Properties of candidate internal sizing agents versus sizing performance

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ABSTRACT

In this study various fatty acids, with either alum or polyallylamine as a mordant, and isocyanate sizing agents were used to determine the effect of the candidate sizing agent on sizing performance and strength properties of bleached hardwood pulp. A variety of observations were made. Sizing agents with 6 or 7 carbon atoms do not give sizing even when they are used in excess and they are well anchored to the fiber surface. Fatty acids with 18 or more carbon atoms may give poor performance if they are not well dispersed. Bulky hydrophobic molecules, such as abietic acid, help to protect the sizing agent-alum-fiber linkage from attack by formic acid. Perfluorinated fatty acid sizing agents do not impart good sizing with either polyallylamine or alum as mordants. Gas chromatographic analysis of stearic acid showed that the passage of time allows free stearic acid to become bound and thereby improve the sizing performance.

Application:

This information should be useful in developing new internal sizing agents and predicting the sizing performance of a wide variety of hydrophobic materials.

PAPER, IF UNTREATED, ABSORBS water very well because of its high porosity and hydrophilic nature. The hydroxyl groups of cellulose and hemicellulose have a high affinity for water, so the contact angle of water with untreated paper ranges from near 0° to 50°, depending on the type of pulp used to make the paper and other variables.

With the exception of tissue and toweling grades, most papers are manufactured with internal sizing agents added to the wet end so that the paper resists water absorption. Internal sizing agents modify the surface energy of the paper as opposed to agents that work by plugging the voids in paper (for example, with starch in a size press). Internal sizing agents are hydrophobic substances which must attach to the paper (through the use of an appropriate functional group) to present a hydrophobic surface. The major sizing agents used commercially are fortified rosin (used with alum as a mordant), alkylsuccinic anhydride (ASA), and alkyl ketene dimer (AKD). Others, like stearic acid, have limited use in specialty papers such as photographic paper *(1)*.

ASA and AKD, although relatively expensive but quite efficient, bond directly to the fibers under neutral to alkaline papermaking conditions with the formation of a covalent bond; therefore, these materials can be used with calcium carbonate filled papers. The hydrophobic portion consists of alkyl chains in both cases. AKD tends to make the paper feel waxy or slippery when used at high dosage levels.

Rosin is a mixture of tricyclic diterpenes ($C_{20}H_{30}O_2$); about 20–40% of the molecules are fortified with fumaric or maleic acid in commercial formulations. It is used with alum to anchor the rosin to the fibers through coordinate bonds. These bonds form through the carboxylic acid moieties of the rosin. Other carboxylic acids can also be used for sizing. Saturated, monocarboxylic acids from C_8 to C_{22} are available to the paper industry, with C_{18} being the most commonly used one *(1)*.

In this study various fatty acids, with either alum or polyallylamine *(2)* as a mordant, and isocyanate sizing agents were used to determine the effect of the candidate sizing agent and its bonding mechanism to paper on sizing performance and strength properties of bleached hardwood pulp. This information should be useful in developing new internal sizing agents and predicting the sizing performance of a wide variety of hydrophobic materials.

RESULTS AND DISCUSSION

Handsheets were made from bleached hardwood pulp with a CSF of 360 mL using 5 L of water at ambient temperature in the British sheet mold. The sizing agent (1% wt/wt on pulp) was dissolved in a small amount of ethanol (to help disperse it) and added to the pulp. Alum (2% on pulp) or polyallylamine (0.5% on pulp) was added to the fiber as the mordant and the pH was adjusted to 4.0 or 7.0, respectively.

Table I shows the results using alum as a mordant. (The handsheets were aged for one week before testing.) Abietic acid, which represents unfortified rosin size, is the best internal sizing agent when 1% formic acid is the test ink. At least 10 carbon atoms are required before a fatty acid gives appreciable sizing, and the C_{14} was the most favorable fatty acid of the ones tested with water at 15–18°C in the British sheet mold. While increasing fatty acid chain length should increase the level of sizing *(3)*, this was not observed above a chain length of 14. Fatty acids decrease in solubility as the chain length increases. It was very difficult to keep the C_{18} and higher fatty acids dispersed in the pulp slurry. Had these materials been added as an emulsion formulation, instead of in a solution form, perhaps the effective-

Sizing agent	Number of carbon atoms	Hercules Size Test 1% Formic acid	Hercules Size Test Neutral ink	Breaking length
Hexyl isocyanate	6	1	1	5.42
Octadecyl isocyanate				5.53
smooth side	18	1026	817	
rough side	18	976	929	

IV. Sizing results using excess hexyl and octadecyl isocyanates

Fatty acid	Number of carbon atoms	Hercules Size Test 1% Formic acid	Hercules Size Test Neutral ink	Breaking length
Abietic acid[1]	20	138	276	5.38
Heptanoic acid	7	0	0	3.39
Decanoic acid	10	6	180	4.89
Myristic acid	14	33	315	4.67
Stearic acid	18	6	174	4.65
Behenic acid	22	2	5	5.00
Tetracosanoic acid	24	0	0	5.28

[1]Not a fatty acid but presented for comparison to rosin sizing

I. Sizing results using fatty acids (1% on pulp) and alum (2% on pulp) at pH 4.0

ness of the higher molecular weight fatty acids as sizing agents would have been improved.

With the fatty acids, generally the higher the level of sizing, the poorer the tensile strength of the paper. Heptanoic acid is an exception. While heptanoic acid gave no sizing, there was a very large decrease in the breaking length of the handsheets when this material was present. Apparently the material was retained and interfered with fiber bonding but was not sufficiently hydrophobic to impart water resistance. This view was tested with the use of hexyl isocyanate, as discussed below. Except for some experiments involving stearic acid, retention of sizing agents was not measured.

Formic acid attacks the fatty acid system to a higher degree than the abietic acid system. The linear fatty acids probably offer less steric hindrance to the formic acid which attacks the alum *(2)* than the abietic acid system. Stated another way, bulky sizing agents appear to help protect the sizing agent-alum-fiber linkage.

In order to improve the solubility of the fatty acids, the pH was raised to 7 with the use of polyallylamine, which has been shown to be a highly effective mordant at this pH *(4)*. The results of this experiment are shown in **Table II**. Under these conditions, myristic acid was still the most favorable (with neutral ink) of the fatty acids tested. The performance of the other fatty acids was very poor. Notably, the strength of the handsheet with myristic acid was lowest of this set. The performance of abietic acid improved appreciably under these conditions. Tables I and II both indicate that the shape of abietic acid is inherently better than that of a fatty acid at giving sizing while maintaining strength.

Several other candidate sizes were tested. Fluorinated hydrocarbons are especially nonpolar. However, the results in **Table III** show that fluorinated fatty acids are not effective sizing agents under these conditions unless added at very high levels. These materials are quite acidic. For example, while acetic acid has a pK_a of 4.76, trifluoroacetic acid has a pK_a of 0.50 at 25°C. Manufacturers warn against using fluorinated hydrocarbons with alum, so we tried using 1% perfluorododecanoic acid with 1% polyallylamine as mordant (at pH 7). The 1% formic acid ink HST test gave only 2.4 seconds and the neutral ink HST test gave only 1.7 seconds using unbleached softwood pulp (where polyallylamine is especially effective as a mordant).

3,4-Dimethylcinnamic acid, an aromatic compound with 11 carbon atoms, was also an ineffective sizing agent. Aromatic compounds, while considered nonpolar, are appreciably more polar than aliphatic compounds and may not be efficient internal sizing agents. The small decrease in strength using this candidate sizing agent indicates it is being retained.

Some handsheets containing no additives were dried in a desiccator over phosphorus pentoxide and treated with excess amounts of two linear-chain isocyanates with 6 and 18 carbon atoms, respectively, in anhydrous tetrahydrofuran as the solvent. Because isocyanate reacts readily with water, this sizing reaction was carried out under anhydrous conditions. However, this method produces a strong covalent linkage to the hydroxyl groups of cellulose and hemicellulose. Unreacted sizing agent was removed by methanol extraction. The handsheets were then equilibrated in the Tappi Standard room.

Table IV shows that the 6 carbon isocyanate gave no sizing, while the 18 carbon isocyanate gave very good sizing. The formic acid sizing test results are high with octadecyl isocyanate because formic acid is not expected to affect this linkage *(2)*. Strength properties were not affected, since the handsheets were already formed before the sizing process. Because hexyl isocyanate was well anchored to the handsheet, one can assume that 6 carbon sizing agents are too short to provide sizing under any conditions. Thus, modifying the exposed hydroxy groups alone is not an effective sizing strategy. One must use relatively large molecules to make the surface sufficiently nonpolar to impart water resistance to paper.

Stearic acid can migrate through the vapor phase to impart sizing in unsized papers *(1, 3)*. Excess sizing agents with carboxylic acid functional groups can act as surfactants to decrease the sizing performance, such as with ASA *(5)*. In order to see whether excess stearic acid might interfere with sizing and might possibly be removed by evaporation, a number of handsheets were sized with stearic acid, air dried, and aged. Some samples were placed in sealed polyethylene bags to prevent volatilization of stearic acid, while other samples were left exposed to the air.

Figure 1 shows the sizing results, using neutral ink with the HST test. Sizing of these air dried handsheets increases with time; furthermore, the handsheets exposed to the air show a larger increase than those in sealed bags.

The stearic acid levels in these handsheets were determined by gas chromatography using methyl esters prepared using BF_3—MeOH complex (Aldrich, Milwaukee, WI) analyzed on an SPB-5 column (Supelco, Bellefonte, PA) using heptadecanoic acid as the internal standard. Two extractions were performed on separate samples for each condition. The first was a hexane (containing internal standard) extraction, followed by evaporation of the hexane, and derivatization of the residue to determine the free fatty acid. The second was an extraction with the BF_3—MeOH complex containing NaF to bind aluminum and liberate all of the stearic acid. **Figure 2** shows the stearic acid content of the handsheets as a function of time.

KEYWORDS

Allyl compounds, aluminum sulfate, amines, bleached pulps, fatty acids, hardwood pulps, internal sizing, isocyanates, mechanical properties, mordants, performance evaluation, size.

Fatty acid	Number of carbon atoms	Hercules Size Test 1% Formic acid	Hercules Size Test Neutral ink	Breaking length
Abietic acid[1]	20	511	582	5.01
Heptanoic acid	7	0	0	5.19
Decanoic acid	10	0	0	5.43
Myristic acid	14	7	538	3.68
Stearic acid	18	2	7	4.24
Behenic acid	22	0	3	4.48
Tetracosanoic acid	24	0	0	4.81

[1]Not a fatty acid but presented for comparison to rosin sizing

II. Sizing results using fatty acids (1% on pulp) and polyallylamine (0.5% on pulp) at pH 7.0

Sizing agent	Number of carbon atom	Hercules Size Test 1% Formic acid	Hercules Size Test Neutral ink	Breaking length
Tridecafluoroheptanoic acid				
1% on pulp	7	0	0	5.51
3% on pulp	7	0	0	5.28
Perfluorododecanoic acid				
1% on pulp	12	2	2	5.10
3% on pulp	12	36	92	4.66
3,4-dimethylcinnamic acid				
1% on pulp	11	0	0	5.29

III. Sizing results using candidate sizing agents with alum (2% on pulp) at pH 4.0

There was little difference in the stearic acid content of the sealed and unsealed samples. There was some loss of stearic acid in both the sealed and the unsealed samples during the first week. Possibly stearic acid was absorbed by the polyethylene of bags used to seal the handsheets, while stearic acid was free to volatilize in the unsealed handsheets. Some of the improvement in sizing observed during the first week may be due to loss of stearic acid that might otherwise act as a surfactant. Improvement in sizing from week one to week four appears to be due to conversion of free stearic acid to bound stearic acid. It is not clear why sizing improves faster in handsheets that are exposed to the air than those in plastic bags.

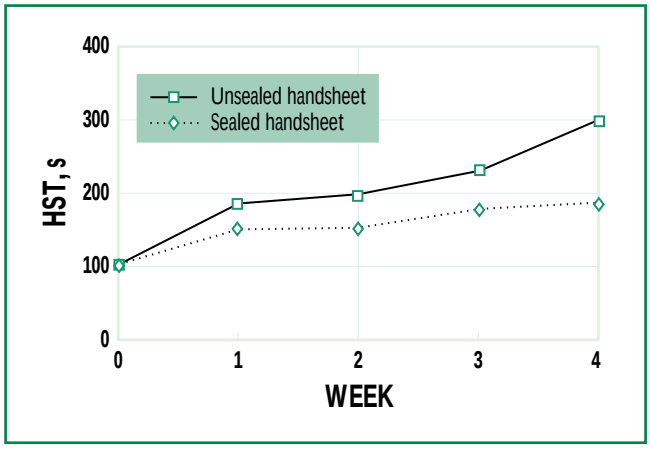
CONCLUSIONS

Sizing agents with 6 or 7 carbon atoms do not give sizing. Even the well anchored hexyl isocyanate that was used in excess did not provide sizing to preformed handsheets. Fatty acids with 18 or more carbon atoms may give poor performance if they are not well dispersed.

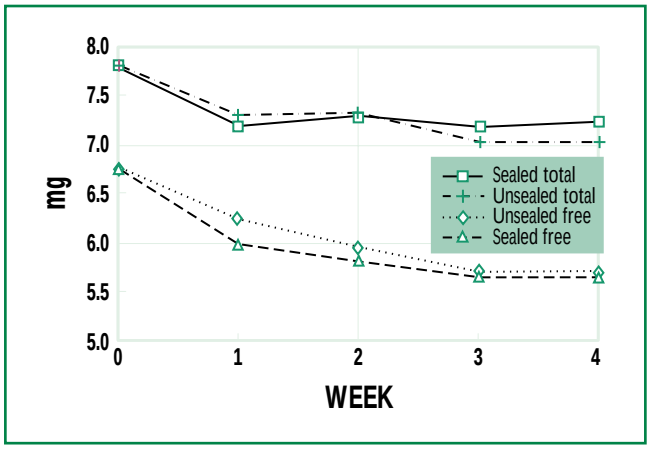
Bulky hydrophobes, such as abietic acid, help protect the sizing agent-alum-fiber linkage from attack by formic acid. They offer the additional advantage of not imparting a waxy feel to paper. The development of alternate, commercially viable anchoring methods for rosin sizing agents that are effective at pH 7–8 should be a milestone to the paper industry.

Development of sizing in air-dried handsheets treated with stearic acid and alum seems to occur partially as some stearic acid is evaporated but mostly as free stearic acid is converted to bound stearic acid.

These results should be useful in developing new internal sizing agents and predicting the sizing performance of a wide variety of hydrophobic materials.



1. HST values with neutral ink for aged handsheets treated with stearic acid and alum



2. Stearic acid content (mg per handsheet) of aged handsheets

EXPERIMENTAL

The sizing agent (1% wt/wt on pulp unless otherwise specified) was dissolved in 100 mL of ethanol (to help disperse it) and added to bleached hardwood pulp (13.2 g dry pulp at 2% consistency and CSF of 360). Alum (2% on pulp) or polyallylamine (0.5% on pulp) was added to the fiber as the mordant and the pH was adjusted to 4.0 or 7.0, respectively. The treated pulp slurry was allowed to stand for 10 min before use. The slurry was diluted to 0.15% consistency and then used to make handsheets using 5 L of water in the British sheet mold. The handsheets were air dried and equilibrated in the constant humidity room (according to TAPPI Test Method T 205 om-88) for one week before testing, unless otherwise stated. While heat drying would have generated interesting sizing results, the strength properties would have been meaningless. Some handsheets using stearic acid were aged for up to three months prior to testing. At least five handsheets were made for each set of conditions. The HST and strength results were averaged.

Handsheets without additives were prepared and air dried. The handsheets were then dried in a desiccator over phosphorus pentoxide. Three handsheets (1.2 g each) were treated with a 20 mL of tetrahydrofuran solution containing 25% of hexyl or octadecyl isocyanate and held at 40°C for 24 h. The reaction of isocyanate with cellulose (R'OH) to form the urethane linkage is depicted as:

$$R—N=C=O + R'OH \rightarrow RNHC(=O)OR'$$

The handsheets were then extracted three times with methanol to remove unreacted isocyanate and air dried in the constant humidity room for two days before testing. The weight gain was below 1% in both cases. The handsheets treated with octadecyl isocyanate had a waxy feel to them.

Stearic acid levels in handsheets were determined by gas chromatography using methyl esters prepared using BF_3—MeOH complex (Aldrich, Milwaukee, WI) analyzed on an SPB-5 column (Supelco, Bellefonte, PA) using heptadecanoic acid as the internal standard. Two extractions were performed on separate samples for each condition. The first used 12 mL of hexane (containing 5 mg internal standard) per half handsheet with shaking at room temperature for 3 h, followed by evaporation of the hexane and reaction of the residue with 3 mL of BF_3—MeOH. The second was an extraction with 15 mL of BF_3—MeOH complex containing 50 mg NaF (to bind aluminum and liberate all of the stearic acid) per half handsheet. In both cases the BF_3—MeOH derivatives were extracted with 1 mL of hexane, and 1 µL of the hexane was injected into the gas chromatograph. **TJ**

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