New insights into the AKD sizing mechanism

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SUMMARY: Paper samples sized with ^{13}C labeled alkylketene dimer (AKD) dispersions were characterized by solid state carbon NMR resulting in direct evidence supporting the formation of AKD-cellulose P-keto esters on AKD sized paper.

A series of AKD reaction products that may potentially result from the paper sizing process, were prepared and characterized. These included the P-keto acid, **3a**, the β-keto calcium salt, **3c**, the P-keto ethyl ester, **6a**, dipentadecylketone, 4, C_{32} alkyl ketene dimer, **1,** and an AKD oligomer, **5.** The AKD oligomer was prepared under conditions previously reported to give **3a.** Sizing efficiencies of the model compounds were determined on a variety of base papers. AKD, **1,** and AKD oligomer, 5, were the only substances that provided significant levels of sizing.

The P-keto acid, **3a**, and P-keto calcium salt, **3c**, were not major AKD sizing products as determined by the NMR study and a supporting liquid chromatography study of extracts from sized handsheets.

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Alkylketene dimer (AKD) based sizing agents have been widely used by the paper industry since their development in the 1950's (Davis et al. 1956; Kincannon, Watkins 1974; Dumas 1981; Evans 1989; Roberts 1991). AKD is particularly effective in alkaline papermaking systems. In recent years, the amount of paper made under alkaline versus acid conditions has been increasing rapidly. This trend has led to a large increase in the use of alkaline sizing agents such as AKD in industry (Crouse 1991).

There is general acceptance that any paper sizing material must be retained, evenly distributed, anchored to the paper, and oriented properly to be effective (Davison 1986). The mechanism by which AKD is anchored to paper has been debated in recent years (Gess 1992; Gess, Lund 1991; Odberg, Lindstrom 1987; Nahm 1986; Dumas, Evans 1986; Merz et al. 1985; Rohringer et al. 1985; Lindstrom, Odberg 1985; Roberts et al. 1985; Lund 1985). The following questions are discussed most often.

- Does AKD react with the hydroxyl groups on cellulose to form covalent β-keto ester bonds?
- Do the P-keto acid or β-keto acid salt hydrolysis products of AKD exist on AKD sized paper and if so, how much do they contribute to sizing?

AKD is typically used commercially at levels varying from 0.05-0.3% based on the weight of the paper. This low level of addition makes it difficult to directly detect AKD reaction products on paper made under realistic conditions. There is a large body of indirect experimental evidence supporting covalent bond formation between AKD and cellulose (Ödberg, Lindstrom 1987; Nahm 1986; Dumas, Evans 1986; Lindstrom, Ödberg 1985). Most of this is based on the fact that not all AKD

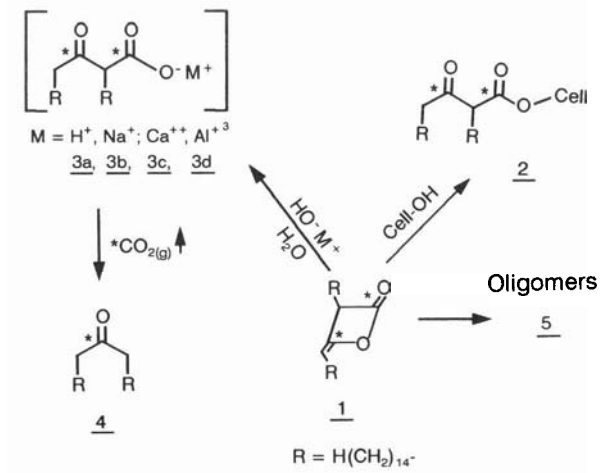

Fig. 1. Possible AKD reaction products produced during the sizing of paper.

can be accounted for after solvent extraction of sized paper, unless the paper is first subjected to conditions typically required to hydrolyze esters. Nahm gave definitive direct evidence that AKD *can* react with cellulosic materials; his experimental conditions, however, were not representative of realistic papermaking conditions (Nahm 1986). Only one piece of direct evidence has been reported. Lindstrom and Odberg recorded IR evidence for ester formation on AKD sized paper (Ödberg, Lindstrom 1987; Lindstrom, Ödberg 1985).

Those who have not favored ester bond formation have generally offered the AKD β-keto acid hydrolysis product and its salts as the major source of sizing when using AKD. This position is based mostly on the work of Rohringer in which he claimed to have synthesized the AKD P-keto acid hydrolysis product. He reported that it was thermally stable and as efficient a size as AKD. However, the sizing study was done using an unrealistically high level of addition (Merz et al. 1985; Rohringer et al. 1985). Gess has also claimed to have observed the P-keto acid on paper (Gess 1991). No spectral evidence supporting the P-keto acid structure has been provided.

Work using CP/MAS solid state NMR and ^{13}C isotopically labeled AKD to study the reactions of AKD directly on paper is discussed in this paper. In the last few years the resolution and sensitivity of solid state ^{13}C NMR have improved markedly due to cross polarization (CP) and magic angle spinning techniques (MAS)(Pines et al. 1973; Schaefer, Stejskal 1976). The level of detection can further be improved by using ^{13}C isotopically labeled compounds. Roberts recently demonstrated the utility of this type of method while studying the reactions of labeled succinic anhydride with paper (Roberts, Tatham 1991 and 1992).

Results and discussion

Some possible reactions involving AKD during the sizing of alkaline paper are illustrated in *fig.* **1.** AKD, **1,** may react with cellulose to form P-keto ester, **2,** with water to