

Quantitative Determination of Alkyl Ketene Dimer (AKD) Retention in Paper Made on a Pilot Paper Machine

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Abstract: There have been some problems reported associated with the use of alkyl ketene dimer (AKD) in alkali papermaking. Excessive use of size emulsion, poor size performance when filler used, problems with back water contamination, poor retention, and formation of pitch deposits on machinery are some of the problems experienced during papermaking operations. In addition, paper containing AKD is reported to lose its resistance, over time against liquid penetration and tends to become slippery. Therefore, in this study, the retention and reaction mechanisms of AKD internal sizing agent in a paper matrix were investigated by capillary gas chromatography (GC) in an attempt to better understand paper sizing with AKD. Results are expressed as the mean value of at least three repetitive tests along with standard deviation (SD) and coefficient of variation (COV). A number of different paper samples were made on a pilot paper machine with different AKD addition levels. AKD levels in wet and machine dry paper were extracted and analysed in GC. Precipitated calcium carbonate (PCC) loading was observed to increase AKD retention. The amount of bound AKD in wet paper significantly increased as a result of drying. Nevertheless, in general the reacted AKD only constituted a very small portion of the total retained AKD. Paper sizing was found to be achieved by bound AKD. This means that an even lower additional level of AKD would be sufficient to ensure good paper sizing provided that it forms a chemical bond with furnish. This result is believed to be important in solving some problems associated with AKD sizing.

Key Words: Alkali paper, AKD sizing, retention, gas chromatography

Alkil Keten Dimer (AKD)'in Pilot Kağıt Makinasında Yapılan Kağıtlardaki Tutunmasının Kantitatif Olarak Belirlenmesi

Özet: Alkali kağıt yapımında Alkil Keten Dimer (AKD) kullanılması ile bağlantılı olan bir takım problemler olduğu bildirilmektedir. Aşırı dozda emülsiyon kullanımı, dolgu maddesi kullanıldığında düşük iç yapıştırma performansı, elek altı suyu kontaminasyon problemleri, zayıf tutunma ve makinalarda yapışkan benekcikler oluşumu gibi problemler kağıt yapımı sırasında karşılaşılan problemlerden bazılarıdır. Ayrıca AKD içeren kağıtların zaman içerisinde sıvılara olan dirençlerini kaybettikleri ve kaygan bir yapıya ulaştıklarında bildirilmektedir. Bu nedenle bu çalışmada, alkil keten dimer (AKD)'in kağıt içerisindeki tutunma ve reaksiyon mekanizması, AKD ile iç yapıştırmayı daha iyi anlayabilmek için kapılar gaz kromatografisi (GC) kullanılarak araştırılmıştır. Sonuçlar en az üç testin ortalaması olarak, standart sapma (SD) ve varyasyon katsayısı (COV) ile verilmiştir. Bir seri kağıt örnekleri, pilot kağıt makinasında farklı AKD katılımları ile üretilmiştir. Islak ve makina kurusu kağıtlar içerisinde bulunan AKD ekstrakte edilmiş ve GC'de incelenmiştir. Kağıt hamuruna çökeltilmiş kalsiyum karbonat (PCC) eklenmesi AKD tutunmasını artırmıştır. Islak kağıtlar içerisindeki selüloz liflerine bağlanmış olan AKD miktarında kağıtların kurutulması sonucu önemli bir artış gerçekleşmiştir. Bununla birlikte genel olarak, bağlı AKD miktarı kağıt içerisinde tutunmuş olan toplam AKD'nin ancak çok küçük bir yüzdesini oluşturmaktadır. İç yapıştırmanın bağlanmış AKD tarafından sağlandığı bulunmuştur. Bu selüloz lifleri ile kimyasal bağ yaptığı sürece çok daha az bir AKD katılmasının iyi bir iç yapıştırma için yeterli olacağını göstermektedir. Bu sonucun, yukarıda bahsedilmiş olan AKD iç yapıştırmasında karşılaşılan bazı problemlerin çözümü açısından önemli olduğuna inanılmaktadır.

Anahtar Sözcükler: Alkali kağıt, AKD iç yapıştırma, tutunma, gaz kromatografi

Introduction

Over the last two decades the paper industry has witnessed a rapid conversion from an acid to neutral/alkali system where alkyl ketene dimer (AKD) is the main sizing agent extensively used in the pH range of 7-10 (Dumas, 1980; Abell, 1985; Wiley, 1989; Crouse and Wimer, 1990). AKDs are waxy materials which are

insoluble in water and have a melting point around 50 °C depending on chain length. Commercial AKD's are prepared from natural fatty acid sources and stearic acid is mainly used for this purpose. Industrial AKD's might have a different side chain lengths due to the fact that the source material itself could have a variety of chain lengths (Roberts, 1996).

In the mixing box of the paper machine, a relatively low level of AKD (0.1-0.5% on oven dry furnish) compared to the traditional rosin sizing (2 to 4% on oven dry furnish) is added to thin stock during internal sizing applications. Therefore, maintaining high machine retention is the first important step in order to have better sizing. It is known that AKD retention is quite sensitive to stock pH and it has been reported to be better at pH 8 (Roberts et al., 1985).

The second important step in AKD sizing is the reaction mechanism with furnishes, though this is still a point of discussion. In general it is believed that AKD reacts with cellulose fibre and forms a beta-keto ester bond, hence making paper hydrophobic (Eklund and Linstrom, 1991; Roberts, 1996). AKD also reacts with water molecules producing an unstable beta-keto acid which then decarboxylates to form a ketone, as illustrated in Figure 1 (Bottroff and Sullivan, 1993). The reaction rate between AKD and water is reported to be faster than that with cellulose fibre (Roberts et al., 1985). There have been different explanations for the sizing effects of these two reaction products. Some researchers claim that the reaction between AKD and cellulose is essential for paper water repellency (Odberg et al., 1987; Eklund and Linstrom, 1991; Roberts, 1996), whereas others believe that such a reaction does not take place at all and is not necessary for sizing (Rohringer et al., 1985; Taniguchi, 1995). Calcium carbonate loading is reported to increase AKD demand in paper. However, the reason remains to

be explained. Therefore, it is important to clarify the point to have a better understanding of not only the sizing mechanism, but also the reasons responsible for some problems, such as size reversion and lower friction, experienced when using AKD sized paper products. The objectives of this study were as follows:

- 1- To better understand the retention mechanism of AKD at the wet end;
- 2- To see the effect of machine drying on AKD reaction with furnish;
- 3- To quantify the reacted and unreacted AKD present in paper, and;
- 4- To study the effects of precipitated calcium carbonate (PCC) on AKD sizing.

Materials and Methods

Materials

The pulp used was a blend of 70% bleached hardwood (Lapponia birch) and 30% bleached softwood (Lapponia pine) beaten to 35° SR in a disc refiner. Filler used was PCC (snowflake) with a particle size of 22 µm. The oil absorbent capacity of PCC used in this study was previously measured to be 19-35 g/100g and the surface area was 12 m² g⁻¹ (Neill, 1996).

AKD sizing emulsion was supplied by Raisio Chemicals, Blackburn, U.K., and the solid content was as

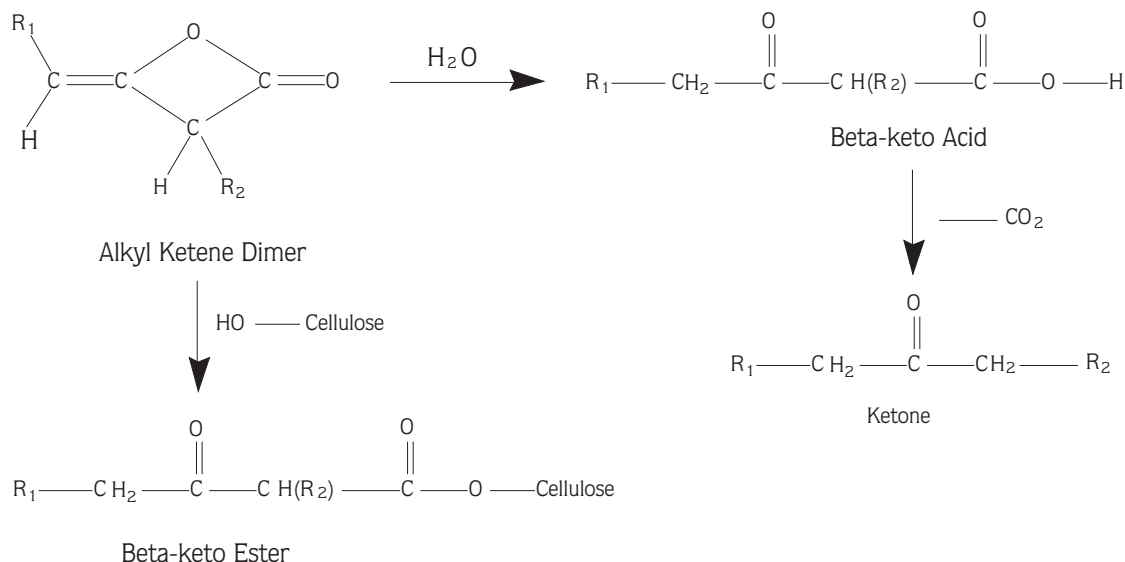


Figure 1. The proposed reaction mechanisms of alkyl ketene dimer with cellulose fibre and water.

follows: 6% AKD, 1.5% cationic starch. Cationic starch (Raisamyl 150 EH) was used as a stabilizer in the emulsion. The retention aid used was a blend of 50% medium and 50% high molecular weight anionic polyacrylamide at an addition level of 0.01% g on dry furnish. All chemicals and solvents used in the extraction procedure were of high quality high performance liquid chromatography (HPLC) grade.

Papermaking

Two different furnishes, one of which was a 70/30% bleached hardwood/softwood mixture and the other was the same fibre mixture with 10% PCC loading, were used to make papers in the UMIST (University of Manchester Institute of Science and Technology) Paper Science Fourdrinier pilot paper machine. The machine was operated with 16 kg cm^{-1} press pressure and at 60 to 90 °C at 10 m min^{-1} production speed.

Only fresh water was used in all trials to avoid building up chemicals and broke in the backwater. The sizing emulsion was diluted with deionised water just before addition. The filler and AKD emulsion were pumped in the system at the mixing box. The machine addition levels for AKD used were chosen for each furnish as 0.1, 0.2, 0.3, 0.4 and 0.5% of actual amount of size on oven dry furnish.

Typical 80 gm^{-2} photocopy papers were produced, conditioned at $23 \pm 2 \text{ °C}$ in $50 \pm 3\%$ relative humidity (RH) for one day and used for testing. The sizing degree of machine dried paper samples were determined by performing a Hercules size test (HST) in accordance with Tappi test method T530 om-96.

AKD extraction and GC study

For extraction work, two different series of paper samples were analysed, one of which was taken just after wet press as undried paper mat, and the other was from the reel as machine dry. The moisture content of wet papers and dry papers were found to be 55% and 6% respectively.

Samples were at first soxhlet extracted with dichloromethane at 60-70 °C for 24 h to take out the unreacted sizing, namely unbound AKD. Then second step extraction work was carried out using the same paper samples. A 22.4 g sample of potassium hydroxide was dissolved in 1 l of methanol to make up the extraction solvent. Paper samples were kept in the solvent at 40-50 °C for 3 h, which followed the acidification with HCl and

repetitive separation with toluene. Collected toluene layers were mixed with anhydrous magnesium sulphate and filtered. Samples from both extractions were evaporated, mixed with internal standard solution (IS) and analysed by gas chromatography (GC).

The Perkin Elmer 1022 GC Plus GC instrument equipped with a Flame Ionisation Detector (FID) was used to analyse the extracts. A 25 m new non-polar capillary column containing the stationary materials of 5% Phenyl and 95% Dimethyl polysiloxane coating the inner wall of the column was used. Hexadecane as an internal standard (IS) and toluene as a solvent were used for GC calibration and study. A typical AKD chromatogram obtained from GC is shown in Figure 2, where four identical peaks for AKD were clearly seen with a peak referring to the IS.

Results and Discussion

Retention of AKD in Paper

Size retention is expressed as the percentage of total sizing extracted from wet paper samples in Table 1. Extraction of AKD particles from wet paper samples was believed to be much easier than that from machine dried paper samples due to the fact that without heat application retained AKD particles were reported to remain on fibres and fillers in paper structure in an unreacted form (Isogai, 1999) which was relatively easy to take out with solvents than that of the reacted form.

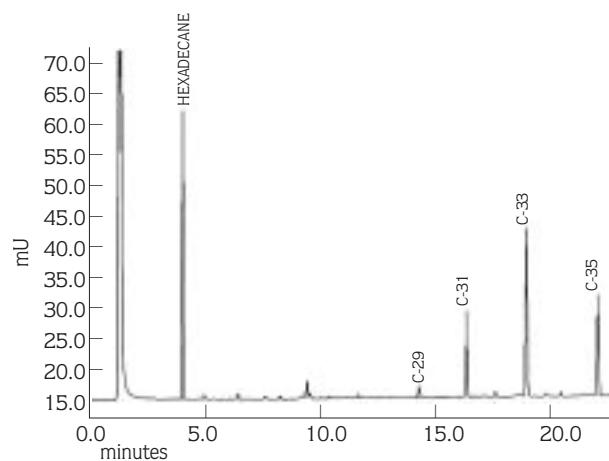


Figure 2. The capillary gas chromatogram of alkyl ketene dimer. (C refers to the carbon atom and the numbers besides C refer to the number of carbon atoms in different chain lengths of alkyl ketene fracture detected in gas chromatography. Hexadecane is the peak of internal standard).

Total AKD Retention Determined on Wet Paper Samples							
Samples with No PCC				Samples with 10% PCC			
AKD Addition (mg/g)	Retention Mean (%)	SD	COV (%)	AKD Addition (mg/g)	Retention Mean (%)	SD	COV (%)
0	0	0	0	0	0	0	0
1	26	3	12	1	58	7	11
2	21	2	11	2	56	4	7
3	31	1	4	3	60	3	4
4	45	2	4	4	63	3	5
5	51	2	4	5	75	3	4

Table 1. Statistical analyses of total AKD retention. It is the combination of both unbound and bound AKD extracted from wet paper samples which was expressed as the percentage of actual added AKD content. Number of test specimens were taken as three. (AKD: Alkyl Ketene Dimer, PCC: Precipitated Calcium Carbonate, SD: Standard Deviation, COV: Coefficient of Variance).

As explained before, size retention in the wet end is chiefly maintained by opposite charge attraction and heterocoagulation where any strong covalent bonds between chemicals and cellulose fibres and fillers have not been formed yet (Isogai et al., 1994; Cooper et al., 1995). Anionic retention aid was naturally expected to create a bridging mechanism between positively charged particles. It seems to work well since the figures were of an acceptable level for industry.

PCC loading was observed to increase size retention around twofold. Cationic starch used as a stabilizer in the emulsion was believed to attach the AKD particles to the negatively charged cellulose fibres and PCC particles, as reported by others (Hedborg and Linstrom, 1993; Voutilainen, 1996). Charge attraction between AKD and PCC was apparently stronger than that between AKD and fibres. It could be also attributed to the larger surface area and oil absorbency property of PCC particles.

Reaction Between AKD and Furnish

It is clearly seen in Figure 2 that in wet paper there was a negligible amount of reacted AKD (bound AKD), which confirms earlier findings (Roberts and David, 1985; Odberg et al., 1987; Marton, 1990). The small amounts of bound AKD found in wet paper samples could be attributed to two factors. One is the possibility of unstabilized AKD molecules present in the emulsion which may have formed a chemical attachment to the cellulose fibre and filler particles. The second factor is the possibility of dissolved AKD molecules trapped in the inner part of the cellulose fibres and filler cavities. These two factors are equally valid in the evaluation of dry paper extractions as suggested by Odberg et al. (1987).

Although PCC increased total AKD retention (Table 1), it did not create a remarkable increase in the amount of bound AKD at the wet end (Table 2). This suggests that PCC particles are much more effective in absorbing and attracting AKD molecules than cellulose fibres as reported before (Hedborg and Linstrom, 1993; Voutilainen, 1996). Furthermore, it also shows that in the wet end AKD retention is almost achieved by physical means rather than via chemical formation.

The amount of bound AKD in wet paper samples was significantly increased as a result of drying as seen in Table 3 and Figure 3, which clearly show the positive effects of temperature on the reaction between AKD and furnish as stated before (Roberts and Garner, 1985; Odberg et al., 1987; Marton, 1990). In the case of filled paper, the increase in bound AKD after paper drying was around fivefold (Table 3 and Figure 3). Having the melting point of 50 °C during drying, retained AKD in paper was thought to melt and eventually resulted in spreading over and penetrating to the inner part of the paper structure. During this mechanism, reactive sites of the furnish and AKD molecules probably had more chance to come into contact leading to a number of chemical reactions. Dried paper having filler evidently seems to have more reacted AKD as seen in Figure 3. This could be attributed to the larger surface area and oil absorbency properties of the filler. Having very small and porous particles, PCC was expected to hold a substantial amount of AKD trapped inside the filler particles (Bottorff, 1993; Bartz et al., 1994; Voutilainen, 1996). It was also possible that there might have been some chemical reaction between AKD and PCC (Jiang et al., 2000).

AKD Extraction From Wet Paper Samples								
Samples with No PCC					Samples with 10% PCC			
Form of AKD Extracted	AKD Addition (mg/g)	Retention Mean (mg/g)	SD	COV (%)	AKD Addition (mg/g)	Retention Mean (mg/g)	SD	COV (%)
Unbound AKD (mg/g)	0	0.00	0.00	0	0	0.00	0.00	0
	1	0.22	0.04	16	1	0.53	0.06	11
	2	0.39	0.06	14	2	1.06	0.09	9
	3	0.86	0.04	4	3	1.72	0.09	5
	4	1.71	0.07	4	4	2.38	0.10	4
	5	2.40	0.10	4	5	3.61	0.13	4
Bound AKD (mg/g)	0	0.00	0.00	0	0	0.00	0.00	0
	1	0.04	0.01	25	1	0.05	0.01	20
	2	0.04	0.01	25	2	0.06	0.01	20
	3	0.07	0.01	16	3	0.09	0.02	18
	4	0.09	0.02	18	4	0.14	0.03	18
	5	0.13	0.02	16	5	0.16	0.03	16

Table 2. Results of wet paper extractions showing the amount of unbound and bound AKD along with statistical analyses. Three samples for each addition levels were analysed for the extraction work. (AKD: Alkyl Ketene Dimer, PCC: Precipitated Calcium Carbonate, SD: Standard Deviation, COV: Coefficient of Variance).

AKD Extraction From Machine Dried Paper Samples								
Samples with No PCC					Samples with 10% PCC			
Form of AKD Extracted	AKD Addition (mg/g)	Retention Mean (mg/g)	SD	COV (%)	AKD Addition (mg/g)	Retention Mean (mg/g)	SD	COV (%)
Unbound AKD (mg/g)	0	0.00	0.00	0	0	0.00	0.00	0
	1	0.19	0.04	19	1	0.37	0.08	21
	2	0.27	0.05	19	2	0.84	0.12	14
	3	0.77	0.09	12	3	1.31	0.13	10
	4	1.36	0.10	8	4	1.70	0.13	8
	5	1.81	0.13	7	5	2.83	0.17	6
Bound AKD (mg/g)	0	0.00	0.00	0	0	0.00	0.00	0
	1	0.09	0.02	16	1	0.24	0.05	19
	2	0.16	0.02	13	2	0.39	0.06	16
	3	0.28	0.04	13	3	0.76	0.10	13
	4	0.28	0.04	13	4	0.81	0.09	11
	5	0.33	0.05	14	5	0.77	0.07	9

Table 3. Results of machine dried paper extractions showing the amount of unbound and bound AKD along with statistical analyses. Three samples for each addition levels were analysed for the extraction work. (AKD: Alkyl Ketene Dimer, PCC: Precipitated Calcium Carbonate, SD: Standard Deviation, COV: Coefficient of Variance).

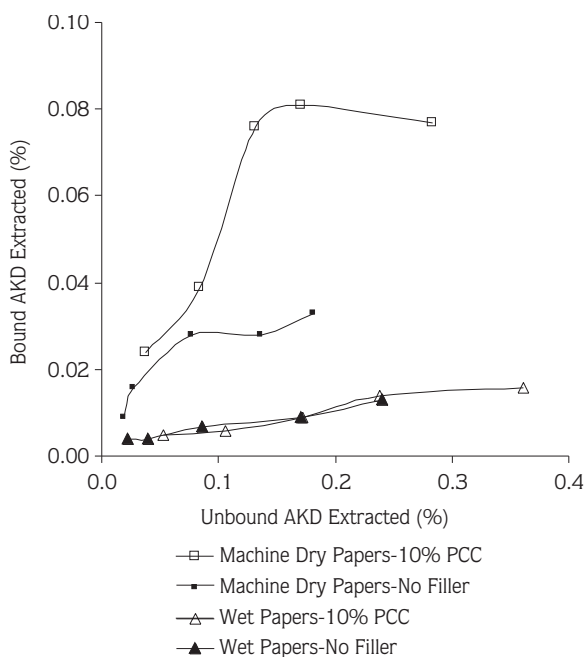


Figure 3. The amounts of bound AKD versus unbound AKD extracted from both wet and machine dry paper samples. (AKD: alkyl ketene dimer, PCC: precipitated calcium carbonate).

It was notable that the amount of reacted sizing agents in dried paper showed a rapid increase until some addition point, and then levelled out (Figure 3). It was postulated that when available reactive groups on furnishes were used, no further reactions would take place. It should be noted that, in general, even the highest amount of extracted AKD could only constitute a very small percentage of reacted AKD in paper (Table 3). This clearly proves that the reaction rate between AKD and fibre as well as PCC is quite slow even at elevated temperatures (Roberts and Garner, 1985; Taniguchi et al., 1993; Isogai, 1999). As seen in Table 3, at the highest AKD addition (5 mg/g) level to the PCC containing paper, the bound AKD was found to be only 0.77 mg/g and unbound AKD was about 2.83 mg/g. Therefore, only 21% of total retained AKD did develop a covalent bond with furnish. In other words, only 15% of added AKD was chemically attached to the cellulose fibres. This is quite a small quantity compared to the paper weight, which is proportionally about 0.077% AKD on dry furnish. If it is the case then the rest of the AKD present in paper is thought to stay on top of cellulose fibres as well as fillers by electrostatic forces. These parts are believed to be ineffective in sizing efficiency (Marton,

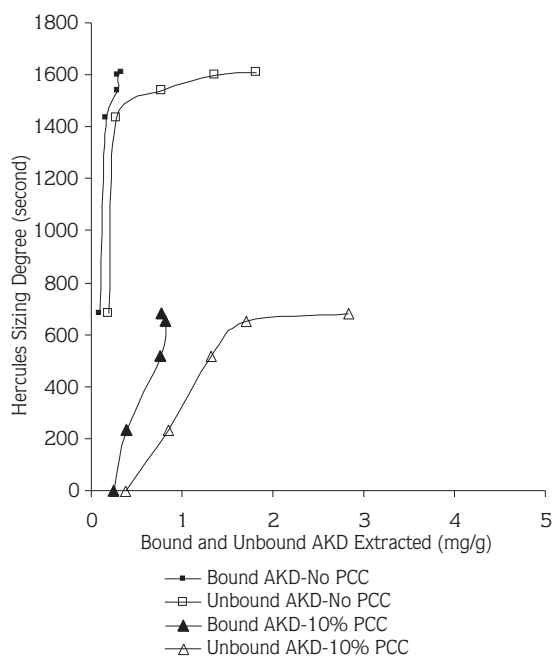


Figure 4. Hercules sizing degree of filled and unfilled paper samples versus the amount of both bound and unbound AKD determined in representative paper samples. (AKD: alkyl ketene dimer, PCC: precipitated calcium carbonate).

1990) and later in time are expected to hydrolyse (Bartz et al., 1994). Unreacted and hydrolysed AKD is also believed to be responsible for the lower frictional properties of papers.

Sizing Degree of Papers

HST values of filled and unfilled papers were plotted against their extracted size contents, as seen in Figure 4. The sizing degree of papers seems to be maintained by bound AKD. It is clearly seen in Figure 4 that when the highest HST values were obtained, constant increases in unbound AKD content in paper had no effect on sizing. This finding is an agreement with earlier reports (Odberg et al., 1987; Roberts 1996).

Although filled papers contained a higher amount of both unbound and bound AKD than unfilled papers (Table 3), interestingly their sizing degrees were significantly lower than those of unfilled papers (Table 4). This was believed to be most probably due to the higher surface area of PCC particles. The surface area of bleached softwood (Odberg et al., 1987) and PCC particles (Gill, 1990; Neill, 1996) were reported to be on average 1 and 12 m² g⁻¹ respectively, which clearly implies that paper containing PCC would require a greater amount of sizing

Hercules Size Degree of Paper Samples							
Samples with No PCC				Samples with 10% PCC			
AKD Addition (mg/g)	HST Mean (Second)	SD	COV (%)	AKD Addition (mg/g)	HST Mean (Second)	SD	COV (%)
1	682	39	6	1	3	2	46
2	1430	57	4	2	222	15	7
3	1533	50	3	3	523	37	7
4	1601	61	4	4	660	40	6
5	1607	60	4	5	664	41	6

Table 4. Results of Hercules sizing tests (HST) of machine dried papers along with statistical analysis. Three samples for each addition levels were analysed for the extraction work. (AKD: alkyl ketene dimer, PCC: precipitated calcium carbonate, HST: hercules sizing test, SD: standard deviation, COV: coefficient of variance).

chemical than unfilled paper to have good water repellency. In addition, the porous particle structure of PCC should also be taken into account since a substantial amount of melted AKD was reported to be trapped inside the voids of fillers and between filler particles in machine dried sheets (Bottorff, 1993; Bartz et al., 1994; Voutilainen, 1996). AKD molecules staying in the voids and cavities of filler could not contribute to sizing as much as those covering the surface area of both cellulose fibres and filler particles. Therefore, it is probably better to use less porous fillers with larger particle size in sizing.

Conclusions

AKD retention at the wet end was quantitatively determined by employing capillary GC. Retention was thought to be due to opposite charge attraction rather than any strong chemical formation. Interaction between

AKD and PCC compared to cellulose fibre was stronger. Paper drying was found to cause a remarkable increase in the reaction between AKD and furnishes. Nevertheless, it was found that in general the reacted part of the sizing chemical was quite small compared with total retained AKD. The rest of the unreacted AKD and those adsorbed on to fillers are of great concern since it is thought they cause a size reversion as a result of hydrolyzation in time (Patton, 1991; Bartz et al., 1994; Jiang et al., 2000). It was shown that it is the bound AKD that makes paper hydrophobic. Therefore, it is concluded that the use of an appropriate amount of AKD in paper should be applied as well as developing some quick way to make them all chemically attached to the furnishes to get a perfect sizing operation. Hence, the overall reacted portion of added AKD was so small that excessive size addition should be avoided by promoting an increase in the quantity of reacted AKD in paper.

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