

## FACTORS INFLUENCING ON RETENTION OF ALKYLKETENE DIMER

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### ABSTRACT

Mechanisms of retention of AKD are studied in terms of effects of cationic polymer additions, and roles of fines and carboxyl groups of pulp fibers. Handsheets were prepared from normal pulp and fines-free pulp under various conditions, and AKD contents in the handsheets were determined by pyrolysis-gas chromatography (PY-GC). The addition of cationic polymer (PAE) to pulp suspension was clearly effective in promoting AKD sizing for both cured and non-cured handsheets, resulting from higher retention of AKD in the sheet by cationic PAE molecules.  $\zeta$ -Potential measurement indicated that the originally cationic AKD emulsions come to have amphoteric surface charges in pulp suspension. The effective AKD retention by PAE may, therefore, be due to ionic bond formation between anionic sites of AKD emulsion surfaces and anionic pulp fibers or fines through cationic PAE molecules. The experiments using fines-free pulp showed that most of the added AKD was adsorbed on fines of beaten pulp. Blocking of carboxyl groups in pulp with nonionic methylamide groups resulted in nearly no sizing degrees and quite low AKD contents. Therefore, it is clear that dissociated carboxyl groups in pulp fibers and

finer are the actual retention sites of AKD emulsion particles at the usual addition levels of AKD. Among chitosan salts and PAE used at 0.1-0.4 % addition levels, chitosan AcOH salt gave the highest effect on AKD retention as well as sizing degrees. Good correlation between AKD contents and sizing degrees was obtained; sizing behavior of AKD-sized handsheets was explainable in terms of their AKD contents determined by PY-GC, and thus retention of AKD is the significant first step for AKD sizing. Solid-state  $^{13}\text{C}$ -NMR analysis of cellulase-treated residues of  $^{13}\text{C}$ -labelled AKD-sized handsheets showed that size components were present in papersheet as structures of either the original AKD or ketones, hydrolyzed AKD, without forming  $\beta$ -ketoesters. SEM observations of AKD-sized handsheets indicated that the effect of curing on AKD sizing is explained in terms of melting of size molecules and their spreading over pulp fiber surfaces.

## INTRODUCTION

Alkylketene dimer (AKD) is one of the typical internal sizes for alkaline papermaking, and generally 0.05-0.2 % addition levels on dry weight of pulp to paper stock give sufficient sizing features to papersheets.

The mechanism of this efficient paper sizing by AKD has been studied from various aspects using some analytical techniques such as  $^{14}\text{C}$ -labelling of AKD, FT-IR, cellulase treatments and some model experiments (1-4). Recently, Bottorff reported using  $^{13}\text{C}$ -labelled AKD and solid-state  $^{13}\text{C}$ -NMR that  $\beta$ -ketoesters were formed between cellulose and AKD in the sheet by curing treatments (5). However, most of AKD-sized papersheets have sizing features even without curing treatments, although the degrees of sizing are lower than those after curing. Therefore, the sizing mechanism of AKD under practical papermaking conditions is still unknown at this point. It was found that in the case of alkenyl succinic anhydride (ASA), another typical reactive size, the reactive structures of ASA are necessary for efficient paper sizing by achieving more homogeneous distribution states of hydrophobic size components on hydrophilic pulp fiber surfaces, without the covalent bond formation between ASA and hydroxyl groups in pulp (6,7).

It is well known that the addition of cationic polymers such as polyamideamine-epichlorohydrin resin (PAE), which is one of the wet-strength additives, to pulp suspension containing AKD emulsion enhances sizing features. This effect of PAE on AKD sizing has been hypothesized to be due to either promoting reactions between AKD and hydroxyl groups of cellulose in papersheet as a catalyst or increasing AKD retention by cationic PAE molecules.

Generally alum is used to some extent even in alkaline papermaking for process controls. For AKD sizing, a small amount of alum has a positive effect, whereas excess alum addition is negative (8,9). In the case of ASA, the alum addition was effective for sizing, due to higher retention of ASA by alum (10). The positive effect of alum on AKD sizing have been assumed to be due to not only higher retention of AKD by alum but also molecular-order interactions between one hydroxyl group of pulp, one aluminum ion and one  $\beta$ -ketoacid molecule, which is the intermediate compound of AKD during hydrolysis, in papersheet (8,9).

Retention of AKD at wet end is a significant first step for AKD sizing, and the above-described effects of PAE and alum on AKD sizing may be related to AKD retention to some extent. The following three mechanisms are possible for explaining AKD retention in the papersheet at wet-end. The first one is that carboxyl groups in pulp, even though their amounts are far smaller than those of hydroxyl groups, govern the anionic surface charges of pulp fibers and fines, and that these carboxyl groups are the retention sites of cationic AKD size emulsions. The second one is that not only carboxyl groups in pulp but also abundant hydroxyl groups, even though their degrees of dissociation must be quite low, participate in AKD retention as anionic sites. The last one is that flocculation of AKD emulsion particles occurs in pulp suspension, and that the AKD flocs thus formed are retained in the pulp fiber mat by filtration effect without any ionic interactions with pulp fibers or fines.

For evaluating retention values of AKD, determination of AKD contents in papersheets is necessary. However, the conventional extraction-GC methods (4) and radioactivity measurements of the sheet samples sized with  $^{14}\text{C}$ -labelled AKD (1,2) are far from on-machine determination methods. Recently, on the other hand, Yano and others (11) reported the

possibility for determining AKD contents in paper samples by pyrolysis-gas chromatography (PY-GC).

In this paper, therefore, mechanisms of retention of AKD are studied using the PY-GC technique from the following aspects: 1) effects of PAE and chitosan salts additions on AKD retention and 2) roles of fines and carboxyl groups of pulp fibers in AKD retention (12-14). Possibility for AKD to form  $\beta$ -ketoesters in handsheets is also studied using  $^{13}\text{C}$ -labelled AKD and solid-state  $^{13}\text{C}$ -NMR.

## EXPERIMENTAL

### Materials

Commercial hardwood bleached kraft pulp was beaten to 470 mL Canadian Standard Freeness with a PFI mill. Fines-free pulp was prepared from the above beaten pulp by 5 repeat of water-feeding and drainage treatments through an 150 mesh wire in the cylinder of handsheet-machine at about 0.171 g/L consistency. Yield of the fines-free pulp was about 94 %. For preparing nonionic pulp, carboxyl groups in the beaten pulp were converted to methylamide by the amidation with methylamine HCl salt and a water-soluble carbodiimide (WSC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide HCl salt, Wako Co. Japan) at pH = 4.75 for overnight using a pH stat, according to the procedure reported previously (15). Based on the carboxyl content, more than 95 % of the carboxyl groups in the original pulp were converted to methylamide ones. For preparing a pulp with higher carboxyl contents, aldehyde groups of the beaten pulp was oxidized with sodium chlorite at room temperature and pH=5 for 24-72 h (16), and then the pulp was washed thoroughly with water. An AKD emulsion and PAE used were commercial products (AS-202 and WS-570, respectively, Japan PMC Co. Japan). The AKD emulsion contained about 12% AKD and 3% cationic starch as the emulsion stabilizer, and had an average particle size of 0.5 $\mu\text{m}$  with a  $\zeta$ -potential of +14mV.

Commercial chitosan and chitin (Chitosan PSH and Chitin PSH,

respectively, Yaizu Suisan Kagaku Co. Ltd. Japan) were used. Chitosan salts were prepared by re-precipitation from aqueous chitosan-AcOH and -HCl solutions into ethanol. Dry chitosan AcOH and HCl salts were obtained by drying of the precipitated gel-like chitosan AcOH and HCl salts *in vacuo*. Water-soluble chitin was prepared from the original chitin sample by the random deacetylation method under homogeneous alkaline conditions (17); one % chitin solution in 10% NaOH was stirred for two days at 20 °C, and the water-soluble chitin was obtained by dialysis of the solution for one week followed by freeze-drying. Degrees of polymerization (DP) and degrees of deacetylation (DDAc) of chitosan samples used in this study are shown in Table I.

<sup>13</sup>C-Labelled AKD was prepared from a mixture of <sup>13</sup>C-labelled stearic and palmitic acids according to the reported procedure (18). One % AKD emulsion containing 3% diethylaminoethyl starch was prepared from the <sup>13</sup>C-labelled AKD and cationic starch (19).

### Handsheet Making

In the typical procedure, an AKD emulsion and a PAE solution were added in this order to 0.15 % pulp suspension with continuous stirring. Handsheets with 60 g basis weight were prepared using tap water according to Tappi Test Method (20). The pH of the pulp suspension was 6.7-7.0. The wet-pressed handsheets were dried at 20 °C and 65 % relative humidity (R. H.) for one day. Some handsheets were cured at 105 °C for 20 min, and then they were conditioned again at 20 °C and 65 % R. H. for more than 1 day before being subjected to sizing tests.

In the case of chitosan-added handsheets, to 0.15 % pulp suspension, calcium carbonate (10 % on dry weight of pulp), the AKD emulsion (0.2 % AKD on dry weight of pulp) and a cationic polymer (0-0.4 % on dry weight of pulp) were added in this order with continuous stirring. Handsheets with basis weight of 60 g were prepared according to Tappi Test Method (20). The pH of the pulp suspension was about 8.0. The wet-pressed handsheets were dried using a drum dryer at about 120 °C for 100 s. The handsheets thus prepared were conditioned at 20 °C and 65 % R. H. for more than 1 day.

## Measurements

Carboxyl contents of pulps were measured according to TAPPI Test Method (21). AKD contents in handsheets were determined using a pyrolysis-gas chromatograph by the modified method reported by Yano et al. (11). About 0.5 mg of a handsheet was set in a small platinum pot for pyrolysis, and the sample was pyrolyzed at 500 °C under a flow of He gas by a vertical microfurnace-type pyrolyzer (GP-1018, YANACO Co. Ltd., Japan), which was directly attached to a gas chromatograph (GC-14B, Shimadzu Co. Ltd., Japan) equipped with a capillary column of OV-1 (60 m × 0.25 mm) and an FID detector. The column temperature was initially set at 200 °C, and then was programmed to 300 °C at 5 °C/min. Injection and detector temperatures were set at 250 and 280 °C, respectively. The AKD contents in handsheets were calculated on the basis of peak areas due to three AKD components in the pyrolysis-gas chromatograms, using a calibration curve obtained from handsheets, whose AKD contents were obtained beforehand by the extraction-GC method (4). Each AKD content expressed in this paper was the average of at least three times' measurements.

Degrees of sizing of handsheets were expressed as Stöckigt sizing degrees (22).  $\zeta$ -Potentials of AKD emulsions were measured by using a micro-electrophoretic apparatus (Rank Brothers, Mark II) at 25°C (23).

Degrees of polymerization of chitosan and chitin were determined by size exclusion chromatography (SEC) using lithium chloride/*N,N*-dimethylacetamide as a solvent (24). Degrees of deacetylation of chitin and chitosan were calculated from nitrogen content. The formation of colloidal chitosan particles was detected by observing scattering behavior of laser light (He-Ne,  $\lambda$  = 632.8 nm) passed through plastic cells containing about 3 ppm of chitosan samples in an alkaline buffer at pH=8.

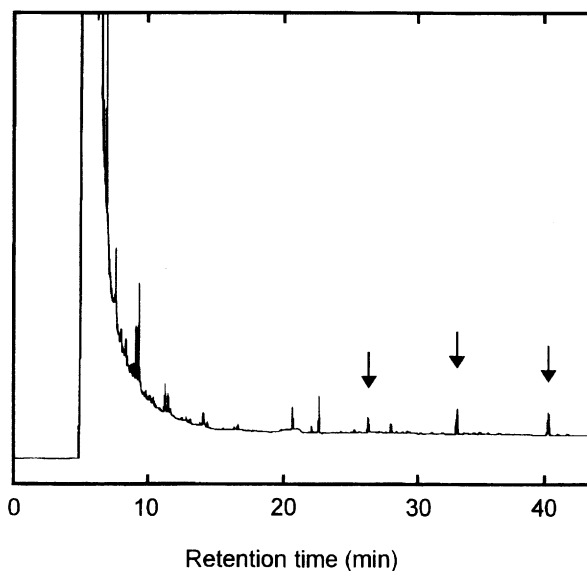
Since the handsheets prepared with  $^{13}\text{C}$ -labelled AKD gave no resonance peaks due to carbonyl carbons in their solid-state  $^{13}\text{C}$ -NMR spectra, the handsheets were treated with cellulase (Meicellase, Meiji Seika, Japan) in an acetate buffer at pH=5 at room temperature for 6 weeks (4). The cellulase-treated residues of the  $^{13}\text{C}$ -labelled AKD-sized handsheets were

collected by centrifugation followed by freeze-drying. Solid-state  $^{13}\text{C}$ -NMR spectra of the cellulase-treated residues were recorded on JEOL JNM-GX 270.

## RESULTS AND DISCUSSION

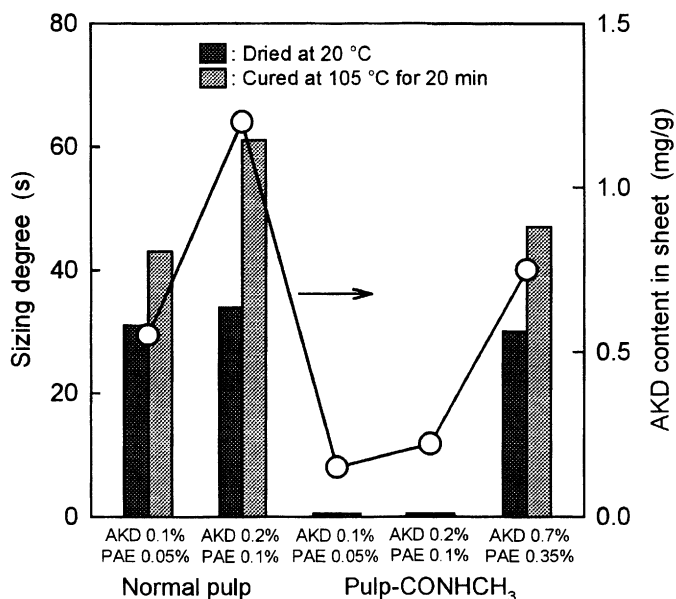
### Determination of AKD in Handsheets by PY-GC

Fig. 1 shows a PY-GC pattern of a typical AKD-sized handsheet. PY-GC-mass spectroscopy revealed that the three peaks in Fig. 1 were assigned to ketones having carbon numbers,  $\text{C}_{31}$ ,  $\text{C}_{33}$  and  $\text{C}_{35}$ , which were derived from the corresponding AKD molecules by hydrolysis (4).



**Figure 1.** Pyrolysis-gas chromatogram of AKD-sized handsheet. Peaks at allows correspond to hydrolyzed products of AKD in handsheet.

Fig. 6 shows sizing degrees and AKD contents of handsheets prepared from normal and nonionic pulps by the additions of AKD and PAE. No sizing features appeared at all on the handsheets prepared from the nonionic pulp at 0.1 and 0.2 % AKD addition levels, whereas the handsheets prepared from the normal pulp had sufficient sizing degrees. AKD content in handsheets decreased from 0.56 and 1.20 mg/g to 0.15 and 0.22 mg/g at 0.1 and 0.2 % AKD addition levels, respectively, by the nonionic blocking of carboxyl groups in the pulp. These results indicate, therefore, that at least in the case of laboratory experiments AKD emulsion



**Figure 6.** Sizing degrees (bar graph) and AKD contents (○) of handsheets prepared from normal pulp and the carboxyl-group-blocked pulp, Pulp-CONHCH<sub>3</sub>.

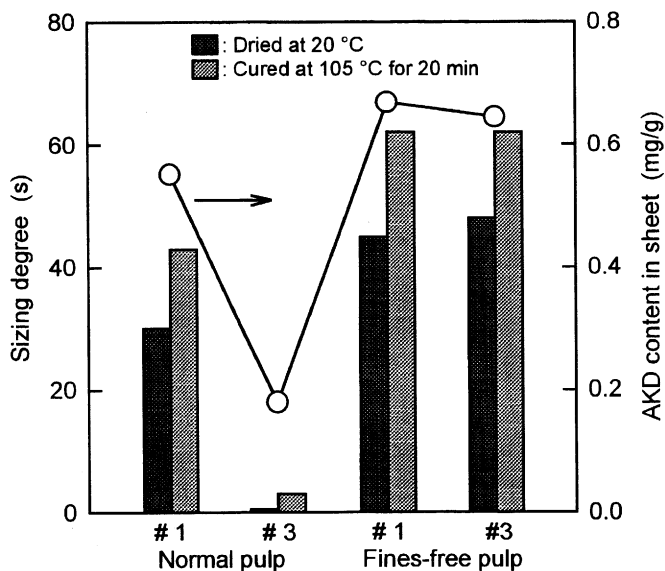


treatment were always 10-25 s higher than those of the handsheets dried at 20 °C. The PAE addition resulted in higher sizing at the usual addition levels of AKD. When PAE was added to pulp suspension with 1 and 2 % AKD on dry weight of pulp, the AKD contents in the handsheets were 0.56 and 1.20 mg/g, respectively. On the other hand, when PAE was not used in the handsheet-making, the AKD contents were only 0.32 and 0.42 mg/g for the 1 and 2 % AKD addition levels, respectively. Hence, more than about twice as much AKD retention values as the cases without PAE can be achieved by the 0.05-0.1 % PAE additions. When the addition level of AKD increased to 0.5 % on dry weight of pulp, the handsheet prepared even without PAE had sufficient sizing because of the sufficient AKD content (0.72 mg/g). Therefore, as long as sufficient amounts of AKD were retained in the sheet, good sizing appeared on the handsheets prepared even without PAE. At similar AKD contents, no particular differences in sizing effects were observed between the handsheets prepared with and without PAE, for both cured and non-cured handsheets. This result revealed that higher sizing obtained by the PAE addition are primarily due to higher retention of AKD thereby for both cured and non-cured handsheets.

### **Effect of Fines Fraction on AKD Retention**

One possibility to explain the above effect of PAE on retention of the cationic AKD emulsion is that the PAE addition increases the retention of fines, where cationic AKD emulsion particles are predominantly adsorbed. Hence, sizing degrees and AKD contents were measured for handsheets prepared from normal and fines-free pulps.

Fig. 3 shows sizing degrees and AKD contents of the handsheets prepared from normal and fines-free pulps with 0.1 % AKD and 0.05 % PAE, where the sequence of water-feeding, agitation and drainage cycle in the cylinder of the handsheet-machine was repeated. Namely, #1 sample in Fig. 3 corresponds to the normal handsheet prepared according to Tappi Test Method. On the other hand, the #3 sample was prepared by repeating the following treatment twice; water was added again to the pulp mat, which was once formed on the handsheet wire by drainage, and the pulp suspension thus prepared was re-agitated and then drained. When the



**Figure 3.** Sizing degrees (bar graph) and AKD contents (O) of AKD-sized handsheets prepared from normal pulp and fines-free pulp by repeat of water-feeding, agitation and drainage cycle in the cylinder of handsheet-machine (see text).

normal pulp was used, the degree of sizing decreased drastically by the repeat treatment of drainage. In contrast, sizing was maintained for the handsheets prepared from the fines-free pulp even by the repeat treatment. As shown in Fig. 3, the patterns of sizing degrees corresponded well to those of AKD contents; AKD content was unchanged for the handsheets prepared from the fines-free pulp, whereas the repeat treatment resulted in a clear decrease in AKD content for the handsheets prepared from the normal (fines-containing) pulp.

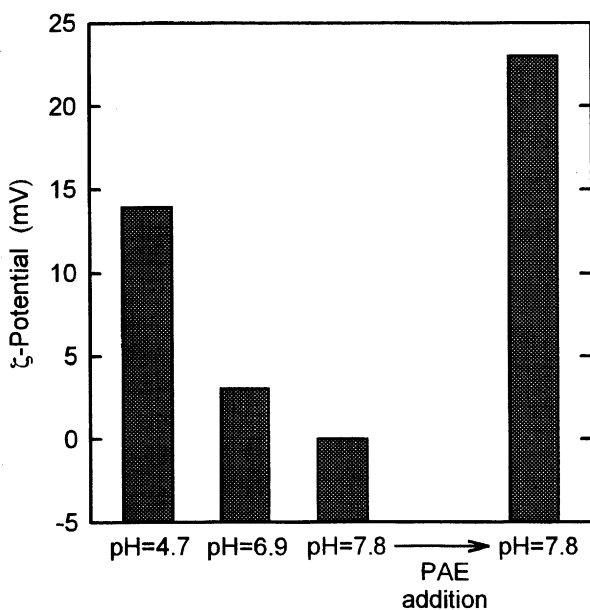
Since the fines fraction had already been removed for the fines-free pulp, the handsheets prepared from this pulp had constant basis weight. On the other hand, the basis weight decreased from 60 g to about 57 g by the repeat treatment due to partial removal of fines from the normal pulp. Therefore, the loss in AKD content or the decrease in sizing of the handsheets prepared from the normal pulp by the repeat treatment is due to the loss thereby of fines. On the basis of AKD content and basis weight, about 75 % of AKD retained in the normal pulp handsheets was adsorbed onto the fines in the pulp suspension. Therefore, the cationic AKD emulsion particles are predominantly adsorbed onto fines of beaten pulp, as Marton reported (25,26).

### **Effect of PAE on AKD Retention for Fines-Free Pulp**

As shown in Fig. 3, when 0.1 % AKD and 0.05 % PAE were used, the handsheet prepared from the fines-free pulp had sizing degrees and AKD contents a little higher than those prepared from the normal pulp. On the other hand, when the handsheets were prepared without PAE, both handsheets prepared from the normal and fines-free pulps had quite low sizing degrees and low AKD contents; the PAE addition was effective in increasing AKD retention also for the fines-free pulp. Thus, PAE molecules plays not only in enhancing fines retention, where AKD emulsion particles are predominantly adsorbed, but also in enhancing AKD retention directly, irrespective of fines in pulp suspension.

### **Retention of AKD by Cationic PAE Molecules**

As shown in Fig. 4, the AKD emulsion used in this study has a  $\zeta$ -potential of +14mV at pH=4.7, and this cationic surface charge originates from cationic starch used for the AKD emulsion stabilizer. However, this cationic charge decreased with increasing pH, and the  $\zeta$ -potential became nearly  $\pm 0$ mV at pH=7.8. Some anionic compounds in the AKD emulsion may lead to the formation of anionic sites on the surfaces of emulsion particles in diluted systems; the originally cationic AKD emulsion particles turn to amphoteric ones in pulp suspension.

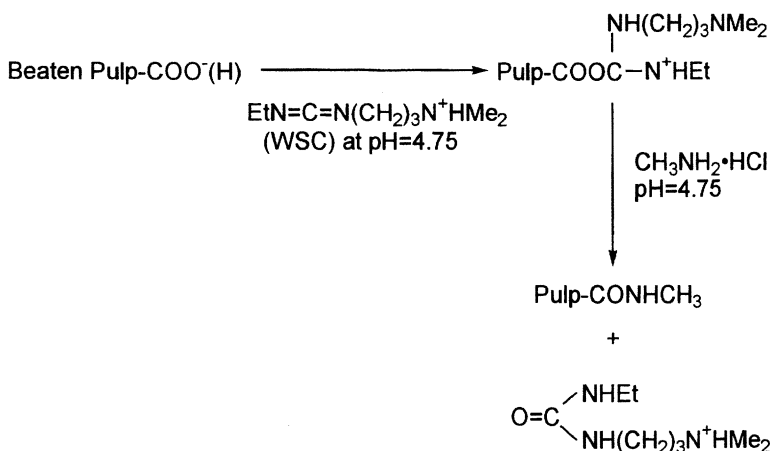


**Figure 4.**  $\zeta$ -Potentials of AKD emulsion particles at various pH, and the effect of PAE addition on  $\zeta$ -potential.

As shown in Fig. 4, when PAE was added to the AKD emulsion at pH=7.8,  $\zeta$ -potentials of the AKD emulsion particles increased from  $\pm 0$  mV to +23 mV. Namely, cationic PAE molecules added are adsorbed onto the anionic sites of the AKD emulsion particles, and the cationic charge of the AKD emulsion particles can be reinforced in pulp suspension by the PAE addition. This increase in cationic surface charge of the AKD emulsion particles by the PAE addition must have resulted in the higher AKD retention both for the normal and fines-free pulps.

### Effect of Blocking of Carboxyl Groups in Pulp on AKD Sizing

In order to elucidate the roles of carboxyl groups in pulp in AKD retention, the carboxyl-group-blocked pulp, Pulp-CONHCH<sub>3</sub>, was prepared, and AKD sizing was examined for this chemically modified pulp. This methylamidation procedure of the beaten pulp was shown in Fig. 5. Carboxyl content decreased from 0.060 to about 0.002 mmol/g by this amidation, and thus more than 95 % of the carboxyl groups present in the original pulp were converted to nonionic groups without any changes in other pulp properties such as freeness.

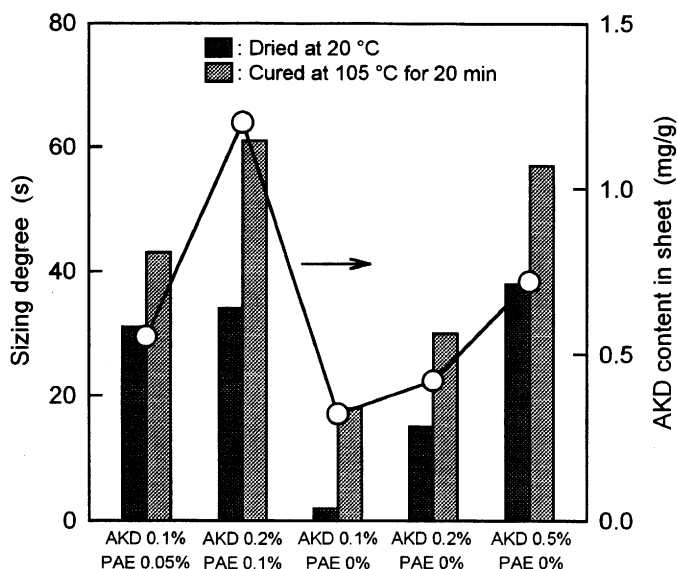


**Figure 5.** Scheme for preparing the carboxyl-group-blocked pulp by methylamidation of carboxyl groups in pulp by water-soluble carbodiimide at pH=4.75.

Quantitative analysis of AKD in papersheet was possible without the freezing-milling treatment of the sheet samples (11) by using standard handsheet samples, whose AKD contents had been determined beforehand by the extraction-GC method (4). Drying methods or curing treatments of handsheets had little influence on AKD contents obtained by this PY-GC method, and the deviations of AKD contents were within the range of  $\pm 3\%$  for one sample in this study.

### Effect of PAE Addition on AKD Retention

Sizing degrees and AKD contents of handsheets prepared with and without PAE are shown in Fig. 2. Sizing degrees after the curing



**Figure 2.** Sizing degrees (bar graph) and AKD contents (○) of handsheets prepared with and without PAE.

particles are retained on pulp fibers or fines primarily at their carboxyl groups at the usual addition levels of AKD; ionic bonds must be formed between dissociated carboxyl groups, *i.e.* anionic sites, of pulp fibers or fines and AKD emulsion particles with cationic PAE molecules.

When the addition levels of AKD increased to 0.5-0.7 % on dry weight of pulp, sizing features then appeared even on the handsheets prepared from the nonionic pulp, because they had sufficient AKD contents for sizing. Since the nonionic pulp had no interaction sites for the ionic bond formation with AKD emulsion particles, AKD components in these handsheets must have been retained in wet web by physical trapping or filtration effect of AKD emulsion particles. Therefore, carboxyl groups in pulp, even though their amounts are far smaller than those of hydroxyl groups in pulp, may play significant roles in the efficient AKD retention.

On the basis of the above mechanisms of AKD retention, the effect of increasing carboxyl content in pulp on AKD sizing was studied. When carboxyl contents were increased from 0.060 to 0.080 mmol/g by the sodium chlorite oxidation of the beaten pulp at room temperature for 24 h, sizing degrees and AKD contents in the handsheets clearly increased, as being expected. Probably aldehyde groups at the reducing ends of hemicellulose are oxidized to carboxyl groups with sodium chlorite, and nearly no depolymerization of the pulp was observed during the oxidation.

### **Effects of Chitosan Salts on AKD Sizing**

Since chitosan has a primary amine group in each glucosamine unit, it is soluble in aqueous acid solutions, forming protonated amine salts. However, it is insoluble in neutral and alkaline solutions. The effects of chitosan on wet and dry strength improvements of papersheet have been already studied (27,28). In this study, two chitosan salts and one water-soluble chitin were used as their aqueous solutions for the addition to alkaline pulp suspension (Table 1). The isolated and freeze-dried chitosan AcOH and HCl salts were completely soluble in water. The water-soluble chitin has acetamide and amino groups randomly distributed at C2 of the repeating unit along the polysaccharide chains (29,30), and it becomes soluble thereby even in neutral and alkaline solutions.

**Table 1.** DPw, DPn, DDAc and cation content of cationic polymers used for handsheet-making

	DPw	DPn	DDAc	Cation content (mmol/g)
Chitosan-AcOH salt	2910	800	85	3.9
Chitosan-HCl salt	2910	800	85	4.3
Water-soluble chitin	1286	220	45	2.4
PAE	-	-	-	3.3

DPw and DPn: degrees of polymerization in weight and number averages, respectively. DDAc: degree of deacetylation.

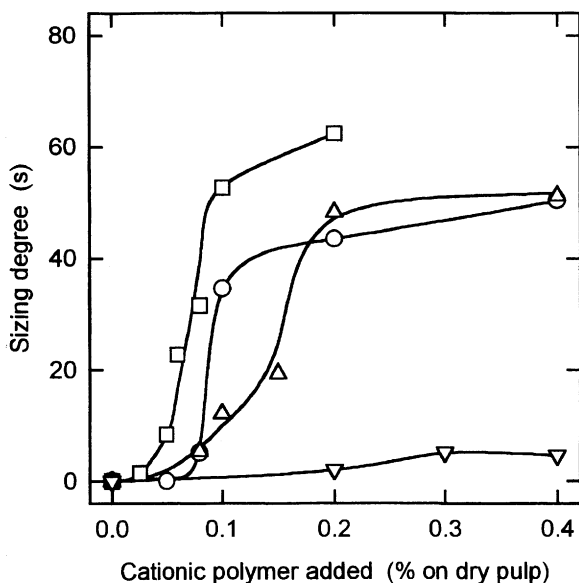
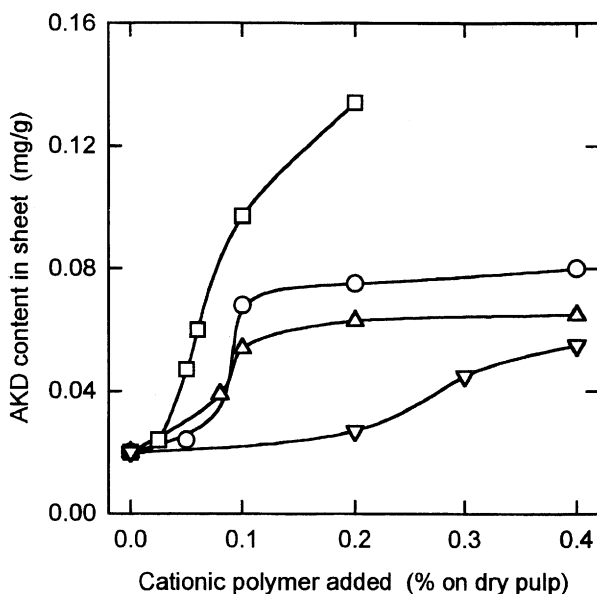
**Figure 7.** Sizing degrees of AKD-sized handsheets prepared with various cationic polymers; chitosan AcOH salt (□), chitosan HCl salt (Δ), water-soluble chitin (▽), and PAE (○).

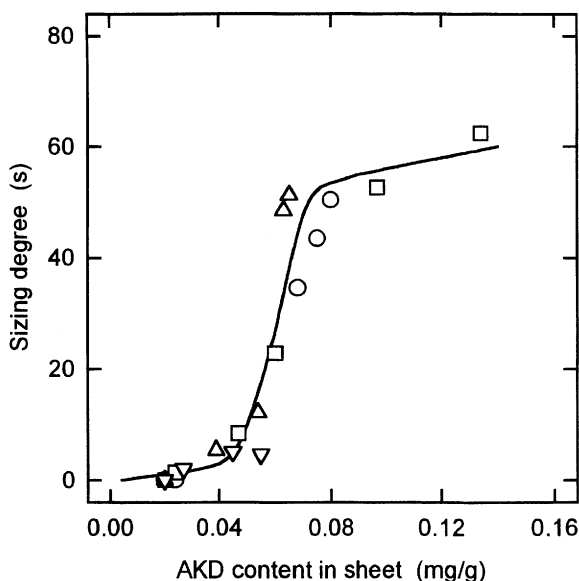


Fig. 7 shows sizing degrees of the AKD-sized and  $\text{CaCO}_3$ -filled handsheets prepared with various cationic polymers. When the handsheets were prepared with calcium carbonate and the AKD emulsion only, no sizing features appeared at all on the handsheets. However, clear sizing features appeared on the handsheets, when the chitosan-AcOH, chitosan-HCl or PAE solution was added to the pulp suspension. Especially, chitosan-AcOH salt had the highest effect on sizing. In contrast, water-soluble chitin had a very low effect on sizing even at the 0.4 % addition level.



**Figure 8.** AKD contents of handsheets prepared with various cationic polymers; chitosan AcOH salt (□), chitosan HCl salt (Δ), water-soluble chitin (▽), and PAE (○).

Fig. 8 illustrates relationships between the amounts of cationic polymers added to pulp suspension and AKD contents in the handsheets. The chitosan-AcOH salt had the highest effect for AKD retention, whereas the water-soluble chitin had the lowest one. Fig. 9 shows relationship between AKD contents in handsheets prepared in this study and their sizing degrees. Sizing features appeared on handsheets at more than about 0.04 mg/g AKD content in the handsheets, and their sizing degrees increased drastically at 0.05-0.07 mg/g AKD content. Thus, the effect of cationic polymers on sizing was roughly explainable by their effects on AKD retention.



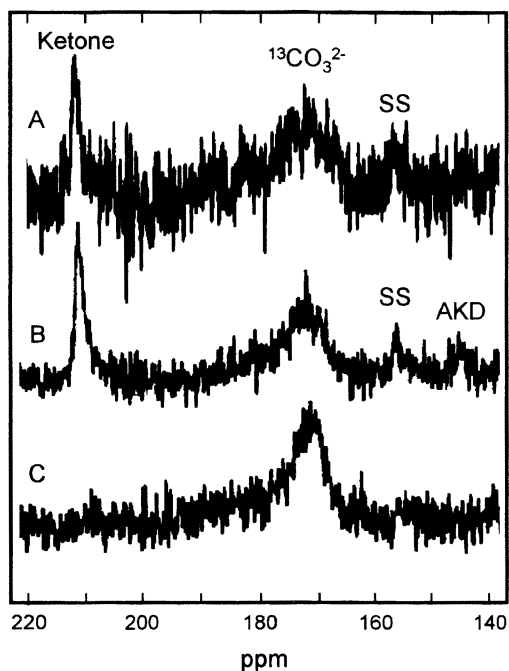
**Figure 9.** Relationship between AKD contents and sizing degrees of AKD-sized handsheets prepared with various cationic polymers; chitosan AcOH salt (□), chitosan HCl salt (Δ), water-soluble chitin (▽), and PAE (○).

As described in the previous section, the enhancement of AKD retention by the addition of PAE to pulp suspension can be explained in terms of higher retention of fines thereby and/or an increase in cationic surface charges of AKD emulsion particles by the adsorption of cationic PAE molecules onto anionic sites of amphoteric AKD emulsion particles in pulp suspension. Therefore, also chitosan salts may have the effect on increasing cationic surface charges of AKD emulsion particles at wet-end. Chitosan AcOH and HCl salts were completely dissolved in water. However, since chitosan has primary amine, it is insoluble in water at pH = 8; the behavior of chitosan in pulp suspension at pH = 8 in the presence of  $\text{CaCO}_3$  filler must be different from that of PAE. Since chitosan formed colloidal particles in alkaline solutions, the immediate precipitation behavior of chitosan molecules on pulp fibers and/or AKD emulsion particles, maintaining cationic charges to some extent, may have resulted in the higher AKD retention.

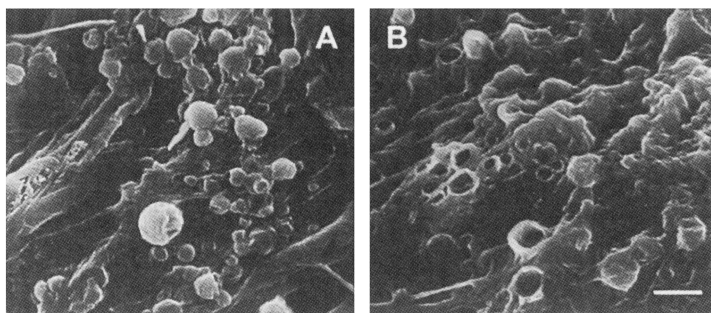
### **Possibility for AKD to form $\beta$ -Ketoesters in Papersheet**

Fig. 10 shows solid-state  $^{13}\text{C}$ -NMR spectra of cellulase-treated residues of the handsheets prepared with 0.1%  $^{13}\text{C}$ -labelled AKD and 0.05 % PAE, and Fig. 10A and 10B were prepared from the cured and non-cured handsheets, respectively. Sizing degrees were 62 and 35 s for the cured and non-cured handsheets, respectively. The patterns A and B are similar to those reported by Bottorff (5). However, no resonance peak due to ketone-carbonyl carbons of  $\beta$ -ketoesters was detected at about 205 ppm in both spectra. Only the resonance peak at 211 ppm due to carbonyl carbons of ketones was observed in both spectra. The broad resonance around 170 ppm is nearly equal to that of ester-carboxyl carbons of  $\beta$ -ketoesters. However, as shown in Fig. 10C, the cellulase-treated residue of the  $\text{CaCO}_3$ -filled handsheets without AKD also had a broad resonance at about 170 ppm. Therefore, the broad resonance detected at about 170 ppm in Fig. 10A and 10B is due to  $^{13}\text{CO}_3^{2-}$  and/or  $\text{H}^{13}\text{CO}_3^-$ , which were formed from  $^{13}\text{C}$ -labelled AKD by hydrolysis and were trapped in the handsheets. As shown in Fig. 10B, the resonance due to AKD is still present in the cellulase-treated residue of the non-cured handsheets; size components are present as the structure of either AKD or ketones, hydrolyzed AKD, in the non-cured handsheets without forming  $\beta$ -

ketoesters. On the other hand, size components present in the cured handsheets are mostly hydrolyzed AKD, *i.e.* ketones.



**Figure 10.** Solid-state  $^{13}\text{C}$ -NMR spectra of cellulase-treated residues of handsheets. A: Cured handsheets prepared with 0.1%  $^{13}\text{C}$ -labelled AKD and 0.05% PAE; sizing degree = 62 s. B: Non-cured handsheets prepared with 0.1%  $^{13}\text{C}$ -labelled AKD and 0.05% PAE; sizing degree = 38 s. C:  $\text{CaCO}_3$ -filled handsheets without AKD. SS: Spinning side band.



**Figure 11.** SEM microphotographs of surface of AKD-sized handsheets before (A) and after (B) curing treatment. Scale bar corresponds to 1  $\mu\text{m}$ .

Fig. 11 shows scanning electron microphotographs (SEM) of surfaces of handsheets prepared with AKD. When the handsheet was dried at 20°C, the AKD emulsion particles with 0.5-1  $\mu\text{m}$  in diameter are observed on pulp fibers. On the other hand, when the handsheet once dried at 20°C was cured at 105°C, only the empty shell-like structures of the emulsion stabilizers are observed on the pulp surfaces. Probably the inside AKD molecules are melted and spread over the pulp surfaces by the curing treatment. It is quite natural that higher sizing degrees can be brought about on handsheets by the curing treatment, because more extended area on pulp surfaces are covered with hydrophobic size molecules (31). These SEM observations and the result of solid-state  $^{13}\text{C}$ -NMR show that the increase in sizing degrees by curing treatments of handsheets is primarily due to melting and spreading of the size molecules on pulp fibers in sheet.

## CONCLUSIONS

In this study, AKD sizing was studied in terms of both retention and sizing mechanisms, and the following conclusions were obtained.

The addition of cationic polymer PAE to pulp suspension was clearly effective in promoting AKD sizing for both cured and non-cured handsheets, resulting from higher retention of AKD in the sheet by cationic PAE molecules.  $\zeta$ -Potential measurement indicated that the originally cationic AKD emulsions come to have amphoteric surface charges in pulp suspension. The effective AKD retention by PAE may, therefore, be due to ionic bond formation between anionic sites of AKD emulsion surfaces and anionic pulp fibers or fines through cationic PAE molecules.

The experiments using fines-free pulp showed that most of the added AKD was adsorbed on fines of beaten pulp. Furthermore, dissociated carboxyl groups in pulp fibers and fines are the actual retention sites of AKD emulsion particles in wet-end at the usual addition levels of AKD.

Among chitosan salts and PAE used at 0.1-0.4 % addition levels, chitosan AcOH salt gave the highest effect on AKD retention as well as sizing degrees. Good correlation between AKD contents and sizing degrees was obtained for all handsheets prepared in this study, and thus retention of AKD is a significant first step for AKD sizing.

Solid-state  $^{13}\text{C}$ -NMR analysis of cellulase-treated residues of  $^{13}\text{C}$ -labelled AKD-sized handsheets showed that most of AKD components were present in papersheet as ketones, hydrolyzed AKD, without forming  $\beta$ -ketoesters. SEM observations indicate that the effect of curing on AKD sizing is explained in terms of melting of size molecules and their spreading over pulp fiber surfaces.

## REFERENCES

1. Lindström, T. and Soderberg, G, "On the Mechanism of Sizing with Alkylketene Dimers, Part 1. Studies on the amount of alkylketene dimer required for sizing different pulps", *Nordic Pulp Paper Res. J.*, **1**(1): 26-33 (1986)
2. Roberts, J. C. and Garner, N., "The Mechanism of alkyl ketene dimer sizing of paper, Part I", *Tappi J.*, **68**(4): 118-121 (1985).

3. Ödberg, L., Lindström, T., Liedberg, B. and Gustavsson, J., "Evidence for b-ketoester formation during the sizing of paper with alkylketene dimers", *Tappi J.*, **70**(4): 135-139 (1987).
4. Isogai, A., Taniguchi, R., Onabe, F. and Usuda, M., "Sizing Mechanism of Alkylketene Dimers, Part 1. Possibility for AKD to form b-ketoesters in papersheets", *Nordic Pulp Paper Res. J.*, **7**(4): 193-199 (1992).
5. Böttorff, K. J., "AKD sizing mechanism: a more definitive Description", *Tappi J.*, **77**(4): 105-116 (1994).
6. Nishiyama, M., Isogai, A. and Onabe, F., "Structures of Alkenyl Succinic Anhydride (ASA) Components in ASA-Sized Papersheet", *Sen'i Gakkaishi*, **52**(4): 180-188 (1996).
7. Nishiyama, M., Isogai, A. and Onabe, F., "Roles of Reactive Alkenyl Succinic Anhydride (ASA) in Paper Sizing", *Sen'i Gakkaishi*, **52**(4): 189-194 (1996).
8. Gess, J. M. and Lund, R. C., "The Strong Bond/Weak Bond Theory of Sizing, Alkyl Ketene Dimer and The Strong Bond/Weak Bond Theory", *Tappi J.*, **74**(1): 111-113 (1991).
9. Patton, P. A., "On the Mechanism of AKD Sizing and Size Reversion", *Proc. Tappi Papermakers Conf.*, p. 415-423 (1991).
10. Isogai, A., Nishiyama, M. and Onabe, F., "Mechanism of Retention of Alkenyl Succinic Anhydride (ASA) on Pulp Fibers of Papersheet", *Sen'i Gakkaishi*, **52**(4): 195-201 (1996).
11. Yano, T., Ohtani, H., Tsuge, S. and Obokata, T., "Determination of Neutral Sizing Agents in Paper by Pyrolysis-Gas Chromatography", *Analyst*, **117**(5): 849-852 (1992).
12. Isogai, A., Kitaoka, C. and Onabe, F., "Effect of Carboxyl Groups in Pulp on Retention of Alkylketene Dimer", *J. Pulp Paper Sci.*, in press.

13. Isogai, A., "Effect of Cationic Polymer Addition on Retention of Alkylketene Dimer", *J. Pulp Paper Sci.*, in press.
14. Hasegawa, M., Isogai, A. and Onabe, F., "AKD Sizing with Chitosan Salts", *J. Pulp Paper Sci.*, submitted for publication.
15. Kitaoka, T., Isogai, A. and Onabe, F., "Sizing Mechanism of Emulsion Rosin Size-Alum Systems, Part 1", *Nordic Pulp Paper Res. J.*, **10**(4): 253-260 (1995).
16. Davidson, G. F. and Nevell, T. P., "The Action of Chlorous Acid on Hydrocellulose", *J. Text. Inst.*, **48**: T356-T361 (1957).
17. Sannan, T., Kurita, K. and Iwakura, Y., "Studies on Chitin 2. Effect of Deacetylation on Solubility", *Makromol. Chem.*, **177**: 3589-3600 (1976).
18. Sauer, J. C., "Ketene dimers from acid halides", *J. Am. Chem. Soc.*, **69**: 2444-2448 (1947).
19. Isogai, A., Taniguchi, R. and Onabe, F., "Sizing Mechanism of Alkylketene Dimers, Part 4. Roles of AKD and ketones on AKD sizing", *Nordic Pulp Paper Res. J.*, **9**(1): 44-48 (1994).
20. "Forming Handsheets for Physical Tests of Pulp", Tappi Test Method, T 205 om-88 (1995).
21. "Carboxyl Content of Pulp", Tappi Test Method, T 237 om-93 (1995).
22. "Testing Method for Stöckigt Sizing Degree of Paper", JIS Method P 8122 (1979).
23. Isogai, A., Hasegawa, M., Onabe, F. and Usuda, M., "Changes in  $\zeta$ -Potentials of Amorphous Cellulose Particles with Chitosan Salts", *Sen'i Gakkaishi*, **48**(11): 655-659 (1992).
24. Hasegawa, M., Isogai, A. and Onabe, F., "Molecular Mass Distribution



- of Chitin and Chitosan", *Carbohydr. Res.*, **262**: 161-166 (1994).
25. Marton, J., "Practical Aspects of Alkaline Sizing, Alkyl Ketene Dimer in Mill Furnishes", *Tappi J.*, **74**(8): 187-191 (1991).
  26. Marton, J., "Practical Aspects of Alkaline Sizing, On Kinetics of Alkyl Ketene Dimer Reactions: Hydrolysis of Alkyl Ketene Dimer", *Tappi J.*, **73**(11): 139-143 (1990).
  27. Allan, G. G., Fox, J. R., Grosby, G. D. and Sarkanen, K. V., "Fiber-Water Interactions in Papermaking", Ed. by Fundamental Research Committee, British Paper and Board Industry Federation, London, pp. 765-794 (1977).
  28. Laleg, M. and Pikulik, I. I., "Wet-Web Strength Increase by Chitosan", *Nordic Pulp Paper Res. J.*, **5**(3): 99-103 (1991).
  29. VÅrum, K. M., Anthonsen, M. W., Grasdalen, H. and Smidsrød, O., "Determination of the Degree of N-Acetylation and the Distribution of N-Acetyl Groups in Partially N-Deacetylated Chitins (Chitosans) by High-Field n.m.r. Spectroscopy", *Carbohydr. Res.*, **211**: 17-23 (1991).
  30. Sashiwa, H., Saimoto, H., Shigemasa, Y., Ogawa, R. and Tokura, S., "Distribution of the Acetamide Group in Partially Deacetylated Chitins", *Carbohydr. Polym.*, **16**: 291-296 (1991).
  31. Ström, G., Carisson, G. and Kiar, M. "Bestimmung der Alkylketene-dimer-Verteilung in Probeblättern mittels Elektronenspektroskopie (ESCA)", *Wochenblatt für Papierfabrikation*, **120**(15): 606-611 (1992).

# Transcription of Discussion

## Factors Influencing on Retention of AKD

*Dr A Isogai, Associate Professor, University of Tokyo, Japan*

*Professor John Roberts, UMIST, UK*

This is very controversial indeed which isn't such a bad thing for a meeting like this. I am just puzzled by the C13 NMR data and why it does not square with the data in the literature which has been published before. I notice you treated the sheets with cellulases. I presume that it is to hydrolyse the cellulose and give you an enhanced signal from the residual AKD-reacted cellulose. You used a period of something like 5 weeks I think at a pH of 5, and I am not entirely sure that a  $\beta$ -keto-ester would withstand that kind of treatment without hydrolysis. It may hydrolyse in that period of time and explain the results that you got. Since the rest of your analysis rests heavily on the assumption that you do not have  $\beta$ -keto-ester formation - it seems a crucial part of your work.

*A Isogai*

We have checked, using model compounds, the stability of  $\beta$ -keto esters under the conditions of the cellulase treatment and found that no cleavage occurred. So, I am sure that the beta keto esters are stable to the conditions of the cellulase treatment.

There are some differences in conditions for preparing samples and for obtaining NMR spectra between my data and those in the literatures. I did not apply the subtractions of NMR spectra, because as long as the cross-polarization technique is used, quantitative resonance peaks cannot be obtained. Furthermore, I did not heat the samples at high humidity for a long time, such as several hours. These differences may have led to the discrepancy between my NMR spectra and those in the literatures.

*Susan Ehrhardt, Research Chemist, Hercules Inc, USA*

It was shown back in the 80's that drying conditions have a large impact on size development. Air drying at 20°C, followed by dry heating does not result in good reaction or good size development. Your experimental conditions might be contributing to the lack of reaction that you are seeing.

*A Isogai*

Indeed, sizing degrees after drum-drying of wet webs are little higher than those after air-drying followed by curing. However, they are not so distinguished.

*Susan Ehrhardt*

Everyone that does work on sizing uses a different measure of sizing - Cobb, HST, Stöckigt - all which differ in their sensitivity. So, big differences in sizing may not show up with the Stöckigt which is less sensitive at high levels of sizing. It would be nice if we all used the same set of sizing tests.

*A Isogai*

In Japan, we adopt Stöckigt sizing degree according to Japanese Industrial Standard. However, we are trying to obtain the relationship in sizing degrees between Stöckigt test and HST. We would like to have a HST.

*Michaela Hofbauer, Hercules European Research Centre BV, Netherlands*

You said you studied the stability of the beta-keto-ester - with the model compound did you include the cellulases in that study?

*A Isogai*

In the case of model experiment, after freeze-drying of the mixture containing the model compound and cellulase in the acetate buffer, the residue was extracted by chloroform. And the chloroform-soluble fraction was subjected to NMR analysis to see the stability of the model compound to the cellulase treatment conditions. So, cellulase was excluded from the model compound.

*Rasik Somaiya, R&D Chemist, Sonoco Products Co, USA*

You know that when you size the paper with AKD you get three forms of AKD in paper. There one which is reacted to cellulose, the unreacted one is found in two states - one not hydrolysed and one hydrolysed which is keto form. Would your GC Pyrolysis method be able to distinguish all these three states and if so how?

*A Isogai*

No it is not. All components come out as the structure of ketones by pyrolysis-gas chromatography.

*Rasik Somaiya*

In that case, you cannot distinguish between free unreacted AKD, free unreacted ketone and reacted AKD using PGC method.

*A Isogai*

No we cannot distinguish. We only see ketone.

*Gil Garnier, Research Engineer, Paprican/McGill, Canada*

You state that tone AKD is more hydrophobic than AKD - do you have any physical evidence to support this statement?

*A Isogai*

We measured contact angles of water drops on AKD and ketones, which were prepared by pouring their chloroform solutions on glass plates. And AKD and ketones had about 70 and 90 degrees, respectively, I think.

*Gil Garnier*

We have done exactly the same thing with ASA and also with Palmitone which is a model for the AKD ketone. We have found that Palmitone has a much lower capacity of sizing than AKD: the contact angle of water is significantly lower than on AKD. We do have physical evidence and proof of that. So we have to disagree with you.

The second point - you extracted your AKD samples 80 times at 60°. I find that a little bit harsh and I think it would be good to have a control experiment. I would suggest you treat a long cellulose ester of low degree of substitution to the same harsh treatment and observed what happens to the ester groups.

*A Isogai*

In your case, probably palmitone forms strong coagulants, thus resulting in the lower sizing or lower contact angle. So, you have to see exactly the distribution states of such hydrophobic compounds on glass plates or other hydrophilic materials. In the case of the Tween 80 treatment we have checked the stability of the ester linkage using model compounds and also you see the Tween 80 itself has the ester linkage. So I don't think it is dangerous to cleave the ester linkage during the extraction treatment.

*G Garnier*

It is an extremely harsh treatment and you can undergo a lot of changes as Prof. Roberts earlier mentioned.

*Professor Tom Lindström comment:*

I would like to put forward a general comment on scientific methodology. If we come up with a new hypothesis, which does not conform with the literature - it's very important that we try to explain what was the problem with the previous theory. A new theory must necessarily emulate previous R&D and explain previous experimental facts on what was the flaw with those experiments.