UV/Vis Spectrometry-Based Analysis of Alkyl Ketene Dimer (AKD) Retention to Solve the Waxy Spot Problem in the Papermaking Process

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ABSTRACT: A sudden surge in the number of translucent and oval-shaped waxy spots caused a serious production loss of the papermaking process. The investigation of the spots revealed that the alkyl ketene dimer (AKD) sizing agent caused the waxy spot problem. A ultraviolet/visible (UV/vis) spectrometry method for the quantitative analysis of AKD was developed and used to reduce the waxy spot problem in paper products. The results showed that the method could be used to quantify AKD in both papermaking stock and white water. The major factors in the papermaking wet end that were associated with the waxy spot problem were evaluated, and practical approaches to solving the AKD retention problem and the waxy spot problem were proposed and implemented. The dosage of a retention aid was found to be the principal factor controlling AKD retention. However, varying the retention aid dosage resulted in the deterioration of the paper formation; therefore, this was not a suitable solution to the waxy spot problem. The type of fixing agent and AKD used was found to be the secondary factor affecting the AKD retention and papermaking system cleanliness. Mill trials were conducted on a paper machine to examine the effects of different fixing agents and AKD types on AKD retention and the waxy spot count at the reel. This approach identified a combination of fixing agent and AKD type that substantially improved AKD retention and reduced the formation of translucent waxy spots in the resulting paper products.

1. INTRODUCTION

The hydrophilicity of the cellulose fiber that forms the basic structure of paper means that paper tends to be highly water absorbing. This limits the use of paper in many types of packaging, printing, and writing. To control the water absorption property of paper, various internal sizing agents have been developed. Alkyl ketene dimer (AKD), which was developed by Downey1 and introduced by Davis et al.,2 is one of the most widely used internal sizing agents for printing and writing grades of paper.

AKD can be anchored to paper without the use of papermaking alum (aluminum sulfate) because it reacts with the hydroxyl group of cellulose to form ester bonds.3,4 However, the slow rate of this esterification reaction5−7 often causes problems that do not occur when conventional rosin-based sizing agents are used. Problems such as slippery paper8,9 and size reversion10,11 are attributable to AKD sizing. In addition to the slow reactivity of AKD with hydroxyl groups, AKD has been shown to react with water,12 resulting in a dialkylketone that has no or low internal sizing ability.6,13

In addition to having the above-described negative effects on paper properties, AKD also causes problems in the paper production stage. For instance, hydrolyzed AKD has been reported to be the main cause of deposit formation in the papermaking process.14,15 Similarly, we have also observed a periodic pipe plugging problem at the final reject line of the screen system of a paper machine producing printing and writing grades of paper. A chemical analysis of the plugged material retrieved from the screen discharge line confirmed that AKD was the main cause of the plugging problem. Moreover, we also observed white granular deposits on the fabric of polydisk filters, which substantially decreased the filtration efficiency, and the chemical analysis showed that the white deposits were hydrolyzed AKD.

These experiences showed us that it was crucial to manage AKD retention in our papermaking machine to ensure a clean production process. Specifically, when the retention level of AKD is low, it circulates through the short or long circulation lines, where it is exposed to high temperatures for a prolonged...
period of time and is thus hydrolyzed. Therefore, a retention analysis of AKD at the papermaking wet end was essential to determine how to better control the internal sizing of the final paper product and how to prevent AKD hydrolysis and subsequent deposit formation.

Several quantitative or qualitative methods have been proposed for use in AKD retention analysis. For instance, Dart,¹⁶ Yano et al.,¹⁷ and Asakura et al.¹⁸ used a gas chromatography/mass spectroscopy (GC/MS) method to investigate the AKD retention determination. Similarly, Zule and Dolenc¹⁹ used solvent extraction and GC methods for AKD analysis. GC/MS is a good analytical tool, but it would be expensive for regular quantitative analysis in a paper mill. The use of radioactive AKD has been explored by Lindström and Söderberg⁶,⁷,²⁰ and Lee and Luner.¹³ However, this method requires radioactively tagged AKD and is thus not applicable in the industrial context. Near-infrared (NIR) or infrared (IR) spectroscopy can be used for the qualitative analysis, but it is limited in its utility for the quantitative analysis of AKD.²¹,²²

Jaycock and Roberts²³ and Min and Shin²⁴ confirmed that ultraviolet/visible (UV/vis) spectroscopy could be used for the qualitative and quantitative analyses of AKD. However, a more thorough investigation is required to determine its suitability for the AKD retention analysis. Furthermore, both the optimal retention level of AKD and the factors affecting the emulsion stability of AKD must be investigated to solve the above-described problems associated with AKD use in papermaking processes.

Accordingly, we have investigated a UV/vis spectrometry-based method for the quantitative analysis of AKD in the papermaking process and also used this for the AKD retention analysis. Based on this method, seven major factors in the papermaking wet end were evaluated to find the most practical methods to increase AKD retention and prevent the production of substandard paper products. These factors included retention aid dosage, fixing agent dosage, AKD type, fixing agent type, filler types, filler dosage, and pulp type. Finally, we carried out mill trials on a paper machine to determine the ability of the two most important factors that we had identified, i.e., the types of fixing agent and AKD, to enhance AKD retention and waxy spot reduction.

2. RESULTS AND DISCUSSION

2.1. Quantitative Analysis of AKD Retention Using UV/Vis Spectrometry. The effect of the reaction time between AKD and 4-dimethyl aminopyridine (DMAP) in chloroform solution was examined, while the ratio AKD/DMAP was kept constant at 1:120. Figure 1 shows that there is a rapid reaction between AKD and DMAP at a constant 1:120 ratio of AKD/DMAP and that the reaction is complete after 90 min. Thus, 90 min was confirmed as the sufficient reaction time for AKD and DMAP. Next, varying the AKD/DMAP ratio with a constant reaction time of 120 min showed that the reaction progressed until the ratio was 120:1 (Figure 2).

The next experiment showed that 10 min of extraction completed AKD extraction (Figure 3). The turbidity of AKD emulsion decreased rapidly as the extraction proceeded, indicating that the AKD emulsion was dissolved by the extraction solvent, resulting in complete solubilization within 30 min. Moreover, the data in Table 1 show that the presence of other stock components such as pulps and fillers had no
influence on the AKD extraction by chloroform, indicating that AKD was completely extracted from the white water.

The $R^2$ values of the calibration lines (Figure 4) were >0.999, validating the suitability of this method for the AKD retention analysis. The absorbance at 338 nm was higher than that at 450 nm; however, the former absorbance was influenced by the presence of minor contaminants. Thus, the calibration line from the absorbance at 450 nm was used for analysis.

2.2. Effect of Papermaking Stocks on AKD Retention.
The AKD retention effects of stocks prepared using hardwood bleached kraft pulp (BKP) 100%, hardwood BKP 50% + bleached chemithermomechanical pulp (BCTMP) 50% (L5B5), and BCTMP 100% were tested, and the results are shown in Table 2. Pulp type had a substantial effect on AKD retention, with retention in the BKP stock being much higher than that in the BCTMP stock, while the L5B5 stock gave AKD retentions between those of the BKP and BCTMP stocks. When anionic AKD-II was used, the hardwood BKP and BCTMP stocks gave retentions of 50.4 and 17.1%, respectively, showing that anionic AKD was retained significantly less in the BCTMP stock. This was attributable to the fact that BCTMP is shorter in fiber length, contains more fines, and possesses more anionic charges.

Fillers are widely used in papermaking, as they provide economic benefits and improve the printing and optical properties of paper. Fillers, however, also cause problems in the papermaking process and in paper properties. Fillers cause strength loss and linting on the printing press. Furthermore, fillers often cause a substantial reduction in sizing. A number of researchers have investigated the desizing effect of precipitated calcium carbonate (PCC) on AKD sizing.

Table 3 shows the effects of different types of filler on the retention of AKD-I and AKD-II. A retention of 51.5% AKD-I was achieved when no filler was used, while the addition of ground calcium carbonate (GCC) and PCC led to 42.5 and 55.8% AKD-I retention, respectively. As AKD-I is positively charged, it was expected to be more adsorbed onto negatively charged GCC. Retention of anionically charged and small filler particles is lower than that of PCC when no retention aid was used, and this resulted in a reduction of AKD retention for the GCC stock.

Many fine materials, such as fillers, sizing agents, and polymeric emulsions, are contained in a papermaking stock. As the particles of these fines are smaller than the opening of the papermaking fabric, their retention is quite low, especially on a high-speed paper machine. Consequently, these fines will drain out with white water and circulate through the white water circuit, unless they can be adsorbed onto long fiber surfaces or extensively flocculated to be retained on the wet web. To increase the retention of fines, a wide variety of retention systems are used. In this study, we used the Hydrocol retention system, which comprises a cationic poly(acrylamide) (PAM) and bentonite, and evaluated its effect on the retention of fines, including AKD. The relationship between the first-pass retention (FPR) and AKD retention is depicted in Figure 5.

The regression coefficient is 0.762, indicating a strong positive correlation between these two variables and thus suggesting that controlling FPR will enable the effective retention of AKD.

2.3. Factors for Improving FPR of AKD. Table 4 shows the experimental layout of the random-sequence seven-run fractional factorial design used to explore the optimization of AKD retention with different additives.

Table 3. Effect of GCC and PCC Fillers on AKD Retention for Hw-BKP Stock

|            | Hw-BKP only | Hw-BKP + GCC | Hw-BKP + PCC |
|------------|-------------|--------------|--------------|
| AKD-I      | 51.5        | 42.5         | 55.8         |
| AKD-II     | 50.4        | 55.0         | 59.8         |

The regression coefficient is 0.762, indicating a strong positive correlation between these two variables and thus suggesting that controlling FPR will enable the effective retention of AKD.

The experimental layout of the random-sequence seven-run fractional factorial design used to explore the optimization of AKD retention with different additives.

Figure 4. UV/vis spectrum of AKD-I/DMAP reaction product (left) and calibration line for AKD-II (right).

Figure 5. Correlation of first-pass retention in wet end and AKD retention in dynamic drainage analyzer (DDA) vacuum drainage.
Table 4. Experimental Layout of Seven-Run Fractional Factorial Designs and AKD Retention

| no. | BCTMP (%) | fixing agent (%/pulp) | AKD | filler (%/pulp) | PAM/bentonite (%/pulp) | AKD retention (%) |
|-----|-----------|-----------------------|-----|----------------|------------------------|------------------|
| 1   | 20        | PAM                   | 0.025 | AKD-I          | GCC 15                | 0.025/0.125 | 88.6    |
| 2   | 20        | PAM                   | 0.050 | AKD-II         | GCC 30                | 0.050/0.250 | 95.3    |
| 3   | 20        | PAE                   | 0.050 | AKD-I          | PCC 15                | 0.050/0.250 | 95.0    |
| 4   | 20        | PAE                   | 0.025 | AKD-II         | PCC 30                | 0.025/0.125 | 93.0    |
| 5   | 40        | PAM                   | 0.050 | AKD-I          | PCC 30                | 0.025/0.125 | 91.3    |
| 6   | 40        | PAE                   | 0.025 | AKD-II         | PCC 15                | 0.050/0.250 | 94.3    |
| 7   | 40        | PAE                   | 0.025 | AKD-I          | GCC 30                | 0.050/0.250 | 94.0    |
| 8   | 40        | PAE                   | 0.050 | AKD-II         | GCC 15                | 0.025/0.125 | 93.0    |

Figure 6 shows a Pareto chart summarizing the effect of different variables on AKD retention. Briefly, a Pareto chart is invaluable for determining the factors that need the most attention to improve a process. A bar graph with values plotted in decreasing order of the effect on a given system is the usual way to present the data on a Pareto chart. Thus, a Pareto chart is a basic tool of quality control, in which independent variables (in this case, AKD retention) are represented in bars of different lengths. The Pareto analysis showed that retention aid dosage, AKD type, and fixing agent type and dosage were the four main factors affecting AKD retention greater than a threshold (standardized) value.

AKD retention increased in proportion to the retention aid dosage, which showed the importance of FPR for AKD sizing. The main effect plot (not shown) for AKD retention from the fractional factorial experiment data showed that AKD-II performed better than AKD-I when various stock components such as cationic starch and fixing agents were used before AKD addition. The use of fixing agent was found to be an important factor affecting the AKD retention. For example, the addition of polyamidoamine-epichlorohydrine (PAE) resin led to better AKD retention than the addition of a PAM-type fixing agent. The strong cationic charge density of the PAE resin made it effective as a fixing agent for AKD.

2.4. Short-Term Mill Trials with PAE Fixing Agent.

Among the seven factors tested, a 0.025% increase in the retention aid dosage was found to be the most effective way to increase AKD retention. This approach, however, deleteriously affected the formation and other properties of paper. As a second option, we compared the efficacies of two fixing agents in mill trials, i.e., PAE resin and highly branched cationic PAM (HB-CPAM). PAE resin has been widely used as a fixing agent, and it often increases AKD retention. Thus, a mill trial was carried out on a paper machine that produced wood-free paper with a basis weight of 80 g/m². The stock was prepared with 15% softwood BKP, 65% hardwood BKP, and 20% BCTMP, with GCC and PCC used as fillers. The proportions of PCC and GCC were 70 and 30%, respectively, and the total ash content in the paper was approximately 26%.

In the first trial, 0.05% PAE increased the ζ-potential of the machine chest and headbox stocks, which resulted in a 3–4% total retention improvement compared to the control run. This increased retention also increased the sizing degree, did not negatively affect paper formation, and decreased the number of waxy spots per spool by 0.9 spots per reel, which was measured using a web imaging system (ULMA, ABB Ltd., Louth, Ireland) installed at the end of the paper machine.

Nevertheless, we required a greater reduction in the number of waxy spots per spool to produce a better-quality paper. To achieve this, in the second trial, we increased the PAE resin dosage to 0.1–0.2% and decreased the addition of sizing agent from 0.48 to 0.35% (Table 5). Despite this decreased addition of sizing agent, the Stöckigt sizing degree increased from 11 to 15 s. In addition, the FPR increased from 75.5 to 84.6%, and the FPR of ash increased substantially, from 31.3 to 44.1%. We also observed a concomitant improvement in the wire drainage and decreased steam consumption for drying, and the number of defective waxy spots per spool decreased from 19 to 14–15. However, 0.1% or more PAE also led to quenching of the optical brightening agent (OBA) dosage from 1.60 to 1.90%. In addition, the FPR increased from 75.5 to 84.6%, and the FPR of ash increased substantially, from 31.3 to 44.1%. We also observed a concomitant improvement in the wire drainage and decreased steam consumption for drying, and the number of defective waxy spots per spool decreased from 19 to 14–15. However, 0.1% or more PAE also led to quenching of the optical brightening agent (OBA) dosage from 1.60 to 1.90%. To solve this UV quenching effect by PAE, other fixing agents were explored.

2.5. Long-Term Mill Trial Using Highly Branched C-PAM and Anionic AKD. Highly branched cationic PAM
(HB-CPAM) was selected as a new fixing agent because of its high charge density and adsorption properties. A preliminary short-term trial was conducted to investigate this agent’s performance, which revealed that HB-CPAM was quite effective in improving retention, wire drainage, sizing, drying energy reduction, and number of waxy spots. We thus conducted a long-term trial, the results of which are shown in Table 6, which indicates that HB-CPAM leads to FPR and ash retention increases of 10.8 and 17.0%, respectively. An increase in the sizing degree indicates that AKD retention also improves, and long-term defective spot numbers decrease substantially from 12.6 to 8.0 spots/reel.

AKD sizing agents are stabilized emulsions that are usually made from cationic starch or charged polymeric stabilizers. However, cationic or anionic synthetic polyelectrolytes also have been used for AKD stabilization. To examine the effect of AKD type on the defective waxy spot count, we carried out two trials using two AKDs. Alternating the use of AKD-I and AKD-II has been a usual practice in the mill. However, laboratory experiments showed that single application of an anionic AKD was better in many respects. For instance, using anionic AKD only improved the Stöckigt sizing degree from 22.6 to 20.8 g/m². Thus, we decided to stop the alternating application of AKDs and switched to single use of anionic AKD-II.

It can be seen in Figure 7 that the number of spots sporadically surged, sometimes to >100 per spool. These surges of spots occurred primarily when low-grammage products were made, because this necessitated the use of 1.5 times more AKD to keep the sizing level for the low-grammage products. Thus, we switched to using only one type of AKD and HB-PAM fixing agent. As can be seen in Figure 7, these changes prevented any surge of spots and led to a substantial decrease in the total number of spots. These results indicated that the use of a new fixing agent and a single AKD application were efficacious in reducing the formation of waxy spots in low-grammage products and allowed cleaner operation of the papermaking process.

| Table 6. Results of Long-Term Trial Using HB-CPAM in Production of 75 g/m² Copy Paper |
|---------------------------------|----------|----------|
|                                | unit     | control  | trial  |
| HB-CPAM dosage                 | %/pulp   | 0        | 0.02   |
| AKD dosage                     | %/pulp   | 0.15     | 0.12   |
| OBA dosage                     | %/starch | 3.3      | 3.0    |
| retention                      | total    | %        | 69.1   | 79.9   |
|                                | ash      | %        | 38.1   | 55.1   |
| wire couch roll vacuum         | kPa      | 73       | 71     |
| dryer steam pressure (#3)      | kg/cm²   | 2.07     | 2.02   |
| formation index                | %        | 62.4     | 63.0   |
| Cobb                           | g/m²     | 21       | 23     |
| sizing degree                  | Stockigt | 27       | 26     |
|                                | HST      | 462      | 403    |
| defective waxy spots           | EA/spool | 12.6     | 8.0    |

![Figure 7. Number of spots observed over 3 years in 60 g/m² wood-free papers.](image)

3. CONCLUSIONS

A UV/vis spectrometry-based method for the analysis of AKD retention was developed, validated, and applied to investigate the role of several important factors on AKD retention. The effects of extraction time, DMAP/AKD ratio, and reaction time were investigated for the quantitative analysis of AKD using UV/vis spectrometry. The AKD retention was determined by extracting the AKD using chloroform and then treating it with DMAP, followed by a UV/vis analysis at 450 nm. The results showed that an extraction time of 60 min, a DMAP/AKD ratio of 120, and a reaction time of 90 min gave consistent and accurate measurements of AKD content in white water and paper stock. This method was used to investigate the effect of stock components on the quantitative measurement of AKD. A strong correlation between AKD retention and total FPR was found with the $R^2$ value of 0.762. This indicated the importance of retention control to AKD sizing.

To find effective ways of improving AKD retention, the effects of seven variables—retention aid dosage, fixing agent dosage, AKD type, fixing agent type, filler types, filler dosage, and pulp type—on AKD retention were tested. Retention aid dosage was found to be the most important, followed by AKD type, fixing agent type, and dosage, and thus the effects of different values of these four variables were examined in both laboratory and mill trials. The results showed that different retention aid dosages negatively affected paper formation, which made this approach impractical. However, a judicious selection of fixing agent and AKD type improved the AKD retention, drainage performance, and sizing efficiency without deleterious effects on paper formation and OBA quenching. Moreover, these optimal conditions led to substantial decreases in the number of waxy spots without any periodic surges in spot number over a long-term period of production.

4. EXPERIMENTAL SECTION

4.1. Materials. Cationic and anionic AKD emulsions, denoted AKD-I (Taekwang Chemicals, Eumseong, Korea) and AKD-II (Laton Korea, Gongju, Korea), respectively (Table 7), were used in both laboratory experiments and mill trials. The particle size and ζ-potential of AKD emulsions were determined using a Malvern Mastersizer (Malvern Instruments Ltd, Almelo, the Netherlands) and an electrophoretic light scattering spectrophotometer (ELS Z-1000, Otsuka Elec-

| Table 7. Properties of Anionic and Cationic AKDs |
|-----------------------------------------------|--------|--------|
| items                                         | AKD-I  | AKD-II |
| solids content (%)                            | 19.9   | 19.6   |
| viscosity (cPs)                                | 6.6    | 7.2    |
| average particle size (µm)                    | 0.41   | 0.39   |
| ζ-potential (mV)                               | +9.8   | -11.9  |
| stabilizer                                    | starch | starch |
| surfactant                                    | polymer| sodium lignin sulfonate |
Table 8. Operation Conditions of DDA Vacuum Drainage

| Start | Drainage | Finish |
|-------|----------|--------|
| time (s) | -90 | -70 | -50 | -31 | -11 | -1 | 0 | +30 |
| furnish | pulp | +AKD | +filler | +PAM | +bentonite |
| stirring rate (rpm) | 400 | 400 | 400 | 800 | 400 | 0 | 0 | 0 |

“Vacuum pressure, 250 mbar; delay time, 1 s; forming time, 30 s.

Table 9. Seven Factors Examined for Their Effect on AKD Retention

| no. | pulp type | variable | type of variable |
|-----|-----------|----------|-----------------|
| 1   | BCTMP 20% | AKD type | AKD-I            |
| 2   | PAM       | fixing agent type | AKD-II          |
| 3   | 0.025%    | fixing agent dosage | 0.5%           |
| 4   | AKD-I     | AKD type | AKD-II          |
| 5   | GCC       | filler type | PCC            |
| 6   | 15%       | filler dosage | 0.16%          |
| 7   | 0.025/0.125% | PAM/bentonite dosage | 0.050/0.250% |

Figure 8. Flow diagram of the gap-former paper machine used for examining the effect of certain variables and showing the points of introduction of additives. Fixing, fixing agent; A-PAM, anionic poly(acrylamide); MP, micropolymer.
stirred at 400 rpm for 20 s. After this time, 0.5% w/w AKD (based on the dry weight of pulp) was added to the stock, and the resulting mixture was stirred for 40 s and then drained. The DDA vacuum level of the dynamic drainage analyzer was adjusted to 250 mbar, and the first-pass retention value was determined from the solids content and turbidity of the drained white water. To determine the AKD retention, a 100 g sample of white water was mixed with 100 g of chloroform in a separation funnel and vigorously shaken for 1 h to extract AKD. Next, a 50 g aliquot of this chloroform solution was taken and treated with DMAP whose weight is equal to the weight of 120 times of AKD, and an aliquot of the resulting mixture was analyzed by UV/vis spectrometry.

The effect of filler types and retention systems on AKD retention were evaluated using the same method used to examine the effect of pulp type. AKD and filler were added after 20 and 40 s of stirring, respectively, and the resulting mixture was drained 20 s after the addition of filler. When the retention aid was used, the addition points and stirring speed shown in Table 8 were used in the experiment. They were chosen to simulate the conditions of the papermaking process.

4.2.3. Influence of Additives on AKD Retention and Mill Trials. To investigate the effect of papermaking raw materials or additives on AKD retention, a fractional factorial experiment design was used. Each of the seven factors shown in Table 9 was examined at two levels to assess the effect of these factors on AKD retention in a laboratory setting, and the resulting data were statistically analyzed.

Next, mill trials were performed to examine the effect of the two most important variables, as determined by the above laboratory experiment, on AKD retention. These trials were performed on a gap-former paper machine producing printing paper and writing grades papers at a machine speed of 1200 m/min. The points at which the additives were introduced are depicted in Figure 8.

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**Notes**

The authors declare no competing financial interest.

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