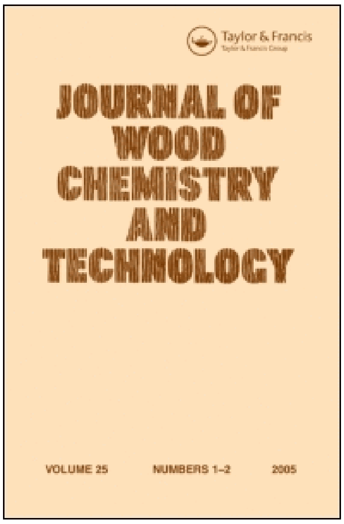

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Asakura, Kazumichi , Iwamoto, Masao and Isogai, Akira(2005) 'Effects of Fatty Acid Components Present in AKD Wax on Emulsion Stability and Paper Sizing Performance', Journal of Wood Chemistry and Technology, 25: 1, 13 — 26

To link to this Article: DOI: 10.1081/WCT-200058233
URL: http://dx.doi.org/10.1081/WCT-200058233

Journal of Wood Chemistry and Technology, 25: 13–26, 2005

ISSN 0277-3813 print/1532-2319 online
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Effects of Fatty Acid Components Present in AKD Wax on Emulsion Stability and Paper Sizing Performance

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Abstract: Commercial alkylketene dimer (AKD) waxes generally contain 80–90% AKD, and the rest of the components are by-products such as fatty acids, fatty acid anhydrides, and AKD oligomers. In this article, the effects of fatty acid components present in AKD waxes on AKD emulsion stability and paper sizing performance were studied using AKD emulsions, which were prepared from an AKD wax mixed with 0–12% stearic and palmitic acids. Repeated temperature shock treatments revealed that the fatty acids–containing AKD emulsions became most unstable at 3% fatty acid content, whereas those with 12% fatty acids were rather stable. When the addition level of fatty acids was increased up to 12%, zeta potentials of the AKD emulsion particles increased from +1.4 mV to +4.4 mV with increasing fatty acid content. This increase in zeta potential may be one of the factors that lead to a decrease in AKD retention ratios in handsheets. Thus, fatty acid components present in AKD waxes not only decrease the pure AKD content in the waxes but also have negative impacts on emulsion stability and paper sizing performance. These results show that fatty acid content in AKD waxes must be sufficiently controlled as low as possible to keep a standard level of the AKD wax quality.

Keywords: Alkylketene dimer, AKD, sizing, stability, fatty acid, emulsion

INTRODUCTION

Internal sizing is one of the significant functionalization processes in paper-making from cellulosic pulps. It adds water-penetration resistance to

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printing and writing papers, packaging papers, and boards as well as base papers for coating and press sizing. Alkylketene dimer (AKD) is one of the typical alkaline sizes, and has been used as an internal sizing chemical in papermaking for more than two decades. AKD is synthesized from fatty acid chlorides by reacting them with triethylamine generally in an organic solvent such as toluene or benzene. Fatty acid chlorides are prepared from fatty acids by chlorination with either phosphorous trichloride or phosgene. In each case, the purity of the AKD in the resultant wax is in the range from 80–90%. So-called AKD oligomers, fatty acid anhydrides, and fatty acids are present in the wax as by-products,[1,2] and the ratios in the wax vary, depending on the AKD preparation method. After emulsification of the AKD in aqueous media, dialkylketones and β-ketoacids are additionally formed to some extent in the wax components by hydrolysis of the AKD.[1]

Although it is difficult to determine exactly the by-product contents in AKD waxes, approximate ratios are 5–6% for fatty acid anhydrides, 0.3–2% for fatty acids, and 7–10% for AKD oligomers, which are determined by size-exclusion chromatographic and titration methods.[1–4] Recently, AKD production without using any organic solvents, that is, solvent-free AKD production, has been developed primarily because of environmental concerns.[5] Under these circumstances, the roles of by-products present in AKD waxes have become significant not only with respect to sizing performance but also the handling or stability of AKD emulsions.[2]

Sizing mechanisms of paper by internal addition of AKD are still controversial; either AKD components covalently bound to the cellulose hydroxyl groups of pulp fibers in paper or ketones formed from AKD by hydrolysis in dried paper contribute to paper sizing.[6,7] However, there is no doubt that the AKD present in the emulsions and retained in paper through the wet-end process eventually contributes to paper sizing. On the other hand, it is unknown whether the by-products present in AKD waxes such as fatty acids, fatty acid anhydrides, and AKD oligomers have negative, positive, or no impact on emulsion stability and paper sizing performance.

In this study, therefore, we first studied the effects of fatty acid components in AKD waxes on emulsion stability and paper sizing performance using model AKD emulsions, whose wax components were prepared by mixing a standard AKD wax with 0–12% fatty acids.

EXPERIMENTAL

Materials

A saturated fatty acid mixture containing stearic and palmitic acids (6:4 by weight) was converted to the corresponding fatty acid chlorides using phosphorous trichloride.[1] A benzene solution (20 g) containing 34.7 g triethylamine (0.343 mol) was added dropwise for 1 h to fatty acid chlorides (100 g; 0.343 mol) dissolved in benzene (80 g) at 25°C, followed by heating the mixture at 50°C for 1 h. Then, water (800 mL) at 50°C was added to the mixture to remove triethylamine HCl salt with the water layer. The benzene layer was collected, and completely dewatered using a drying agent. AKD wax (called the standard AKD wax hereafter) was then obtained by evaporation of the benzene solution.[8] The AKD content of the wax was 85%. The other components were fatty acids (2%), fatty acid anhydrides (5%), and AKD oligomers (8%). The components were analyzed by gas-chromatography and size-exclusion chromatography under standard conditions.[9] A quaternary cationic starch with a degree of substitution of 0.04–0.05 originating from waxy maize was used for emulsification of the AKD waxes. De-ionized water was used for preparation and dilution of cationic starch solutions and AKD emulsions.

Fatty acids–containing AKD emulsions were prepared according to the scheme in Figure 1. The standard AKD wax (100 g) and fatty acids (0–12 g) were melted by heating at ca. 85°C, and a 3.2% cationic starch solution (488 g) at ca. 85°C containing small amounts of aluminum sulfate and an organic sulfonate (naphthalene-formalin resin sulfonic acid Na salt) was added to the melted mixture. The fatty acids–containing AKD emulsions were then prepared by treating the mixture twice with

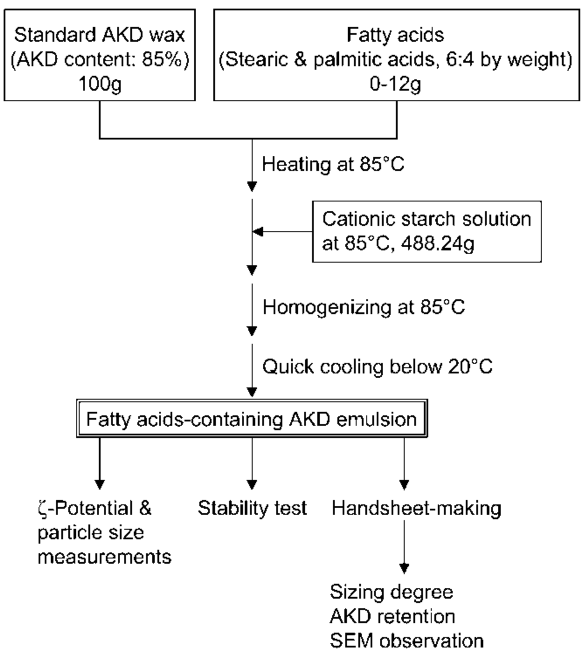

Figure 1. Scheme for preparing AKD emulsions containing fatty acids.

Table 1. Fatty acid-containing AKD emulsion samples prepared and used in this study

Emulsion sample	Mixing ratio in wax: Standard AKD wax[a]: Fatty acids	Pure AKD content in wax (%)	Total wax content in emulsion (%)	Pure AKD content in emulsion (%)
AKD-FA0	100:0	85.0	17.0	14.5
AKD-FA3	100:3	82.5	17.4	14.4
AKD-FA6	100:6	80.2	17.8	14.3
AKD-FA12	100:12	75.9	18.7	14.2

[a]Pure AKD content in the standard AKD wax is 85%.

a high-pressure homogenizer (Manton-Gaulin; APV Co., USA) at 40 MPa and 85°C, followed by quick cooling below 20°C with an ice bath. Components in the emulsions thus prepared are listed in Table 1.

Handsheet-Making

A commercial hardwood bleached kraft pulp with ζ-potential of −17.8 mV and 86% α-cellulose was beaten to 350 mL Canadian Standard Freeness (CSF) using a Niagara beater. To a 0.9% pulp slurry, the AKD emulsion (0.15% standard AKD wax on dry weight of pulp) and a cationic starch solution (1% cationic starch on dry weight of pulp) were added sequentially and handsheets with a basis weight of 65 g/m^2 were prepared using tap water (pH 7.5, conductivity 200 $\mu S/cm$) according to the TAPPI Test Method T 205 sp-95 (1995). Wet webs were dried at either 23°C for one day or directly dried using a drum-dryer at 105°C for 2 min. Part of the handsheets once dried at 23°C were then heated in an oven at 105°C for 30 min. AKD emulsion particles maintained their particle shapes without melting in the handsheets dried at 23°C, and thus they were subjected to scanning electron microscopic observation. The drum-drying was used for evaluation of the sizing degree of the handsheets dried under conditions close to the practical papermaking. Heating of the handsheets once dried at 23°C was adopted for evaluation of sizing potentials of the AKD-sized handsheets. Generally, heating at 105°C for 30 min for the once-dried handsheets gave the highest sizing degree in the three drying methods.[10] The sizing degree of the handsheets was evaluated by the Stöckigt sizing test according to JIS P 8122 (1979).

Characterization of AKD Emulsions

Viscosities of AKD emulsions were measured at 20°C using a B-type viscometer (Digital Viscometer DLV-B, Tokyo Keiki, Co., Ltd., Japan). Zeta potentials of 0.004% AKD emulsions, which were prepared by dilution of the original emulsion with de-ionized water, were determined at 20°C using an electrophoretic light scattering apparatus (EIS-6000; Otsuka Electric Co., Ltd., Japan). Average particle sizes of AKD emulsions were measured using a laser diffraction particle size analyzer (SALD-2100, Shimadzu Co., Japan). Temperature-shock treatment was applied to the AKD emulsions for evaluation of their stabilities. One temperature-shock cycle consisted of the following two steps: keeping the emulsion at 35°C for 24 h followed by cooling it at 5°C for 24 h. This temperature-shock cycle was repeated up to 4 times. The treated emulsions were subjected to the measurements of viscosities, average particle sizes, and scum weights formed and filtered off on a 330-mesh wire.[11]

Analyses

The AKD content of the handsheets were determined by pyrolysis-gas chromatography.[12] Surfaces of the handsheets were observed using a field-emission-type scanning electron microscope (S-4000, Hitachi Co., Japan) after platinum coating for 150 s.

RESULTS AND DISCUSSION

Effects of Fatty Acid Components in AKD on Emulsion Stability

When the standard AKD wax was mixed with 0–12% (on the dry weight of the wax) fatty acids followed by emulsification with cationic starch solutions, no differences in apparent form were observed between the emulsions by optical microscopy (Figure 2); in all cases the particles were well dispersed without forming any agglomerates in the emulsions. Figure 3 depicts zeta potentials and pH values of the emulsions. Expectedly, the pH values of the emulsions were hardly affected by the fatty acid addition. In contrast, even though fatty acids were mixed with the AKD wax, zeta potentials increased from +1.4 mV to +4.4 mV by the 12% fatty acid addition. The value of +1.4 mV for the original AKD emulsion under such diluted zeta potential measurement conditions at about pH 7 is brought about by charge valance on emulsion particles between dissociated amino groups of cationic starch and sulfonate groups of the compound co-added at the emulsion preparation; cationic charges due to the amino groups slightly suppress anionic charges due to the sulfonate groups. The changing pattern of zeta potential in Figure 3 is unexpected, because fatty acids are thought to contribute to an increase in anionic charges if dissociated fatty acids are present on the emulsion particle surfaces. In this experiment, the addition level of cationic starch was constant. Thus, fatty acid components present on the emulsion particle surfaces may attract more cationic starch

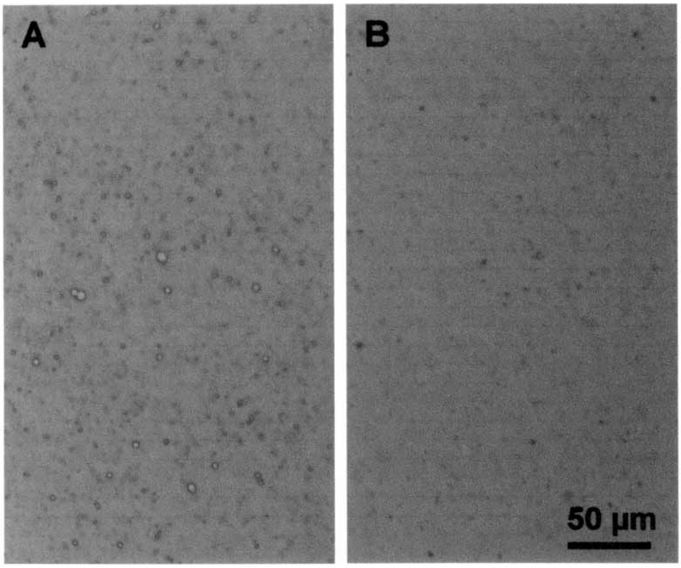

Figure 2. Optical microphotographs of AKD emulsions, which were prepared by adding 0% (A) and 12% (B) fatty acids to the standard AKD wax.

molecules to each emulsion particle by electrostatic interactions, thus resulting in the increased zeta potentials. It is not plausible that anionic fatty acids and the anionic organic sulfonates have some interactions in each emulsion particle. These increased cationic charges of the fatty acids–containing AKD emulsions might influence the AKD retention behavior in handsheet-making, which will be discussed later.

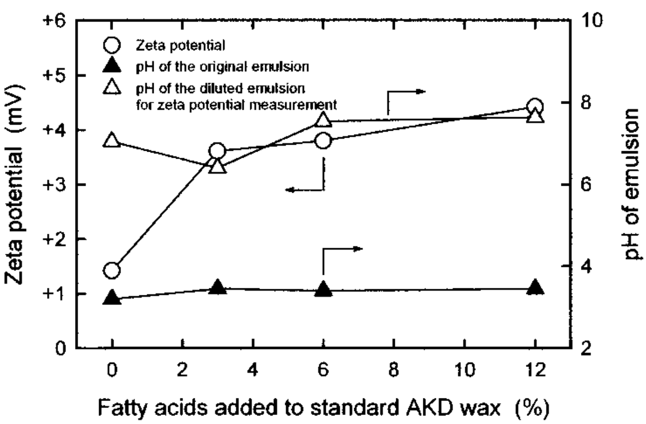

Figure 3. Effect of fatty acid addition to standard AKD wax on zeta potential and pH of the emulsions.

Changes in the viscosity of fatty acid–containing AKD emulsions by the temperature-shock treatment are shown in Figure 4. In all cases, AKD emulsion viscosities clearly increased with increasing the number of the temperature-shock treatment cycles. This treatment probably promotes instability of the AKD emulsions because of some detachment of emulsion stabilizers such as cationic starch and organic sulfonate from each emulsion particle. On the other hand, changing patterns of the viscosities varied depending on the fatty acid content in the wax. Especially the AKD emulsion prepared by adding 3% fatty acids to the standard AKD wax was the most unstable emulsion examined. When 12% fatty acids were added to the AKD wax, the corresponding emulsion had rather lower viscosities. The value of surface charge of the diluted AKD emulsion prepared by the addition of 3% fatty acids, that is, +3.6 mV in Figure 3, cannot directly explain the unstable behavior of the AKD emulsion with high wax content in Figure 4. There may be some discrepancy in surface charges between AKD emulsion particles determined at such low and high AKD wax contents.

Similar results were also observed in the average particle size measurement of the AKD emulsions (Figure 5), although differences between the samples were not so clear in comparison with the results of the viscosities in Figure 4. Again, the AKD emulsion prepared by adding 3% fatty acids to the standard AKD wax had relatively greater particle sizes. Some scum was formed in the AKD emulsions during the temperature-shock treatment. This scum was collected by filtration, and weighed after drying to determine scum content in the AKD emulsions formed (Figure 6). Clear differences in the scum content were observed between the samples. The AKD emulsion

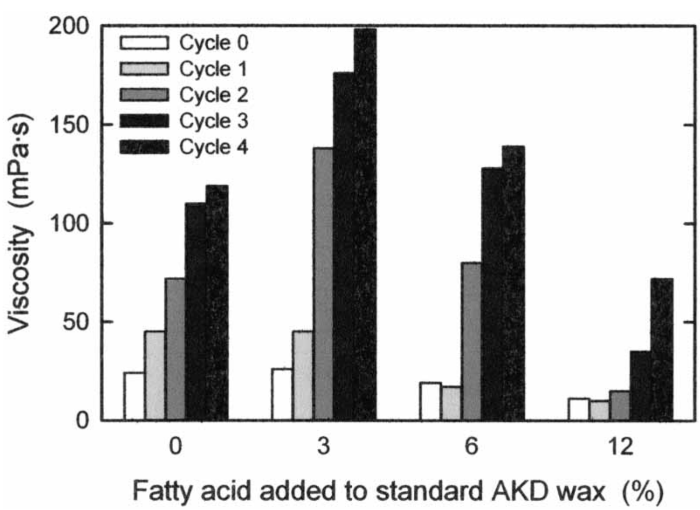

Figure 4. Effect of fatty acid addition to standard AKD wax on viscosity of the emulsions by temperature-shock treatment. One cycle: 32°C for 24 h → 5°C for 24 h.

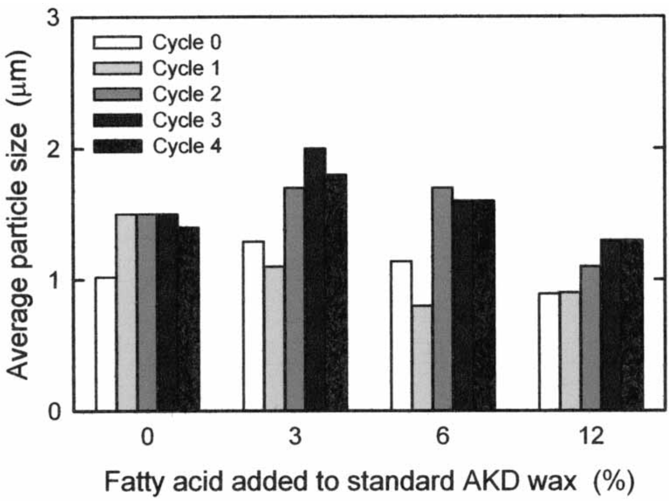

Figure 5. Effect of fatty acid addition to standard AKD wax on average particle size of the emulsions by temperature-shock treatment. One cycle: 32°C for 24 h → 5°C for 24 h.

prepared by adding 3% fatty acids to the standard AKD wax gave the highest scum content especially after the temperature-shock treatment.

These stability tests of the AKD emulsions show that fatty acid components, whose addition levels to the standard AKD wax are around 3%,

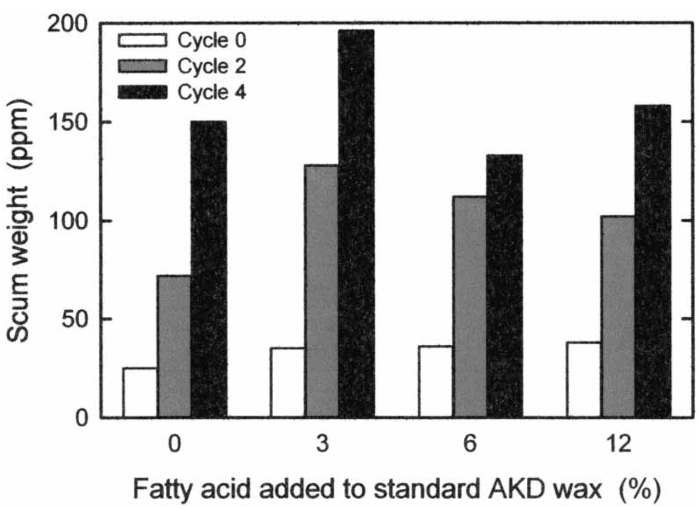

Figure 6. Effect of fatty acid addition to standard AKD wax on the weight of scum formed in the emulsions by temperature-shock treatment. One cycle: 32°C for 24 h → 5°C for 24 h.

have the maximum negative effects on emulsion stability. Thus, the fatty acid content in AKD waxes must be sufficiently controlled for improving AKD emulsion stability. In contrast, when fatty acid contents increase to around 12%, stabilities of the emulsions are improved.

Effects of Fatty Acid Components on Sizing Performance

The fatty acid–containing AKD emulsions prepared according to the scheme in Figure 1 were used to make handsheets using 1% cationic starch as a retention aid, where the added amounts of pure AKD were adjusted to 0.15% on the dry weight of the pulp. The wet webs were dried by the following two methods: drying on a metal plate at 23°C for one day and direct drum drying at 105°C for 2 min. The handsheets dried once at 23°C were subjected to scanning electron microscopic analysis for observing AKD emulsion particles attached on pulp fibers in the sheets. Parts of the handsheets dried once at 23°C were subsequently heated at 105°C for 30 min for evaluation of the sizing potentials.

The results of the sizing degree experiments are plotted in Figure 7. The handsheets dried at 23°C and those dried in the drum-dryer had similar sizing levels. The once-dried and then heated handsheets had the highest sizing levels in the three drying methods. Although the drum-drying is the best method for evaluation of sizing degree in terms of the practical papermaking process, the heating of the once-air-dried handsheets seems to be suitable for evaluation of sizing potentials for not only AKD but also other internal sizes, because migration of size components due to steam streams can be excluded as possible.[13] In all cases, the sizing levels appeared to decrease with

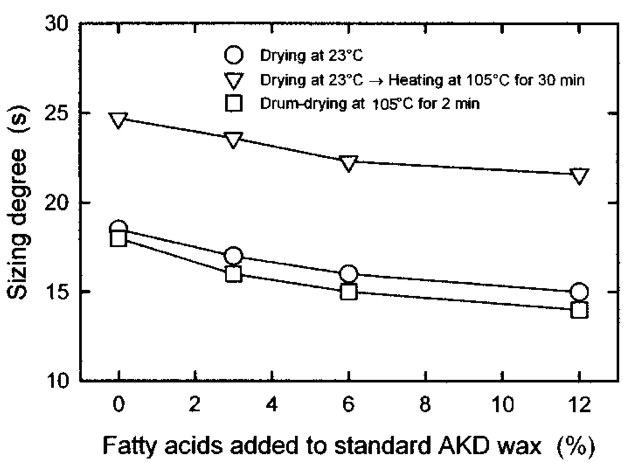

Figure 7. Sizing degrees of handsheets prepared with AKD emulsions containing fatty acids.

increasing fatty acid addition to the standard AKD wax, indicating that fatty acid components present in AKD waxes have negative effects on sizing performance.

Figure 8 shows the AKD content or AKD retention ratio of the handsheets. The AKD content decreased essentially linearly with increasing fatty acid content in the wax. When the degrees of sizing of the handsheets containing different AKD contents are estimated as those having the same AKD content (0.988 mg/g) by proportional calculation between sizing degrees in Figure 7 and AKD contents in Figure 8, fatty acid components retained in the handsheets do not seem to have negative impacts on the sizing levels (Figure 9). Thus, the decrease in sizing level of the handsheets prepared by the AKD emulsions with increasing levels of fatty acids (Figure 7) is explained primarily in terms of the decreased AKD retention. As shown in Figure 3, the zeta potential of the AKD emulsion increased with increasing addition of fatty acids to the wax. This increase in zeta potential, which was brought about by the fatty acid addition to the AKD wax, may have brought about in turn the decreased AKD retention value. However, the increasing pattern of zeta potential of the AKD emulsions by the fatty acid addition in Figure 3 do not exactly correspond to the linear decreasing pattern of AKD retention (Figure 10). Some other factors in addition to the changes in zeta potential of the AKD emulsions may have brought about the decreased AKD retention values. In any cases, the presence of fatty acid components in AKD waxes leads to negative effects on the size retention at the wet-end, resulting in lower sizing performance.

In the case of internal sizing, not only size retention values but also some other factors, that is, distributions of emulsion particles on pulp fibers, often govern the resultant sizing patterns. Figure 11 displays scanning

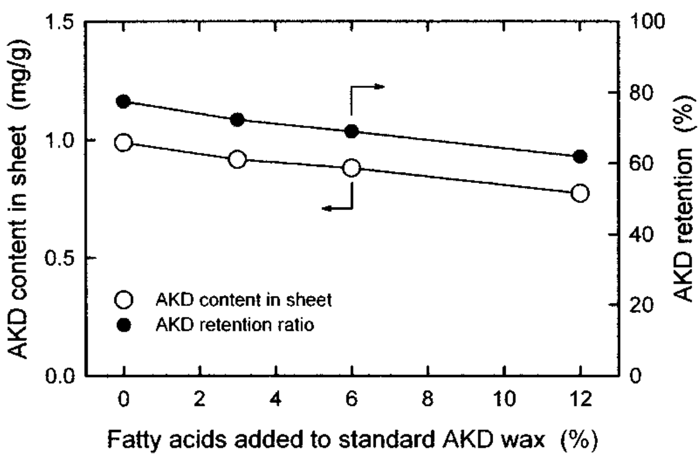

Figure 8. AKD content and AKD retention ratio in handsheets prepared with AKD emulsions containing fatty acids.

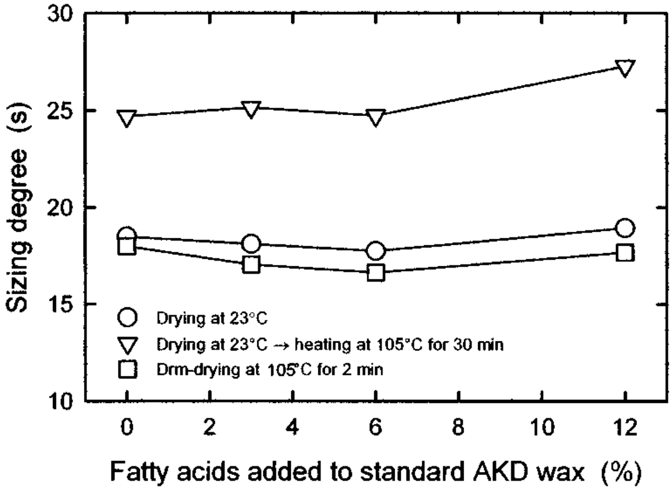

Figure 9. Sizing degrees at the same AKD content (0.988 mg/g) plotted by proportional calculation between sizing degree in Figure 7 and AKD content in Figure 8.

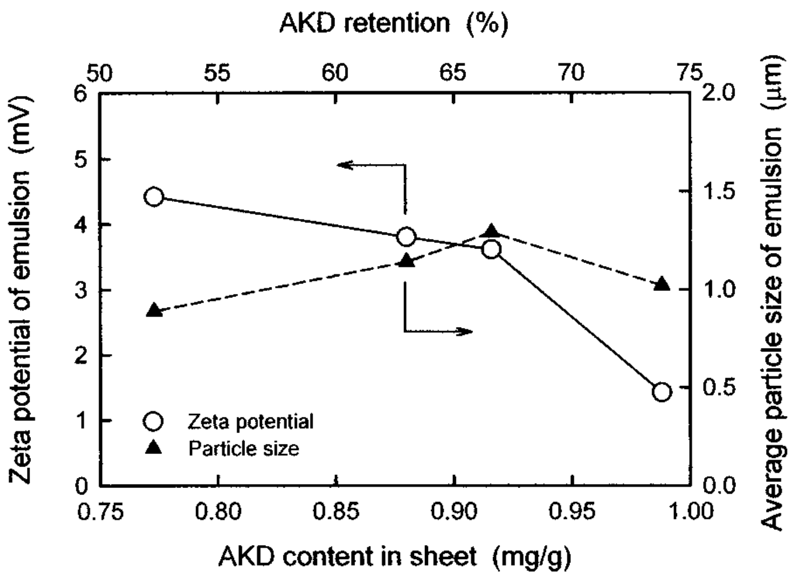

Figure 10. Relationships between AKD content or AKD retention ratio in the handsheets and either ζ-potential or average particle size of AKD emulsions containing fatty acids.

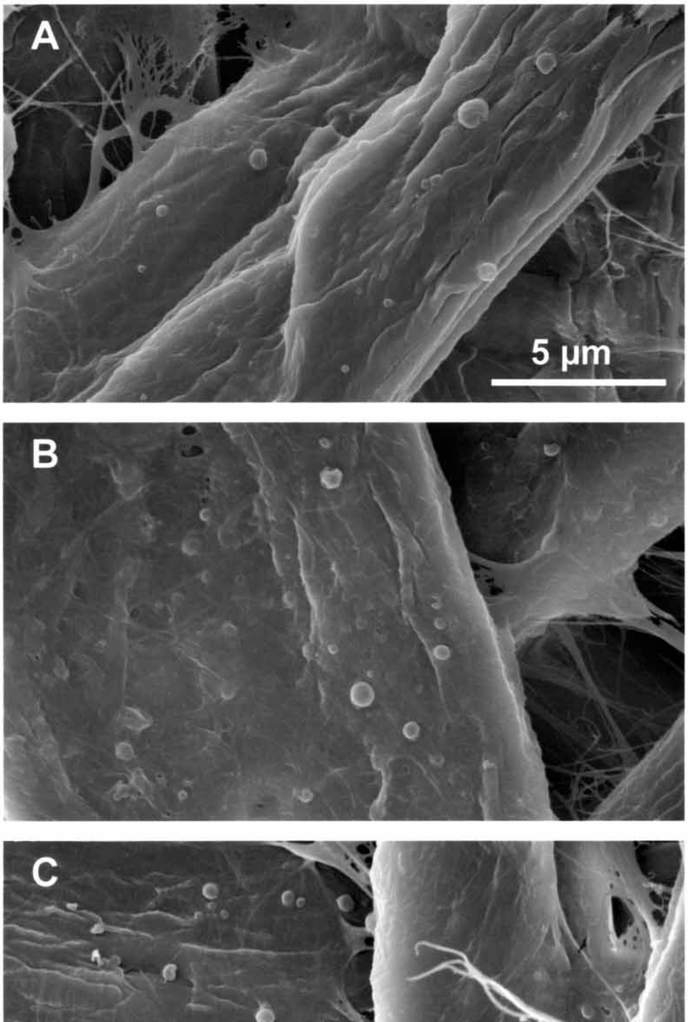

Figure 11. SEM microphotographs of handsheet surfaces prepared with AKD emulsions and dried at 23°C without heating. The emulsions were prepared from standard AKD wax with 0% (A), 3% (B), and 12% (C) (on dry weight of the standard AKD wax) fatty acids.

microphotographs of surfaces of the air-dried handsheets prepared with the AKD emulsions prepared from the standard AKD wax and 0, 3, or 12% fatty acids. In all cases, each emulsion particle is independently adsorbed on pulp fiber surfaces without any agglomeration or uneven distribution, and no particular differences in distribution pattern of the emulsion particles were observed among the AKD emulsions prepared by adding 0, 3, and 12% fatty acids to the standard AKD wax. These results show that fatty acid components present in AKD wax do not affect distribution behavior of emulsion particles on pulp fibers but have influences on emulsion stability, retention behavior, and the resultant sizing performance of paper.

CONCLUSIONS

Fatty acid components added to the standard AKD wax have negative impacts on emulsion stability and paper sizing performance of the AKD emulsions prepared thereof. When fatty acid components added to the standard AKD wax increased up to 12%, zeta potentials of the AKD emulsion particles increased from +1.4 mV to +4.4 mV with increasing the addition level of fatty acids to the standard AKD wax. This increase in zeta potential may be one of the factors to decrease AKD retention ratios in the handsheet-making system used, resulting in a decrease in the sizing levels. The temperature shock treatment revealed that the fatty acids–containing AKD emulsions became most unstable at 3% fatty acid addition level, whereas those at 12% fatty acid addition level were rather stable. Thus, fatty acid content in AKD waxes must be well controlled as low as possible to keep a standard level of the AKD wax quality.

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