On the mechanism of sizing with alkylketene dimers

Part 1. Studies on the amount of alkylketene dimer required for sizing different pulps

Tom Lindstrom and *Gunnel Soderberg*, Swedish Forest Products Research Laboratory, Stockholm

Keywords: Kraft pulps, Mechanical pulps, Sizing, Alkylketene dimers*, Reaction mechanisms, Radioisotopes.

SUMMARY: The amount of alkylketene dimer (AKD) required to size different pulps has been investigated. The quantities of AKD retained on the fibers and reacted with the fibers were determined using radioactive labelled (^{14}C) AKD. Unreacted AKD was removed from cured paper sheets using a procedure involving a preswelling stage in H_2O and subsequent solvent exchange to tetrahydrofuran and Soxhlet extraction with the same solvent. It is shown that no sizing is obtained unless AKD reacts chemically with the cellulose fibers.

Unreacted AKD contributes to sizing provided that there is some reacted AKD on the fiber surfaces. Reacted AKD is however 2-3 times (depending on pulp type) more efficient than unreacted AKD. No AKD-hydrolysis could be discerned during drying under the laboratory conditions employed. The reaction between AKD and cellulose is shown to start when the paper sheet is almost dry (>80% solids content). Small quantities of reacted AKD, ranging from 0.008 to 0.038% (depending on pulp type) are required to obtain a sized paper (Cobb,, = 25 g/m^2).

It is shown that the amount of reacted AKD required to reach a specified sizing threshold (Cobb, = 25 g/m^2) is closely related to the BET-surface (Brunauer-Emmet-Teller) area (N_Z-adsorption) of the paper sheets and not to the wet hydrodynamic surface area of the papers.

From the relationship between the sizing threshold and the BET-surface area and surface balance measurements on AKD-wax, it was calculated that a surface coverage of 4% POML (Planar Oriented Mono Layer) is required for a sizing to a $Cobb_{60}$-value of 25 g/m^2.

The surface energy requirements for spreading of AKD are discussed and a mechanism for AKD-sizing is proposed. The mechanism explains certain experimental facts e.g. why fiber to fiber bonds are unsized and why the sizing threshold is related to the BET-surface area of the paper.

ADDRESS OF THE AUTHORS: Swedish Forest Products Research Laboratory, Box 5604, S-114 86 Stockholm, Sweden.

Alkylketene dimers (AKD) are widely used in order to size paper and board products, i.e. to control the rate of penetration of liquids into the paper structure (1-7).

AKD belong to the class of reactive sizes, i.e. the AKD reacts with the cellulosic fibers thereby rendering the fiber surface hydrophobic. The degree of sizing depends on the extent of chemical reaction, and sizing is not immediately developed as with the more commonly used rosin-alum based system, where the anchoring of the rosin to the cellulosic surface is achieved by electrostatic interactions.

In spite of the fact that AKD has been widely used in the paper industry for many years, very little information on AKD-sizing has been released in the literature (1-7).

It is generally assumed that the sizing efficiency of an AKD-dispersion is dependent on at least the following factors:

- AKD-retention
- AKD-particle distribution on the fiber surfaces
- Spreading and extent of chemical reaction

Few attempts have, however, been made to study these factors and sort out the different parameters affecting each step. The object of this series of papers is to fill this gap and to clarify the mechanism of AKD-sizing. The experimental approach has been to use radioactive labelled ^{14}C-AKD to determine the small quantities of AKD retained and reacted to the fibers.

This paper deals with the sizeability of different pulps with AKD, i.e. the amount of reacted AKD which is required to size a specific pulp, with the manner in which unreacted AKD contributes to the degree of sizing and finally with spreading and reaction phenomena during paper consolidation and drying.

A brief account of some of the results included in this paper has already been presented (8).

General background

Alkylketene dimers (AKD) used as sizing agents in papermaking are formed from the higher fatty acid chlorides (C_{12}-C_{18}) via their ketenes. The reaction is catalysed by tertiary amines. In commercial preparations fatty acid mixtures are used and the composition of the final product is determined by the combinations of the fatty acids. Each fatty acid can form diketenes either with itself or with its homologues. The product is insoluble in water and is generally added to the paper stock as a cationic aqueous dispersion.

The dispersion is usually stabilized by the addition of a cationic starch. Various cationic sizing accelerators are also often added, depending on the specific end use of the product. The particle size of commercial dispersions is in the range between 0.2 pm and 2 pm. The alkylketene dimers are believed to react with cellulose hydroxyl groups to form β-keto-esters (see *fig. 1*). Ring opening always occurs at the acyl-oxygen bond. Alkylketene dimers can also react with water, forming an unstable β-keto acid, which decarboxylates to the corresponding ketone.

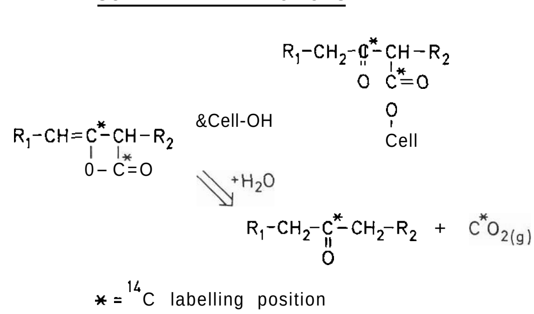

Fig. 1. Some possible AKD-reactions.