

The effect of alum on the mechanism of alkylketene dimer sizing

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ABSTRACT We studied the effect of aluminum sulfate (papermaker's alum) and pH on the retention of radioactively labelled tetradecylketene dimer on paper. Adding alum during sizing with the dimer leads to a loss in sizing on the sheet. This adverse effect of alum on alkylketene dimer sizing arises from a complex formation between the dimer and the adsorbed aluminum species on the fiber. This theory is suggested by the ionic mobility of the crystalline cellulose in the presence of alum and our results from the solvent extraction of the dimer-treated sheets.

KEYWORDS

Alum
Chemical
analysis
Papermaking
Retention alcls
Size

Papermaker's alum (hydrated aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}$, where $x = 14 \dots 18$) is extensively used as retention aid in rosin sizing systems (1). However, alum is detrimental to the development of sizing in the case of alkylketene dimer sizing (2-4). Alum adversely affects sizing even though the dimer is retained on the sheet of paper. Therefore, it is the mechanism of retention of the dimer in the presence of aluminum ions that must be interfering with the development of sizing.

When aluminum sulfate is added to a papermaking medium (usually water containing cellulosic fibers), both the dissolved and precipitated aluminum ion species are absorbed onto the fibers (5). Complete absorption takes place because hydrated aluminum sulfate is completely dissociated into hydrated aluminum ions and sulfate ions at a low concentration and is partially dissociated at other concentrations. In the solid state, hydrated aluminum sulfate is com-

pletely ionized, and the aluminum ion is coordinated to six molecules of water, thus being separated from the sulfate ions within the crystal lattice. Also, in water, aluminum ions are hydrolyzed readily and reversibly into hydrated species (5).

Papermaking fibers are cellulosic in nature. Prior to sheet formation, they are usually refined to become fibrillated and are cut into smaller pieces, thereby creating a wide adhesive surface area for the retention of paper additives. Alkylketene dimers are made from fatty acids, such as in the reaction involving hexadecanoic acid to obtain tetradecylketene dimer. (See the appendix.)

As sizing agents, the dimers are effective in neutral and alkaline conditions. Rosin, conversely, requires an acid medium. This gives alkylketene dimer size the advantage because the neutral or alkaline condition of the product sheets enhances the durability of the paper (3). Although its mode of retention and sizing development has

been generally attributed to the reaction with the cellulosic fibers at the hydroxyl groups to form $\alpha\beta$ -keto ester bond (3), the evidence to justify this assumption conclusively has not been substantiated (6).

Here, we examine the retention of tetradecylketene dimer on paper made in the presence of aluminum sulfate. We propose the mechanism of retention of the dimer and aluminum ion species on the sheet, showing how the presence of aluminum ions interferes with the proposed mechanism of alkylketene dimer sizing.

Results and discussion

Variation of size retention, water absorbency capacity, and penetration time

Tables I and II and Figs. 1-3 show the effects of hydrated aluminum sulfate on alkylketene dimer retention, water absorbency capacity of the sheet, and penetration times. Both unextracted and solvent-extracted

sheets were internally sized with radioactively labelled tetradecylketene dimer. Each stock preparation contained 2.24 mg of the labelled tetradecylketene, and sheets were made with two levels of alum addition in the stock, 1-10% ($0-0.28 \times 10^{-4}$ moles of alum $\text{Al}_2(\text{SO}_4)_3 \times 8 \text{H}_2\text{O}$) and 0-80% ($0-2.4 \times 10^{-4}$ moles) based on dry pulp.

The unextracted sheets. The results show that the retention of the dimer decreased from 67.4% to 45.1% (Figs. 1 and 2) as the concentration of aluminum sulfate in the stock increased from 0% to 80%. However, the pH decreased from 5.7 to 4.4 (Table II), and the specific retention decreased by 1.17 mg/g to 0.78 mg/g (Fig. 3). (The units "mg/g" refer to milligrams of tetradecylketene dimer per gram of paper).

At a low percentage of alum addition (0.25%), the penetration time decreased rapidly and then gradually to 2.7 s. The water absorbency capacity increased to 1.12 g/g at 80% addition. When we compared these results with the control sheet sized without alum (1.00 mg/g retention, 30 s penetration time, and 0.51 g/g of water absorbency capacity), we found that the sheet was not sized even though there was enough retention of tetradecylketene dimer to have caused sizing to develop. The results show that aluminum sulfate has little effect on the retention of tetradecylketene dimer. However, the alum greatly reduced the extent of sizing, because a retention of 0.75 mg of tetradecylketene dimer per gram of paper should have been adequate for sizing to develop in a sheet made without aluminum sulfate (6).

Solvent-extracted sheets. The specific retention, 0.04 mg/g of the nonsolvent-extractable size in the sheet made from 1% and 2% alum-treated stock was lower than that of the control sheet (0.09 mg/g) (Table III). Thus, alum-treated papers readily lost the size on extraction. The tests for both the water absorbency capacity (1.47 g/g and 1.55 g/g) and the penetration times (2.7 s and 2.8 s) confirmed that the extracted alum-treated sheets were not sized at all (Table IV).

The effect of a change in pH

The dissociation of aluminum sulfate in water decreases the pH of the solution (5). (See the appendix.) Table

I. Retention and degree of sizing of alkylketene dimer in the presence of alum (0-10%)

Alum, %	pH	Total retention, mg	Retention, mg/g	Retention, %	Water absorbency capacity, g/g	Penetration time, s
0	5.8	2.16	0.80
0.0	5.8	1.51	1.17	67.4	0.65	20.90
0.5	5.4	1.24	0.98	55.4	0.65	6.85
1.0	5.2	1.32	1.06	58.9	0.75	9.00
2.0	4.9	1.24	0.99	55.4	0.76	8.02
3.0	4.8	1.20	0.95	53.6	0.72	8.65
5.0	4.6	1.21	0.96	54.0	0.80	8.00
10.0	4.5	1.02	0.81	45.4	0.88	6.30

*Based on 2.24 mg of labelled tetradecylketene dimer added to the stock.

II. Retention and degree of sizing of alkylketene dimer in the presence of alum (0-80% based on dry fiber in the stock)

Alum, %	pH	Total retention, mg	Retention, mg/g	Retention, %	Water absorbency capacity, g/g	Penetration time, s
0	5.7	2.10	0.9
0	5.7	1.39	1.00	62.1	0.51	30.0
2	5.0	1.22	0.90	54.5	0.81	6.6
10	4.6	1.12	0.80	50.0	0.96	4.9
20	4.6	1.07	0.77	47.8	0.78	4.0
40	4.5	1.03	0.76	46.0	0.77	4.1
60	4.4	1.02	0.75	45.4	0.96	4.4
80	4.4	1.01	0.75	45.1	1.21	2.7

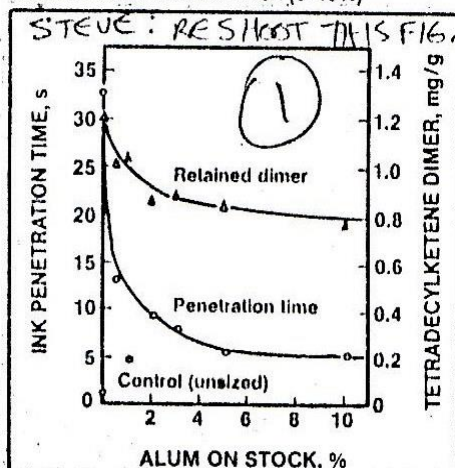
*Based on 2.24 mg of labelled tetradecylketene dimer added to the stock.

III. The effect of extraction and hydrolysis on the retention of size on sheets made in the presence of alum

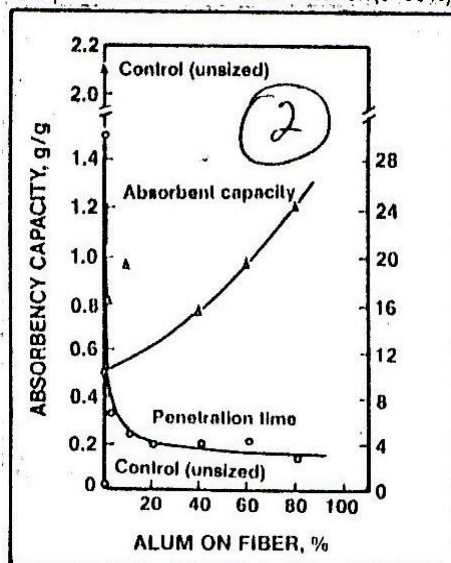
	Alum, %		
	0	1	2
Unextracted sheet			
Specific retention, mg/g	1.09	0.723	0.720
Residual retention, %	100	100	100
Solvent-extracted sheet (6 h)			
Specific retention, mg/g	0.09	0.04	0.04
Residual retention, %	8.3	5.5	5.6
Neutral hydrolysis (6 h) and solvent extraction (6 h)			
Specific retention, mg/g	0.05	0.02	0.02
Residual retention, %	4.60	2.77	2.78

2.26 mg of tetradecylketene dimer added to the stock per handsheet. Residual retention is based on unextracted sheet retention.

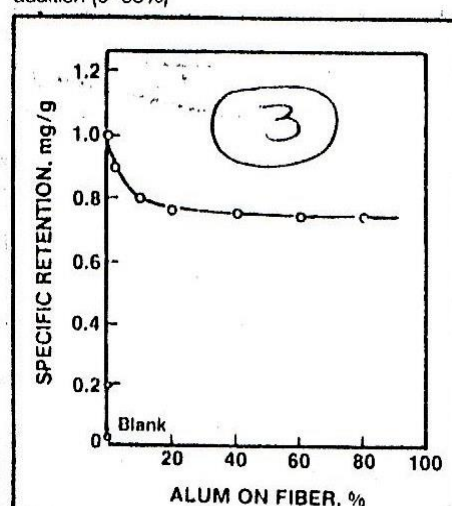
1. The variation of size retention and penetration time with alum addition (0-10%)



2. The variation of water absorbency capacity and penetration time with alum addition (0-80%)



3. The variation of size retention with alum addition (0-80%)



IV. The effect of extraction and hydrolysis on water absorbency capacity and the penetration time of sheets made in the presence of alum

	0 ^a	Alum, %		
	0	1	2	
Unextracted sheet				
Absorbency capacity, g/g	2.16	0.63	0.70	0.66
Penetration time, s	1.0	30.0	9.0	0.0
Solvent-extracted sheet (6 h)				
Absorbency capacity, g/g	2.22	0.90	1.47	1.55
Penetration time, s	0.1	17.1	2.7	2.5
Neutral hydrolysis (6 h) and solvent extraction (6 h)				
Absorbency capacity, g/g	3.0	2.4	2.8	2.7
Penetration time, s	0.10	10.1	0.60	0.60

2.26 mg of tetradecylketene dimer added to the stock per handsheet.
^aFor the control (unsized) sheet.

V and Fig. 4 compare the results of adjusting the pH of the paper with sulfuric acid, acetic acid, and alum solution. The specific retentions of tetradecylketene dimer on the unextracted sheets made from stocks adjusted to pH 5.0 and 4.3 with acidic acid were 0.84 mg/g and 0.76 mg/g, respectively. The values for stocks adjusted with sulfuric acid were 0.85 mg/g and 0.80 mg/g, respectively. The specific retentions of the alum system were 0.67 mg/g and 0.38 mg/g at the two pH values.

Thus, compared with the alum sample, there was a much smaller change in retention between the control sample (0.95 mg/g) and the sulfuric-acid-treated paper—a differ-

ence of 0.19 mg/g at a pH of 4.3. The same was true for the sample treated with acetic acid, with a difference of 0.15 mg/g at a pH of 4.3. This difference for the alum-treated sheet was 0.57 mg/g (0.95 mg/g - 0.38 mg/g), showing that only 40% of the amount retained by the control sheet was retained when alum was present. The water absorbency measurements ($\text{H}_2\text{SO}_4 = 0.72 \text{ g/g}$, $\text{ACOOH} = 0.53 \text{ g/g}$, and control = 0.58 g/g at pH 4.3) indicated that the sheets were still fairly well sized. In the alum-treated paper, the water absorbency capacity increased to 0.81 g/g at the same pH, showing that the sheet was not sized at all. The tests for penetration time confirmed the same variation. Both

the residual retention and the degree of sizing of the solvent-extracted sheets showed a pattern of variation similar to that observed with the unextracted samples.

Hydrolysis of tetradecylketene dimer

In neutral hydrolysis of the nonsolvent-extractable size on the alum-treated sheets, the residual retention reduced to only 0.02 mg/g (Table III). This amount is only 40% of the amount retained in the control sample, which had passed through the same process of hydrolysis for 6 h. Therefore, the residual nonsolvent-extractable size in alum-treated paper hydrolyzed much more readily than the nonsolvent-extractable size in the control sheet.

The hydrolysis product obtained after 6 h of hydrolysis of the alum-treated sample was identified as methyl 2-tetradecyl-oxo-octadecanoate (palmitone) (6). Such a compound was identified as the product of neutral hydrolysis only after 160 h and as the product of acid hydrolysis (sulfuric acid) only after 24 hours. Thus, the presence of acid also increases the rate of hydrolysis of tetradecylketene

Electrophoretic mobility of microcrystalline cellulose

Microcrystalline cellulose consists of negatively charged particles. In an electrophoretic mobility apparatus, they are attracted to the anode, with the measured mobility being affected by the size of the particles and the pH of the medium of flow.

V. The effect of pH on retention and penetration time in alkylketene dimer sizing

IV	pH 6.2		ACOOH	pH 5.0		Alum	pH 4.3		Alum
	Unsize control	Size control		H ₂ SO ₄	ACOOH		H ₂ SO ₄		
Unextracted sheet									
Retention, mg/g	...	0.95	0.85	0.84	0.67	0.80	0.76	0.38	
Relative retention, %	...	100	89.5	88.4	70.5	84.2	80.0	40.0	
Absorbency capacity, g/g	2.2	0.58	0.52	0.70	0.62	0.53	0.72	0.81	
Penetration time, s	1.0	172.6	80.1	97.1	19.6	31.2	30.1	10.0	
Solvent-extracted sheet (6 h)									
Retention, mg/g	...	0.15	0.14	0.14	0.07	0.13	0.13	0.05	
Relative retention, %	...	100	93.3	93.3	46.7	86.7	86.7	33.3	
Absorbency capacity, g/g	2.2	0.59	0.80	0.62	1.0	0.9	0.95	1.02	
Penetration time, s	1.0	109.7	7.30	55.1	1.7	6.7	6.4	1.7	
2.24 mg of tetradecylketene dimer added to the stock per handsheet.									

2.24 mg of tetradecylketene dimer added to the stock per handsheet.

Table VI presents the mobilities of the microcrystalline cellulose when the pH was adjusted with sulfuric acid, acetic acid, and alum solution to pH 4.3. These values were 89.5%, 87.5%, and 31.3%, respectively, of that of the control run at a pH of 5. In this way, the presence of aluminum ions contributes to the decrease of electrophoretic mobility of microcrystalline cellulose.

Looking through the line of flow, we also observed that the particles in the alum-treated system became coagulated, increased in size, and finally dropped out from the line of flow to the anode. These observations may be explained in terms of electrostatic attraction between the negatively charged microcrystalline particles and the positively charged aluminum species in the cellulose sol. Because of the difference in charges, the two particles flocculate to form bigger particles that slow down their mobilities. After coagulation, these particles drop out of the line of flow.

This experiment was performed to illustrate what might happen in the papermaking stock containing many fines and aluminum ions. Jaycock and Pearson (8) have also observed that fines in a fiber furnish that contains aluminum sulfate became flocculated first before adsorption onto the fibers, leading to uneven distribution of the fines or other similarly charged additives on the paper surface.

Conclusions

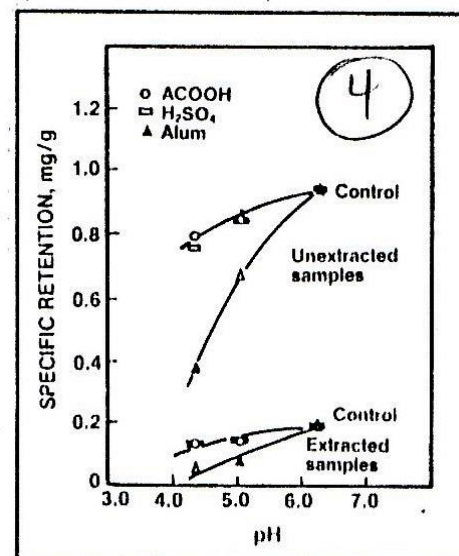
First, poor sizing development in the alkylketene dimer-alum system (Table IV) may be caused by poor anchorage and uneven size distribution on the fiber surface. These inadequacies may be caused by the preferential adsorption of the cationic starch-stabilized tetradecylketene particles on the positively charged aluminum ion in the stock. Thus, a smooth monomolecular layer of alkylketene dimer (such as tetradecylketene dimer) did not develop, and such a layer is necessary for sizing development.

Second, the fact that most of the size in alum-treated paper was readily extracted with chloroform (Table III) suggests that most of the dimer molecules were not directly attached to the cellulosic fibers by any chemical bond. Therefore, aluminum ions must have interfered with such interactions.

Third, since retention was reduced and sizing was lost when the pH of the stock was adjusted with alum solution, as opposed to the case of acids only, the presence of aluminum ions must affect the general orientation of the size particles on the fiber surface. The low mobility and coagulation of microcrystalline cellulose particles as observed in the electrophoretic mobility apparatus tend to support these observations.

These results should be consistent with the mechanism of alkylketene dimer size-aluminum ion retention proposed in Fig 5. This figure illustrates that in the papermaking medi-

4. The variation of specific retention of tetradecylketene dimer with stock pH



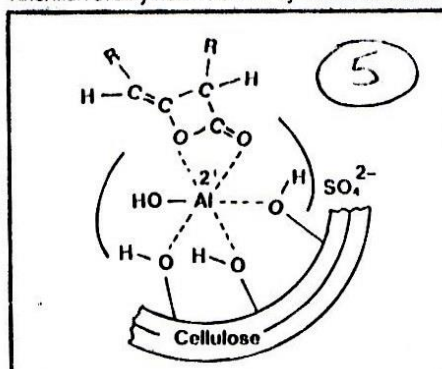
um under consideration, different aluminum ion species in the system (5) can coordinate with water molecules cellulosic fibers, and alkylketene dimer molecules. (See the appendix.) However, the water molecules are driven off when the paper is dried, leaving coordination with only the cellulosic fibers and the dimer.

By this orientation, there is no direct interaction between the cellulosic fibers and the dimer for a possible chemical reaction, which is generally assumed to be the mechanism of alkylketene dimer sizing (1-3). In this way, the presence of aluminum sulfate in the stock inhibits the formation of the proposed β -keto ester bond between the fibers and the dimer

VI. The effect of pH on electrophoretic mobility of microcrystalline cellulose

pH	Adjusted with	Electrophoretic mobility, $U \times 10^8 \text{ m}^2/(\text{s} \cdot \text{V})$
5	...	4.8
4.3	ACOOH	4.2
4.3	H ₂ SO ₄	4.3
4.3	alum	1.5

5. Possible coordination mechanism for the retention of alkylketene dimer by cellulosic fibers



Literature cited

1. Internal Sizing of Paper and Paper Board (Swanson, J. W., Ed.), TAPPI PRESS, Atlanta, 1971.
2. Davis, J. W., and 7COAUTHORS? Tappi 39(1): 2(1956).
3. Weisberger, C. A. and Henford, C. B., Tappi 43 (12): 178A(1960).
4. Davison, R. W., Tappi 58(3): 48(1975).
5. Priest D. J., Alum usage, in PAPER '82 Int. Paper Industry Tech. Association Conf. Papers. 7SPONSOR7.
6. Roberts, J. C., Garner D. N., and Akpabio U. D., Sizing and the mechanism of alkyl ketene dimer sizing, Trans. of the 8th Fund. Research Symposium at Oxford 2, 7SPONSOR7, Oxford, England, 1985, pp. 815-837, 1121-1124.
7. Akpabio U. D., A study of control of water penetration in paper by diketene derivatives, Ph.D. thesis, U.M.I.S.T., Manchester, U.K., 1985.
8. Second Report of the Pulp Evaluation Committee to the Technical Section, Papermakers Association, 7SPONSOR'S CITY OF HEAD-

molecules during sizing. Thus, the presence of alum is detrimental to the development of sizing in papers made with alkylketene dimer (6).

Materials and methods

The radioactively labelled tetradecylketene was synthesized by the Rothman method (7) using radioactive hexadecanoic acid. The cationic starch-stabilized emulsion of known specific activity was prepared from the radioactively labelled tetradecylketene and cationic starch by heating the starch at 80°C for 5 min before passing it twice through a homogenizer.

The handsheets were formed from Kajaani sulfite pulp after 3 min of beating in the Medway Benter, according to the British standard (8).

The absorbency capacity test was carried out by immersion method, while a Hercules size tester was used in determining the penetration time. Solvent extraction of the sheet was done with chloroform in soxhlet extraction apparatus. Retention was determined with a Liquid Scintillation Counter, type LKB (Wallace) 1217, Rackbeta, using a 2,5-diphenyl-oxazole primary scintillator and a 2,2-p-phenylene-bis (5-phenyloxazole) secondary scintillator.□

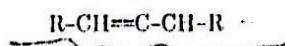
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Appendix: chemistry explanations

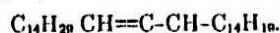
Alkylketene dimers

The alkylketene dimers are represented by



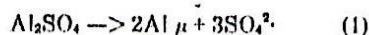
where R is an organic group.

These dimers are made from fatty acids. An example is hexadecanoic acid (C₁₄H₂₀CH₂COOH), which under goes reaction to yield tetradecylketene dimer:

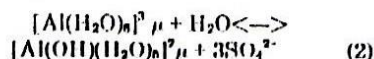


Aluminum sulfate

The dissociation of aluminum sulfate takes place as follows:



The hydrolysis equilibrium of aluminum ion hexahydrate is:



Proposed coordination bonds for the hydroxy aluminum ion pentahydrate are shown in Fig. 6.

