THE EFFECT OF KETENE DIMER MELTING POINT ON THE RATE OF SIZING DEVELOPMENT

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SUMMARY

Two studies were carried out in an effort to gain a better understanding of how ketene dimers develop sizing. In the first study, eight ketene dimers with a range of melting points, vapor pressures, and molecular weights were evaluated for rate of sizing development. Ketene dimer melting point had a clear effect on the rate of sizing development. High melting ketene dimers initiated sizing at higher sheet moistures than low melting dimers. High melting dimers also developed their ultimate level of sizing faster than low melting ketene dimers. These results suggest that solid and liquid ketene dimers have different mechanisms of sizing development. Ketene dimer vapor pressure and molecular weight had no consistent effects on the rate of sizing development.

Pseudo first order rate constants for sizing development were then measured for a high melting solid ketene dimer and a liquid ketene dimer over dryer temperatures ranging from 55 °C to 85 °C. The rate constants measured for the liquid ketene dimer increased steadily as dryer temperature increased. An Arrhenius plot of the rate constants obtained for the liquid ketene dimer yielded an activation energy of 11 kcal per mole for sizing development. These results are consistent with the hypothesis that the chemical reaction of the lactone ring is the rate determining step in sizing development for liquid ketene dimers. The high melting

solid ketene dimer followed more complex kinetics and probably developed sizing by a combination of mechanisms. It is likely that the differing sizing responses measured for the solid and liquid ketene dimers are due to differing sizing contributions from the unreacted and hydrolyzed ketene dimers.

INTRODUCTION

Ketene dimer sizing agents have been widely used throughout the paper industry for over 40 years [1–4]. Their remarkable efficiency against a wide range of penetrants make them the sizing agent of choice in a number of packaging and printing and writing applications.

Over the years, the ketene dimer sizing mechanism has received a great deal of attention. In 1986, Davison proposed a four step mechanism for ketene dimer sizing development [5]. Each step in the mechanism – retention, spreading, orientation, and anchoring – is critical to the sizing performance of the ketene dimer.

A number of authors have made important contributions to our understanding of each step in the ketene dimer sizing mechanism [6–22]. Several important questions, however, remain unanswered. One of the more interesting unanswered questions is which of the three final steps – spreading, orientation, or anchoring – is the rate determining step in ketene dimer sizing? Many chemists find it natural to assume that the chemical reaction of the lactone ring on the ketene dimer is the rate determining step in sizing development. In a series of papers, Lindstrom showed that reaction of the lactone ring is the rate determining step in the formation of non-extractable, bound ketene dimer [8–11]. An activation energy of 13–17 kcal/mole was measured for the reaction. Lindstrom also found a clear relationship between the amount of bound ketene dimer in the sheet and non-extractable Cobb sizing. Unreacted ketene dimer contributed to solvent extractable sizing, but only in the presence of reacted ketene dimer.

The earliest stages of sizing development, however, have received relatively little attention. As described below, two studies were carried out under mild drying conditions in an effort to gain a better understanding of the earliest stages of sizing development at high sheet moistures. In the first study, a series of ketene dimers with a range of melting points, vapor pressures, and molecular weights were evaluated for rate of sizing development. The results of this study showed that ketene dimer melting point has a significant effect on the rate of sizing development. A second study was then carried out to study the

effects of ketene dimer melting point on the rate of sizing development over a wide range of dryer temperatures.

RESULTS AND DISCUSSION

Effect of ketene dimer melting point, vapor pressure, and molecular weight

Ketene dimer melting point and chemical structure are known to have significant effects on sizing efficiency [1]. For example, Brungardt and Zhang [23] showed that ketene dimers with melting points below room temperature have similar sizing efficiencies. Ketene dimers with melting points above room temperature generally gave higher sizing efficiencies. For the ketene dimers with melting points above room temperature, ketene dimer efficiency increased as melting point increased.

A similar series of ketene dimers was made for the current study in an effort to determine the effects of ketene dimer melting point and structure on the rate of sizing development. As shown in Table 1, ketene dimers were made from pure C_{10}, C_{12}, C_{14}, and C_{16} saturated fatty acid feedstocks. Ketene dimers were also made from a technical grade high C_{18} saturated fatty acid feedstock, and blends of C_{12}/C_{14} (saturated), C_{16}/C_{18} (saturated), and oleic/linoleic fatty acids.

The melting point of each ketene dimer was measured using Differential Scanning Calorimetry (DSC, 0.5 °C per minute, second heat). As shown in Figures 1 and 2, these ketene dimers represent a wide range of melting points.

Table 1 Ketene Dimer Melting Point, Volatility, and Rate of Sizing Development

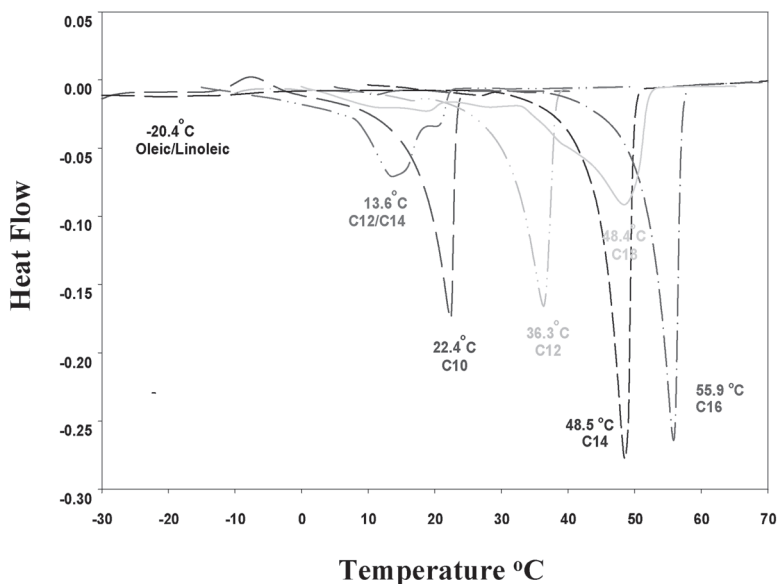| Dimer Feedstock	Ketene Dimer Melting Point	TGA – 50% Weight Loss	Rate Constant (s^{-1})	Regression	
				% of Endpoint	R^2
Oleic/Linoleic fatty acid blend	−20 °C	270 °C	7.5×10^{-3}	97%	99%
C_{12}/C_{14} fatty acid blend	13.6 °C	220–240 °C	7.1×10^{-3}	90%	94%
Pure C_{10} fatty acid	22.4 °C	180 °C	8.6×10^{-3}	100%	95%
Pure C_{12} fatty acid	36.3 °C	220–240 °C	7.2×10^{-3}	97%	99%
C_{16}/C_{18} fatty acid blend	49.4 °C	270 °C	1.6×10^{-2}	100%	73%
Technical grade high C_{18} fatty acid	48.4 °C	270 °C	1.8×10^{-2}	100%	78%
Pure C_{14} fatty acid	48.5 °C	220–240 °C	2.0×10^{-2}	97%	94%
Pure C_{16} fatty acid	55.9 °C	270 °C	2.1×10^{-2}	98%	93%

Figure 1   Ketene Dimer Melting Point.

The oleic/linoleic acid ketene dimer had the lowest melting point, −20 °C. Increasing the molecular weight of the fatty acid from C_{10} (22 °C), to C_{12} (36 °C), to C_{14} (48 °C), to C_{16} (56 °C) gave a steady increase in the melting points of the ketene dimers made from the pure fatty acid feedstocks. The ketene dimers made from blended fatty acid feedstocks had significantly lower melting points than the corresponding ketene dimers made from pure fatty acids. For example, the ketene dimer made from the C_{12}/C_{14} fatty acid blend had a melting point of only 14 °C. The melting points of a series of ketene dimers made from C_{16}/C_{18} fatty acid blends, including the 40/60 palmitic/stearic acid blend used in the current study, are shown in Figure 2. All three blends had melting points (49–51 °C) significantly lower than the melting points of the pure C_{16} (56 °C) and pure C_{18} (61 °C) ketene dimers.

Several authors, most recently Garnier [21, 22], have proposed that vapor phase migration is a critical step in ketene dimer spreading and sizing development. As shown by the thermogravimetric weight loss curves in Figures 3 and 4, the series of eight ketene dimers evaluated in the current study represent a wide range of volatilities (0.5 °C per minute, N_2 atmosphere, open platinum container). Although the thermogravimetric method
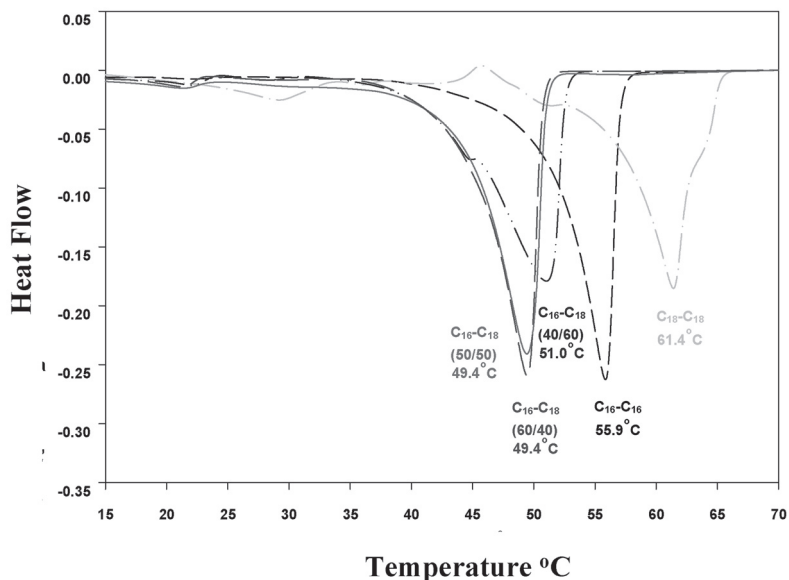
Figure 2 Ketene Dimer Melting Point.

used in the current study does not give an absolute measure of ketene dimer vapor pressure under papermaking condition, it does accurately rank the relative volatilities of the eight selected dimers. As expected, increasing fatty acid molecular weight reduced the volatility of the resulting ketene dimer. For example, the ketene dimer made from the pure C_{10} fatty acid feedstock lost 50% of its initial weight by 180 °C. The ketene dimers made from the pure C_{12} fatty acid, the pure C_{14} fatty acid, and the C_{12}/C_{14} fatty acid blend gave similar weight loss curves. All three ketene dimers lost 50% of their initial weight by 220–240 °C. The ketene dimers made from the pure C_{16} fatty acid, the oleic/linoleic fatty acid blend, and the technical grade C_{18} fatty acid also gave similar weight loss curves. All three ketene dimers lost 50 % of their initial weight by 270 °C. Weight loss curves for a series of five ketene dimer made from C_{16}/C_{18} blends, including the 40/60 blend used in the current study, are shown in Figure 4. All five ketene dimers gave similar weight loss/temperature profiles, even though they had significantly different melting points. It should be noted that none of the ketene dimers showed a significant amount of weight loss due to evaporation at the temperatures used to dry paper. Based on these results, residual
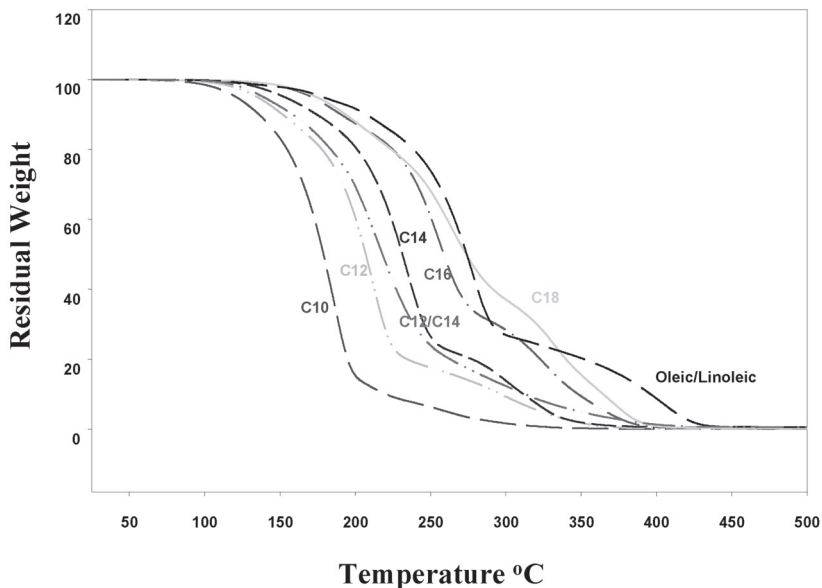
Figure 3   Ketene Dimer Volatility.

fatty acid left over from the manufacturing process is probably the only significant component of the dimers that is volatile under paper drying conditions.

From a physical property perspective, the ketene dimers evaluated in this study represent a broad spectrum of melting point and volatility combinations. For example, the ketene dimer made from the blend of oleic and linoleic acid had a low melting point and a low volatility. The ketene dimer made from pure C_{16} fatty acid had a similar volatility, but a much higher melting point. The ketene dimer made from the pure C_{10} fatty acid had a relatively low melting point and a high volatility. Interesting comparisons can also be made between the ketene dimers made from pure fatty acid feedstocks and the dimers made from blends of fatty acids. For example, the ketene dimer made from the blend of C_{12} and C_{14} fatty acids had a volatility close to that of the corresponding ketene dimers made from the pure fatty acids, but a much lower melting point.

Once their physical properties had been determined, the rate of sizing development of each ketene dimer was measured using the size press addition
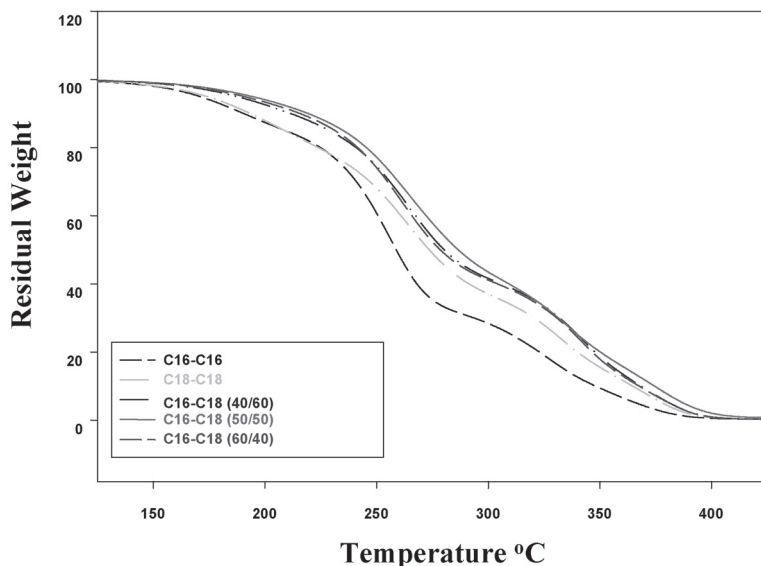
Figure 4 Ketene Dimer Volatility.

method described by Varnell [24]. The size press addition method was selected to minimize any effects caused by differences in ketene dimer retention. An unsized, highly-filled sheet made on the Western Michigan University pilot machine was used as the substrate (75 g/m², 15% medium particle size precipitated calcium carbonate, 11 m²/g). 5% oxidized corn starch was added with the ketene dimer at the size press. Standard hard water, 50 ppm hardness and 50 ppm alkalinity, was used to cook and dilute the size press starch. Dryer can temperature was fixed at 65 °C. Ketene dimer addition level was fixed at 0.1% (based on emulsion formula dimer). A starch based emulsion of each ketene dimer similar to that described in Reference 25 was used. A more complete description of the size press procedure is given in the Experimental section.

All eight ketene dimers progressed through three stages of sizing development (See Figure 5). An initial stage in which little or no HST sizing was developed was observed at drying times between 0 and 40 seconds. A second stage in which all eight ketene dimers gave a steep, linear increase in sizing as drying time increased from 40 to 240 seconds. And, a third stage in which sizing leveled off at drying times between 240 and 360 seconds. All eight
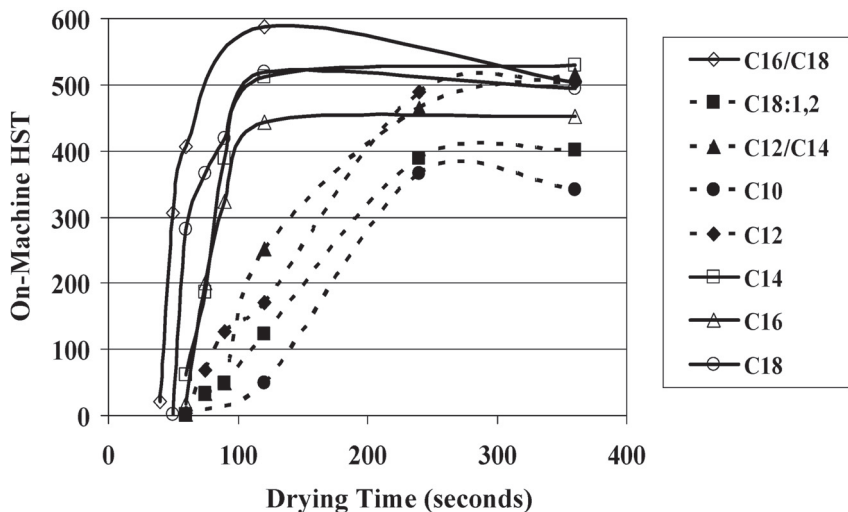
Figure 5   Sizing Response Curves.

ketene dimers gave high levels of sizing after 360 seconds of drying (350–500 HST seconds).

Ketene dimers develop sizing by a complex process. Unreacted ketene dimer, hydrolyzed dimer, ketene dimer oligomers, and covalently bound beta-keto ester formed by the reaction of ketene dimer with cellulose are all known to contribute to sizing [8, 9, 15, 16]. Each ketene dimer reaction product contributes differently to HST sizing. For example, covalently bound beta-keto ester is believed to be a more efficient sizing agent than hydrolyzed dimer. Based on this sizing model, HST sizing development should not follow simple kinetics.

Nevertheless, approximate rate constants for sizing development were calculated for each ketene dimer using the slope of the linear increase in sizing in the second stage of sizing development and the ultimate level of sizing reached after 360 second of drying. The calculation was carried out as follows. First, a standard least squares regression method was used to calculate the slope of the increase in sizing during the second stage of sizing development (See Figure 5). The regression equation was then used to calculate the length of time needed for sizing to increase from 0 seconds of HST sizing to half of the ultimate level of sizing. This "half-life" was then converted to a rate constant using the standard equation for first

order kinetics, where k_1 is the first order rate constant, and τ is the half-life in seconds.

$$k_1 = \ln 2 / \tau \qquad (1)$$

In most cases, excellent fits were obtained to at least four half-lives of sizing development, confirming that the linear fit is a good model for the sizing development process (See Table 1, at least 94% of the ultimate level of sizing). It should be noted that two key assumptions went into this calculation. First, it was assumed that the concentration of ketene dimer is proportional to the rate of formation of each of the reaction products that contributes to sizing. And, it was assumed that the water, cellulose, and starch components of the paper that react with ketene dimer are present in large molar excess.

Ketene dimer melting point had a clear effect on the rate of sizing development (See Table 1 and Figure 5). The four lowest melting ketene dimers (C_{10}, C_{12}, C_{12}/C_{14}, and oleic/linoleic dimers) gave parallel slopes in the second stage of the sizing development curve and similar rate constants for sizing development (approximately 7×10^{-3}/sec). The four high melting ketene dimers (C_{14}, C_{16}, technical C_{18}, and C_{16}/C_{18} dimers) formed a second set of parallel slopes in the second stage of the development curve and gave significantly higher rate constants for sizing development (approximately 2×10^{-2}/sec). Based on these rate constants, the high melting ketene dimers developed their ultimate level of sizing three times faster than the low melting ketene dimers. It should also be noted that the high melting ketene dimers initiated sizing at shorter drying times and higher sheet moistures than the low melting ketene dimers (See Figure 5). These results suggest that liquid and solid ketene dimers have significantly different mechanisms of sizing development under mild drying conditions.

Finally, it should be noted that ketene dimer volatility and molecular weight had no consistent effects on the rate of sizing development. For example, the liquid ketene dimer made from oleic and linoleic acid and the high melting ketene dimer made from palmitic and stearic acids had similar volatilities, but very different rate constants for sizing development. These results suggest that vapor phase transport of ketene dimer is not involved in the rate determining step of sizing development. Vapor phase migration may still be important for the development of permanent, non-extractable sizing.

Effect of dryer temperature on rate of sizing development

A second study was then carried out in an effort to gain a better understanding of how ketene dimer melting point affects the rate of sizing development.

As shown in Tables 2 and 3, the rates of sizing development of the solid ketene dimer made from a mixture of palmitic (C_{16}) and stearic (C_{18}) acids and the liquid ketene dimer made from oleic and linoleic acids were measured over dryer temperatures ranging from 55 °C to 85 °C. Ketene dimer addition level was again fixed at 0.1% (based on emulsion formula dimer). The remaining size press treatment conditions were kept as close as possible to those used in the preceding study. The sheet moistures measured over the entire range of drying conditions are shown in Figure 6.

Table 2 Effect of Sheet Moisture on Rate of Sizing Development

Dryer Temperature	Palmitic/Stearic Solid Ketene Dimer		Oleic/Linoleic Liquid Ketene Dimer	
	Sizing Initiated (s)	% Sheet Moisture	Sizing Initiated (s)	% Sheet Moisture
55 °C	30	19	60	11
60 °C	20	19	–	–
65 °C	35	17	60	8
75 °C	20	19	40	11
85 °C	15	16	20	15

Table 3 Effect of Dryer Temperature on Rate of Sizing Development

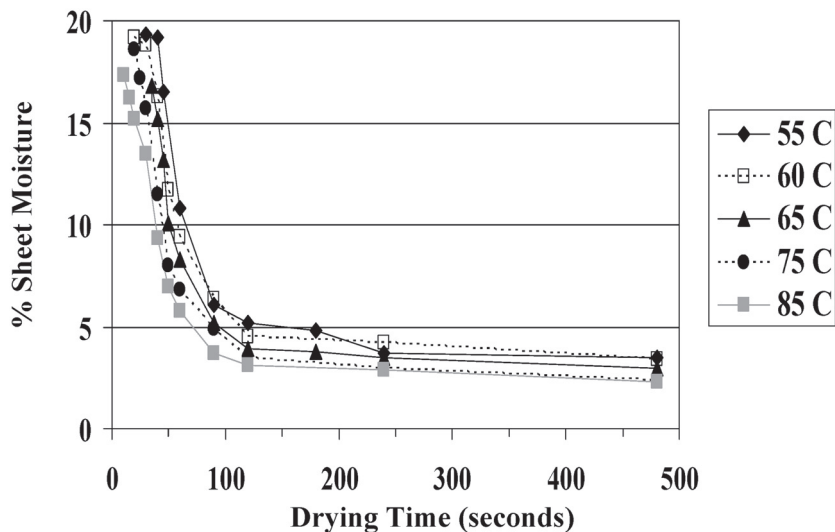| Dimer	Dryer Temperature	Rate Constant (s^{-1})	Regression	
			% of Endpoint	R^2
Oleic/Linoleic Acid Ketene Dimer	55 °C	5.6×10^{-3}	87%	95%
	65 °C	8.1×10^{-3}	100%	99%
	75 °C	1.7×10^{-2}	100%	99%
	85 °C	2.0×10^{-2}	84%	90%
Palmitic/Stearic Acid Ketene Dimer	55 °C	5.6×10^{-3}	90%	98%
	60 °C	5.5×10^{-3}	86%	97%
	65 °C	4.0×10^{-2}	94%	86%
	75 °C	4.5×10^{-2}	90%	93%
	85 °C	3.0×10^{-2}	82%	97%

Figure 6   Sheet Moisture vs. Drying Time.

Both ketene dimers gave similar patterns of sizing development over the entire range of drying conditions tested (See Figures 7 and 8). As in the previous study, an initial drying time with no measurable HST sizing was followed by a steep linear increase in sizing, and a leveling off at long drying times. The drying time needed to initiate sizing generally decreased as dryer temperature increased for both ketene dimers.

Consistent with the results of the preceding study, the solid palmitic/stearic acid ketene dimer developed sizing at significantly shorter drying times, and much higher sheet moistures, than the oleic/linoleic acid ketene dimer (See Table 2). For example, the palmitic/stearic acid ketene dimer required only 30 seconds of drying at 55 °C to initiate sizing. The oleic/linoleic acid ketene dimer required 60 seconds to initiate sizing at the same dryer temperature. As shown in Table 2, the palmitic/stearic acid ketene dimer initiated sizing over a narrow range of sheet moistures, regardless of drying temperature (16–19%). Significantly lower sheet moistures were needed to initiate sizing with the oleic/linoleic acid ketene dimer (8–15%). These results are consistent with the hypothesis that the palmitic/stearic acid and oleic/linoleic acid ketene dimers initiate sizing by different mechanisms.

Pseudo first order rate constants for sizing development for the palmitic/ stearic acid and oleic/linoleic acid ketene dimers were then calculated using
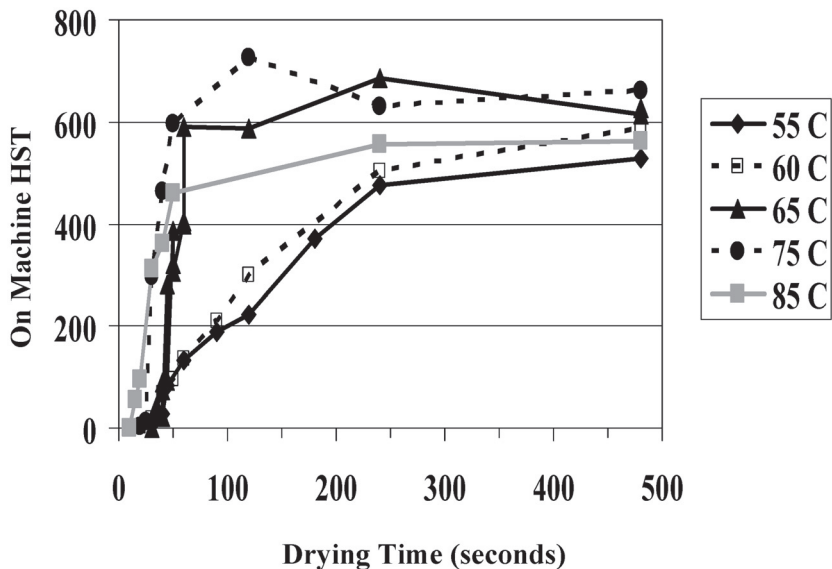
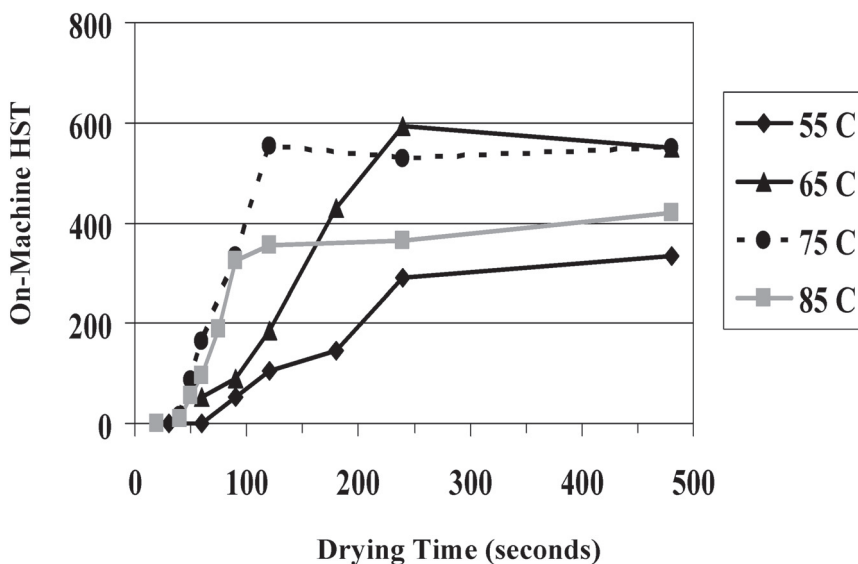**Figure 7** C_{16}/C_{18} Sizing Response Curves.

Figure 8   Oleic/Linoleic Sizing Response Curves.

the method described in the preceding section (See Table 3 and Figures 9–10). In almost every case, a good linear fit to the initial steep increase in sizing was obtained for the first three half-lives of sizing development (87% of the ultimate level of sizing).

As shown by a plot of the natural log of the sizing development rate constants versus temperature (See Figure 11), both ketene dimers gave similar rates of sizing development at the extremes of dryer temperature used in this study (55 °C and 85 °C). Very different results, however, were obtained at intermediate dryer temperatures. The liquid oleic/linoleic acid ketene dimer gave a steady, increase in rate of sizing development as dryer temperature increased from 55 °C to 85 °C. The palmitic/stearic acid ketene dimer gave a discontinuous increase in the rate of sizing development between 60 °C and 65 °C. This discontinuity in rate of sizing development was measured on three separate occasions with identical results. Increasing dryer temperature from 65 °C to 75 °C to 85 °C gave no additional increase in the palmitic/stearic acid ketene dimer's rate of sizing development.

An Arrhenius plot of the rate constants obtained for the oleic/linoleic acid ketene dimer between 55 °C and 85 °C yielded an activation energy of 11 kcal per mole for sizing development (See Figure 12, $R^2 = 96\%$). This value in a
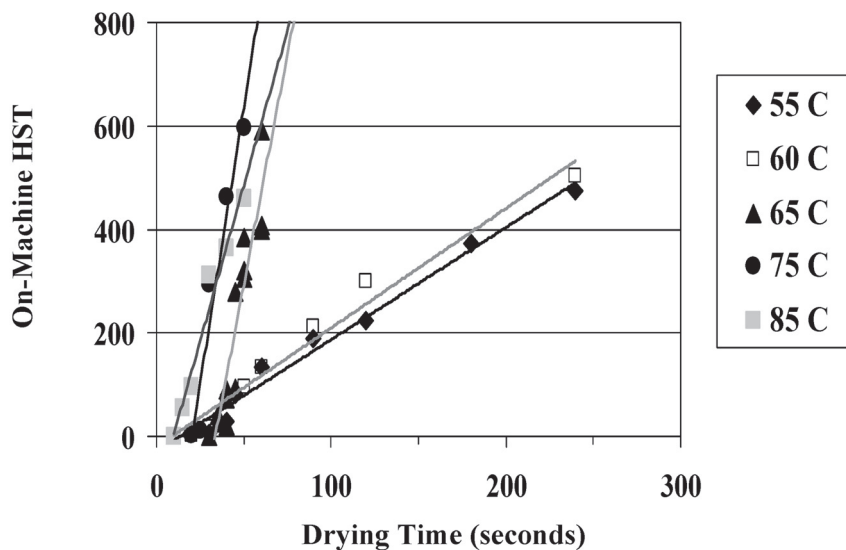

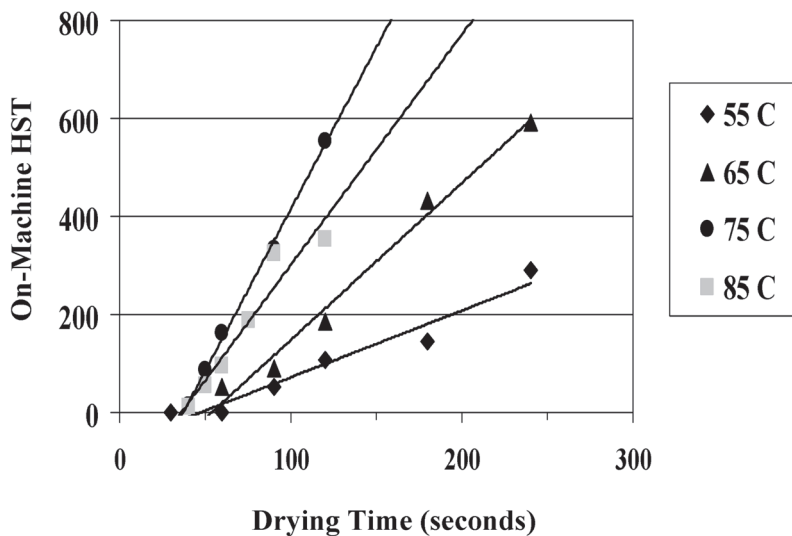**Figure 9** C_{16}/C_{18} Regression Analysis.

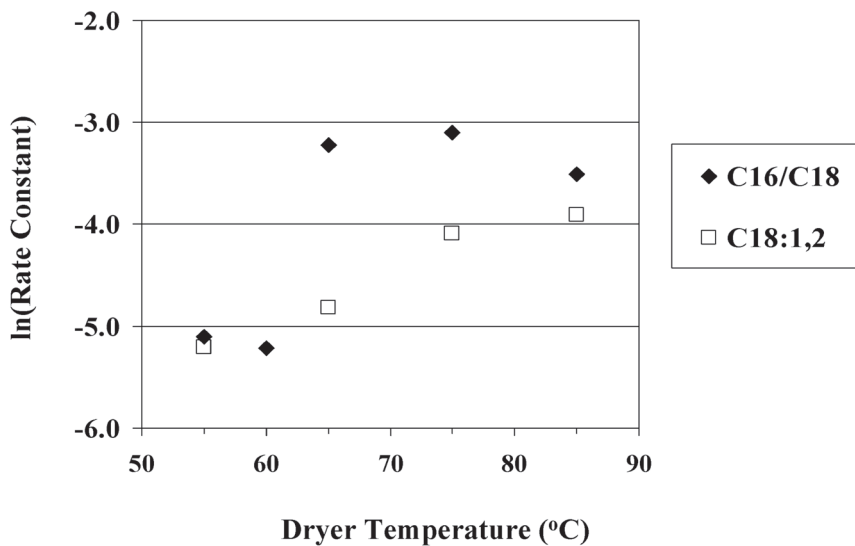**Figure 10**   Oleic/Linoleic Regression Analysis.

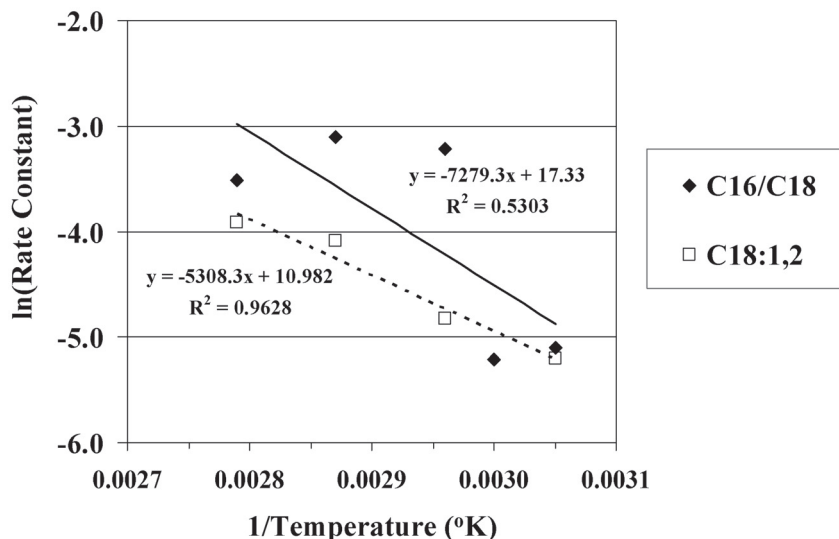**Figure 11**   Rate Constants vs. Dryer Temperature.

Figure 12 Arrhenius Equation Activation Energy.

highly alkaline system is somewhat lower than the activation energies (13–17 kcal per mole) measured by Lindstrom for the rate of bound ketene dimer formation in an internally sized, unfilled alkaline sheet [9]. The activation energy measured for the oleic/linoleic acid ketene dimer in the current study is also somewhat lower than the activation energy measured by Garnier for vapor phase transfer of hydrophobicity from a ketene dimer sized sheet to a cellulose surface (15 kcal/mole) [22]. Lindstrom reported a drop in activation energy as the pH of the papermaking system increased. It is possible that the increased alkalinity of the sheet can account for the relatively low activation energy measured in the current study.

An Arrhenius plot of the rate constants obtained for the palmitic/stearic acid ketene dimer between 55 °C and 85 °C yielded an activation energy of 15 kcal per mole. Due to the poor fit, the standard deviation associated with this value is relatively large. It should also be noted that the Arrhenius plot shows that the palmitic/stearic acid ketene dimer develops sizing with only a very small energy barrier between 65 °C and 85 °C.

Based on these results, it is likely that the palmitic/stearic acid and oleic/linoleic acid ketene dimers initiate and develop sizing by substantially different mechanisms. The oleic/linoleic acid ketene dimer followed relatively simple kinetics. The rate of sizing development increased steadily as dryer

temperature increased. An activation energy of 11 kcal per mole was measured. These results are consistent with a simple mechanism in which the chemical reaction of the lactone ring is the rate determining step in sizing development for liquid ketene dimers.

The palmitic/stearic acid ketene dimer followed more complex kinetics and probably developed sizing by a combination of mechanisms. It is likely that the palmitic/stearic acid ketene dimer developed a significant fraction of its sizing by the chemical reaction of the lactone ring. Sizing developed by this mechanism should follow a simple rate law similar to that found for the oleic/linoleic acid ketene dimer. This hypothesis is supported by the equal rate constants for sizing development measured for the palmitic/stearic acid and oleic/linoleic acid ketene dimers at the highest and lowest temperatures used in this study (55 °C and 85 °C).

A second sizing mechanism superimposed on the chemical reaction mechanism is needed to explain how the palmitic/stearic acid ketene dimer developed sizing at higher sheet moistures and shorter drying times than the oleic/linoleic acid ketene dimer. It is likely that both reacted and unreacted ketene dimer were present under these drying conditions. Lindstrom showed that unreacted ketene dimer can contribute to sizing in the presence of bound dimer [8, 9]. Based on his result, it is likely that unreacted palmitic/stearic acid ketene dimer can also contributed to sizing at the short drying times used in this study. This hypothesis is further supported by work reported last year by Varnell [24]. Using the same size press addition method used in the current study, he showed that almost all of the initial sizing development obtained from a palmitic/stearic acid based ketene dimer is solvent extractable. High levels of extractable HST sizing were obtained well before the formation of significant non-extractable sizing was observed at longer drying times. Solid waxes are generally known to be more efficient sizing agents than liquid waxes. Therefore, it is likely that the differing sizing responses measured for the solid palmitic/stearic acid and liquid oleic/linoleic acid ketene dimers at very short drying times were due to differing contributions of the unreacted ketene dimers. Some hydrolyzed dimer may also be present and contribute to sizing at this point. An alternative explanation also deserves mention. It is possible that the palmitic/stearic acid ketene dimer can order itself into a monolayer, spread, and react more readily than the oleic/linoleic acid ketene dimer [20].

A third sizing mechanism superimposed on the chemical reaction mechanism is needed to explain the palmitic/stearic acid ketene dimer's discontinuous increase in rate of sizing development at 65 °C, and the absence of a significant energy of activation for sizing development between 65 °C and 85

°C. All of the dryer temperatures used in the current study were well above the melting point of the unreacted ketene dimer (49 °C). So it is not likely that the discontinuity in rate of sizing development represents an increased contribution to sizing from the unreacted ketene dimer as it melts and flows. It is more likely that the discontinuity in rate of sizing development represents the increased contribution of hydrolyzed ketene dimer. Hydrolyzed ketene dimers are known to contribute to sizing, particularly if some bound ketene dimer is present [15, 16]. The hydrolyzed palmitic/stearic acid ketene dimer used in the current has a DSC melting point of 70–75 °C in its pure form. A mixture of hydrolyzed and unreacted ketene dimer should have a lower melting point. At dryer temperatures below 65 °C, it is possible that hydrolyzed palmitic/stearic acid ketene dimer cannot melt and flow and contribute efficiently to sizing. At higher temperatures, hydrolyzed palmitic/stearic acid ketene dimer should be able to melt and flow and contribute efficiently to sizing. The increased contribution of hydrolyzed ketene dimer could easily mask the changing rate constant for the chemical reaction of palmitic/stearic acid ketene dimer between 65 °C and 85 °C. Since melting and flowing of the hydrolyzed ketene dimer should have a relatively low activation energy, an increased contribution from the hydrolyzed palmitic/stearic acid ketene dimer could yield an Arrhenius plot with little or no energy of activation over this temperature range.

The liquid oleic/linoleic acid ketene dimer used in the current study forms a liquid hydrolyzate at room temperature. Since the hydrolyzate is a liquid over the entire range of drying conditions, whatever contribution hydrolyzed oleic/linoleic acid ketene dimer makes to sizing should not be affected by dryer temperature.

Future plans

Additional work is needed to answer some of the questions raised by these studies. Additional sizing data using solvent extracted paper is needed to separate the effects of bound, unreacted, and hydrolyzed dimer. And, add back experiments are needed to determine the relative contributions of unreacted oleic/linoleic acid and palmitic/stearic acid ketene dimers and their hydrolyzates in the absence of bound beta-keto ester.

Experimental

Rate of sizing development testing was carried out on a laboratory puddle size press. A highly-filled, unsized sheet made on the Western Michigan University pilot machine was used as the substrate (75 g/m², 70:30 HW:SW,

15% medium particle size scalenohedral PCC – 11 m^2/g, 0.5% cationic potato wet end starch, 0.25% alum, no size press treatment).

An oxidized corn starch was added with the ketene dimer sizing agents on all runs The size press starch was prepared by cooking at 95–100 °C for 45 minutes. 50 ppm hardness, 50 ppm alkalinity water was used to cook and dilute the starch. Starch concentration was adjusted to compensate for water loss during cooking. Starch solutions were stored in a water bath at 70 °C prior to use. All starch solutions were used within six hours of preparation.

Ketene dimer concentration in the size press starch solution was based on wet pick-up measurements (average of three measurements). Wet pick-up measurements ranged from 95–100% of the original substrate sheet weight. Based on these measurements, a 5% solids starch solution was used to give 5% starch pick-up. Similarly, a 0.1% ketene dimer concentration was used to give 0.1% pick-up (based on emulsion formula dimer). The ketene dimer emulsion was added to the starch solution immediately before use. An emulsion formulation similar to that described in Reference 25 was used.

Individual sheets (11 cm × 28 cm) for sizing development testing were treated in the size press as follows. Hot water was run on the rollers before each run to preheat them to the desired temperature. A 100 mL aliquot of the treatment solution was then poured into the size press nip and the substrate sheet was passed through the rollers. The sheet was immediately dried on a drum dryer at the desired temperature. The level of HST sizing was measured immediately after drying (one front and one back measurement, 80% reflectance, Hercules #2 ink). Two sheets were tested at each combination of drying time and temperature, for a total of four HST measurements per condition. Sheet moisture was also measured for each combination of drying time and temperature (average of five measurements).

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THE EFFECT OF KETENE DIMER MELTING POINT ON THE RATE OF SIZING DEVELOPMENT

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Tom Lindström   STFI-Packforsk AB

When it comes to the activation energy for the AKD-reaction I think that there is a danger in trying to determine activation energies from the Hercules Sizing Test (HST) instead of reacted amount of AKD. The HST is certainly nonlinear with reacted amount of AKD, and for solid AKD, our data (that were published years ago) are in direct conflict with your data. We did not go down to the very low temperatures, but in the upper region we had a considerable activation energy.

Secondly, coming to your interpretation, which I think is interesting. Looking at your data regarding the kinetics, we can see that they apparently fall into two groups. One difficulty in judging those curves is that the efficiency of the liquid AKD's is much lower than the efficiency of the solid AKD's, which will shift the curves for the liquid AKD up, if you compare them against the amount of reacted AKD.

Clement Brungardt

I think if you did plot them versus the reacted amount they would have similar rates of sizing development. Several questions were involved there. If I go back to your 1986 paper, I think it was the second Nordic Pulp and Paper article (see reference 9 in the paper). What you showed was energies of activation between 14 and 17 *kcals/mol* and you saw energy of activation dropping as the alkalinity of the system went up or the pH of the system went up. We are working in a much higher alkalinity system, we are in a highly filled

Discussion

paper and we are not just tracking reacted dimer. Whereas your paper looked at the development of non-extractable permanent sizing; that 10.5 *kcal* number that I am quoting really encompasses several processes, sizing from dimer, sizing from hydrolysate, sizing from ketene dimer oligomer, all of those processes. So, I would expect to get an energy of activation that suggests there is a chemical reaction going on. I would not necessarily expect to get the same energy of activation as you got for just one of those reactions. As far as the HST sizing goes, the sizing agent addition levels were chosen so that we would get very high sizing levels for all eight ketene dimers. They were all in the ranges of 400, 500 or 600 seconds. We are looking at substantial sizing for all of them. HST does not correlate linearly with the chemical reaction, but then that really was not my purpose, I was not trying to track the chemical reaction. What I was trying to track was the rate of sizing development. I was trying to answer the question that our sales managers were asking as I stated in the introduction. We have got the solid ketene dimers. We have got the liquid ketene dimers. Why are they developing sizing at different rates? Those different rates of sizing development were not affecting the size press starch pickup. What they were affecting was size press starch absorption in the sheet and that absorption was affecting print quality and surface strength.

Tom Lindström

Looking at your conclusions, you said that the hydrolyzed material has a contribution. Looking at our more recent hydrolysis trials I would say that there would be no hydrolysis, even at highly alkaline conditions, for handsheets. You have to have pretty harsh conditions for hydrolysis to occur.

Clement Brungardt

Evidence supporting the hydrolysis of ketene dimer on the paper machine is given in Reference 16 of the paper. See Table III on page 114.

K. J. Bottorff. AKD sizing mechanism: a more definitive description. *Tappi J*. **77**(4):105–116, 1994.

Bottorff found that ketene dimer was almost completely hydrolyzed on the surface of PCC (precipitated calcium carbonate) after 5 minutes at 70 ℃. This is well within the range of the drying conditions used in this study (55–85 ℃, with drying times up to 6 minutes). For comparison to Bottorff's work,

the PCC used in this study was a scalenohedral PCC with a surface area of 11 m^2/g. We used 0.1% ketene dimer and 15% PCC, yielding a concentration of 0.67% ketene dimer to PCC. Bottorff found that ketene dimer hydrolyzes much more slowly on GCC than PCC. Perhaps this explains the differing experience in Europe and North America.

We have done a lot of work in the last 2 or 3 years on analysing the components, the final products of AKD, in paper. Bill Scott at Miami, Ohio made ketene dimer radio-labelled paper for us. Unfortunately, the work is not published. So we actually have radio-labelled data on ketene dimer products in a variety of papers under a variety of conditions where we have actually been able to get closure on what each one of the products is in the paper. We do find a fair amount of hydrolyzed material in the paper. What we do not find in the finished paper is unreacted dimer and I will just say that we do find the bound ketene dimer and we find an awful lot of what we would call ketene dimer oligomer that greatly complicates the whole analysis process. The extraction process, the extraction method used can significantly change what you consider bound dimer and unbound oligomer. The oligomer is often very difficult to extract and can be misinterpreted as bound ketene dimer. The answer to your question is: we do find hydrolyzed dimer on the paper machine.

Tom Lindström

Understand me correctly, I mean in the handsheet experiment, I would not expect much to be hydrolyzed, but on the paper machine there is a lot of hydrolysis occurring. We should compare our hydrolysis data.

John Roberts

I think probably, to some extent, it depends upon how long you wait after the sheet is made and my feeling is that hydrolysis in the sheet is going to be a very slow process. I agree with you. It may be more difficult to say on a paper machine.

Clement Brungardt

If you go back to organic chemistry and you look at the chemical reactivity of water versus an alcohol group on cellulose. They have very similar nucleophilicities and you would expect them to have very similar rates of reaction. Since there is a whole lot more water in a headbox, particularly on a mole

basis, than there are alcohol groups on the cellulose, I would be surprised if hydrolysis did not occur at least as fast as the reaction to form bound dimer.

Tom Lindström

Let us compare the data when they are in the literature.

Murray Douglas   McGill University

You talked about the effect of drying on the development of sizing. You have 4 to 5 temperatures of drying. What are those temperatures? Is it the temperature of the air in which the sheet is dried or the temperature of a hot plate on which they are mounted? What is the drying condition?

Clement Brungardt

The temperatures in the paper refer to the temperature of the starch that we were adding at the size press and they are also the temperature of the drum drier itself. When you are looking at the drying temperatures that we used, you can probably convert it to sheet temperature as well. If I were going to pick a hole in this study, what I would say is that we didn't measure rate of sizing development at 100°C. We didn't use higher drying temperatures because the reaction was too fast to measure in the lab.

Roger Gaudreault   Cascades Canada Inc

What prevents us from trying to do some industrial vapour sizing? Laboratory vapour phase sizing has been published many years ago.

Clement Brungardt

I want to make it clear that I am talking mostly about non-permanent sizing and the initial rate of sizing development in this study. We did not see any correlation between ketene dimer vapor pressure and the rate of sizing development in this study. Vapor phase migration of ketene dimer may still be important for the development of permanent sizing. Vapor phase migration has been shown to be important under some papermaking conditions. It just did not show up as important for the initial rate of sizing development in this study. For non-extractable sizing it very well could be important. For the reaction to form bound ketene dimer, vapor phase migration of ketene dimer could be the rate turning step. I would like to take the paper sized with the

eight ketene dimers used in this study, extract the sheets and look at the rate constants for the formation of non-extractable sizing or bound ketene dimer. I do not want to say that paper phase transmission is not important because I honestly think it may be.