Octadecylamine as an internal sizing agent

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ABSTRACT

Octadecylamine is effective as an internal sizing agent when used alone, or without alum as a mordant. With unbleached kraft pulp, 0.25% octadecylamine (on dry pulp) was enough to induce sizing. Bleached kraft pulp required 0.5% octadecylamine. The sizing efficiency depended on the temperature, the presence of metallic ions, and the storage time of the stock. The optimum pH range was 7–10. Paper strength decreased with the use of octadecylamine. However, cationic starch can be added to overcome the strength loss.

Application: *Octadecylamine is a new internal sizing agent that may offer superior sizing performance in some specialized applications.*

SIZING CONSTITUTES THE PAPER'S ability to resist the wetting and penetration of aqueous solutions such as water, ink, or milk. Wood fibers naturally attract water molecules through extensive hydrogen bonding as a result of the hydroxyl groups of cellulose and hemicellulose. Internal sizing treatments convert the hydrophilic fiber surfaces into hydrophobic surfaces, causing them to repel the water molecules.

For an internal sizing system to be effective, it must meet all of the following requirements (*1*, *2*):

1. The sizing agent must be highly hydrophobic.
2. The sizing agent and its anchoring system must be retained during papermaking.
3. The sizing agent must have good coverage on the fiber surface.
4. The sizing agent must be anchored to the fiber surface of the paper.
5. The sizing agent and its anchor must be chemically inert to the liquid.

Rosin soap with alum as a mordant has been the principal internal sizing system used in the paper industry since the early 1800s. The optimum pH of the pulp slurry for this sizing system is in the range of 4.5–5.5. Even with some modifications, its use is not often practical for neutral to alkaline papermaking processes in which calcium carbonate is used as a filler. Other sizing agents are usually used for these grades of paper, including alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). However, these materials have several disadvantages: high cost, the formation of static electricity on the sized paper, paper surface slipperiness, and fugitive sizing (*3*).

It would be advantageous to develop new internal sizing agents that could induce sizing under alkaline conditions. In our laboratory, efforts have focused on (a) determining the mechanism of action for mordants based on coordination chemistry and (b) developing new mordants for rosin sizing soap that would be effective under alkaline conditions (*4–7*). When polyamine was applied as a substitute for alum as a mordant in rosin sizing, highly effective sizing was achieved at high pH.

Although neither polyethylenimine (PEI) nor polyallylamine (PAA) alone could induce sizing, their functions as mordants inspired us to try aliphatic amines as internal sizing agents. The hypothesis is that these materials would be self-substantive since they have both high hydrophobicity from a long aliphatic chain and an amine group to provide direct anchoring to the fiber. Thus, octadecylamine, $CH_3(CH_2)_{17}NH_2$, was selected as a candidate agent for internal sizing.

RESULTS AND DISCUSSION

Sizing results

Unbleached kraft (600 mL CSF) and bleached kraft (380 mL CSF) softwood pulps were used to make laboratory handsheets with 0.1–1.0% octadecylamine (based on the mass of oven-dry pulp) as an internal sizing agent. The sizing levels in these handsheets were compared to control sheets prepared with 1% rosin and 2% alum sizing at pH 4.5. Some handsheets were air dried, while others were dryer-dried at 250°F for 4 min.

The degree of sizing was determined by the Hercules size test and Cobb size test values. These results are shown in **Table I**. In general, the Cobb size test does not show changes in well-sized papers, and those values are not discussed here. Size tests were repeated after various lengths of time of up to two months with very little change in values. In other words, there is no apparent curing time requirement and no apparent fugitive sizing.

For handsheets made from unbleached kraft softwood pulp and dryer-dried, we found that 0.25% octadecylamine imparts a high level

Sizing method	Hercules size test, s: 1% formic acid ink	Hercules size test, s: Neutral ink	Cobb test, g/m²	Breaking length, km
Unbleached, air-dried				
Octadecylamine, %				
1.0	3073	1567	24.5	3.25
0.5	865	729	31.5	4.06
0.25	369	294	40.3	4.35
0.1	5	3	soaked	4.56
Rosin–alum	695	3175	22.8	4.24
Control	…	…	…	5.15
Unbleached, dryer dried				
Octadecylamine, %				
1.0	4446	2931	22.8	3.06
0.5	3546	1310	26.3	3.63
0.25	1312	534	28.9	4.21
0.1	5	4	soaked	4.64
Rosin–alum	695	3175	22.8	4.24
Control	…	…	…	5.14
Bleached, air dried over night				
Octadecylamine, %				
1.0	104	175	29.8	3.06
0.5	7	23	36.8	3.67
0.25	1	0	soaked	3.71
0.1	0	0	soaked	4.03
Rosin–alum	64	174	27.1	4.20
Control	…	…	…	4.35
Bleached, dryer dried				
Octadecylamine, %				
1.0	941	805	23.6	2.64
0.5	130	162	24.5	3.18
0.25	5	3	soaked	3.64
0.1	1	2	soaked	4.09
Rosin–alum	201	426	20.1	3.78
Control	…	…	…	4.18

Stock adjusted to pH 7.2 for amine sized pulp; cold tap water in sheet mold. For rosin-alum systems, 1% rosin and 2% alum were used at pH 4.5. Dryer-dried handsheets were dried at 250°F for 4 min after press cycle.

I. The effect of the amount of amine size and drying method on sizing efficiency and paper strength

Starch added, %	Hercules size test, s: 1% formic acid ink	Hercules size test, s: Neutral ink	Cobb test, g/m²	Breaking length, km
Unbleached, 0.5% octadecylamine				
0.0	3546	1310	26.3	3.63
0.5	3540	1573	29.8	4.42
1.0	2138	1218	29.8	4.66
2.0	2200	1400	32.4	5.21
Bleached, 0.5% octadecylamine				
0.0	130	162	24.5	3.18
0.5	60	86	26.3	3.53
1.0	84	81	26.3	3.88
2.0	92	106	29.8	3.93

Sheets were formed at pH 7.3 in cold tap water and were dryer dried at 250°F for 4 min.

II. Effect of cationic starch on sizing and strength

Starch pH	Hercules size test, s: 1% formic acid ink	Hercules size test, s: Neutral ink	Cobb test, g/m²	Breaking length, km
Unbleached, 0.25% octadecylamine				
6	12	9	soaked	…
7	780	427	28.88	4.31
8	1359	614	28.88	4.34
9	1360	580	30.63	4.36
10	1265	393	30.63	4.16
11	528	186	31.50	4.45
Bleached, 0.5% octadecylamine				
5	0	0	soaked	4.79
6	8	29	soaked	4.54
7	44	63	27.13	3.78
8	158	146	24.50	3.83
9	195	196	25.38	3.51
10	195	208	24.50	3.48
11	100	142	27.13	4.54

Sheets were formed in cold tap water and were dryer dried at 250°F for 4 min.

III. Effect of pH on sizing and paper strengthproperty

of sizing (Hercules test values are 1312 s with 1% formic acid ink and 534 s with neutral ink). For handsheets made with unbleached kraft pulp and octadecylamine, interestingly, the Hercules values with 1% formic acid ink are always much higher than the values for the tests run with neutral ink instead. In the rosin–alum sizing system, the opposite is observed. In the case of AKD sizing, Hercules test values for tests run with the 1% formic acid ink are approximately the same as values for tests run with neutral ink (*8–9*).

For the handsheets made with bleached pulp and octadecylamine, on the other hand, the Hercules size test values with the 1% formic acid ink were not consistently lower or higher than the values determined using the neutral ink. Furthermore, paper made with bleached pulp was not easily sized by octadecylamine compared with paper made from unbleached pulp. Moreover, a higher dosage of octadecylamine was required to keep the sizing efficiency comparable to that of the rosin–alum system. These results indicate that at least two mechanisms are involved in the sizing process with octadecylamine.

The drying conditions of the handsheets affected the extent of sizing. Higher levels of sizing were found in handsheets that were oven-dried at 250°F for 4 min than in those that were air-dried, for both bleached and unbleached sheets. For example, air-dried handsheets made with bleached softwood pulp and

0.5% octadecylamine had Hercules size test values of 7 s with 1% formic acid ink and 23 s with neutral ink. In contrast, the corresponding dryer-dried handsheets had values of 130 s with 1% formic acid ink and 162 s with neutral ink. Drying the sheets for longer periods of time in dryers increased the sizing efficiency to a limited degree. For example, handsheets made with unbleached kraft softwood pulp and 0.25% octadecylamine and dryer-dried for 4 min had average Hercules values of 1312 s with 1% formic acid ink. In contrast, handsheets that were dryer-dried for 30 min had average Hercules values of 1802 s with 1% formic acid ink. (Values for 30 min are not shown in the tables.)

The tensile strength of paper decreases with the use of rosin–alum sizing systems, as a result of interference with hydrogen bonding. Therefore, it is important to determine how octadecylamine affects paper strength. As shown in Table I, the higher the level of sizing achieved with octadecylamine, which corresponds with the amount of octadecylamine added, the lower the tensile strength, which is reported as the breaking length. As shown in **Table II**, cationic starch overcomes the decrease in strength, but it also results in a decrease in the level of sizing.

The effect of the pH of the pulp stock on sizing with octadecylamine is shown in **Table III**. The optimum pH range for effective sizing with a rosin–alum sizing system is 4.5–5.5. In this range, the aluminum–rosin complex formed can be retained onto fibers from aqueous solutions (*3*). The optimum pH range for sizing with octadecylamine is relatively broad, and effective sizing was achieved for handsheets in the range of 7–10. The upper limit of this range was near the p*K*a of the conjugate acid of octadecylamine (approximately 10.65 using the p*K*a of octylamine for comparison). The equilibrium equation of octadecylamine in aqueous solution is:

$$C_{18}H_{37}NH_3^+ \rightleftarrows C_{18}H_{37}NH_2 + H^+ \quad pKa = 10.65$$

Therefore, at a pH above 10.65, the concentration of octadecylamine is higher than that of protonated octadecylamine (the cationic form), and the concentrated form probably is not an active sizing agent. The lower limit of the optimum pH range, on the other hand, might be related to the fiber performance. Below pH 7, carboxylate groups on the surfaces of fibers may become less anionic as they become protonated (going from anionic to neutral charge).

The addition of metal ions has been shown to increase the level of sizing when polyamine is used as a mordant for rosin sizing (*5*). When selected metallic ions are added with octadecylamine, however, the sizing efficiency of handsheets decreases, as shown in **Table IV**. Coloration in the handsheets treated with Fe^{2+} and Cu^{2+} salts indicates the retention of these salts.

Type of ion	Hercules size test, s: 1% formic acid	Neutral ink
Unbleached, 0.25% octadecylamine		
Fe^{2+}	6	6
Cu^{2+}	23	191
Zn^{2+}	637	456
Al^{3+}	19	10
Control	1312	534
Bleached, 0.5% octadecylamine		
Fe2+	42	6
Cu2+	20	91
Zn2+	30	10
A13+	1	2
Control	130	162

Sheets were made from stock at pH 7.3 in cold tap water and were dryer dried at 250°F for 4 min.

IV. Effect of metallic salts (1%) on sizing

An increase in temperature of the pulp stock while handsheets were being made decreased the level of sizing with octadecylamine, especially at temperatures above 30°C, as shown in **Table V**. A long storage time of pulp stock with the octadecylamine already added lowered the level of sizing in the handsheets. For example, if the bleached softwood pulp with 0.5% octadecylamine added was stored for 1 h before handsheets were made, the sheets had Hercules values of 33 s with neutral ink as compared with 162 s from Table I. Therefore, in our tests, the stock was not kept longer than 30 min before the handsheets were made.

Temp., °F	Stock Hercules size test, s: 1% formic acid	Neutral ink
20	3596	1698
30	3390	1424
35	1851	957
40	211	142
50	16	29
60	5	14

Sheets were made from stock at pH 7.3 in cold tap water and were dryer dried at 250°F for 4 min.

V. The effect of stock temperature on sizing of unbleached kraft softwood pulp

Table VI shows sizing results obtained with octadecylamine on bleached kraft hardwood pulp and TMP softwood pulp. There are two kinds of TMP pulps used in our test: fresh pulp and "old" pulp. The "old" pulp had been refrigerated as an aqueous slurry for over two years and had a dark color. The sheets made from the "old" pulp did not appear to be very uniform. Interestingly, the sizing results are remarkably different. The "old" pulp is easily sized by octadecylamine in contrast to the fresh pulp. Sizing behavior differences attributable to the aging of unbleached kraft softwood pulp were not apparent.

The mechanism of sizing

As mentioned, there may be several mechanisms involved in the sizing process with octadecylamine. Differences probably center on the anchoring mechanism. Octadecylamine has

Pulp type	ODA, %	CSF, mL	Hercules size test, s 1% formic acid	Neutral ink
Hardwood	0.5	590	243.0	240.0
Old TMP	1.0	200	>8,000.0	>8,000.0
OldTMP	0.5	200	493.0	996.0
Fresh TMP	2.0	103	1303.0	643.0
Fresh TMP	1.0	103	4.7	3.5

Sheets were made from stock at pH 7.3 in cold tap water and were dryer dried at 250°F for 4 min. ODA = octadecylamine.

VI. Sizing with bleached kraft hardwood and TMP softwood pulps

a very long carbon chain as its tail. This long carbon chain provides the hydrophobic group to resist wetting by aqueous solutions. The amine group must provide the anchoring mechanism.

The amine is largely unprotonated above pH 10.64 and is largely protonated below pH 10.64. Recent work summarizes cationic–π interactions (*10*) that form between cations and aromatic structures. In sizing with octadecylamine, lignin contains aromatic groups, while protonated octadecylamine acts as a cation. The plausibility of this mechanism is supported by the observation that unbleached pulp is more easily sized than is bleached pulp. Similarly, basic dyes, which contain cationic amine groups, have high affinities for lignin but not for bleached pulps.

The cationic–π interaction is a noncovalent interaction involving a quadrupole moment of the aromatic group. While a relatively weak interaction, it can be much stronger than hydrogen bonding. For example, NH_4^+ and $N(CH_3)_4^+$ have binding energies to benzene of 19 kcal/mol and 9 kcal/mol, respectively. (For comparison, the interaction of NH_3 with benzene is 1.4 kcal/mol).Therefore, protonated primary amines should be more effective sizing agents than protonated secondary, protonated tertiary, and quaternary ammonium amines in unbleached pulp. We found that neither 1% didecylamine (on pulp) or 1% octadecyl trimethyl ammonium bromide gave sizing with unbleached kraft pulp at pH 7. For that matter, 1% diphenylmethaneamine, 1% adamantanamine, and 1% aminoanthracene did not give sizing, either.

KEYWORDS

Amines, bleached pulps, drying, hand sheets, internal sizing, kraft pulps, pseudotsuga, size, sizing tests, softwood pulps, test methods, unbleached pulps.

It is also possible that lignin, being less hydrophilic than either cellulose or hemicellulose, makes unbleached pulp easier to size. The fact that bleached pulp can be sized indicates that other interactions beside cationic–π interactions must be possible. The high effectiveness of the sizing system using polyallylamine as a mordant for rosin sizing of bleached kraft hardwood pulp (*4*) must be attributable to other types of interactions involving carboxylate groups of rosin and fibers.

Interactions between cationic surfactants (octadecylamine) and polyanionic solid polymers (cellulose and hemicellulose) in aqueous solutions are described as "cooperative binding" (*11*). This interaction provides the possibility of retention of amine onto cellulose. One characteristic of the cooperative binding model is that binding is highly dependent upon the temperature, the pH of the aqueous solution, and the ionic strength (*11*, *12*). Higher temperatures and the existence of some electrolytes are known to decrease the degree of binding, as was observed in our work.

A sizing agent that should be preferable to octadecylamine would be rosin amine (*13*) because of its shape. However, commercial rosin amine (Rosin Amine D, Hercules) on unbleached kraft pulp gave a Hercules size test value of only 15 s with neutral ink. Also, 1% dehydroabietylamine (Aldrich) on unbleached kraft pulp gave a Hercules test value of 15 s with neutral ink. Tetra-decylamine (Aldrich) on unbleached kraft pulp was not as effective as octadecylamine; the Hercules size test value was only 23 s with neutral ink.

CONCLUSIONS

Octadecylamine was shown to be a highly effective sizing agent for unbleached kraft Douglas-fir pulp at an addition level of 0.25% on pulp. It did not require the use of a mordant, such as alum; indeed, alum interferes with sizing when octadecylamine is the sizing agent. Octadecylamine was less effective on bleached kraft Douglas-fir pulp at an addition level of 0.5%.

The pH range of the pulp slurry that gave the highest degree of sizing was pH 7–10. Notably, the sized handsheets made from unbleached kraft pulp were more resistant to formic acid ink than to neutral ink by the Hercules size test. An elevated temperature (40°C) or the presence of alum in the British sheet mold decreased the degree of sizing drastically.

EXPERIMENTAL PROCEDURES

The unbleached Douglas-fir kraft pulp had a Canadian standard freeness (CSF) of 600 mL and a 40-mL permanganate number of 62. The bleached Douglas-fir kraft pulp had a CSF of 380 mL. The TMP pulp consisted of over 70% western hemlock. Six grams (air dried basis) of moist pulp were added to 450 mL of water, and the slurry was blended in a food blender for 3 min until the stock was well dispersed.

The desired amount of octadecylamine solution was added (1% wt./vol. in ethanol, since octadecylamine is not water soluble), and the mixture was stirred for another 2 min. Cationic starch or metal ions were added at this point. The pH was adjusted to the desired value, the slurry was diluted to a consistency of 0.15%, and the pH value was readjusted. In some experiments, hot water was heated in advance, and the temperature was adjusted and kept consistent as necessary.

Handsheets of a grammage of 60 g/m^2 were made according to TAPPI T 205 sp-95 in the British sheet mold. The standard press cycle was used, and the sheets were either dried in a sheet dryer at 250°F for 4 min or air-dried according to the test method. Dryer-dried sheets were conditioned at 72°F and 50% relative humidity for at least 4 h prior to testing.

Five handsheets were made under each condition, and the test results were averaged for all five. Cobb size values were determined by TAPPI T 441 om-90. Ink penetration resistance was determined on a Hercules Sizing Tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution. Paper tensile strength was tested according to T 494 om-88.

Cationic starch was obtained from Grain Processing Corp., under the brand name of "Chargermaster R430 Cationic Starch." It is a corn starch containing quaternary ammonium groups at a degree of substitution of 0.032. Octadecylamine was obtained from Aldrich Chemical Company (Milwaukee, Wis.) with a stated purity of 98%. All metal ions were in the form of reagent-grade chemicals. The percentages are the mass of chemical relative to that of oven-dry pulp. Al^{3+} is as $Al_2(SO_4)_3 \cdot 16H_2O$, Cu^{2+} is as $CuSO_4$, Fe^{2+} is as $FeSO_4 \cdot 7H_2O$, and Zn^{2+} is as $ZnCl_2$. For example, 1.0% Al^{3+} is 1.0% alum based on the mass of dry pulp. TJ

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