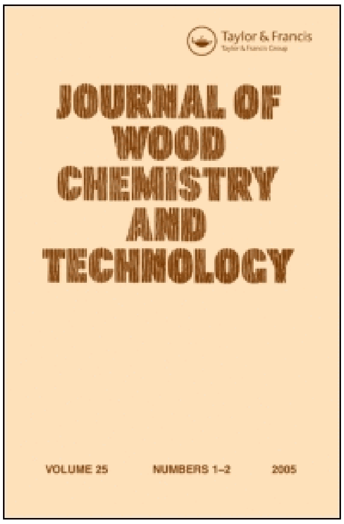

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The Role of Lignin in the Mechanical Permanence of Paper: Part II. Effect of Acid Groups

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THE ROLE OF LIGNIN IN THE MECHANICAL PERMANENCE OF PAPER: PART II. EFFECT OF ACID GROUPS

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ABSTRACT

The effect of sulphonic acid groups on the mechanical permanence of paper was studied by accelerated aging of thermomechanical pulp (TMP) that was sulphonated to different levels. Results showed that acid groups in the *hydrogen form* have a significant negative effect on the mechanical permanence of paper. However, neutralization of these groups by treatment with sodium hydroxide or calcium carbonate significantly improved the mechanical permanence of paper. Sulphonated mechanical pulp after washing with tap water has good mechanical permanence because the acid groups are mostly in the calcium form due to the ion exchange during washing.

KEYWORDS: Acid groups, Lignins, Paper Properties, Durability, Mechanical Properties, Aging, Calcium Carbonate.

INTRODUCTION

There is increased concern by workers in the paper conservation field about the rapid deterioration of books and documents in libraries and archives. Such concerns have resulted in an increased demand for "permanent" paper. Several organizations have laid down standards to define permanent paper; these standards require that papers have at least 2%

calcium carbonate, a pH range between 7.5 to 10.0, and a lignin content less than 1%[1].

Earlier studies on the permanence of lignin-containing pulps have focused primarily on papers made of stone groundwood furnishes which were sized with alum-rosin. This produced papers with poor mechanical permanence, which was often attributed to the presence of lignin. However, it was not clearly demonstrated whether this lack of permanence was due to lignin or the acidic papermaking conditions generated from the use of alum-rosin. Recent results showed that mechanical pulps have good retention of strength properties with accelerated aging (mechanical permanence) as long as they were manufactured under neutral or alkaline conditions[2-9].

A recent review of the existing literature on paper permanence points towards acid hydrolysis of the cellulose as the primary cause of paper deterioration[10]. The external sources of acidity in the sheet have been thought to originate from the use of alum during the rosin sizing process and from atmospheric contaminants[10]. There is speculation in the literature that acid groups in the fibre wall may be another important source of acidity and lead to the loss of mechanical permanence[11]. Moreover, there is concern about the formation of acid groups by oxidation of fibre chemical components, particularly lignin, during aging. This is one of the reasons for the exclusion of lignin in standards for permanent paper. However, there is no published scientific data to confirm these speculations.

Acid groups originate in the cell wall of wood or may be introduced into the hemicellulose and lignin components of the fibre wall during pulping and bleaching processes. Under normal papermaking conditions these groups are carboxylic and sulphonic acid groups. The carboxylic acid groups are primarily associated with the hemicellulose component of the cell wall, and in the hydrogen form they dissociate in water only to a small degree. Sulphonic acid groups are introduced with the sulphite treatment during chemithermomechanical pulping (CTMP), chemimechanical pulping (CMP) or sulphite pulping. These groups are almost exclusively associated with the lignin component of the fibre wall and they readily dissociate in water.

The objective of this study is to determine the effect of acid groups on the mechanical permanence of paper to further clarify the role of lignin.

EXPERIMENTAL

Pulp Preparation

To identify the effect of acid groups on mechanical permanence, samples with a range of acidic group content were prepared by sulphonating a commercial softwood thermomechanical pulp (TMP) with sodium bisulphite for different time intervals. The sulphonation reactions were carried out at a temperature of 135 °C and pH of 7. Pulps after sulphonation were thoroughly washed with tap water and fines were removed.

Ion exchange of acid groups: To ensure that all acid groups were in their hydrogen form, pulps from the above treatment were treated by alternate soaking at 1% consistency in 0.1 N hydrochloric acid and 0.1 N sodium chloride solution ending with an acid soak. The pulps were then washed with deionized water until free of chloride ions. To further convert acid groups to their sodium form, pulp with the acid groups in the hydrogen form was soaked at 1% consistency in a 0.1 N solution of sodium chloride and adding sodium hydroxide to bring the pH to 8.5-9.0. This soaking treatment lasted 30 minutes and the pulp was then washed with deionized water. Soaking and washing treatments were repeated three times. After the complete conversion to the sodium form, all pulps were washed free of sodium and chloride ions using deionized water.

Loading of calcium carbonate: Twenty-four grams of pulp with the acid groups in the hydrogen form was added into 1 liter of water with 30 grams of calcium carbonate and then disintegrated for 15 minutes at 3,000 rpm in a British disintegrator. The calcium carbonate content in paper was determined by measuring the ash content of the handsheets according to CPPA standard testing method G. 11. This loading treatment gave a 17.7% calcium carbonate content (based on the oven-dry paper weight) in the handsheets.

Preparation and Testing of Handsheets

After the above treatments, handsheets were prepared according to the CPPA standard procedure. Deionized water was used to ensure that the water used for the formation of handsheets did not introduce any new ions into the pulps. Handsheets were then cut into 1.5 cm wide strips and randomly mixed for further testing and aging.

The folding endurance (M.I.T.) was measured according to CPPA standard method D. 17, but with a tension of 400 grams instead of the normal 1,000 grams due to the low fold endurance of the mechanical pulp. To get an indication of fibre strength, zero-span tensile strength was measured using the Pulmac apparatus[12].

The cold extraction pH of paper in deionized water was measured according to CPPA standard testing method G. 25. The cold extraction pH of paper in 0.1 N NaCl solution was also measured in order to obtain the hydrogen ion concentration inside the fibre wall[13].

The lignin content was obtained by adding the acid-insoluble and acid-soluble lignin results. Acid-insoluble lignin was determined by CPPA standard testing method G. 9 and acid-soluble lignin was measured by UV spectrophotometry following Tappi useful method UM 250.

The content of acid groups including carboxylic and sulphonic acid groups in the handsheets was determined by conductometric titration[14]. The handsheets were disintegrated in deionized water before the titration.

Accelerated Aging

To evaluate the retention of sheet strength properties, accelerated aging experiments were carried out at a temperature of 80°C and a relative humidity of 75%. Paper strips were suspended in sealed glass bottles. A glass tube with a saturated salt solution was also enclosed in the bottles to obtain the desired relative humidity. The glass bottles were placed in an oven whose temperature was set to 80°C. After accelerated aging, the samples were conditioned at 23°C and 50% RH for at least 24 hours and then tested.

RESULTS AND DISCUSSION

Effect of Acid Group Content

The acid group content of the pulps after sulphonation to different levels is summarized in Table I. Sample 1 is the non-sulphonated TMP and Samples 2-5 are TMP samples with increased levels of sulphonation. As can be seen, lignin content of the pulps remains nearly constant with sulphonation. This allows us to clearly identify the effect of acid group content. The hydrogen ion concentrations (pH) of the samples are directly related to the amount of acid groups present in the pulps (Table I). The pH values determined in deionized water are always higher than those in 0.1 N NaCl solution. The presence of a salt overcomes Donnan equilibrium and allows a more uniform distribution of hydrogen ions between the fibre wall and the external solution[13]. The pH values in 0.1 N NaCl solution can also be estimated from the acid group content by assuming complete dissociation of both carboxylic and sulphonic acid groups. The estimated pH values from one gram oven-dry paper in 70 mL 0.1 N NaCl solution are indeed very close to those measured in 0.1 N NaCl solution, particularly for the samples with more sulphonic acid groups (Table I). The larger pH difference for samples with fewer sulphonic acid groups may be due to the incomplete dissociation of the carboxylic acid groups.

The initial physical properties of the handsheets prepared from the pulps are shown in Table II. Due to the mild chemical treatment, there is no significant difference in the initial physical properties. The percent retentions of zero-span tensile strength and of fold endurance as a function of accelerated aging time are shown in Figures 1 and 2. The fold endurance is

TABLE I

Initial Chemical Properties of the Sulphonated Samples

Sample	*1*	*2*	*3*	*4*	*5*
Lignin Content (%)	*30.*	*28.6*	*28.7*	*28.9*	*28.5*
Carboxylic Acid Group Content (meq/kg)	*75*	*122*	*129*	*139*	*133*
Sulphonic Acid Group Content (meq/kg)	*0*	*22*	*63*	*82*	*129*
Total Acid Group Content (meq/kg)	*75*	*144*	*192*	*221*	*262*
pH In Cold Deionized Water	*4.6*	*4.5*	*4.1*	*4.0*	*3.9*
pH In 0.1 N NaCl Solution	*3.6*	*3.0*	*2.8*	*2.7*	*2.5*
pH (Estimated)	*3.0*	*2.7*	*2.6*	*2.6*	*2.4*

TABLE II

Initial Physical Properties of the Sulphonated Samples

Sample	*1*	*2*	*3*	*4*	*5*
Zero-Span Tensile Strength (km)	*8.7*	*8.9*	*9.1*	*9.2*	*9.4*
MIT Double Folds	*391*	*468*	*305*	*535*	*553*

Sample 1: non-sulfonated TMP

Sample 2: TMP sulfonated for 10 minutes.

Sample 3: TMP sulfonated for 20 minutes.

Sample 4: TMP sulfonated for 40 minutes.

Sample 5: TMP sulfonated for 120 minutes.

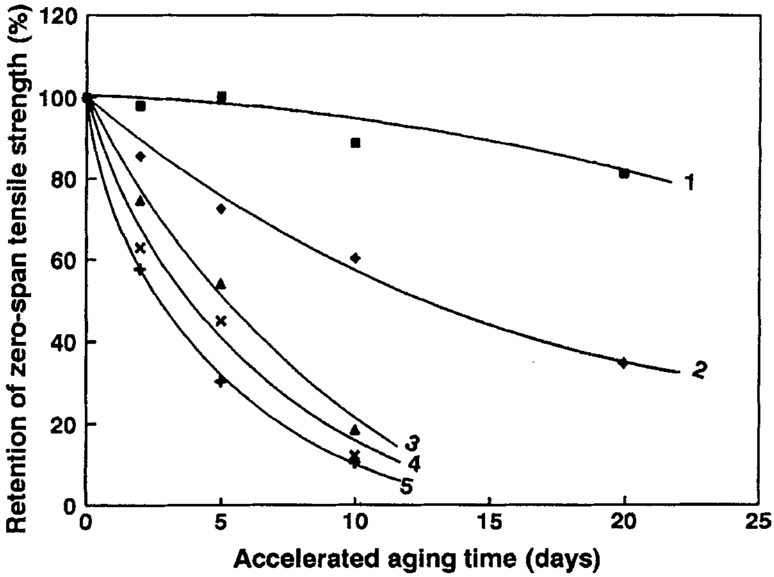

Figure 1. Effect of acid group content on the retention of zero-span tensile strength.

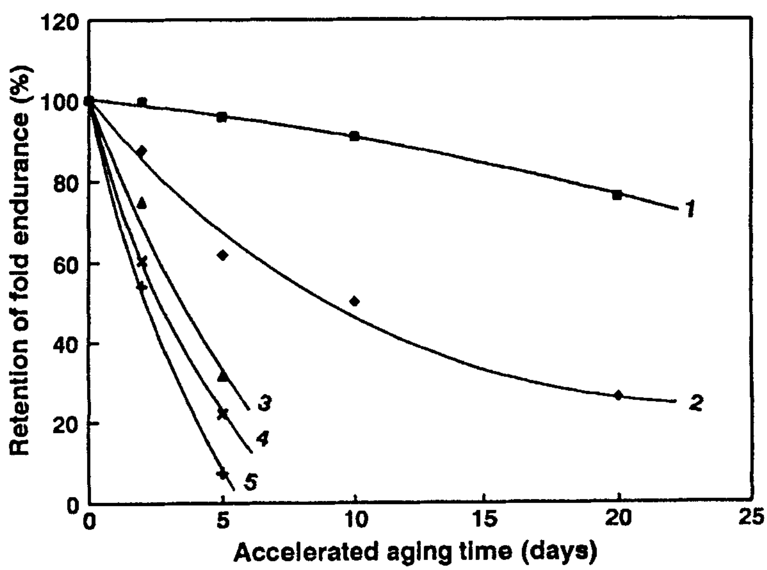

Figure 2. Effect of acid group content on the retention of fold endurance.

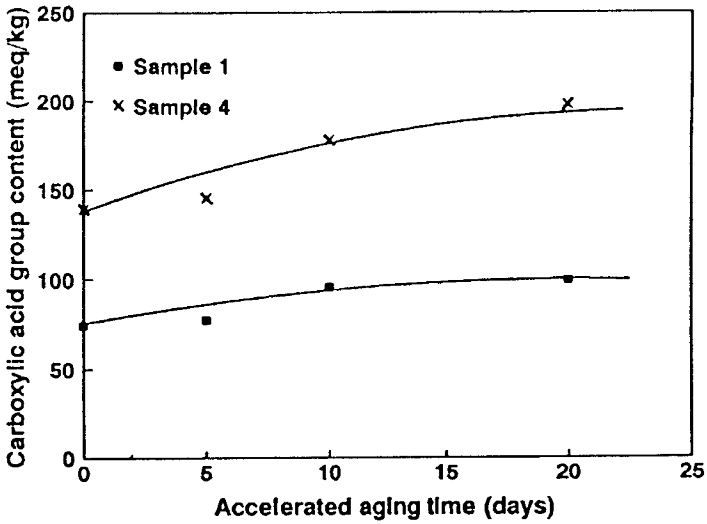

Figure 3. Effect of accelerated aging on the formation of acid groups.

calculated as the logarithm of MIT double folds[15]. The results show a significant loss of strength with increased acid group content, indicating that the sulphonic acid groups in their hydrogen form have a very detrimental effect. The degradation is attributed to a very low pH inside the fibre wall due to the complete dissociation of sulphonic acid groups. These results further support acid hydrolysis as the main mechanism of paper degradation[16].

There is speculation that during aging of lignin-containing paper, lignin and hemicellulose are oxidized to produce additional carboxylic acid groups[11]. To clarify this, the acid group content was measured after accelerated aging. The results for TMP (Sample 1) and sulphonated TMP (Sample 4) are shown in Figure 3. As can be seen, there is indeed an increase of acid group content with increased aging time. The increase of acid groups is due to the formation of carboxylic acid groups (sulphonic acid group content measured was constant during accelerated aging), most likely on lignin and hemicellulose since for pure cellulose there was no increase in acid group content[16].

TABLE III

Initial Properties of the Neutralized and Tap Water Washed Samples

Sample	*4-TW*	*4-Na*	*4-Ca*
pH in 0.1 N NaCl solution	*5.9*	*6.0*	*8.7*
Zero-span tensile strength (km)	*9.9*	*10.6*	*8.1*
MIT double folds	*861*	*770*	*40*

Sample 4-TW: TMP sulphonated and subsequently washed by tap water

4-Na: Sample 4 converted to sodium form

4-Ca: Sample 4 loaded with calcium carbonate

However, due to the low dissociation of these acid groups we do not anticipate any significant effect on strength properties.

<u>**Effect of Neutralization of Acid Groups by Sodium Hydroxide**</u>

The acid groups of Sample 4 in the hydrogen form were converted into the sodium form by soaking in a solution of sodium hydroxide (neutralization):

$$R-SO_3H + NaOH = R-SO_3^{\ominus}Na^{\oplus} + H_2O \quad (1)$$

$$R-COOH + NaOH = R-COO^{\ominus}Na^{\oplus} + H_2O \quad (2)$$

(R represents lignin, hemicellulose and cellulose).

After complete conversion and washing with deionized water, this sample (Sample 4-Na) had a pH of 6.0 in 0.1 N NaCl solution (Table III), same as

TABLE IV

Neutron Activation Analysis Data of the Samples

Sample	4-TW	4	4-Na	4-Ca	Tap Water
Ca (ppm)	4109	579	753	37370	31.0
Na (ppm)	870	467	4095	670	4.0
Al (ppm)	249	154	260	238	0.1
Mg (ppm)	955	392	444	546	2.7
K (ppm)	205	98	179	134	0.9
Total metal content (meq/kg)	355	101	298	1972	—

Sample 4-TW: TMP sulphonated and subsequently washed by tap water

4: Sample 4-TW converted to hydrogen form

4-Na: Sample 4 converted to sodium form

4-Ca: Sample 4 loaded with calcium carbonate

the pH of 0.1 N NaCl solution alone, indicating complete neutralization of the acid groups to their sodium form. This is verified by a high sodium concentration in the handsheets determined by neutron activation analysis (Table IV). In fact, the total metal concentration is close to that required for the complete neutralization of acid groups. Testing of the samples after accelerated aging of this sample shows a very high retention of both zero-span tensile strength and fold endurance (Figures 4 and 5). These results indicate that even with high lignin content and high acid group content, sheets from sulphonated TMP are permanent when the acid groups are neutralized.

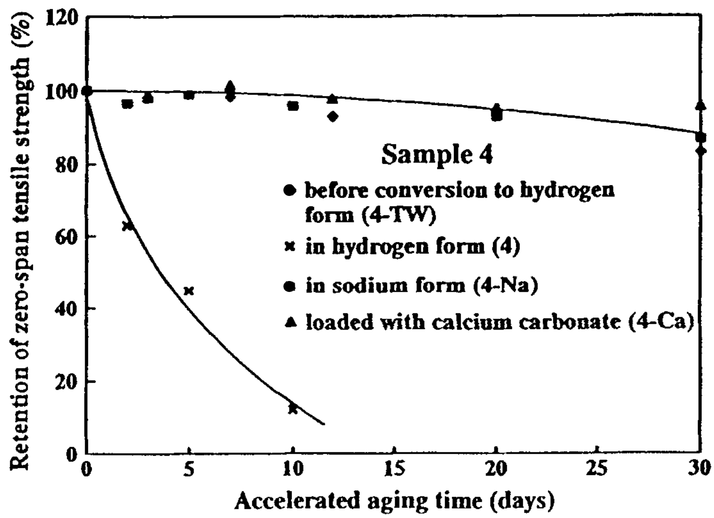

Figure 4. Effect of neutralization on the retention of zero-span tensile strength.

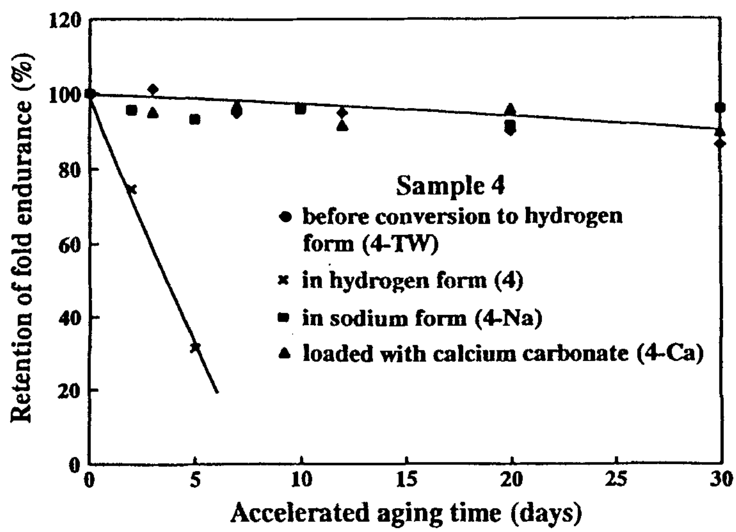

Figure 5. Effect of neutralization on the retention of fold endurance

It should be noted that the neutron activation analysis shows that some metal ions are still present in the handsheets of Sample 4 (Table IV) even though they should be completely removed by ion-exchange treatment. These metal ions may be introduced from the contact with blotter paper during the process of handsheet formation and replace some hydrogen ions. However, the acid groups (the part in hydrogen form) are determined from disintegrated handsheet strips and not from the pulp, thus the effect of the metal ions introduced during the formation of handsheets can be excluded.

Effect of Loading with Calcium Carbonate

The sheets loaded with calcium carbonate (Sample 4-Ca) had a pH of 8.7 in 0.1 N NaCl solution (Table III). The initial strength properties, particularly MIT double folds as shown in Table III are decreased due to the loading of a large amount of calcium carbonate (in practice, such a large loss of strength is prevented by reinforcing the paper with a beaten kraft pulp or dry and wet strength additives). The total metal ion concentration is much higher than required to neutralize acid groups as shown in Table IV. Accelerated aging results show an excellent retention of zero-span tensile strength and fold endurance (Figures 4 and 5). This suggests that the hydrogen ions from the acid groups were neutralized by the loading treatment. Moreover the extra calcium carbonate present in the paper may also neutralize any acid groups formed during aging.

Permanence of Sheets Washed with Tap Water after Sulphonation

Also plotted in Figures 4 and 5 are the results for Sample 4 just after sulphonation and washing with tap water but without conversion to the hydrogen form (Sample 4-TW). This may be representative of actual mill pulp samples. Sample 4-TW has a very good aging resistance because all hydrogen ions from the acid groups are likely replaced by the calcium ions in the tap water. If sufficient washing steps are used as would be in a mill, all the hydrogen ions attached to the acid groups could be replaced by calcium ions. This was confirmed by measuring the concentration of metal elements in Sample 4-TW with neutron activation analysis (Table IV). It is seen that a high concentration of calcium exists in the sheets after tap water washing. The total ion concentration is 355 meq/kg, indeed higher than that required to neutralize all acid groups. The analysis of tap water indicates a high calcium concentration (31 ppm, as shown in Table IV). In fact, previous work showed that washing acidic book papers with tap water made paper more permanent than washing with deionized water[17]; but the cause of this was not clearly identified. Based on the finding of our study, previous results can be explained by the concept of ionic conversion of the acid groups after tap water washing; deionized water can only wash out the external acids. In practice, when a pulp is thoroughly washed by tap water before forming a sheet, the acid groups are neutralized and are predominantly in the calcium form. Therefore, assuming that neutral or alkaline papermaking conditions are used, the high acid group content in commercial CTMP and BCTMP should not be a problem for permanence.

The findings of this study suggest that sheets with a high acid group and high lignin content can be very stable with respect to their mechanical properties during aging when all the acid groups are in the sodium or calcium form.

CONCLUSIONS

Controlled experiments with sulphonated TMP of different acid group content have demonstrated that the acidic groups in the "hydrogen form" do have a significant negative effect on the mechanical permanence of paper. However, the neutralization of all acidic groups into the sodium form significantly improves the permanence of these pulps. Loading calcium carbonate into the pulp before disintegration and sheet formation can also achieve a high mechanical permanence. Washing pulps with tap water containing calcium ions can improve paper permanence by changing the ionic form of the pulp. This work further confirms that the presence of lignin has no negative effect on the mechanical permanence of paper as long as neutral or alkaline papermaking conditions are used.

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