

SIZING MECHANISMS AND THE EFFECT OF FILLERS

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ABSTRACT

The mechanism of sizing with soluble rosin soap size differs from the sizing mechanism of dispersed rosin acid size. Cationic fixing agent has to be used with the latter size to assure proper attachment of the size to furnish components. The problem of size attachment is not unlike that for the alkaline AKD size emulsion. The relative extent of attachment is assessed by a high shear stirring test.

Sizing involves a complex array of interactions in which surface reactions play an important role. The large surface area fines and fillers in the furnish reduce sizing efficacy. Size accumulates on fillers/fines to a higher extent than expected from surface area alone. On the basis of experimentally determined adsorptivities, size distribution in a furnish can be estimated. Size on fiber appears to be more efficient than on fillers/fines, compared at equal surface coverage. This requires that we minimize the amount of fine particulates in the furnish. Fillers/fines capture a significant amount of applied size; thus, first pass fillers/fines retention has to be maximized to retain size in the sheet. Size distribution also can be affected by the proper choice of process conditions.

INTRODUCTION

Internal sizing is an important process step in the wet end operations of the paper machine. The purpose of sizing is to modify the surface of fibers to control water penetration. Sizing materials are among the most

frequently applied wet end additives. Table 1 indicates the market share in 1981 of various size preparations in the United States. Two types of rosin size, soap and dispersed acid size were used in the largest quantities. The production of synthetic (reactive) size was not very significant in 1981, but in the last three years their market share has grown.

Size	Price, ¢/lb.		Use Tons	Market Value Million \$
	As is	Solids		
Soap Paste	38	54	95,000	72
Dispersed Acid	28	80	90,000	50
Synthetic/Alkaline	180	180	6,000	22

Source: Pulp and Paper Magazine, 1981.

Table 1 US Size Consumption - 1981

The present paper deals with mechanistic aspects of rosin sizing with only lateral inclusion of synthetic sizes, where applicable. The focal point of our discussion will be the effects of filler and pulp fines on the sizing of paper and board.

There is no need here to review fully the history of sizing mechanisms. At the 1965 Cambridge symposium, Schwalbe (1) presented an informative review. More recently, Swanson (2), Griggs (3), Strazdins (4, 5) and Dumas (6) discussed, among others, the more significant progress achieved in the past decades.

In the development of rosin sizing theories, two major approaches emerged for explaining sizing mechanisms: one school has proposed that the fiber surface is the site of the interaction of rosin with alum, the central step of the sizing reaction (7); while others proffered that these interactions occur in solution (8) and a resulting rosin-aluminium complex adsorbs on the fiber surfaces (9). A rational resolution of these two proposals is at hand (4,10,11). We will deal briefly with some of the pertinent experimental evidence.

The mechanisms involved in alkaline reactive sizing are discussed by Roberts (12) at this Symposium. The main sizing steps there proceed on surfaces. The solution reactions of reactive sizes are side reactions which only eliminate the reactive groups of size by competitive hydrolysis.

Almost all practical papermaking furnishes contain fine particulates (pulp fines and mineral fillers) in addition to the papermaking fibers. Fines contribute a considerable portion of the surface available for sizing interactions; thus, they also affect the sizing process in a significant manner. There are common features in the surface interactions of the chemically different fillers and fines, but we may also expect specific reactions dependent also upon the mechanisms involved in the interactions of the various sizes.

The outline of our present discussion is the following:

Selected aspects of sizing mechanisms.

Attachment of sizes to surfaces. Charge effects.

Effect of various fillers and fines on sizing efficiency.

Distribution of sizes on furnish components.

The experimentation was conducted with commercially available size preparations. Never-dried medium-refined bleached hardwood pulp was used in the laboratory experiments, the mill furnishes also contained 20-30% pine

fibers. In some laboratory studies, radioactive ^{14}C -labeled rosin sizes were used (11, 13). The fillers were commercially used pigments. Experimental conditions are indicated in the text or on the tables, and further details can be found in the references given.

MECHANISTIC ASPECTS OF SIZING

Surface vs. Solution Interactions

To start our discussion on the fundamental aspects of rosin sizing, the first objective is to establish the site of the main reaction - where and in what order will the reaction between the fiber and sizing agents occur? Critical experiments were designed (10,11) to separate the surface and solution interactions of rosin and alum.

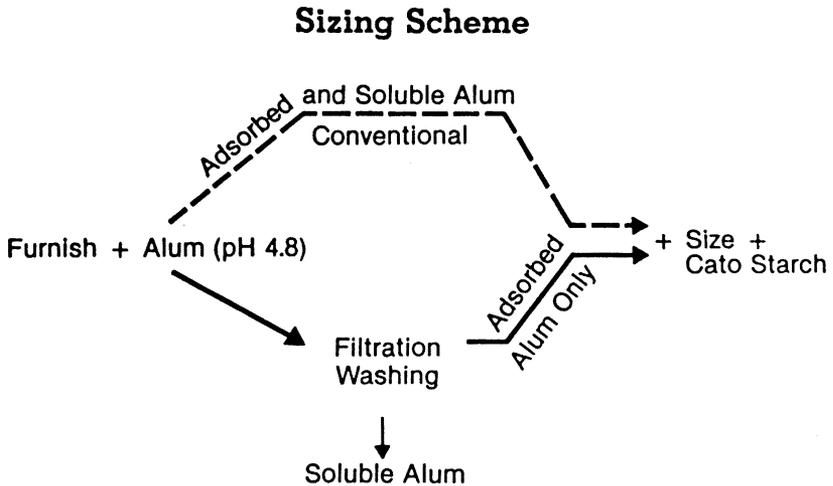


Fig 1—Sizing Scheme

As the upper route in the scheme (Figure 1) indicates, alum was added to pulp furnish as in conventional reverse sizing at pH 4.8. Part of the alum is adsorbed on the pulp, another part will remain in solution. Alum addition was followed by addition of size, and finally by application of cationic starch. In a second experiment, the sizing sequence was interrupted after alum addition, as the lower branch of the scheme shows, and the soluble aluminium ions were removed by filtration and careful washing of this second portion of the pulp furnish. Analysis revealed that about 70 to 80% of the alum remained adsorbed on the pulp and there was no alum left in solution after washing. The treated pulp samples were resuspended and the sizing sequence was continued by adding the size and, finally, cationic starch. Handsheets were made and tested on the Hercules Sizing Tester (HST).

Condition	Applied		% Rosin Found	Analysis	Sizing Value HST, sec.
	% Size	% Alum			
Conventional	0.5 Dispersed Acid	1	0.38	¹⁴ C	531
Pretreated	0.5 Dispersed Acid	(1)	0.38	¹⁴ C	500
Conventional	1 Paste Size	2	0.7	GLC	350
Pretreated	1 Paste Size	(2)	0.4	GLC	176
Conventional	1 N-Soap	2	0.6	GLC	247
Pretreated	1 N-Soap	(2)	0.4	GLC	58

Furnish: 415 mL CSF hardwood pulp, reverse sizing, pH 4.6-4.8, 0.3% cationic starch.

Table 2 Interaction of Rosin Sizes with Preadsorbed
Alumina

Table 2 presents the sizing values obtained in three such paired experiments. With dispersed size there was only a minimal difference, 531 vs. 500 sec, between the sizing values of the conventionally-sized sheet vs. sheets prepared from washed pulp. We would expect a major loss in sizing value if reactions between rosin and alum in solution were a dominant part of the sizing mechanism. Therefore, with dispersed rosin size, good sizing is not dependent on the interaction with dissolved alum. The rosin-alum interaction must occur later on the fiber surface after adsorption of the two reactants.

In the next pair of experiments, commercial soap paste size was used which also contained about 10% free rosin acid. The sizing value with the washed pulp dropped to only half that obtained in the conventional sizing, with alum in solution.

The last two lines in Table 2 highlight experiments using fully neutralized soap size (N-soap). In the conventional sizing mode, where alum and soap size are both in solution, the sizing value was 247 sec. On the other hand, the sizing value of the pretreated pulp was very low, only 58 sec, after the soluble alum had been removed by washing. To produce effective sizing, soap size molecules must react with alum in solution and not with alum adsorbed on the fiber surface. Here, surface interaction is minimal.

These experiments also showed the superiority of dispersed size in achieving high sizing values. Half as much dispersed size gave penetration times over twice as high as those obtained with soap. But there can be other considerations, too, in the choice of size, that are discussed later.

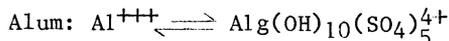
Sizing with Soluble Rosin Soap Size

Dissolved rosin soap size and soluble aluminium ions interact in solution and form positively charged insoluble aluminium-rosinate flocs which subsequently adsorb on the electronegative furnish (cf. ref. 2,4,9). The sizing steps are outlined as follows:-

Sizing With Soap Size

Size: Rosinate in Molecular Solution

or < 0.1 μm Particles



pH: 4.1 - 4.7

Preferred Reaction Sequence

1. $\text{Al-Ions}^+ + \text{Rosinate}^- \rightarrow (\text{Al-Rosinate})^+ \text{ Floc}$
2. $(\text{Al-Ros})^+ \text{ Floc Adsorbs on Fiber}^-$
3. Curing: Floc Heat-Softens, Spreads, Positions on Fiber.

There is a pH-dependent competition between dissolution and adsorption of the various Al-complexes forming in a solution; pH over 4.5 promotes alum adsorption on fiber/fines (14). Under typical soap sizing conditions (pH 4.1-4.6), enough Al-ions are dissolved to form the cationic aluminium rosinate complex. There is no need in this pH domain to supply additional cationic assistance to attach the size particles to the furnish; it would be added primarily to improve fines retention. Table 3 supports this conclusion. With pasted soap size, addition of 0.3% cationic starch increased the sizing values (10,11) by only 25 percent. This increase can be explained by the increased fines retention and by the different response of free rosin acid in the soap size paste.

Sizing with Dispersed Sizes (Size Emulsions)

Emulsions of synthetic, so-called "reactive sizes" are non-ionic and have to be attached to the fiber surface through the assistance of cationic emulsifiers and stabilizers. The emulsified particles are usually quite large (0.5 to 2 μm), and high efficiency sizing relies on spreading of the low melting size on the fiber surface in very thin layers during the drying operation (6).

Sizing Mode	Cationic Starch	HST Sec.	% Rosin Found (GLC)
Conventional			
Reverse	-	280	0.4
Reverse	+	350	0.7
Direct	-	376	0.5
Direct	+	475	0.8

Furnish: 415 mL CSF hardwood pulp, 2% alum, 1% pale soap size paste, pH 4.6, 0.3% cationic starch

Table 3 Cationic Starch at rosin Soap Sizing

Sizing Mode	Cationic Starch	HST sec	% Rosin Found	Analysis
Reverse				
Conventional	-	67	0.3	GLC
Conventional	+	531	0.4	¹⁴ C
Al-pretreated	-	15	0.05	¹⁴ C
Al-pretreated	+	500	0.4	¹⁴ C

Furnish: Hardwood pulp, 1% alum, 0.5% size, pH 4.8, 0.3% cationic starch

Table 4 Cationic Starch at Dispersed Rosin Acid Sizing

The dispersed rosin acid sizes are mostly anionically stabilized emulsions (15) with particle sizes in the range of 0.2-0.4 μm . Each discrete particle contains millions of aggregated rosin acid molecules, only a fraction of which are on the outer surface and able to react with the solution. To assure attraction between the negatively charged furnish and the anionic size droplets, cationic assistance is necessary (11). There are usually three types of cationic additives which can be utilized to promote attachment:

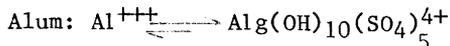
- a. Soluble Al^{+++} or higher charged polynuclear Al^{n+} species ($n=4-5$)
- b. Cationic starch
- c. Synthetic polyelectrolytes and retention aids.

Results in Table 4 with ^{14}C -labeled size clearly bring out these effects. The radioactivity measurements (11) indicated that about 76% of the 0.5 percent dispersed rosin acid size applied was retained in the handsheets formed in the presence of cationic starch. Lack of dissolved Al-ions did not make a difference in this case. In the absence of cationic starch, however, size retention suffered, and consequently, sizing values dropped. These results indicate that we need cationising agents to achieve good size retention through electrostatic attraction. The main steps of sizing with dispersed rosin can be outlined in the following way.

Sizing With Dispersed Acid Size

Size: Rosin Acid Particles in

Finely Dispersed Form

0.2 - 0.4 μm 

pH: 4.5 - 5.0

Preferred Reaction Sequence

1. (Al-Ions)⁺ Adsorb on Fiber⁻
2. (Rosin A)⁻ + Retention Aid⁺ \rightarrow (Rosin A)⁺
3. (Rosin A)⁺ Adsorbs on (Fiber + Al)⁻
4. Curing: Rosin A Melts, Spreads, Reacts with Al

The interactions between rosin and alum are complex and delicate. Rosin sizing can be disrupted in the presence of complexing agents which bond Al more strongly than rosin acid does. This disruption can happen before curing with e.g., oxalic acid, or after curing in the presence of lactic acid. Our present picture is that electrostatic attraction (ionic bonding) is the main force. It is likely that other types of forces (London, Van der Waals, H-Bonding) may also be involved in the interaction of fiber and rosin, especially in self-sizing where no aluminium is available to anchor the rosin to the surface. However, such weakly adsorbed rosin can overturn on the fiber surface through interaction with strongly polar liquids (2).

Attachment of Size

The sizing additives are usually added to the furnish in some preferred order (e.g., size first \equiv direct, or alum first \equiv reverse) in the stock preparation system. The

electrostatically attached size is subjected to strong shearing forces in the fan pump, cleaners, screens, headbox and also on the wire. A recently published study of Pelton (16) suggests that the high shear rates of the paper machine ($10^4 - 10^7 \text{ sec}^{-1}$) may even disrupt covalent bonds. Pelton also showed that similarly high shear rates can be generated in the Dynamic Drainage Jar of Britt (17). This latter equipment was utilized in our assessment of the relative strength of size attachment to fiber in strong shear fields (25).

The size and additives were applied to a pH-adjusted, 1% consistency slurry of a coarse fiber fraction (separated over 200 mesh screen from a medium refined hardwood pulp). The sized furnish was stirred at high speed (1000 rpm) for 10 minutes in the Britt Jar. The fiber fraction was separated from the liquid, gently washed and freeze dried. The adsorbed size was determined by extraction and gas chromatography. The non-attached portion of size also was recovered by extraction from the filtrate. Due to the multiple manipulations, the material balances showed as much as 20% deficiency.

(2% alum, 1% dispersed rosin acid size, reverse sizing mode at 400 and 1000 rpm)

pH	Cationic Starch 0.3%	At 400 rpm			At 1000 rpm		
		% of Applied Size Recovered from			% of Applied Size Recovered from		
		Fiber	Water	Unaccounted for	Fiber	Water	Unaccounted for
4.8	-	59	32	9	43	41	16
4.8	+	69	12	19	78	20	2
5.8	+		N.D.		57	24	19
6.8	+		N.D.		50	29	21

Table 5 Size Distribution in High Speed Stirring Experiments - Dispersed Rosin Acid Size

Typical results at two stirrer speeds, presented in Table 5, show that increasing shear rate may promote either detachment or shear coagulation and deposition. In the absence of cationic assistance, increasing shear (from 400 to 1000 rpm) reduced the size retained on fiber; in the presence of cationic starch, however, the size portion which became attached to fiber, increased to almost 80% (of the applied size amount). The size concentration at 1000 rpm on fiber almost doubled after addition of 0.3% cationic starch. Increasing pH reduced size attachment.

The high speed stirring experiments also confirmed the lesser role of cationic assistance in sizing with rosin soap (Table 6). The portion of applied size recovered from the fiber fraction only increased at the regularly used pH 4.6 from 68% to 73% in the presence of cationic starch. Increasing pH reduces solution interactions between alum and rosin. Over pH 6, the retained portion of size on fiber was found to be small, even in the presence of cationic starch.

Retention of the larger particles of emulsified synthetic sizes on the surface of fibers is still more critical because of the hydrolytic sensitivity of free-floating size in the white water. Some examples with two commercial AKD sizes are shown in Table 7. The charge conditions have to be well-balanced to assure efficient electrostatic attachment, hence the need to use additional cationic promoters occasionally.

(2% alum, 1% fully neutralized liquid rosin soap size, reverse sizing mode at 1000 rpm)

pH	Cationic Starch 0.3%	% of Applied Size Recovered from Fiber
4.6	+	73
4.6	-	68
5.8	-	16
6.8	+	13

Table 6 Attachment of Rosin Soap Size to Fiber

AKD Emulsion	Emulsifier Type	Additional Promoter*	% of Applied Size Recovered From		
			Fiber, with Solvent	Fiber after Hydrolysis, with Solvent	Water, with Solvent
Weakly cationic	Cationic starch	-	N.D.	15	79
Weakly cationic	Cationic starch	+	53 - 60	14 - 18	33 - 16
Strongly cationic	Synthetic resin	-	40 - 72	20 - 21	18 - 11

CONDITIONS: 5.5 g coarse hardwood fiber, 0.3-0.4% size solids (12-15 mg AKD), 4-8 mg strongly cationic medium m.w. resin*, stirred at around pH 7 to 8 in Britt Jar, for 10 min. at 1000 rpm.
Solvent: CHCl_3 ; hydrolysis by boiling with ethanolic NaOH.

Table 7 Attachment of AKS Size Preparations to Fiber

Practical experience indicates (6) that the attachment is quite shear-sensitive, which also is corroborated by the results of Table 7. Two commercial AKD size preparations were used in these high shear experiments, one weakly cationic emulsion (ζ potential = 17mV) stabilized with cationic starch, and a strong cationic emulsion (ζ potential = +32 mV) prepared with a presumably polyamine-polyamide based cross-linked resin. Most of the AKS from the weak cationic preparation was detached from the fiber (almost 80% was recovered from the water phase) after 10 minutes stirring in the Dynamic Drainage Jar. Application of an additional cationic promoter reduced the soluble AKD portion to 16-33%. In the case of the second strongly cationic ADK preparation, only 11 - 18% of the applied size was found in the water phase.

We could conclude from these and other pertinent studies (25) that efficient size retention requires the creation of shear resistant attachment of size to furnish before the stock reaches the wire. Molecular and colloidal forces, especially electrostatic attraction, play an important role in the process of attaching size to furnish components. Anionic dispersed rosin size and weakly cationic AKD sizes may need an additional cationic bridging

agent for appropriate size retention. The available dissolved positive aluminium ions usually are not effective enough to create strong attachment for the dispersed rosin acid size. Studies indicated that cationic starch is more effective, (10,18). With rosin soap size, cationic starch is used primarily as a retention aid for fines. Retention of the fines and fillers is very important as will be discussed later.

EFFECTS OF FILLERS AND FINES ON SIZING EFFICIENCY

Hardwood and groundwood furnishes contain a large amount of pulp fines (< 200 mesh). Some fine paper furnishes are composed of less than half coarse fibers, the majority being pulp fines and inorganic fillers. Fines and fillers are needed to obtain desirable optical and printability properties in the sheet.

Brecht (19) observed in 1937 that fillers strongly affect the sizing response of handsheets sized with 3% fully neutralized rosin soap size and 5% alum at pH 5.5. Dye penetration time increased with increasing loading of talc and CaSO_4 pigments; CaCO_3 and, still more strongly, clay decreased the sizing values. Brecht explained the negative effect of clay by the high surface area and hydrophilic nature of kaolin. Weigl (20) further developed Brecht's ideas, proposing that the sizing effect also depends on the free surface energy of the filler. He concluded that low surface energy (hydrophobic) talc and CaCO_3 should increase, and the high surface energy clay should decrease the sizing values.

Observations with unfilled bleached hardwood furnish (11) indicated that the sizing loss caused by addition of pulp fines was higher than expected from their surface area contribution. One would not expect major difference in surface energetics between fibers and pulp fines in spite of some subtle differences in their chemical nature. We concluded, therefore (18), that the surface energy hypothesis of Brecht and Weigl is not applicable to cellulosic "fillers", i.e., pulp fines.

In addition, the nature of the size used in a given experiment constitutes a further complicating factor for generalizing the sizing interactions in a multicomponent furnish. We can rightfully expect differences, for instance, in the interactions of rosin soap size used by Brecht and the more recently developed emulsified rosin acid sizes.

Handsheet Study with Various Fillers

In our related handsheet experiments (18), 0.5% dispersed rosin acid size or 1% fully saponified size (marked as N-soap) were used (Table 8). All sizing values were greatly reduced by the presence of fillers in the furnish, both with acid and soap sizes. With acid size, talc and coating clay which have similar surface areas gave identical HST sizing values. With soap size, talc appeared to give less sizing loss than other pigments. Clays reduced sizing values in direct proportion to their respective surface areas. TiO_2 exerted in both cases a moderating influence on sizing loss caused by filler clay.

Filler	1% N-Soap Size			0.5% Dispersed Acid Size		
	% Alum	% GC Size	HST sec.	% Alum	% GC Size	HST sec.
PDM Filler Clay	1.3	0.90	270	0.93	0.40	216
PDM Clay + TiO_2 (12:8)	1.2	0.80	260	0.64	0.30	244
No. 2 Coating Clay	1.4	0.85	174	0.66	0.30	153
Talc	1.0	0.85	326	0.90	0.40	154
$CaCO_3$	1.3	0.25	46	0.84	0.03	1
No Filler	1.3	0.80	500	0.70	0.40	543

CONDITIONS: 410 ml. CSF bleached hardwood pulp, 20% filler, reverse sizing, 0.8% cationic starch used. Dispersed acid size: 1% alum, pH 4.8, 0.5% size. Fully saponified N-soap size: 2% alum, pH 4.6, 1% size. HST sec. normalized to 68.5 g/m² basis weight.

Table 8 Effects of Fillers on Handsheet Sizing

Pulp	Hydrodynamic ₂ Surface Area, m ² /g
65 sec. Blend Pulp	2.1
62 sec. Hardwood Pulp	2.2
Coarse 62 sec. Hardwood Fibers	1.2
<200 Mesh Hardwood Pulp Fines	6.0

Filler	N ₂ -Surface Area m ² /g
Filler Clay	10.5
No. 2 Reg. Coating Clay	14.6
Talc	14.0
TiO ₂ Powder	9.9
Precipitated CaCO ₃	8.5
Ground CaCO ₃ Filler, H-30	6
Finely Ground CaCO ₃ , H-65	14

It is assumed that:

- a) hydrodynamic surface area = available area for sizing reactions.
- b) for fillers, N₂ area = hydrodynamic surface area.

Table 9 Surface Area

Precipitated CaCO₃ gave a low but still appreciable HST reading of 46 sec, with the soap size, while the sheet remained waterleaf with acid size. In the presence of CaCO₃ filler, sizing pH was > pH 6, but pH did not remain constant. The surface of the CaCO₃ particles is alkaline, further contributing to the observed sizing loss. To moderate the negative effect of CaCO₃, several practical approaches are available (e.g., 21, 22).

According to Weigl's proposal (20), one would expect major differences in the sizing contributions of the various fillers. Our data in Table 8 indicate that all fillers decrease sizing compared to pigment-free furnishes. The effect is larger with dispersed acid size application than with soap sizing. With dispersed acid

size, a main variable appears to be the surface area of the filler (Table 9). The hydrophobic surface of talc may have caused less deteriorating effect with rosin soap sizing, but no special influence was observable with dispersed rosin acid sizing. TiO_2 , which is considered to be a hydrophilic filler, reduced the sizing value of either size to a lesser extent than expected from the surface area effect alone. The low surface energy and alkaline $CaCO_3$ had a strong negative effect with both sizes. These observations are at variance with Weigl's proposition (20). Furthermore, in mill furnishes, adsorption of dissolved colloids (e.g., hemicelluloses) on fillers and fines may equalize both charges and surface energies (23).

The Role of Surface Areas. Pulp Fines

Since sizing is a surface chemical interaction, the surface area of furnish components should affect sizing efficiency (24). Refining increases the surface area of pulps because of the increasing amount of fines and fibrillation of fibers. The same amount of size applied to this increased area would be expected to give decreased coverage of the surface and decreased water repellency. In a related study (11), hardwood pulp was increasingly refined, portions of the pulps were fractionated, and the hydrodynamic surface areas of the preparations were determined. 0.3 - 0.5% dispersed rosin acid size and 1% alum were used to size the furnishes, and handsheets were made to test sizing values. It has been assumed that the size retention was the same in all handsheets. As a first approximation, eventual influence on HST values of changes in porosity and caliper also was neglected. The observed ink penetration times are plotted in Figure 2 as a function of calculated surface coverage (mg size added/m² surface area). The sizing values in the range studied increased almost linearly with increasing surface coverage.

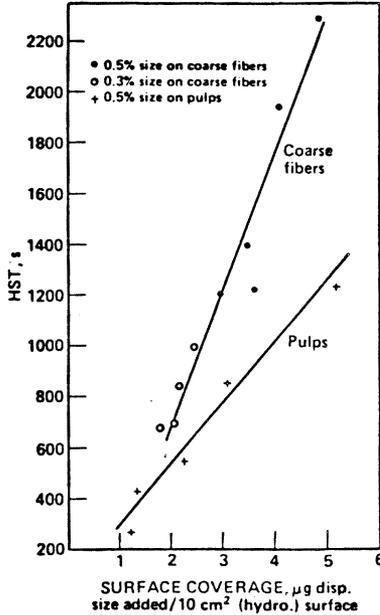


Fig 2—Sizing efficacy vs coverage

Figure 2 conveys an unexpected message, namely that size on coarse fiber gives better sizing efficiency than size on pulp that contains fines when compared at the same level of surface coverage. We will see later indications that fillers and fines accumulate rosin acid size well above that expected on the basis of specific hydrodynamic surface areas. Such a heavy coverage may be inefficient. Figure 2 suggests that size on coarse fiber is more efficient than on pulp containing fines. Fines are needed for sheetmaking, and fines also carry a great deal of rosin size. To achieve a good compromise and effective sizing, we should strive for the minimum amount of fines in the headbox furnish, and for high retention of them on the wire while the sheet is being formed. Since recirculating fines are not effective in developing sizing, the appropriate

strategy is high first pass retention to enhance sizing and achieve the best condition for other sheet properties. These points are further corroborated (10, 11) by the following experiments.

Sheet Preparation	Found	
	% Dispersed Size	Sizing Value sec.
A. Conventionally sized pulp	0.4	540
B. Coarse fiber sheet Fines removed after sizing	0.05	1
C. 80% unsized fiber 20% presized fines	0.4	455
D. Coarse fibers sized Fines removed before sizing	.35	1200

Table 10 Fines in Handsheets

Table 10 indicates that 0.4% dispersed size retained on a conventionally-sized unfilled hardwood pulp can produce a sizing value of approximately 540 seconds. When pulp fines are removed after sizing by screening the sized furnish to form a coarse fiber sheet, the majority of the added size has been taken away. The size content, found now on the coarse fibers, drops to about 0.05% and the sizing value of the coarse fiber sheet drops correspondingly to 1 second. The major portion of the applied size associated itself with the fines.

When 20% of presized fines, heavily sized in a separate step, were added back to 80% of the separated or even fresh unsized coarse fibers, the original size content returned, and the sizing value increased to 455 seconds. This is a high level, although still 100 seconds lower than observed in the control condition. This experiment underlines the importance of retaining the fines in the sheet and retaining them during the first pass on the wire.

In our final experiment we removed the fines from the pulp before sizing; thus, all the size was added to the coarse fiber fraction. The sizing value now jumped to 1200 sec, indicating that the retained 0.35% size covered the coarse fibers more efficiently than it would a mixture of fibers and fines in a whole pulp. (Removal of fines changed the porosity and caliper of the handsheets confounding the evaluation of sizing results. These effects need further study).

These experiments throw light on the dualistic role the fines play in the context of sizing efficiency. Best sizing is achieved when minimal fines are used in the headbox furnish and the fines are retained in the paper. Alternatively, increasing the relative size concentration on the coarse fiber portion would improve sizing efficiency

ADSORPTION OF SIZING ADDITIVES ON FURNISH

The previously described experiments indicate that sizing efficiency in a multicomponent furnish depends not only on the applied amount, but also the location of the size and its distribution on the surfaces of furnish components. This distribution is affected by processing conditions (application points, consistency of furnish), by the chemical environment (pH, dissolved substances, concentrations of size and sizing additives), furnish composition and the adsorptive behaviour of the sizes themselves. The distribution of rosin sizes in a typical sizing condition was determined (18), see Table 11.

¹⁴C-labeled dispersed rosin acid and fully neutralized rosin soap (N-soap) sizes were added after alum application at pH 4.6-4.8 to a bicomponent hardwood furnish, consisting of either pulp with 20% fines or blends of coarse fibers and 10% filler. The sized fibers and fillers (fines) were separated on the 200 mesh screen of the Britt Jar, and alum and size concentrations (w/w) were determined both on furnish and in the liquid. The ratio of surface concentrations is expressed as adsorption ratio in the Tables. Material balance was better than 90%, size retention was over 80%.

When 0.5% dispersed acid size and 1% alum were used in the sizing, the weight concentrations of alum adsorbed on pulp fines: fillers: coarse fiber were close to the ratio of 3:2:1, while the corresponding ratios for ^{14}C -acid size ranged from 20:20:1 to 60:200:1. In cases where the coarse fiber retained only a small amount of size (<0.05%), the precision of size determination is low, and the derived ratio is unrealistically high. TiO_2 could not be separated completely from the fibers which strongly retain the TiO_2 -size coprecipitate on the fiber surface. To facilitate comparison, Table 11 shows values calculated for ash-free fibers. Size retention on pigments was generally quite high, but CaCO_3 adsorbed very little size; this effect may have contributed to its low sizing efficiency in handsheets.

Furnish	^{14}C -Size	Alum %	Alum Adsorption Ratio	Size Adsorption Ratio	Size Conc., %	
			(w/w)	(w/w)	Fiber	Filler
			Fiber/Filler	Fiber/Filler	Fiber	Filler
Pulp ^{a)}	0.5% Acid	1	1:3	1:57	0.03	1.7
Fiber and Fines	0.5% Acid	2.5	1:4.3	1:19	0.10	1.9
	1% N-Soap	2	1:4.8	1:17	0.19	3.2
Fiber + Filler Clay	0.5% Acid	1	1:2	1:22	0.06	1.3
	1% Acid	2	1:1.8	1:16	0.22	3.5
	1% N-Soap	2	1:2	1:4	0.49	1.9
Fiber + Coating Clay	0.5% Acid	1	1:2.2	1:67	0.03	2.0
	1% N-Soap	2	1:5	1:17	0.18	3.1
Fiber + Talc	0.5% Acid	1	1:2.4	1:38	0.05	1.9
	1% N-Soap	2	1:6	1:21	0.16	3.3
Fiber + TiO_2 } (Corrected) ² } ^{b)}	0.5% Acid	1	1:2	1:200	0.01	2.0
	1% N-Soap	2	1:5.6	1:34	0.09	3.1
Fiber + CaCO_3 } (pH ~ 6)	0.5% Acid (50% size ret.)	1	n.d.	1:35	0.02	0.7
	1% N-Soap (5% size ret.)	2	1:15	1:30	0.01	0.3

CONDITIONS: ^{a)} Furnish: 410 mL CSF bleached hardwood pulp; pulp fines are separated. In all other cases, furnish is a combination of coarse fiber fraction and filler. Sizing conditions, see Table 8; except, labeled ^{14}C -sizes and only 0.3% cationic starch used.

^{b)} Calculated for ash free fiber; for the TiO_2 -containing fiber, the size adsorption ratios are around 1:16.

Table 11 Distribution of Rosin Sizes in Filled Furnishes

Sizing values obtainable with soap size are usually lower than with dispersed acid size. Thus, higher amounts, 1% soap size and 2% alum were used in most experiments. In that case, the alum distribution in the furnish shifted

even further toward the fillers. Fines and fillers adsorbed 5 to 6 times more alum per unit weight than did the fibers. On the other hand, only sixteen to twenty times more size by weight was found on filler than on coarse fibers. In almost every case, fillers accumulated a greater portion of the added dispersed acid size than of the soap size.

	N-Soap Size			Dispersed Acid Size		
	Headbox	Tray Water	Couch Trim	Headbox	Tray Water	Couch Trim
pH	4.3			4.1		
Dissolved Al ³⁺ , mg/L	6.7	6.1		19	18	
ζ potential, mV		-1			0	
Dissolved rosin, mg/L	4	4		3	5	
Adsorbed alum, %	1.4	5.2	1.3	1.3	3.3	1.3
Adsorbed GC-rosin, %	0.6	0.84	0.4	0.5	1.6	0.25
Fines in solids, %		87	15		52	15

Table 12 Distribution of Rosin Sizes and Alum on a Board Machine

Mill experience corroborates the laboratory observations, although the actual processing conditions and recycling may cause significant shifts in the adsorption ratios. It also is possible that some redistribution and equalization of the uncured size may occur in the drying section. It is useful to compare headbox, tray water and couch trim or raw stock solids and adjust the distributions according to the actual fines and fiber contents. Table 12 shows original data from two mill experiments with a soap size (0.6%) and dispersed rosin size (0.4%) carried out subsequently on the same machine using unfilled bleached furnish. The adjusted ratio of adsorbed alum on fines vs. fibers was 5.6-5.8 to 1. The concentration ratio of adsorbed acid size on fines vs. fibers was about 12:1, about four times higher than the corresponding ratio for the soap size, confirming laboratory observations.

The distribution of a synthetic reactive size on various fillers was established in a similar way. In laboratory experiments, 0.45% of a commercial highly cationic synthetic size preparation was used at pH 8 (the preparation contained 40% AKD). The isolated fiber fractions retained some portion of the filler; thus, the concentration ratios are expressed both for the fiber fraction as is (unadjusted), and also for fiber adjusted as ash-free (see Table 13 for details). The residual pulp fines content is estimated. The distributions are not unlike the distribution of rosin sizes. Data in Table 14 show the (unadjusted) distribution of the same size preparation (applied at a rate of 0.28%) in a filled fine paper furnish, once again corroborating - in a qualitative manner - the laboratory observations.

Distribution of a Reactive Synthetic AKD Size Preparation in the Furnish
(65 sec. hardwood fiber, 15% filler, 0.45% size preparation, pH 8, Britt jar)

Furnish:	Pulp (w/fines)	Fiber Filler Clay	Fiber Filler CaCO ₃ (H-30, Ground)	Fiber Coating Clay	Fiber Coating CaCO ₃ (H-65, Ground)
Found % of Added Size on:					
Fiber (ash and fines-free)	18	25	33	<1	<1
Filler/fines	77	69	52	87	84
Solution	11	1	1	2	<1
Unaccounted	(6)	5	14	11	14
Size Concentration Ratios:					
Adjusted Fiber:Filler ratio	1:21	1:16	1:11	1:~100	1:~70
Unadjusted Fiber:Filler ratio	1:12	1:9	1:9	1:60	1:40
% of Added Filler on Fiber	(~20)	32	13	10	13
Filler Recovery, % total	(100)	89	79	87	89

Table 13 Distribution of a Reactive Synthetic AKD Size Preparation in the Furnish

	<u>Headbox</u>	<u>Tray Water</u>	<u>Couch Trim</u>
pH	7.2	7.1	
Dissolved Al ³⁺ , mg/L	0.1	0.1	
ζ-Potential, mV	0	+2	
Dissolved Size, mg/L	12	10	
Adsorbed Alum, %	0.4	1.1	0.3
Filler, %	18	46	12.6
Adsorbed Size, %	0.20	0.90	0.24
Unadjusted Ratio of Size Concentrations	1	4	1

Table 14 Distribution of a Commercial AKS Size Preparation in a Mill Furnish

Furnish Content % Component	Relative Specific Surface Areas of Components	Relative Adsorption Intensities ^{a)}		
		Alum	N-Soap Size	Disp. Acid Size
60% Fiber	1	1	1	1
20% Fines	5	3	16	20
20% Filler Clay	9	2	4	16

^{a)} based on weight concentrations

Table 15 Rosin and Alum Adsorptivities in a Model Furnish

The analytical findings suggest an accumulation of sizes on the surface of fillers and fines. In those cases when this accumulation is large, size may be deposited in inefficient thick multilayer patches, while on coarse fibers, sizes tend to extend to a more efficient thinner film. While there are significant differences among sizes and among fillers, the basic mechanism of the "filler-effect" appears to be general.

One can estimate the probable distribution for any furnish (18). Table 15 shows the derived relative adsorption intensities in a hypothetical fine paper furnish model (cf. Table 11). It can be calculated from the weighted adsorption data (% furnish component x relative adsorption intensity) that the pulp fines carry in such a furnish about 27% of the retained alum, but over half of the rosin size (Table 16). Filler clay carries relatively more of the dispersed rosin acid size than of the soap size, leaving on the fibers less acid size than found with soap sizing. Consequently, on paper machines with low filler retention, soap size does relatively better than dispersed acid size. The correct solution is to improve filler retention with proper retention aids. We have to emphasize that these distribution models were established on the basis of room temperature laboratory experimentation. The response of various sizes at high operational temperatures changes, and this aspect also has to be taken into consideration.

Distribution of Size and Alum
(Retention 80%)

Furnish Component	% of Retained		
	Alum	N-Soap Size	Disp. Acid Size
60% Fiber	55	13	8
20% Fines	27	70	51
20% Filler Clay	18	17	41

Table 16 Distribution of Size and Alum

Retention Aid 0.05%	Cationic Starch, %	Dispersed Acid Size	Pale Paste Size	HST sec.	Cobb ² g/m ²	Filler Retention, %
---	---	✓		281	23	46
---	---		✓	124	25	45
---	0.3	✓		354	21	60
---	0.3		✓	164	26	58
---	0.8	✓		423	20	80
---	0.8		✓	144	25	80
P-2	---	✓		221	22	82
P-2	0.3	✓		275	22	86
P-2	0.8	✓		413	23	87
P-2	---		✓	70	27	81
P-2	0.3		✓	80	29	76
P-3	---		✓	92	25	86
P-3	0.3		✓	139	24	87
P-3	0.3	✓		400	19	86
P-3	0.8	✓		568	18	87
P-7	---		✓	92	25	86
P-7	0.3	✓		322	22	83
P-7	0.8	✓		526	18	87
P-7	0.3		✓	139	24	87

CONDITIONS: Hardwood Pulp, 20% PFM filler clay, reverse sizing at pH 4.6 (soap size) or pH 4.8 (acid size). In all cases: 2% alum and 1% size used.

Table 17 Filled Hardwood Pulp Handsneets - Retention Aids

RETENTION OF FILLERS AND FINES IN THE SHEET

In all practical furnishes, retention aids have to be used to optimize retention of both filler and size. Cationic starch appeared to be a very efficient fixing agent for size retention. Table 17 shows that the usually applied cationic polyacrylamide (PAA) polymers give good filler retention, but poor sizing in the absence of cationic starch. In a handsheet study (18) comparing the efficiency of three high molecular weight PAA polymers (with increasing charge densities) and cationic starch, the best results were obtained by the contribution of the medium charge density PAA used together with 0.8% cationic starch.

Experimental observations (25) may explain the superiority of cationic starch in size retention compared to polyacrylamide. The data indicate that size accumulation on fines and clay filler increases with PAA, 1.5 to 3 times that obtained with starch. The thicker the size layer on fines, the lower becomes their relative sizing efficiency.

CONCLUDING REMARKS

The sizing mechanisms of soluble (rosin soap) sizes differ significantly from the mechanism of dispersed sizes where surface interactions play the dominant role. Sizing conditions have to be adjusted to the respective sizing mechanism to optimize results. With dispersed sizes, cationic fixing agents have to be used to assure proper attachment of size to the surfaces of furnish components. Cationic starch appears to be a very efficient additive for this purpose. Sizing conditions have to be chosen to assure size attachment strong enough to withstand the shearing forces in the machine system. Experimental techniques for comparative assessment have been described.

All fillers decrease the sizing response of paper. Higher surface area fillers depress sizing more, but surface area is only one of the factors involved. Size on fiber is more efficient than size on fillers and fines, compared at equal surface coverage.

Size accumulates on fines and fillers to a higher extent than expected from surface area alone. The filler interactions are different for the various sizes; the nature of interactions is not fully understood at present. With dispersed rosin acid size, the combination of cationic starch and medium charge density polyacrylamide gave good retention and sizing. Retention aids have less influence on sizing values achieved with rosin soap size. Polymeric retention aids without cationic starch gave high filler retention, but rather low sizing values with rosin sizes. Synthetic sizes have to be formulated with cationic agents present.

On the basis of experimentally determined adsorptivities, the distribution of sizes and sizing additives in a furnish can be predicted. The distribution of reactive AKD size is not unlike that of rosin sizes. Precautions have to be taken to maximize the size concentration on coarse fibers rather than allowing the fines to capture the added size.

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Transcription of Discussion

Sizing Mechanisms and the Effect of Fillers

by J. Marton

Davison I think that most people would agree that the surface charge on the fines is similar to that of the fibres themselves, as indicated by Herrington's paper earlier this week. Therefore, I have some trouble understanding why rosin size should prefer the pulp fines surfaces to the fibre surfaces. I wonder if it could be that the rosin size particles that are being adsorbed onto these relatively small fines are encountering less shear forces in an agitated slurry than the particles adsorbed onto the relatively large fibres. Could you comment on that?

Prof J. Marton I cannot really give you a definitive explanation. Accumulation of size on fillers and fines appears to be a rather general phenomenon and the process/mechanism is still under investigation. You first point questions whether fines have the same surface charge as fibres have. We had a long discussion about related questions earlier in the week. It is generally true that in a neat pulp system, the surface charges are closely the same, both for coarse fibres and pulp fines, but what I described is not a pure system. We have cationic and anionic agents which are adsorbed on the surfaces of different adsorbents; so, it is difficult to be dogmatic about whether the charges are the same or not in such a situation.

Your second point questions the mechanism why do the size particles adsorb preferentially onto the fines. As I said, this is still under study. The contribution of shear is a probable factor. Shear can promote co-flocculation of size with fines and fillers, but it also can enhance the detachment of size from the coarse fibres, in the manner you are suggesting.

Prof M. Miller Miami University, Oxford, U.S.A.

The Hercules Sizing Test is a wonderful test, but it does have some limitations in that if you have different basis weights, different colour or different thicknesses, you have to make some re-calculations. With your coarse fibres, I think you would obtain a different sheet thickness and I wonder if you re-calculated for that? Secondly, I would like to know if you have tested the sheet some other way, e.g. using the Cobb test.

Marton I agree with you as to the limitations in the HST test. Cobb tests were done, but not on all of the sheets involved in this study. Some Cobb results were given in the cited papers published earlier in TAPPI Journal. Generally, we made 50lb/r handsheets with rather small caliper variance and normalised the results where necessary. However, due to the more complex situation with coarse fibre sheets, we gave the directly observed data. These handsheets are bulkier and more porous than the pulp sheets. These properties, however, are antithetical in HST measurements. The coarse fibre handsheets were so well sized that it could not possibly have been due solely to the effect of caliper increase.