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NEUTRAL SIZING AND THE MECHANISM OF ALKYL KETENE DIMER SIZING

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ABSTRACT

The principle of reactive sizing is discussed, and the variety of sizes which have been considered is reviewed.

The reactivity of tetradecyl ketene dimer towards water and model compounds for cellulose has been shown to be very low and the results suggest that very little β-keto ester formation would be expected under normal papermaking conditions.

A study has also been made of the retention of C-14 labelled tetradecyl ketene dimer in laboratory handsheets, and of the degree of sizing which is induced. The results show that the dimer is present in the sheet predominantly in its unreacted form, but that a small percentage is present in a form which is not amenable to extraction by chloroform. This residual size exerts a considerable sizing effect, and the amount present in the sheet is related to the curing conditions used. The nature of the unextractable material has been studied by mild hydrolysis and the results are compatible with a low level of β-keto ester formation. Comparisons have been made with C-14 labelled hexadecyl hexadecanoate, a compound of similar structure and physical characteristics but which is unable to undergo reaction with cellulose.

A study has also been made of the influence of aluminium sulphate on alkyl ketene dimer sizing. The retention of size in sheets made in the presence of aluminium sulphate is reduced, but not to a sufficiently low level to account for the loss in sizing which is observed. An explanation in terms of the inhibition of reaction of the dimer with cellulose as a result of adsorbed aluminium species is proposed.

INTRODUCTION

The internal sizing of paper is achieved by retarding the rate of penetration of a fluid, usually water, through capillaries formed both within and between fibres. The rate of capillary rise of fluids into paper has been effectively described by the Washburn equation (1) and modifications of it (2). These approaches assume that the penetration of a fluid into paper is analogous to the penetration of a fluid into a single capillary. Retardation is brought about by increasing the contact angle formed between a drop of liquid and the fibre surface and thus decreasing both the wettability and the rate of penetration. Contact angles have been shown to be sensitive to molecular packing, surface morphology and chemical constitution (3-5), and it is the latter which is influenced during the internal sizing of paper.

All internal sizing agents attempt to modify the fibre surface free energy by virtue of introducing hydrophobic molecular groups on to the surface. This has to be done in a way which will allow a good distribution of the sizing molecule through the body of the sheet but which will not interfere with interfibre bonding (cf. fibre softening agents). Thus internal sizes are introduced at the wet end of the papermaking system, usually as colloidal suspensions, which are incorporated into the fibre network during sheet formation and are able to migrate and undergo molecular reorientation during and after drying. The development of sizing in this period after sheet formation and drying is often referred to as curing.

The most well known of these internal sizes are the naturally occurring resin acids related to abietic acid. These are used in conjunction with aluminium sulphate in an acidic system, and sizing is brought about by the retention in the sheet of precipitates of aluminium mono- and di-resinate together with some free resin acid. The mechanism for the retention of these precipitates in paper is primarily electrostatic, as the size precipitates assume a positive charge and are strongly adsorbed by the anionic fibre surfaces (6). Orientation of the size takes place during and after drying.

Rosin-alum sizes do not form any covalent attachment to the cellulose of the fibre cell wall and their effectiveness as sizing agents depends upon correct orientation of the hydrophobic groups at the fibre surface. Changes in pH, particularly high pH, can lead to the size being retained in an inappropriately oriented form and to complete loss of sizing. For this reason and also because of the desirability of making paper under neutral or alkaline conditions, a number of so called reactive sizes have been developed over the course of the last thirty years. These all depend upon the size molecule undergoing covalent attachment to the fibre surface through some form of reaction, often esterification, with the cellulosic hydroxyl groups. A list of the most common compounds which have been considered is shown in Table 1.

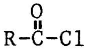
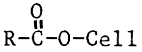
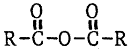
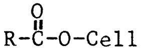
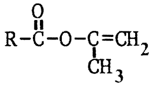
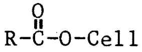
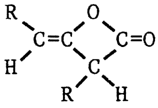
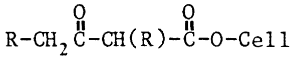
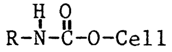
COMPOUND	STRUCTURE	R	CELLULOSE DERIVATIVE	REF
ACID CHLORIDE	 $R-\overset{O}{\overset{\parallel}{C}}-Cl$	$C_{14}-C_{18}$	 $R-\overset{O}{\overset{\parallel}{C}}-O-Cell$	7,8
ACID ANHYDRIDE	 $R-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-R$	$C_{17}H_{35}$	 $R-\overset{O}{\overset{\parallel}{C}}-O-Cell$ (+ RCOOH)	9-11
ENOL ESTER	 $R-\overset{O}{\overset{\parallel}{C}}-O-\underset{CH_3}{\underset{\vert}{C}}=CH_2$	$C_{17}H_{35}$	 $R-\overset{O}{\overset{\parallel}{C}}-O-Cell$ (+ $(CH_3)_2CO$)	12
ALKYL KETENE DIMERS		$C_{14}-C_{16}$	 $R-CH_2\overset{O}{\overset{\parallel}{C}}-CH(R)-\overset{O}{\overset{\parallel}{C}}-O-Cell$	13,14
ALKYL ISOCYANATE	R-N=C=O	$C_{17}H_{35}$	 $R-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\parallel}{C}}-O-Cell$	15

Table 1 Reactive sizes for cellulose

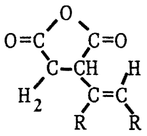
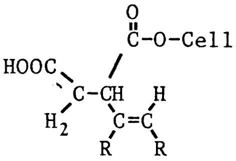
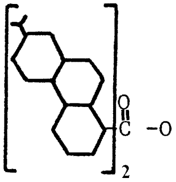
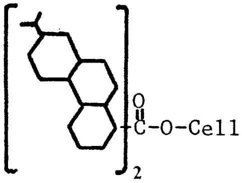
COMPOUND	STRUCTURE	R	CELLULOSE DERIVATIVE	REF
ALKENYL SUCCINIC ANHYDRIDE		C_6-C_8		16
ROSIN ANHYDRIDE				17

Table 1 Reactive Sizes for Cellulose (Continued)

The most commercially successful of these sizes are the alkyl ketene dimers (AKD) and the alkenyl succinic anhydrides (ASA), and these have slowly been replacing the traditional rosin-alum method in many applications.

As these sizes are able to react with water, their hydrolytic stability must be sufficient for them not to undergo hydrolysis either during storage or during the wet formation process. However, they must have a melting point which is low enough to allow dispersion during drying and must also be sufficiently reactive at these temperatures to participate in reaction with cellulosic hydroxyl groups.

Whilst it has always been assumed that reaction takes place during drying, the nature and extent of this reaction and also of the competitive hydrolysis has received little study. This paper describes some of the research which has been carried out in the field of alkyl ketene dimer sizing over the past few years, and also reports on the effect of aluminium sulphate on this sizing system.

GENERAL REACTIVITY OF ALKYL KETENE DIMERS

Alkyl ketene dimer sizing agents were first patented in 1953 (13) and were reported in the open literature in 1956 (18). They are believed to form a direct covalent linkage with cellulose via β-keto ester formation. The reaction is not specific to cellulose, and the dimers are also able to undergo hydrolysis with water to form an unstable β-keto acid which eliminates carbon dioxide to form a ketone. The general mechanism for this and the competitive hydrolysis reaction is shown in Figure 1. The evidence for direct β-keto ester formation with cellulose is rather tenuous and based on the observation that the dimer appeared not to be extracted from paper by organic solvents, and also on the observation that treatment of the dimer sized fibres with cuprammonium solution (a solvent for cellulose) left an insoluble shell behind, presumed to be the reacted external surface of the fibre (18). Recent research with C-14 labelled dimers (19,20), however, has shown that significant quantities of the dimer can in fact be extracted by organic solvents such as chloroform or tetrahydrofuran.

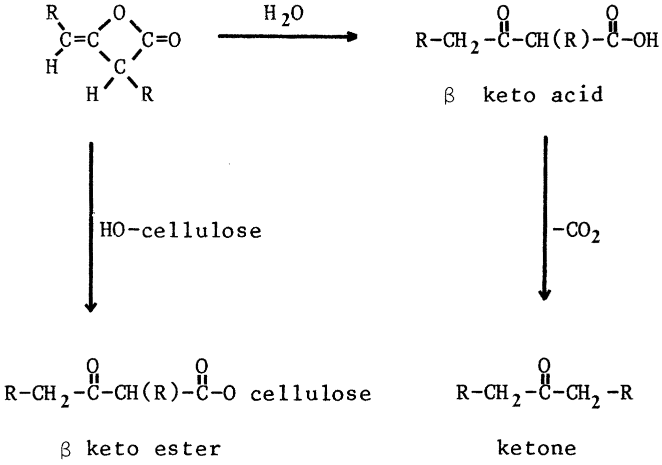


Fig 1—Reaction of diketene (R = H) and alkyl ketene dimers (R = $C_{14}H_{29}$ to $C_{16}H_{33}$) with cellulose and water.

The selection of alkyl ketene dimers as potential sizing agents for cellulose seems to be based on the work of Staudinger and Eicher in 1952 (21) in which the parent molecule of these dimers, diketene, was used to acetoacetylate cotton in glacial acetic acid using a sodium acetate catalyst (Figure 1). Kirillova and Padchenko later extended this work to a range of conditions and catalysts (22). However, these non-aqueous conditions are very different from those used in the papermaking process, and the reaction cannot be assumed to occur so readily in an aqueous system.

The possibility of some form of polymerisation being involved in sizing has not been given sufficient consideration, for diketene is known to undergo polymerisation even at room temperature (23) and, at higher temperatures, may polymerise explosively in the presence of appropriate initiators. A number of workers have studied polymer formation by diketene, and both polyester and polydiketone structures have been proposed (24-30). The nature of the polymer also seems to be dependent upon the type of catalyst used (28).

Roberts and Garner (31) studied the general reactivity of diketene and alkyl ketene dimers towards water and primary and secondary alcohols. Diketene itself was found to be surprisingly unreactive even in homogeneous dioxane solution at 50 °C. Reaction was only 50% complete after about 40hours (Figure 2). Attempts to form the β-keto ester of methyl β D-cellobioside in glacial acetic acid were also unsuccessful as shown by the fact that the characteristic proton nuclear magnetic resonance spectrum of the undisrupted β -lactone ring was still clearly visible after 72 hours (31).

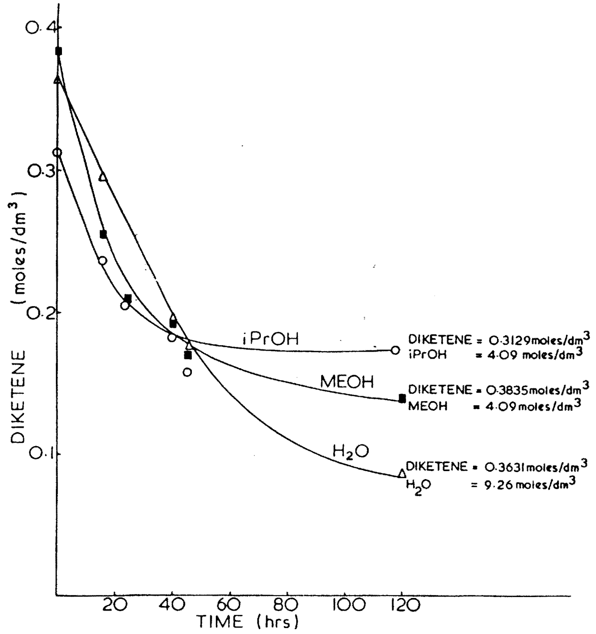


Fig 2—Rates of reaction of diketene with water, methanol and propan-2-ol.

The general reactivity of the higher analogues of diketene, the alkyl ketene dimers, would be expected to be lower than that of diketene because of the steric crowding of the reactive lactone ring by the two long chain alkyl groups. This has been confirmed for tetradecyl ketene dimer (31). Its rate of hydrolysis in a neutral aqueous dioxane solution was very slow ($T_{1/2} \sim$ 30 hours) and no reaction could be detected after 59 hours between the dimer and either methanol or propan-2-ol in chloroform (Table 2). However, under basic conditions, reaction with water and methanol took place more readily although no reaction could be observed with propan-2-ol (Table 2).

Substrate	Substrate conc. moles dm^{-3}	Tetradecyl ketene dimer conc. moles dm^{-3}	NaOH conc. moles dm^{-3}	Temp °C	Solvent	$T_{1/2}$ hours
water	4.27	0.065	-	92	1,4 dioxane	30
	4.27	0.065	0.64	92	1,4 dioxane	0.5
methanol	3.53	0.120	-	53	$CHCl_3$	>>59*
	3.63	0.120	1.20	53	$CHCl_3$	3
propan 2-ol	1.88	0.120	-	60	$CHCl_3$	>>59*
	1.88	0.120	1.20	60	$CHCl_3$	>>29*

* no reaction could be observed in the time stated

Table 2 The reaction of tetradecyl ketene dimer with water, methanol and propan 2-ol.

These results suggest that reaction between alkyl ketene dimers and cellulose in the papermaking system is likely to be slow, and in particular it is likely to be slower than the competitive hydrolysis with water. Pisa and Murckova (32) and Rohringer et al (33) offered some confirmation of this by studying the multiple internal reflectance infra red spectra of sheets of paper sized with alkyl ketene dimers. They were unable to detect the presence of β -keto ester linkages but were able to detect the characteristic infra red bands associated with the unreacted dimer.

REACTIVITY OF ALKYL KETENE DIMERS TOWARDS CELLULOSE

Isotopic (C-14) labelling techniques have proved to be very successful in investigating the reactivity of the dimers towards cellulose and water in paper prepared under standard handsheet conditions (19,20). The route to the synthesis of these labelled compounds is shown in Figure 3. When the starting material is palmitic or stearic acid, which is labelled at the C-1 carboxyl group, the dimer which is produced is labelled at two positions in the lactone ring. The technique is particularly useful because hydrolysis of the dimer leads to a β-keto acid (Figure 1) which readily decarboxylates to eliminate a molecule of labelled carbon dioxide, thus causing a 50% loss in activity. The activity balances may then be used to measure the extent of the competitive hydrolysis reaction.

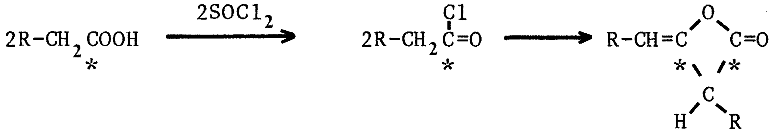


Fig 3—Formation of C – 14 labelled tetradecyl ketene dimer (R = $C_{14}H_{29}$)

Roberts and Garner (19) carried out a comparative study of the behaviour of two C-14 labelled compounds, tetradecyl ketene dimer and hexadecyl hexadecanoate (Figure 4). The latter was used for comparison purposes, as it is unable to undergo covalent reaction with cellulose.

Tetradecyl ketene dimer   Hexadecyl hexadecanoate

Fig 4—C – 14 labelled sizing compounds used in ref.19

The retention characteristics of starch stabilised emulsions of these two compounds were studied as a function of pH (Figure 5), and both display a pH optimum at about 8-9. This suggests that retention is a characteristic of the cationic starch used for stabilisation rather than of the sizing compounds themselves. It also supports the view that any reaction occurring between the dimer and cellulose does not take place at the wet end of the process. The low retention observed at low pH can be explained in terms of reversal of the dissociation of cellulose carboxyl groups, which in turn leads to a reduction in surface charge and a reduced electrostatic interaction with the cationic stabilised emulsion (34,35).

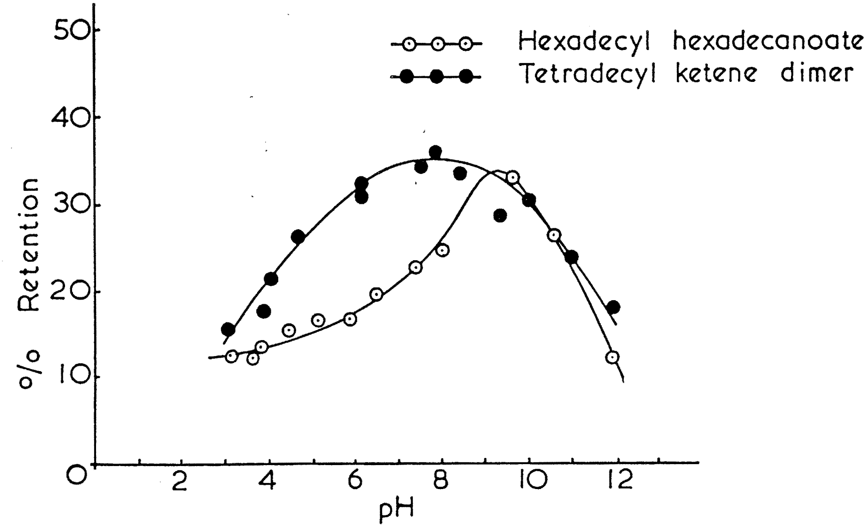


Fig 5—Retention of cationic starch stabilised emulsions of tetradecyl ketene dimer and hexadecyl hexadecanoate in handsheets as a function of pH

Handsheets containing either of these sizing agents, which had been conditioned at 50% relative humidity and 20 °C, but which had received no heat treatment, showed virtually no resistance to water penetration as measured by a water-absorbency test. However, heat treatment of the conditioned handsheets caused water resistance to develop for both compounds (Table 3).

HEAT TREATMENT		HEXADECYL HEXADECANOATE				TETRADECYL KETENE DIMER			
		BEFORE SOLVENT EXTRACTION		AFTER SOLVENT EXTRACTION		BEFORE SOLVENT EXTRACTION		AFTER SOLVENT EXTRACTION	
Temp °C	Time min	size content mg/g	AC g/g	size content mg/g	AC g/g	size content mg/g	AC g/g	size content mg/g	AC g/g
50	5	2.39	1.61	0.030	2.02	2.27	1.52	0.059	1.79
100	5	2.55	1.34	0.039	2.03	2.17	0.65	0.065	1.39
100	10	2.49	0.95	0.037	1.97	1.87	0.62	0.077	1.04
100	30	2.61	0.57	0.044	1.88	2.07	0.54	0.101	0.61

Note:AC=Absorbency Capacity (water absorbed per g of paper in 15 seconds);solvent extraction with chloroform for 50 hours.

Table 3 The Effect of Heat Treatment on Sizing development by Hexadecyl Hexadecanoate and Tetradecyl Ketene Dimer.

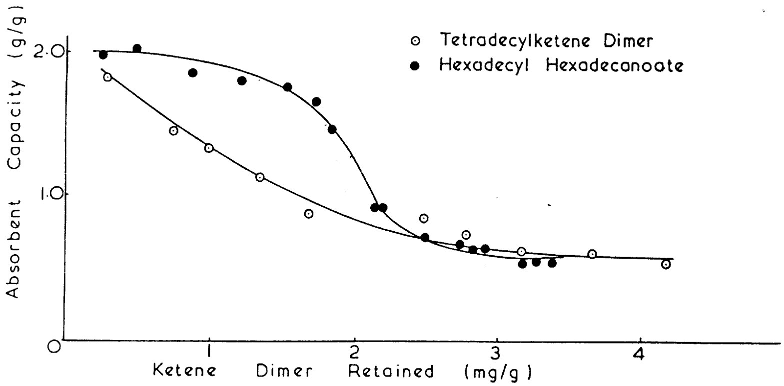


Fig 6—The relationship between absorbent capacity and the retention of tetradecyl ketene dimer and hexadecyl hexadecanoate

Heat treatment seems to be essential for the development of sizing by alkyl ketene dimers, and this observation has also been made by Lindstrom (20). It is also in agreement with the observation that during the industrial use of these dimers, the development of sizing takes place after drying and during reel-up. Although both compounds caused decreases in the degree of water absorption as a result of heat treatment, the sheets containing the dimer became hard sized after only five minutes at 100°C, whereas the sheets treated with the ester required extensive heating to achieve the same degree of sizing. Figure 6 shows the relationship between the retention of each of these compounds in the range 0 to 4mg/g and the degree of sizing induced.

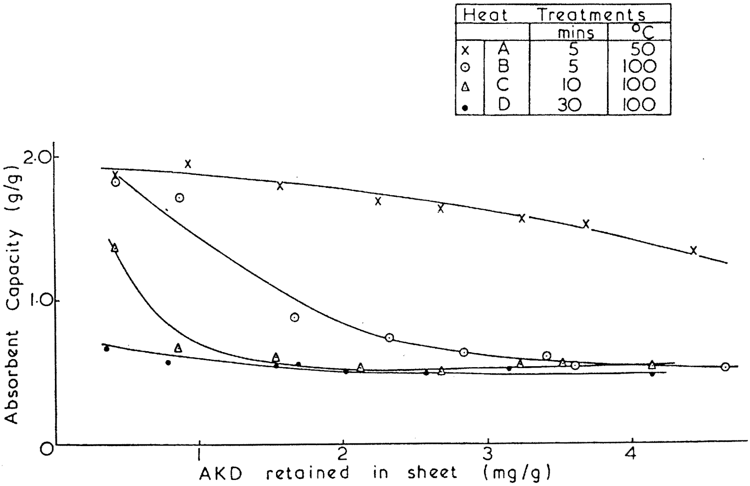


Fig 7—The effect of heat treatment on the absorbent capacity of sheets containing tetradecyl ketene dimer

At levels above 2.5mg/g, both compounds were equally effective, but at lower levels of retention the dimer was much more effective. Furthermore, in the case of the dimer, the more severe the heat treatment the lower was the level of retained dimer which was necessary to induce good sizing (Figure 7).

The difference between these two compounds is unlikely to be due to differences in their physical redistribution in the sheet during heating, for both compounds have almost identical melting points (hexadecyl hexadecanoate 53.5-54.5° (36) and tetradecyl ketene dimer 55.5-56° (37)) and both would be expected to be dispersed to a similar degree. The autoradiographs in Figure 8 show that dispersion and diffusion of the dimer occurs during heating. The difference in behaviour between the two compounds is more likely to be due to the formation of a β-keto ester during heat treatment in the case of the dimer. This would be expected to give rise to two highly orientated hydrophobic alkyl groups at the fibre surface which would inhibit the approach of advancing water molecules. Such a reaction would be impossible in the case of hexadecyl hexadecanoate, and the relatively small decrease in water absorbency which occurs on heat treatment of handsheets containing this ester (Table 3) is presumably due to diffusiion and spreading of the size in a relatively randomly oriented form.

In an attempt to assess the extent to which these compounds have become irreversibly 'bound' or reacted with the cellulose, a study has been made of the effect of chloroform extraction on the level of retained sizing agent and the absorbency capacity of the extracted sheets. Sheets which had been sized with labelled compounds and then heat-treated for different periods of time, were extracted with chloroform in a soxhlet extractor for 50hours, and their size content and water absorbency remeasured. The results are shown in Table 3.

In the case of sheets treated with hexadecyl hexadecanoate, the size content could be reduced to less than 2% of its original level by chloroform extraction and this also restored the water absorbency of the sheet to its unsized condition. Furthermore, the amount of material which was retained after solvent extraction was influenced very little by the severity of heat treatment. However, the dimer could not be solvent extracted so completely. Approximately 3% of the original activity remained after solvent extraction of sheets which had been heated at 50°C for 5 minutes, and this rose to about 5% for sheets which had been treated for 30 minutes at 100°C.

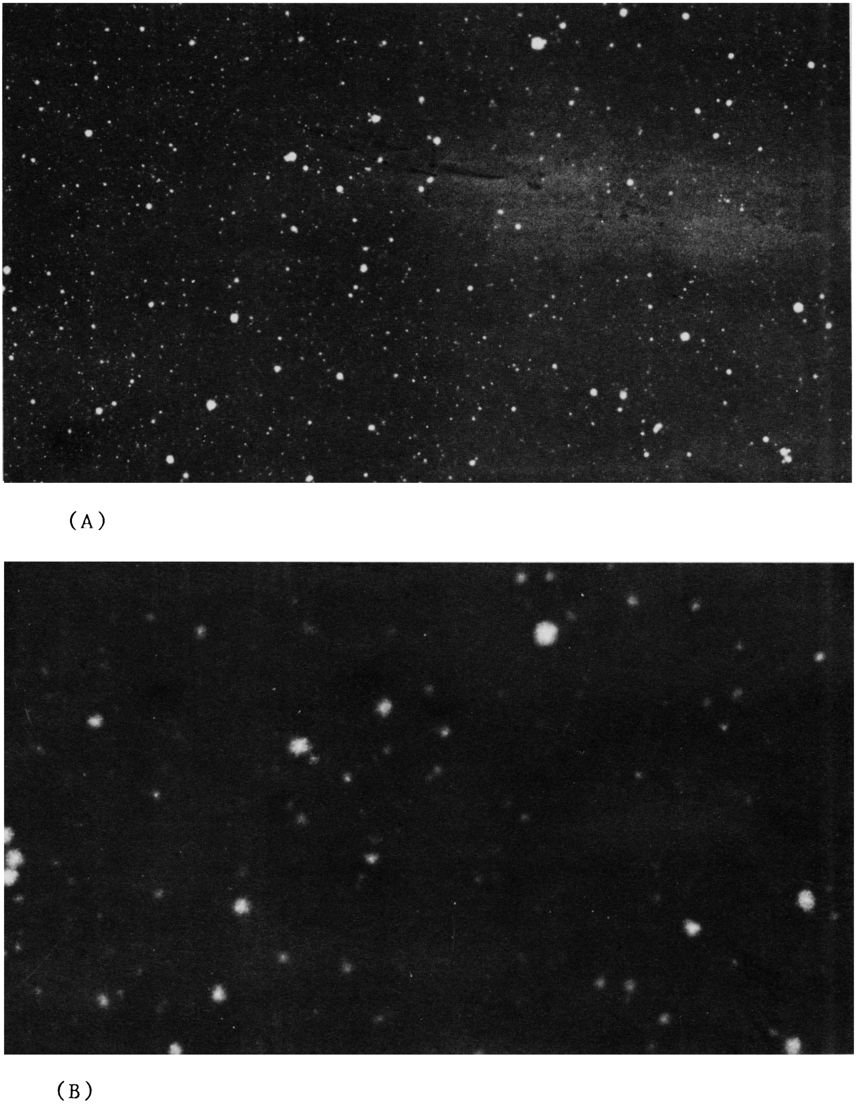


Fig 8—Autoradiographs of sheets containing tetradecyl ketene dimer before heat treatment (A), and after heating at 100 C for 10 minutes (B).
Identical fields ($\approx$ times 2)

Furthermore, the absorbency capacities of the solvent extracted sheets did not return to that of the unsized sheets, and in the case of the most severe heat treatment, the sheets remained hard sized. Similar results were observed by Lindstrom (20) for alkyl ketene dimers derived from stearic acid using a tetrahydrofuran extraction procedure.

These results demonstrate a marked difference in the behaviour of these two compounds. Clearly, hexadecyl hexadecanoate is able to control wetting and penetration of the sheet by virtue of its bulk presence, the distribution of which is improved by heat treatment. Solvent extraction removes virtually all of the ester and, with it, the sizing of the sheet. Tetradecyl ketene dimer is also present in a largely unreacted form as confirmed by the fact that over 95% of it can be extracted by chloroform, and that the extract has an identical infra red spectrum to the unreacted dimer. Its bulk presence does give rise to a limited amount of sizing (Table 3), but dispersion clearly occurs during heat treatment (Figure 8), and this in turn leads to an increase in the amount of non solvent-extractable material (Table 3). Unlike hexadecyl hexadecanoate, however, the residual unextractable material exerts a powerful sizing effect (Table 3).

The nature of this residual non solvent-extractable material has been studied in order to establish whether it is present as a β-keto ester. Experiments have been carried out in which the residual material present after chloroform extraction has been subjected to mild hydrolysis by refluxing sheets in deionised water for 20 hours and then subjecting them to further chloroform extraction. The results are shown in Table 4.

Sheets, when treated in this way, regained all their water absorbency, and their size content was reduced to negligible levels. Tetradecyl ketene dimer is known to undergo slow hydrolysis under these conditions (see Table 2) but the hydrolytic stability of β-keto esters under these conditions is not known. In order to ascertain the stability of both tetradecyl ketene dimer and a β-keto ester derived from it, labelled methyl 2-tetradecyl-3-oxo octadecanoate has been prepared (Figure 9).

	CONTROL (UNSIZED)	SIZED SHEET BEFORE SOLVENT EXTRACTION	SIZED SHEET AFTER SOLVENT EXTRACTION*	SIZED SHEET AFTER SOLVENT EXTRACTION HYDROLYSIS AND SOLVENT EXTRACTION **
Retention of Dimer mg/g	0	1.05	0.100	0.030
Absorbency Capacity g/g	2.13	0.49	0.71	2.50

* Soxhlet extraction with chloroform for 6 hours.
** as above, plus 20 hours refluxing with water, followed by soxhlet extraction with chloroform for a further 6 hours.

Table 4 The Effect of Neutral Hydrolysis of Residual Dimer on Retention and Water Absorbency of Handsheets.

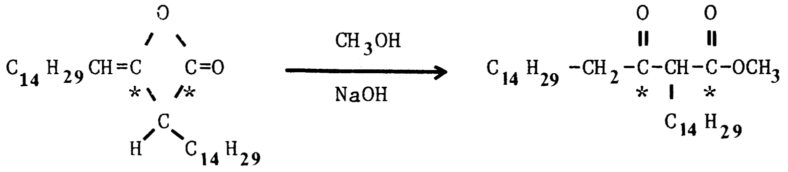


Fig 9—The Preparation of Methyl 2–tetradecyl–3–oxo octadecanoate from Tetradecyl Ketene Dimer

The specific activity of this ester and of tetradecyl ketene dimer has been measured before and after aqueous hydrolysis for 160 hours and the results shown in Table 5.

	INITIAL SPECIFIC ACTIVITY µCi/g	SPECIFIC ACTIVITY AFTER NEUTRAL HYDROLYSIS*
Tetradecyl Ketene Dimer	90.1	48.2
Methyl 2-tetradecyl 3-oxo octadecanoate	83.8	51.8

* Hydrolysis carried out by refluxing in approx. 20% aqueous dioxane for 160 hours.

Table 5 The Neutral Hydrolysis of Tetradecyl Ketene Dimer and Methyl 2-tetradecyl 3-oxo octadecanoate.

The specific activity of each compound dropped to about half of its original value after this time, confirming that hydrolysis to the β-keto acid and decarboxylation (with loss of one labelled carbon atom as CO_2) had occurred. Further confirmation was obtained by isolating and characterising the palmitone produced in each case. The results in Table 4 are therefore consistent with the presence in paper of either β-keto ester or a strongly 'bound' alkyl ketene dimer molecule. The possibility of polymer formation seems less likely, as compounds of the polydiketone and the polyester type would not be expected to undergo hydrolysis under such mild conditions.

It is therefore not possible, by hydrolysis, to distinguish with certainty between a strongly bound dimer molecule and β-keto ester formation, but the fact that the amount of material which is not amenable to solvent extraction increases with both pH and temperature (19,20) suggests that β-keto ester formation is the more likely.

The most likely mechanism of action of these dimers during industrial usage is therefore one of retention in the sheet by electrostatic hetero-coagulation processes followed by dispersion and migration during drying. At this stage the dimer is likely to undergo a low level of both hydrolysis to the ketone and of ß-keto ester formation with cellulose once the local water has been consumed. The extent of these processes being dependent upon the pH of the system and the contact time and temperature attained during drying.

THE EFFECT OF ALUMINIUM SULPHATE ON ALKYL KETENE DIMER SIZING

Aluminium sulphate is known to have an adverse effect on the alkyl ketene dimer sizing system (18). The effect of alum addition in the range 0 to 10% (based on fibre) on both retention and degree of sizing (penetration time) has been studied and is shown in Table 6.

ALUM %	pH	AKD RETENTION* mg/g	% RETENTION OF AKD	PENETRATION TIME** sec	ABSORBENCY CAPACITY g/g
0	5.8	1.17	67.4	26.9	0.65
1	5.2	1.06	58.9	9.0	0.75
3	4.8	0.95	53.6	8.65	0.72
5	4.6	0.96	54.0	8.0	0.88
10	4.5	0.81	45.5	6.3	0.81

* Initial size addition = 2.24mg per 1.2g handsheet; all sheets heat treated at 105°C for 10mins after conditioning.
**Hercules Size Tester.

Table 6 The Effect of Alum Addition on Size Retention and Degree of Sizing.

These results show that the addition of alum in the range 0-5% to the fibre suspension prior to sheet formation caused a relatively small reduction in the retention of the dimer (13%), but a large decrease in the degree of sizing as measured by the penetration time method. An increase in absorbency capacity was also observed, but this method of sizing measurement proved to be less sensitive to alum addition than the penetration time test. The fact that the dimer at these retentions and with this heat treatment would normally induce good sizing (Figure 7) demonstrates that alum interferes with the action of the dimer rather than with the mechanism of its retention in the sheet. In order to confirm this, the effect of chloroform extraction has been studied and the results are shown in Table 7.

ALUM	UNEXTRACTED SHEET			SOLVENT EXTRACTED SHEET*		
%	AKD RETENTION mg/g**	AC g/g	PENETRATION TIME sec	AKD RETENTION mg/g	AC g/g	PENETRATION TIME sec
0	0	2.16	1.0	0	2.22	0.1
0	1.09	0.63	30.0	0.09	0.90	17.1
1	0.723	0.70	9.0	0.04	1.47	2.7
2	0.720	0.66	8.0	0.04	1.54	2.5

* Chloroform for 6 hours.
**2.26mg of AKD added to 1.2g of fibre in each handsheet machine.

Table 7 The Effect of Chloroform Extraction on Retention of Alkyl Ketene Dimer, Absorbency Capacity (AC) and Penetration Time.

In the case of sheets prepared in the presence of 1 and 2% alum, the amount of size retained in the sheet after solvent extraction was less than half of that in sheets prepared in the absence of alum. The absorbency capacity and penetration times for alum treated sheets after solvent extraction were found to be close to those values for completely unsized sheets, whereas the sheets which had not been treated with alum retained a high proportion of sizing even after solvent extraction.

The results are consistent with inhibition of β-keto ester formation by aluminium sulphate. It is possible that adsorption of hydrated aluminium species on the fibre surface creates sites for competitive coordination of the dimer molecules, thus inhibiting ester formation with cellulose. A speculative proposal for the mechanism of this interaction is given in Figure 10.

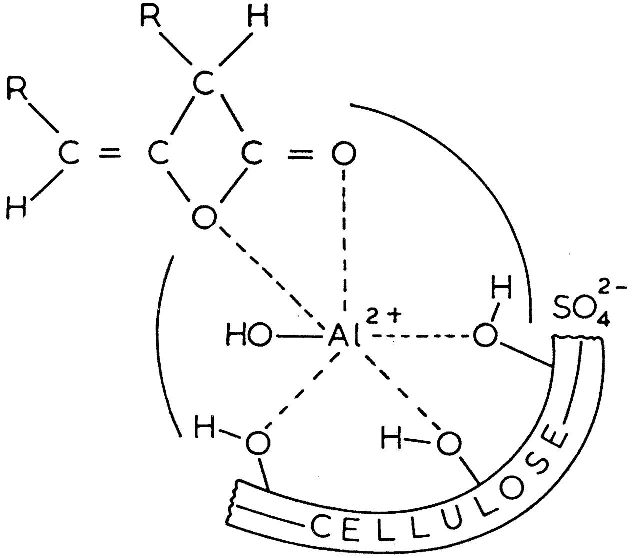


Fig 10—A proposed machanism for the inhibition of ß keto ester formation by absorbed alumium species

EXPERIMENTAL

A once dried bleached Softwood Sulphite pulp, beaten to 23 SR in deionised water, was used throughout this work.

The preparation of C-14 labelled tetradecyl ketene dimer, hexadecyl hexadecanoate and their emulsions, and the radioassay procedures, determination of water absorbency capacity, sheet making and solvent extraction procedures are described in Reference 19.

Spectroscopic and other methods used in the studies of reactivity of diketene and tetradecyl ketene dimer towards water, alcohols and model compounds are described in Reference 31.

Penetration time measurements were made with a Hercules Size Tester using Number 2 ink ($10cm^3$) containing 10% formic acid. The mean of three measurements was determined for each handsheet.

Hydrolysis of solvent - extracted sheets containing radiolabelled material was carried out by taking the remaining part of a 1.2g handsheet (after scintillation counting and absorbency capacity measurement) and refluxing it with distilled water ($200cm^3$ per g of paper) for 20 hours. The paper was then dried and extracted with chloroform (soxhlet extractor) for 6 hours using the method described in Reference 31.

The preparation of C-14 labelled methyl 2-tetradecyl 3-oxo octadecanoate was achieved by refluxing C-14 labelled tetradecyl ketene dimer ($0.2g, 4x10^{-4}$ mol) in chloroform ($20cm^3$), methanolic sodium hydroxide (0.2cm of 0.025molar) and methanol ($2cm^3$) for 2 hours. After removal of volatile solvents, the product was recrystallised from methanol, m.p. 48-50°C.

Neutral hydrolysis of tetradecyl ketene dimer and methyl 2-tetradecyl 3-oxo octadecanoate was carried out by refluxing each substance (0.05-0.1g) in 1,4-dioxane ($100cm^3$) and distilled water ($10cm^3$) for 160 hours. The reaction was monitored by the disappearance of infra red bands associated with the lactone ring ($1720cm^{-1}$ and $1855cm^{-1}$) or the β-keto ester ($1720cm^{-1}$ and $1750cm^{-1}$) and the appearance of the characteristic single carbonyl stretching frequency of palmitone ($1710cm^{-1}$). Palmitone was recovered by removal of volatile solvents and recrystallisation from methanol (m.p. 81-83 °C). The specific activities of the crude products were determined and are quoted in Table 5.

Aluminium sulphate ($Al_2(SO_4)_3.16H_2O$), when required, was dissolved in distilled water at the appropriate concentration and added to the sheet machine prior to sheet formation.

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Transcription of Discussion

Neutral Sizing and the Mechanism of Alkyl Ketene Dimer Sizing
by J.C. Roberts, D.N. Garner and U.D. Akpabio

Dr. T. Lindström STFI, Stockholm, Sweden

It seems that different research groups around the world are able to obtain different results for the amount of reaction between AKD and fibres. Our own published work shows that it is possible to achieve quite high levels of reactivity, about 50 - 60%, under certain conditions, as shown in Figure 1. I am also concerned that your paper quotes our own research as being in agreement with you on the levels of reactivity, whereas I do not think that this is the case.

Dr. L. Ödberg and I have also looked for the presence of infra red bands associated with β keto ester formation in solvent extracted sheets. This has been done using the Fourier transform technique with very long accumulation times. These results, which are to be published shortly, show a weak band at around 1741 cm^{-1} which we have assigned to the β keto ester. Moreover, on extracted sheets there are strong absorption bands at 2920 cm^{-1} and 2852 cm^{-1} (CH_2- vibrations from the alkyl-chain) and a complete lack of absorption bands in the region between 1800 and 1900 cm^{-1} where unreacted AKD has a strong absorption from the carbonyl group in the lactone ring.

Dr. J.C. Roberts

Firstly, let me say that, in our paper, we said that both your own and our results show that 'significant quantities of the dimer could be extracted by organic solvents'. I think you will agree that the figure which you have shown demonstrates that, at comparable pH (in our case around 7), and drying conditions, the level of reacted AKD is only about 20 - 30%. I think that 70 - 80% of unreacted dimer could, therefore, justifiably be described as 'significant'.

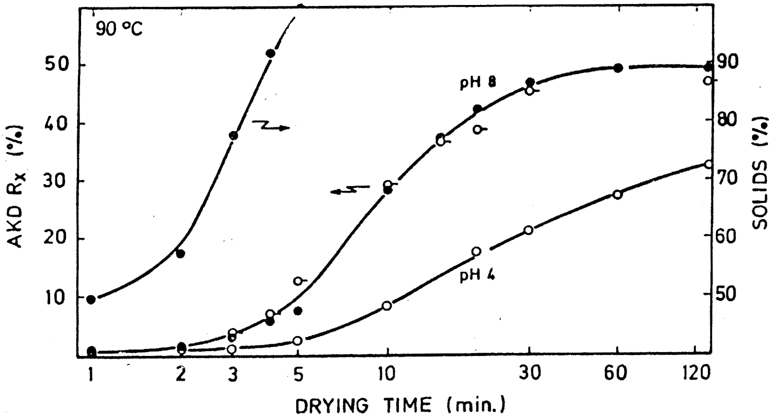

Fig 1—The effect of drying time, at 90°C, and pH on the reactivity of AKD

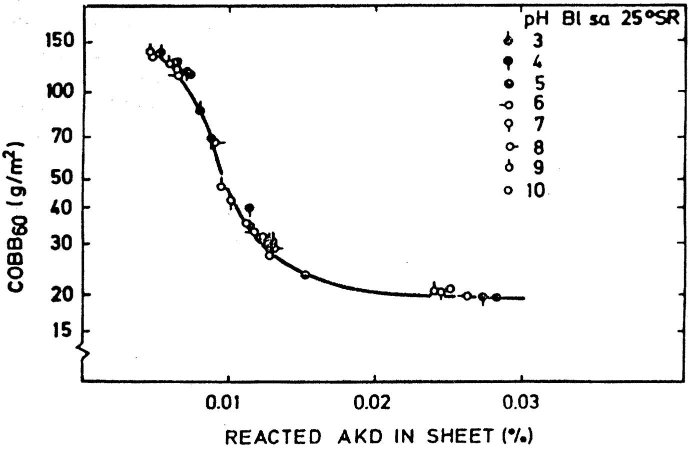

Fig 2—The relationship between levels of reacted AKD and Cobb sizing at various levels of pH

However, on the whole, the use of percentages is very misleading and we have generally tried to avoid it. Some of your own data from your 1982 Stockholm presentation on A.K.D. sizing will help to demonstrate the point. The figure (Figure 2) shows that you achieved optimum Cobb values at around 0.015% of **AKD** retained in the sheet after solvent extraction. This is equivalent to 0.15 mg/g and agrees very well with both our own results, and also with those of Merz our co-workers (see table).

Because of the different amounts of **AKD** retained before solvent extraction, the percentage figures are not in such good agreement.

	Amount retained before solvent extraction (mg/g)	Amount retained after solvent extraction (mg/g)	% reacted
Roberts	2.07	0.10	5
Lindstrom	0.57	0.17	30
Merz	1.68	0.17	10

I would also like to point out that we are talking about 0.15 mg/g, which is 150 gm per tonne of pulp. I would like to suggest that users of **AKD** sizes should think carefully about how much they put into their wet end system in order to achieve this level of reaction and what they think might be happening to the excess.

Aspler I would like to make a comment on Dr. Lindstrom's contribution. You show these 1741 cm^{-1} infra red peaks as being proof of the β keto ester bond formation. I would be cautious about that conclusion because a peak at this position is diagnostic for almost any alkyl ester. The work you illustrated which showed the absence of the unreacted ketene is much more convincing.

Davison The amount of AKD reacted in the sheet, of course, is the most important criterion. Our own radioactive AKD sizing experiments have shown that 50-70% of the retained AKD in handsheets can be reacted in paper and cannot be solvent extracted. That would agree quite well with Dr. Lindstrom's results. These figures would refer to perhaps 0.05 to 0.1% AKD being retained in the sheet. However, with 1% AKD in the sheet and, say, 0.05% reacted, then that would only be 5% of the total AKD. All of the rest of the retained AKD would be sitting there with nothing to react with because you only have a limited amount of exposed cellulose surface for AKD to react with. In other words, an excess of retained AKD will provide you with an apparently very low percentage reactivity.

Roberts I have provided you with our published work on C^{14} labelled dimers and it is not very easy for me to respond to what I might call anecdotal evidence just quoted and not published in the open literature. I know Hercules are in the process of preparing a publication and I will look forward to reading that.

Atalla To what type of interaction would you attribute the retention of some fraction of the non-reactive model compound after the extraction? Does it suggest some kind of Van der Waal interaction of the extended chains with hydrophobic surfaces on cellulose?

Roberts I have not given this matter any thought until you raised the point. We have always assumed that it would be difficult to remove the last traces of C^{14} labelled material simply because they are high activity materials. Therefore even small traces are going to yield some residual counting after solvent extraction. However, on hearing your comments, I became less certain that this may be right.

It is obviously something to which we should direct our attention.