

Alkylketene dimer sizing: vapor-phase deposition of tetradecyl ketene dimer on paper

U. D. Akpabio

Lecturer I, Dept. of Pure and Applied Chemistry, University of Cross River State, P. M. B.
1017, Uyo, Cross River State, Nigeria

J. C. Roberts

Senior Lecturer, Paper Science Dept., U.M.I.S.T., Manchester, U.K.

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Earlier observations (1, 2) have shown that paper internally sized with alkylketene dimers develops sizing only after heat treatment. Roberts and Garner (1), by autoradiography, also observed spreading of the dimer particles in heat-treated sized sheets, whereas such spreading was not observed in samples that were not heat treated. The spreading should allow good anchorage and suitable orientation of the size particles on the cellulosic fiber surface such that even distribution and effective coverage are achieved for good sizing development (3). Therefore, an alternative method of achieving sizing with alkylketene dimer under similar temperatures should be the vapor-phase deposition of the dimer onto the paper. Our experiment was aimed at studying a possible mechanism for alkylketene dimer sizing.

Results and discussion

Tables I and II and Fig. 1 show the retention of tetradecylketene dimer by vapor-pressure transfer onto unsized sheets at various temperatures and deposition times. Retention increased with temperature and exposure time at 140°C. At 105°C (the curing temperature of the test sheets), there was only moderate transfer. The results also show that the size is retained preferentially at the surface: when 5.6% of the thickness was removed from the surface of a sheet by peeling, about 20% of the size was removed from the sheet at 150°C.

I. Variation of retention and water absorbency capacity with exposure temperature for vapor-phase tetradecylketene dimer sizing

	105°	120°	150°
Unextracted sheet, control			
Retention, mg/g	0
Absorbency capacity, g/g	2.6
Unextracted sheet			
Retention, mg/g	0.04	0.26	1.30
Absorbency capacity, g/g	2.3	2.1	2.0
Unextracted sheet less 5.6%*			
Retention, mg/g	0.03	0.16	1.04
Absorbency capacity, g/g	2.4	2.1	2.0
Solvent-extracted sheet, control			
Retention, mg/g	0
Absorbency capacity, g/g	2.8
Solvent-extracted sheet (6 h)			
Retention, mg/g	0.005	0.005	0.006
Absorbency capacity, g/g	2.4	2.3	2.2

*5.6% of the thickness peeled from the surface.

In all cases, the residual amount of this material in the sheet after solvent extraction with chloroform was insignificant as compared with earlier results (4), when the tetradecylketene dimer was internally applied in cationic starch emulsion.

All the sheets containing the tetradecylketene dimer showed no sizing development before and after solvent extraction, which is also in marked contrast to the emulsion results. The minimum water absorbency capacity was 2 g/g of paper (unsized sheet), whereas the minimum water absorbency capacity of paper with emulsion-applied sizing was 0.71 g/g (4) even after solvent extraction. Thus, the vapor-phase-transferred tetradecylketene dimer was unable to size the sheets.

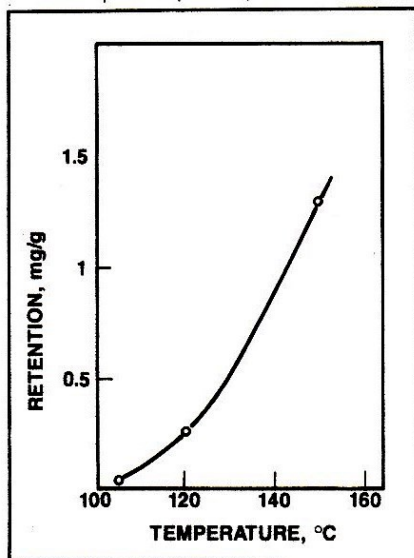
The reason for this failure may be that the conditions were not those

II. Variation of retention and water absorbency capacity with exposure time to 140°C for vapor-phase tetradecylketene dimer sizing

	5 min	10 min
Unextracted sheet		
Retention, mg/g	0.28	1.73
Abs. capacity, g/g	2.2	2.0
Solvent-extracted (6 h)		
Retention, mg/g	0.006	0.02
Abs. capacity, g/g	2.3	2.0

necessary for good sizing development (3). On the other hand, it could be that the dimer underwent chemical modification during the process of transfer and deposition in a form which could not size the sheet. It was possible to test the second hypothesis to some extent by analyzing the material that had condensed and solidified on the side of the vessel used for the transfer. The

1. The variation of retention of tetradecylketene dimer with temperature at constant time of exposure (10 min)



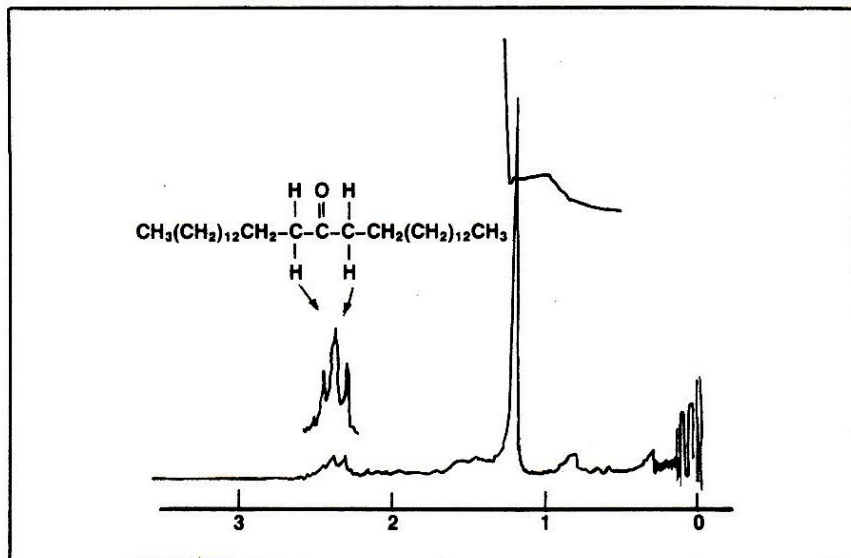
compound was identified as 16-hen-triacontanone (palmitone) by several methods.

First, the mixed melting point determination gave 80.5–82.5°C for the mixture and 81–83°C for authentic palmitone prepared by hydrolysis of tetradecylketene dimer with sodium hydroxide in a dioxan–water mixture. Second, the infrared spectrum displayed an absorption band at 1710 cm^{-1} , corresponding to the carbonyl stretching frequency of palmitone. Third, the NMR spectrum corresponded with the spectrum of authentic palmitone (Fig. 2):

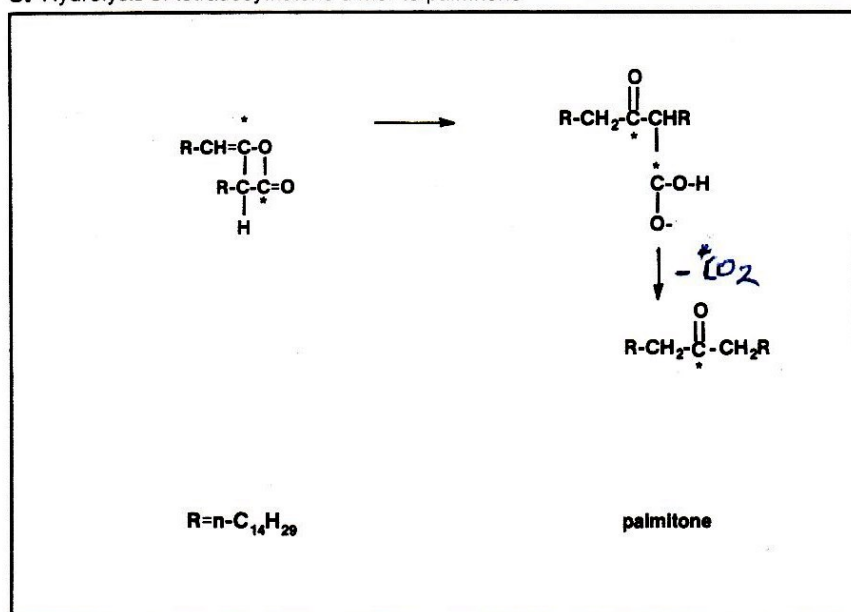
- A triplet at $\delta = 2.35$ for the 4 hydrogens on the α carbons
- A shoulder at $\delta = 1.6$ for β carbon atom protons (4 H)
- A spike at $\delta = 1.26$ for main chain protons (48 H)
- A small peak at $\delta = 0.85$ for terminal methyl protons (6 H).

It is likely, therefore, that it was palmitone that was deposited onto the paper during the vapor-phase transfer of tetradecylketene dimer. The infrared spectrum of the solid extract from the treated sheet also indicated an absorption at 1710 cm^{-1} . Theoretically, 1 g of tetradecylketene dimer requires only about 0.04 g of water to completely convert it to palmitone. Therefore, in a sheet of paper having a moisture content of 8%, there would easily be enough water vapor to hydrolyze the dimer to palmitone at the transfer temperature by the reaction pathway proposed as shown in Fig. 3.

2. The NMR spectrum of the deposited material was that of palmitone.



3. Hydrolysis of tetradecylketene dimer to palmitone



Conclusions

Vapor-phase deposition of alkylketene dimer on dry paper does not lead to sizing development because a preferential reaction takes place with water vapor obtained from the sheet itself at the transfer temperature. The unreactive compound palmitone deposited on the sheet can also be easily removed by solvent extraction.

The implication of these results for the mechanism of alkylketene dimer sizing in paper is that the nonsolvent extractable material observed earlier (4) could not have been in the form of strongly absorbed, unreacted dimer

molecules. During the heat treatment of the internally sized sheets, any monolayer of initially adsorbed alkylketene dimer molecules would be likely to react with cellulose at the accessible hydroxyl groups to form a β -ketoester as initially proposed (4).

Experimental procedures

Preparation of radio-labelled tetradecylketene dimer

Radioactively labelled tetradecylketene dimer was synthesized from radio-labelled hexadecanoic acid through formation of hexadecanoyl chloride and further dechlorination

with triethylamine to form the dimer (5) with a specific activity of 90.1 $\mu\text{Ci/g}$.

Handsheets

Standard handsheets were made from bleached Kajaani sulfite pulp according to the British Standard procedure (6) using deionized water. Cationic starch was used as retention aid.

Vapor-phase deposition of tetradecylketene dimer on paper

Radioactively labelled tetradecylketene dimer (50 mg) was placed in a clean Pyrex glass beaker 5 cm deep.

An unsized, uncured sheet was placed over the open end of the beaker and secured tightly with a piece of wire. The system was heated in an oil bath, without immersing the sheet, at various temperatures and exposure times.

Determination of absorbency capacity

Absorbency capacity of the sheet in grams of water per gram of paper was determined by immersion in distilled water.

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