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Effect of Spreading of Neutral Sizing Agent, Alkylketene Dimer, on Sizing Development

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ABSTRACT

The objective of this work was to investigate the effect of spreading behavior of the sizing agents (AKD or dialkyl ketone) on the sizing development of AKD-sized paper. There was a direct relationship between the spreading behavior of the sizing agents and their melting points. Both AKD and dialkyl ketone showed no substantial spreading until the temperature reaches to their melting points. Consequently, dialkyl ketone did not provide sizing development when the paper was heat-treated below 75℃, while AKD provided sizing effect even the paper heated at 50℃. The ketone, however, provided rather higher sizing effect than that of AKD, when the paper was heat-treated over 100℃. This result means that the ketone also gives sizing development to paper, moreover the ketone could give higher sizing effect to paper than AKD when it was melted and well spreaded on the fiber surface. While the ketone introduced to papers from hydrolyzed AKD emulsion could not contribute to sizing development.

Keywords : alkylketene dimer, spreading, ketone, sizing agent, sizing development, AKD sizing

1. Introduction

It was well known that a dialkyl ketone was produced by the hydrolysis of AKD in AKD-sized paper. Zhou (1) reported that considerable amounts of AKD were hydrolyzed during storage from the observation of the IR spectra of the extracts of AKD sized paper. Akapio and Roberts (2) suggested that one gram of tetradecyl ketene dimer required theoretically only 0.04 g of water to completely convert it to palmitone, therefore, about 8% moisture content of paper would be enough to hydrolyze the dimer to palmitone. However, it was reported (1-4) that hydrolyzed AKD(ketone) did not provide sizing effect to

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AKD-sized paper because the ketone could not react with cellulose to form a covalent linkage. Isogai et al. (5) reported that the partial hydrolysis of AKD on the surface of emulsion particles probably brings about the remarkable decrease in dispersibility of the emulsion with the increase in hydrophobicity of emulsion, and that the decrease of dispersibility leads to the decrease in sizing effect.

In previous paper (6), it was known that AKD reacted rarely with cellulose in the presence of water and most of AKD was converted to a dialkyl ketone through the reaction with water. Therefore, the actual sizing agents should not be β-ketoesters of cellulose, but unreacted AKD and hydrolyzed AKD(ketone). Comparing hydrophobicity of the sizing agent, it was shown that the ketone could give higher hydrophobicity to cellulosic fibers than unreacted AKD.

In this study, the effect of the melting and spreading features of AKD and its ketone on the sizing development of AKD-sized paper were investigated at various temperatures by scanning electron microscopy(SEM). Stöckigt size degree was also measured before and after the heat treatment.

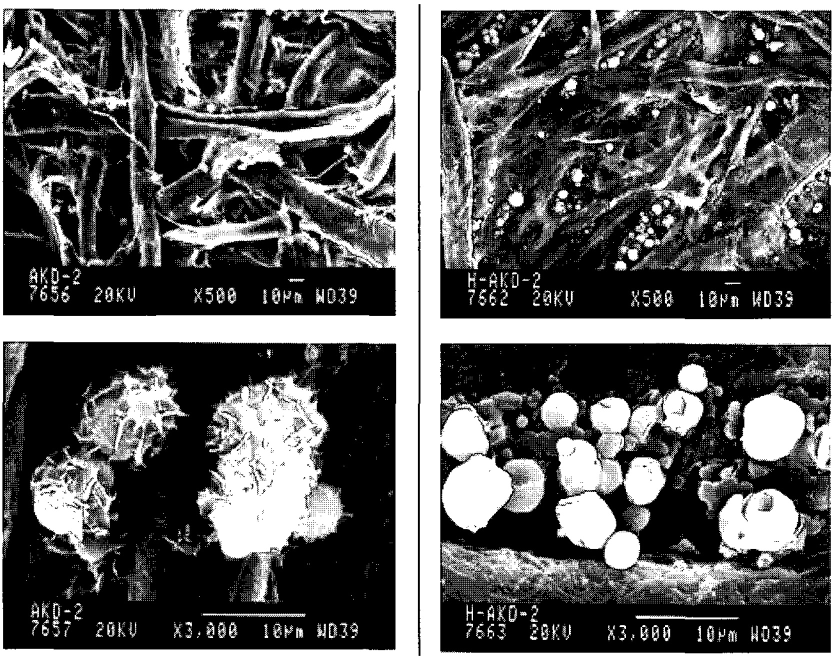
2. Experimental

2.1 Materials

Alkylketene dimer(AKD) of commercial product (Nippon Oils Co. Ltd.) was used in this study. Hydrolyzed AKD (ketone) was made from the hydrolysis of AKD as previous paper(6). AKD and ketone were recrystallized from hexane solution for three times, and characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. Whatman No. 1 filter paper was used as a base paper for sizing. HPLC-grade dimethylformamide (DMF) was purchased from Aldrich Chem Co. Inc., and used without further purification.

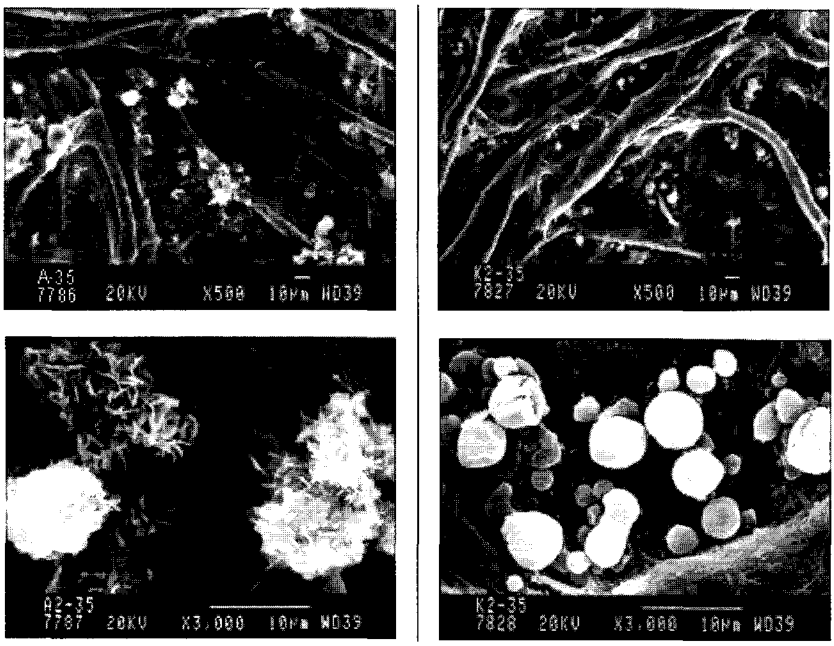
2.2 Procedures

DMF was used as a solvent for AKD and ketone. AKD and ketone solution (1.0 wt.%) in DMF was prepared by stirring at 50℃ over 3 h, respectively. Whatman No. 1 filter paper was immerged in 50 ml of the solution at 50℃, and then 50 ml of 30℃ distilled water was added to produce particles of both AKD and ketone in the paper web. By the addition of water, which acted as a non-solventfor both AKD and ketone solved in DMF solution, AKD and ketone were much less soluble in the solution. Consequently, AKD and ketone homogeneously solved in DMF solution were to be small particles in the paper web and on the paper surface. Finally, DMF was removed from the papers by careful washing with distilled water. After washing, these samples were dried at room temperature. SEM-micrographs of AKD or ketone particles in the paper web and on the paper surfacewere taken from JEOL JSM-840A. Retention of AKD and ketone in the filter paper was 9.30 wt.% and 8.85 wt.% respectively. The papers including AKD or ketone particles in its web were heated on a rotary drum dryer for 30 s at various heating temperatures. Before and after heat treatment, the papers were used for the observation of SEM and the measurement of Stöckigt size test according to KS M7025. Differential scanning calorimeter(DSC) was used for measurement of melting points. DSC spectra were obtained with TA Instrument Model No. 1200 42910 DSC at the heating rate of 5℃/min in nitrogen atmosphere.



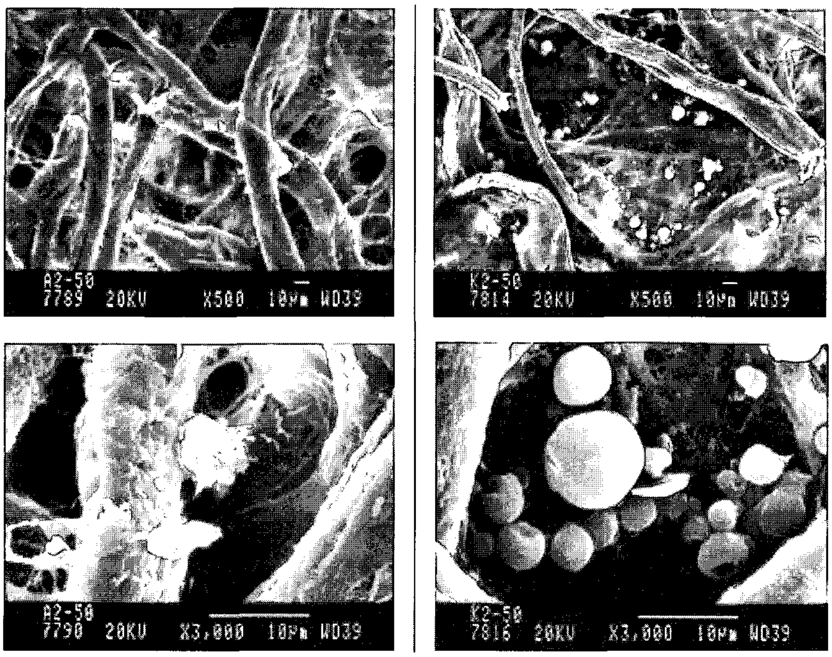
(A) (B)

Fig. 1. SEM-micrographs of papers treated with (A) AKD and (B) ketone before heat treatment.



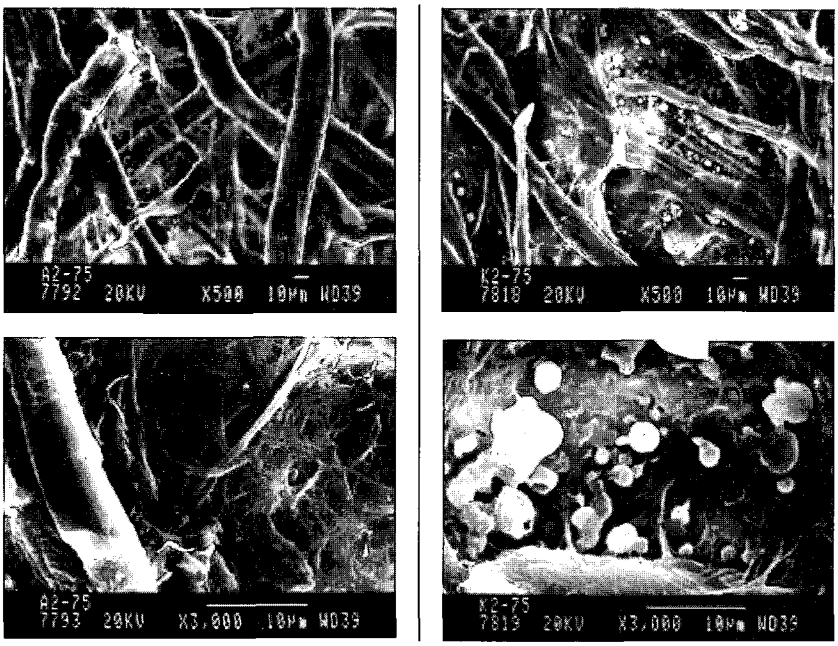
(A) (B)

Fig. 2. SEM-micrographs of papers treated with (A) AKD and (B) ketone after heat treatment at 35℃ for 30 s.



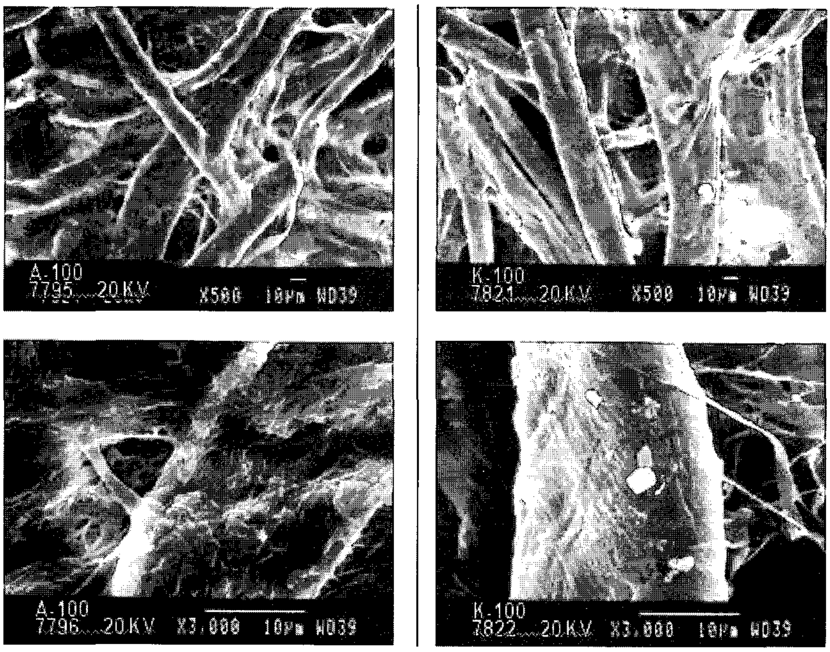
(A) (B)

Fig. 3. SEM-micrographs of papers treated with (A) AKD and (B) ketone after heat treatment at 50℃ for 30 s.



(A) (B)

Fig. 4. SEM-micrographs of papers treated with (A) AKD and (B) ketone after heat treatment at 75℃ for 30 s.



(A) (B)

Fig. 5. SEM-micrographs of papers treated with (A) AKD and (B) ketone after heat treatment at 100℃ for 30 s.

3. Results and Discussion

The papers including the particles of AKD or ketone were heated on the rotary drum dryer at various temperatures for 30 s. Before and after the heat treatment, the morphology of the particles in the paper was observed by scanning electron microscope(SEM) and their SEM-micrographs were shown in Fig. 1 ~ Fig. 5.

Fig. 1 showed the surfaces of the sample papers before heat treatment, which contain the particles of AKD and ketone. Particle shapes and sizes of AKD and ketone were different. The spreading behaviors of both AKD and ketone particles were easily observed from changes in particle shapes and sizes from the SEM-micrographs.

In the SEM-micrographs (Fig. 2) of the papers heated at 3℃, no changes in both AKD and ketone particles on the paper were observed. In the case of heat treatment at 50℃, most of AKD particles disappeared, while the ketone particles remained with no changes in its morphology as shown in Fig. 3. In Fig. 4, it was shown that AKD particles lost their shapes and the ketone particles started to melt when heat treated at 75℃. Finally, Fig. 5 showed that both AKD and ketone lost their particle shapes by heating at 100℃. Disappearance of the particles meant that the particles of both AKD and ketone melted and then spread on the fibers.

Fig. 6 showed DSC spectra of AKD and ketone. From the spectra it could be known that the melting points of AKD and ketone were about 50℃ and 75℃, respectively. These temperatures correspond with the temperatures that AKD and ketone particles disappeared in

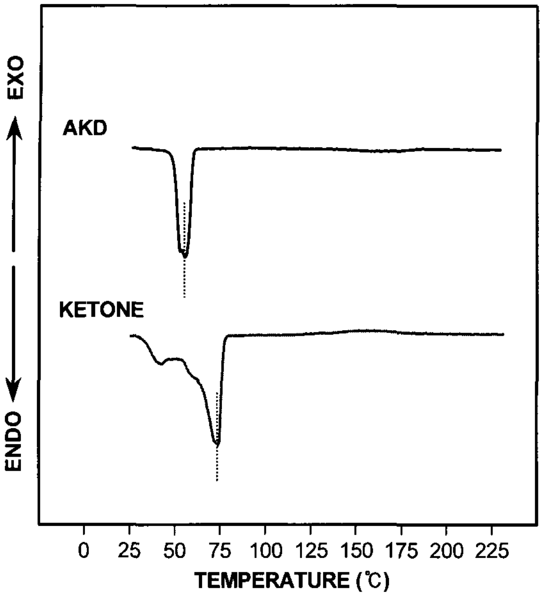


Fig. 6. DSC spectra of AKD and ketone.

the paper. Therefore, it could be known that the spreading behaviors of AKD and ketone were related directly to their melting points.

After heating of the papers containing AKD or ketone particles, their sizing degrees were measured by Stöckigt test method and illustrated in Fig. 7. AKD treated papers showed about 40 s and 60 s of Stöckigt size degree when they heat treated at 50℃ and 75℃, respectively, while the papers treated with ketone did not show any sizing effect. However, in the case of heat treatment over 100℃, the ketone showed superior sizing effect. This result indicated that ketone could also contribute to sizing development of AKD sized paper, when it spreads well to the fiber surface. Especially, ketone treated papers showed higher sizing degree than the paper treated with AKD, when they heated over 100℃. In other words, ketone could give higher sizing effect than unreacted AKD when it spreads well on the fiber surface.

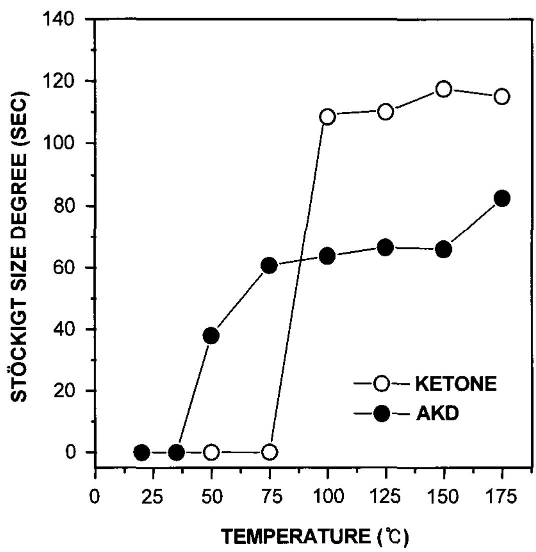


Fig. 7. Stöckigt size degree of the papers treated with AKD or ketone.

However, it had been thought that ketone could not contribute for sizing development. Ketone could be introduced to AKD sized papers by using old AKD emulsion partially hydrolyzed to ketone. Marton (7) reported that a commercial AKD emulsion lost about 15% of its reactive groups through the hydrolysis during five weeks storage at room temperature. It was reported that an old AKDemulsion brought about a remarkable decrease in sizing development. The reason was thought as decreasing of the reactivity of AKDby its hydrolysis and poor spreading of hydrolyzed AKD (ketone).

Ketone could also be introduced in AKD sized paper during drying and storage processes of the AKD sized papers by the hydrolysis of AKD retained in paper. Zhou (1) reported that there was no ketone just after drying, but considerable amounts of ketone was detected after 23 d storage of AKD-sized paper. In this case, ketone should not exist in the form of solid particle, but in the form of well spreaded thin-layer on AKD-sized paper. The reason was that ketone was produced by the hydrolysis of AKD, which already melted and spread on the fiber surface. Therefore, it was proposed that the ketone which produced by the hydrolysis of AKD in AKD sized paper would contribute to the AKD sizing development.

4. Conclusions

The objective of this work was to investigate the effect of spreading behavior of the sizing agents (AKD or ketone) on the sizing development of AKD sized paper. Morphological changes in the particles of AKD and ketone were observed by SEM-micrographs of the papers containing AKD or ketone when they were heated at various temperatures. Stöckigt sizing degrees of the papers were also measured before and after heat treatment at various temperatures.

It was shown that there was a direct relationship between the spreading behavior of the sizing agents and their melting points. Both AKD and ketone showed no substantial spreading until the temperature reached to their melting points. Consequently, ketone did not provide sizing effect when the paper was heat-treated below 75℃, while AKD provided sizing effect even the paper was heated at 50℃. Ketone, however, provided rather higher sizing effect to paper than AKD when the paper treated over 100℃. This result meant that ketone also gives sizing effect to paper, moreover ketone could give higher sizing effect to paper than AKD when it melted and spread well on the fiber surfaces.

Ketone would be existed in the form of well spreaded thin-layer on AKD sized paper, since ketone was produced by the hydrolysis of AKD, which already melted and spreaded on the fiber surface. Therefore, it could be suggested that the hydrolysis of AKD in sized papers during drying or storage could contributed to sizing development of AKD-sized paper. While a ketone introduced to papers from an hydrolyzed AKD emulsion could not contribute for sizing development.

Acknowledgements

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