

Sizing with saponified alkenyl succinic acid

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ABSTRACT *Radioactive Carbon-14 labeling has been used to study the retention of saponified alkenyl succinic acid size. The effect of pH, alum addition level, stock consistency, and stock temperature on size retention have been studied. The structure of size precipitates, which were prepared under various conditions, has also been examined by Fourier transform infrared analysis (FTIR). Size retention seems to be mostly affected by alum addition level and stock consistency but not by pH. On the other hand, the structure of the size precipitate is affected by pH. The degree of size coagulation is affected by stock temperature. An alum addition level of at least 1.0%, a pH of less than 5.5, and precipitation in thick and low-temperature stock are the recommended conditions for the use of this size.*

KEYWORDS

Alum
Additives
Retention
Rosin
Sizing

Rosin soap size has been used extensively since its first development in 1804 (1). Although the type of rosin soap size has changed from natural saponified rosin paste to fortified soap, the basic retention mechanism is believed to be the same. Here, we report on a retention study for saponified alkenyl succinic acid size under various conditions. The size is a synthetic one obtained from isoalkenes and maleic anhydride (Fig. 1). It has been used for 15 years, mostly in Japan but also more recently in Europe. It can be used in the same way as rosin soap size, and the retention and sizing mechanisms can probably be considered to be the same.

Rosin soap size is known to be rather ineffective at high pH (1) and at low

additions of alum (2). It also tends to be precipitated in dilute stock (3) or in high-temperature stock (4, 5). It has been suggested that soap size is precipitated and retained by reaction with alum (1, 6). Under conditions in which the soap size shows poor performance, this reaction with alum is thought to be affected (5).

Many mechanistic studies have been carried out with rosin soap size, including ^{14}C labeling to give labeled fortified rosin (7, 8), but this product is a complex mixture of compounds in which molecules may have different numbers of carboxyl groups. Such variation creates difficulties. However, saponified alkenyl succinic acid consists of molecules that always contain precisely two carboxyl

groups. Therefore, we used saponified alkenyl succinic acid in our retention study and IR (infrared) study to understand the mechanism of soap sizing and ascertain the best conditions for its use.

Results and discussion

Comparison with rosin size

In Fig. 2, saponified alkenyl succinic acid size is compared with conventional rosin soap size. The figure shows greater effectiveness at low addition levels.

Influence of pH

The effect of pH on size retention and sizing efficiency was examined using ^{14}C -labeled saponified alkenyl succin-

ic acid size (Table I and Fig. 3). The pH was adjusted by keeping the alum addition constant (1.5%) and varying the amount of added NaOH. Sizing efficiency declined as pH increased, but size retention was almost constant.

The size precipitates were prepared at various pHs. The carboxyl groups were examined by FTIR (Fourier transform infrared analysis), and the results are shown in Fig. 4. The saponified size shows carboxyl absorption bands at 1560 cm^{-1} and 1410 cm^{-1} . However, when precipitated as the aluminum salt at pH 4.5, these bands are missing, and new bands appear at 1580 cm^{-1} and 1460 cm^{-1} . This suggests that the precipitated aluminum salt at pH 4.5 contains few residual saponified carboxyl groups. About 20% of the carboxyl groups were still saponified at pH 5.5, and almost half were saponified at a pH of 6.5. The alkaline (K^+ or Na^+) salt is hydrophilic (9), so the size precipitate formed at high pH is less hydrophobic, and this trait may lead to a drop in sizing efficiency at high pH.

Papermaking at high pH can also be achieved by a low level of alum addition, and this may also affect size retention.

Influence of alum addition level

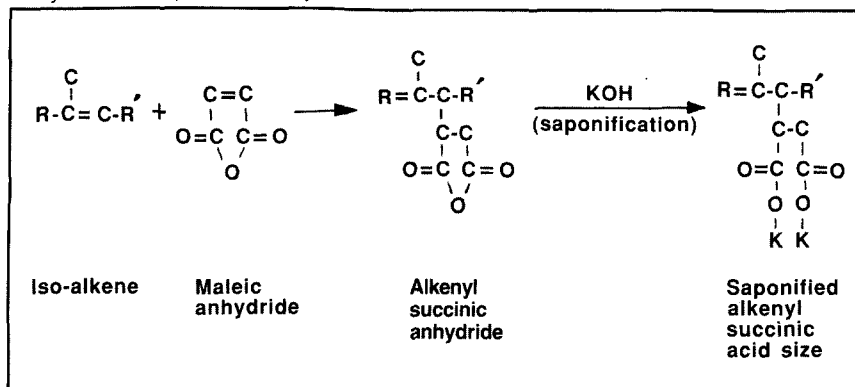
Table II and Fig. 5 show the influence of the alum addition level (at constant pH = 5.5) on size retention and sizing efficiency. As the alum addition was decreased, size retention dropped. This drop is probably the cause of the reduction in sizing efficiency.

Using FTIR, we compared the size precipitates prepared at different additions of alum. As Fig. 6 shows, no particular difference could be observed, which suggests that the alum addition level only has an effect on size retention and not on the structure of the size precipitate.

Influence of stock consistency

To study the influence of stock consistency on sizing retention and efficiency, we precipitated the size in thick stock (2%) and in thin stock (0.5%). Table III shows that a higher sizing efficiency was obtained when the size was precipitated in thick stock, and this higher efficiency seems to arise from higher retention.

1. Synthesis of saponified alkenyl succinic acid size



Influence of stock temperature

The influence of stock temperature was studied by precipitating size and making handsheets at 50°C (Table IV). Size retention showed a slight decrease, but sizing efficiency decreased to a large extent. Size precipitates prepared at 50°C and 20°C were compared by FTIR (Fig. 7), and the results suggested a small increase in the number of saponified carboxyl groups. However, these differences were too small to explain the big decrease in sizing efficiency.

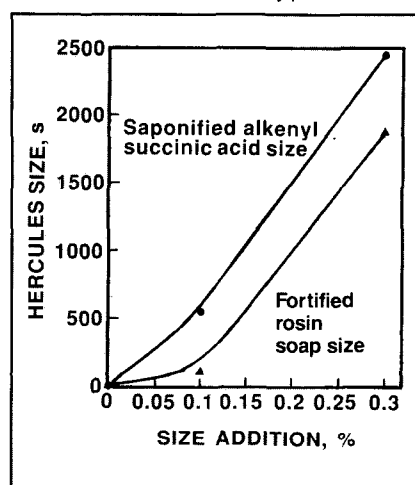
Air-dried handsheets, sized at 50°C and 20°C, were prepared. We used scanning electron microscopy (SEM) to examine the magnitude of the size precipitates on the fiber (Fig. 8). The size precipitates retained at 50°C are larger than those retained at 20°C. This change in the degree of coagulation might lead to a drop in sizing efficiency at high temperature.

Size addition level and sizing efficiency

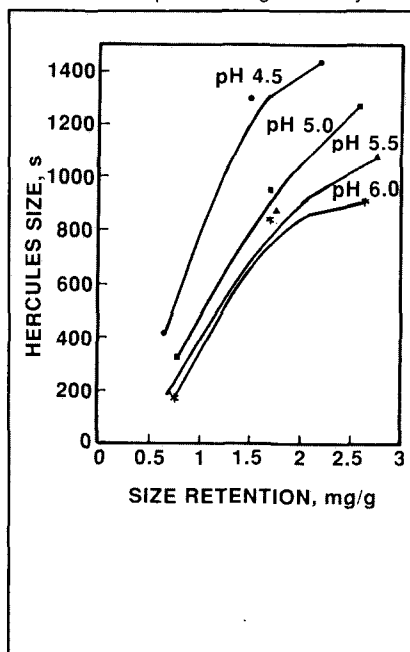
The relationship between size addition and sizing efficiency is shown in Fig. 9. Sizing efficiency increased with increased addition. However, the efficiency reached a maximum after a certain size addition level, even though there was a constant level of size retention.

Adsorption sites for size retention are still available even after maximum sizing has been achieved. Apparently, maximum surface coverage is not essential for optimum sizing. This condition may be the result of the steric influence of the hydrocarbon chains, or it may result from drying if drying leads to more effective coverage of the surface by these groups.

2. Comparison of sizing efficiency between saponified alkenyl succinic acid and fortified rosin soap size (pH = 4.7. Pulp = 490 mL CSF hardwood. Size: commercially produced size.)



3. Influence of pH on sizing efficiency



I. Influence of pH on sizing

pH	Size addition, %		
	0.1	0.2	0.3
<u>HST value, s</u>			
4.5	415	1297	1436
5.0	324	951	1268
5.5	192	873	1075
6.0	170	840	911
<u>Size retention, %</u>			
4.5	64	75	73
5.0	78	85	86
5.5	70	88	92
6.0	76	85	88

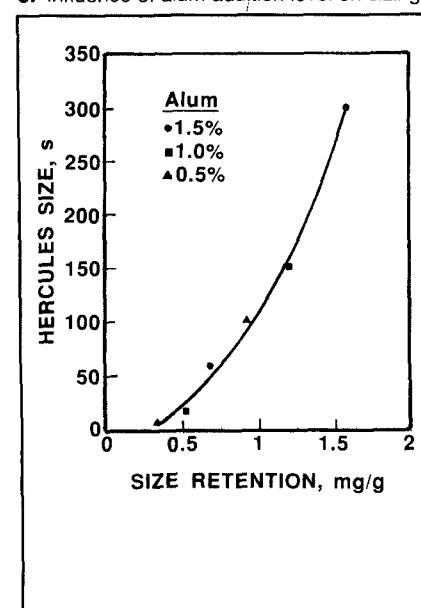
450 mL CSF hardwood.

II. Influence of alum addition on sizing

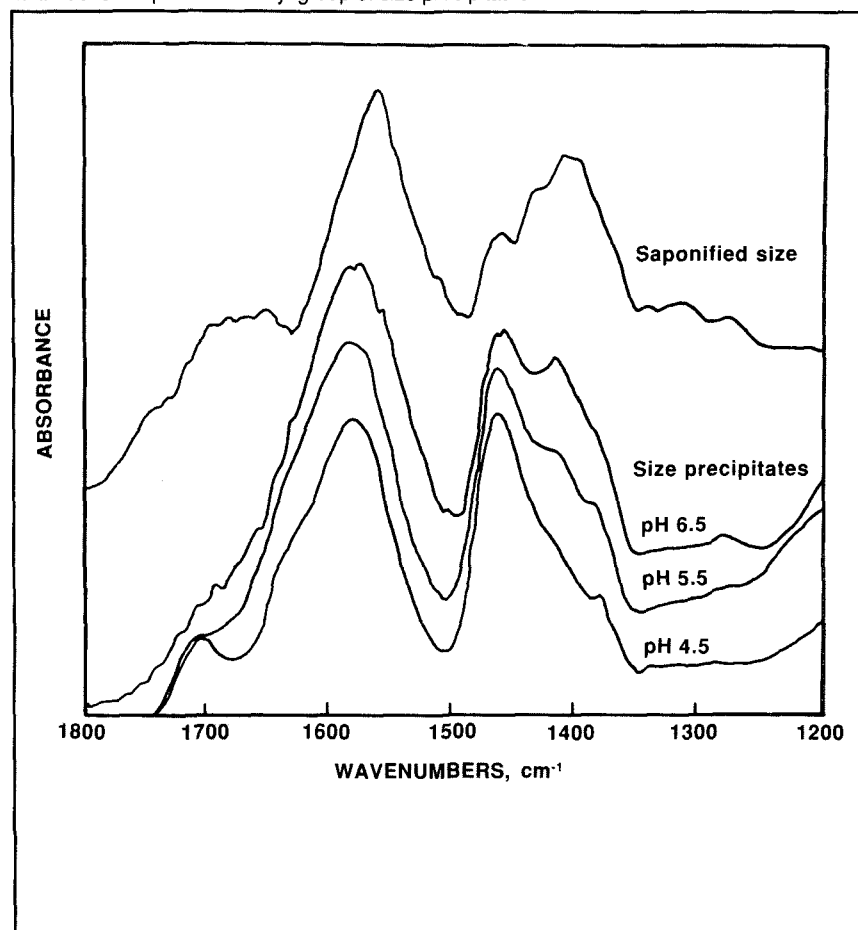
pH	Size addition, %	
	0.1	0.2
<u>HST value, s</u>		
1.5	59	300
1.0	17	151
0.5	7	101
<u>Size retention, %</u>		
1.5	68	79
1.0	52	60
0.5	33	46

pH = 5.5.
310 mL CSF softwood.

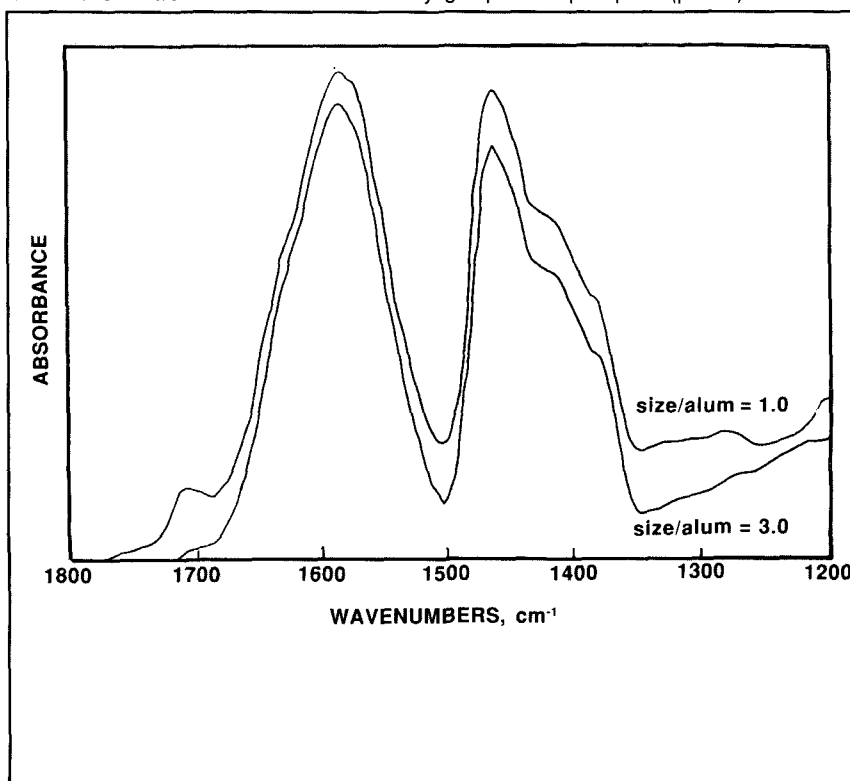
5. Influence of alum addition level on sizing



4. Influence of pH on carboxyl group of size precipitates



6. Influence of alum addition level on carboxyl group of size precipitate (pH 5.5)

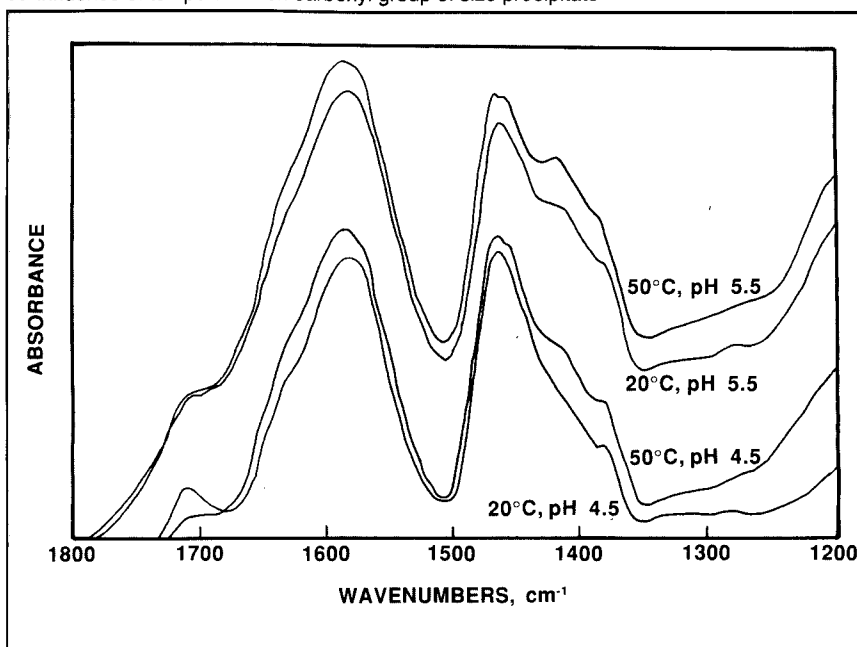


III. Influence of stock consistency on sizing

Stock cons., %	Size addition, %	
	0.1	0.2
HST value, s		
2.0	61	444
0.5	6	226
Size retention, %		
2.0	79	80
0.5	37	53

pH = 5.0.
400 mL CSF softwood.

7. Influence of temperature on carboxyl group of size precipitate

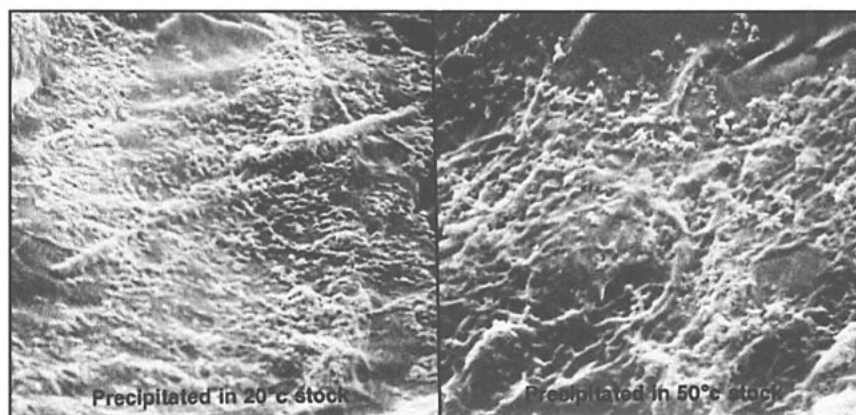


IV. Influence of temperature on sizing

Temp., °C	Size addition, %	
	0.1	0.2
HST value, s		
20	61	444
50	21	210
Size retention		
20	79	80
50	68	73

pH = 5.0.
400 mL CSF softwood.

8. Scanning electron micrographs of size precipitates on fiber (X10,000, size addition level : 0.54.)



Experimental methods

Preparation of ¹⁴C-labeled size

The ¹⁴C-labeled alkenyl succinic anhydride was synthesized from a mixture of C10-C14 iso-alkenes (average carbon no. = 12) and 2,3-¹⁴C maleic anhydride. These were heated in a sealed glass tube reactor at 190°C for three days. The alkenyl succinic anhydride was separated by distillation and saponified into soap size (10% solids concentration). The specific activity (in curies/gram) of the anhydride was 16.68 μ Ci/g, and that of the saponified alkenyl succinic acid size (10% solid concentration) was 1.26 μ Ci/g.

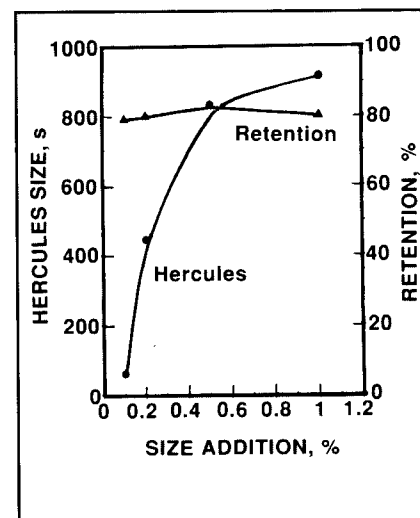
Preparation of handsheets

Handsheets were prepared from either *Oulu* hardwood bleached sulfate or *Lapponia* softwood bleached sulfate pulps. These were beaten in a Medway beater and were diluted to a consistency of 2%. Size and other chemicals were normally added to the 2% slurry in the following order:

1. NaOH, to enable alum addition at a certain pH
2. ¹⁴C-labeled size
3. Alum (normally 1.5% based on pulp).

The slurry was diluted into 0.5% and divided into several portions which were used for preparing handsheets using a British standard sheet machine (basis weight = 60 g/m²). Water

9. Size addition level and sizing efficiency (pH = 5.0, 400 mL CSF softwood pulp)



adjusted to the appropriate pH was used for dilution and for sheet formation. After pressing, handsheets were dried on a drum dryer at 100°C for 3 min.

Testing

Sizing efficiency was tested using a Hercules size tester (HST) with acid-free ink. Size retention was determined using a liquid scintillation counter.

FTIR study of size precipitates

Commercially produced saponified alkenyl succinic acid size (Diasize NSP: Mitsubishi Oil Co. Ltd.) was used for FTIR studies. Size was precipitated in the same manner as it would have been precipitated in a 2% slurry for handsheet preparation. That is, a certain amount of NaOH (with the amount dependent on pH), size (0.02 g), and alum (0.06 g) were added to water (400 mL) in that order. The precipitate was filtered through a 0.45- μ m membrane filter and dried

at 100°C. The FTIR study was carried out using the diffuse reflectance technique.

SEM studies of size precipitates on the fiber

Sized handsheets prepared at 50°C and 20°C were air dried. After gold coating, they were examined by scanning electron microscopy with a 10,000 times magnification.

Conclusions

An alum addition level of at least 1% and precipitation in thick stock are the main two factors that contribute to good retention of saponified alkenyl succinic acid size. A pH below 5.5 gives a size precipitate that is sufficiently hydrophobic. To use this size in high-temperature stock, some of the suggestions proposed for the use of rosin soap size at high temperature (10) could probably be applied to maximize the efficiency of size. □

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