Stock Preparation Strategies In Quality Paper Manufacturing: Part 1-Normal and Reverse Sizing

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ABSTRACT

18 sets of stock preparation experiments have been conducted for comparing the sizing efficiency in normal and reverse mode. Alum variation from 0 to 3.5% has been made fixing rosin content to 1% with talc addition level to 25%. Rosin has also been varied from 0.6 to 1.2% fixing alum to 2%. Filler addition levels have also been changed from 20 to 45% fixing alum to 2% and rosin to 1%. The pH has been varied from 4.5 to 7.0, covering thus acid to neutral sizing range.

The optimum cobb value attained in reverse sizing is ~ 16 g/m² with ash content of 15.9%. Results of different hand sheets prepared are discussed for cobb, ash content, drainage time, brightness, opacity, smoothness, porosity, bulk, tear and burst factors, breaking length and double fold values. Based on the results obtained, reverse sizing is explained to be better than normal sizing requiring 2% of alum and 1% of rosin for 25% of filler addition level. Sizing in near neutral pH region ie. 6-6.4, accomplished with 2% alum, is also highlighted.

INTRODUCTION

Alum-rosin sizing is being used since more than 180 years but the mechanism is reported very recently still not to have been understood (1,2). The two important modes of sizing are:

1. Normal sizing (also called as direct sizing), and

2. Reverse sizing.

In normal sizing, rosin is added first followed by alum whereas in reverse sizing rosin addition follows alum (3-5).

The ultimate sizing depends not only on alum and rosin but also on the fibre characteristics, namely the fine percentage (6). Sometime the fibre is pretreated with alum separately and then redissolved for rosin addition (7). Rosin can be in emulsion form (dispersed rosin), soap or paste. Alum is $Al_2(SO_4)_3 \cdot 18H_2O$. Papermaker's alum is alum sulphate (8) though ferric and nonferric alums are available.

Apart from the sequence in which alum and rosin are added, amount of these two additives is also important (9,10). Similarly the addition stage of filler can play some role, specially for filler retention property (11,12). Water quality again has bearing on the effectiveness of alum addition (13,14). It was considered therefore worthwhile conducting experiments in the laboratory with systematic variations of all these factors to arrive at the right stock preparation strategy for quality paper manufacturing and attempt to throw light on the sizing mechanism (1,2).

It has been found that the level of alum used in India is somehow very high and the primary objective of this work is to show that it can be reduced to 2%. The properties are shown to have improved on using lower level of alum. The results have allowed to analyse the various mechanisms reported in the literature and conceive the sizing on a different perspective. The majority of works carried out on the

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subject are in abroad where the fillers used are other than talc and therefore these results may be quite useful for Indian paper manufacturers.

EXPERIMENTAL

The hand sheets were prepared in a British pulp evaluation apparatus by taking bamboo-mixed hard wood (80:20) bleached kraft pulp of 40°SR freeness. The rosin in the form of emulsion and alum having 15.45% of Al_2O_3 were used for the stock preparation. Water passed through a mixed bed resin columns with a polishing unit has been used for preparation of stock and the hand sheets.

About 20g of pulp in the form of slurry in 2 lt. water is mixed with the sizing and filler additives in the laboratory disintegrator. A period of 5 minutes stirring is given to the pulp slurry after addition of each chemical. After filler addition, only 2 minutes of stirring is made after which the slurry is diluted with 5 lt. of water. The pH of stock is measured by a digital pH meter. About 450 ml of slurry is withdrawn for preparation of 60 gsm hand sheets.

Elrepho brightness tester (Carl Zeiss, West Germany) has been used for determination of brightness and opacity. Bendtsen porosity meter has been used for measurement of smoothness and porosity.

Tappi standard methods (15) of testing have been followed to determine the properties of hand sheets.

RESULTS AND DISCUSSION

18 sets of experiments have been conducted with alum variation of 0 to 3.5%, rosin from 0.6 to 1.2% and filler addition of 0 to 45%, the resulting pH being 4.5 to 7 **(Table-1).** Results of only representative sets have been presented. pH of 4.5 to 7 is meant for acid to neutral sizing though our objective is to improve performance essentially in acidic range as employed in most of the Indian paper mills.

The discussion of the results obtained will be made to compare performance between normal (Set N0. I-V) and reverse sizing (Set No. VI to XVII) specially with recourse to alum dosing. The set XVIII consists of rosin-filler-alum sequence. In set I to XVII, filler was added at the end.

Table-2 contains the cobb, ash and drainage time in normal sizing with rosin content of 1% and alum at 0, 2, 2.5, 3 and 3.5%, the corresponding pH being 6.99, 6, 5.16, 4.81 and 4.51. The pH value decreases with increase in alum percentage which is normal. It can be seen that the pH can be varied from practically neutral medium to acidic range of 4.5.

Table-1

Compositions and pH of different sets studied

Set No.	Alum(%)	Rosin(%)	Filler addition%	pH
I	0	1.0	25	6.99
II	2	1.0	25	6.0
III	2.5	1.0	25	5.16
IV	3.0	1.0	25	4.81
V	3.5	1.0	25	4.51
VI	2	1.0	25	6.36
VII	2.5	1.0	25	5.12
VIII	3.0	1.0	25	4.80
IX	3.5	1.0	25	4.51
X	2.0	0.6	25	5.42
XI	2.0	0.8	25	5.72
XII	2.0	1.2	25	6.15
XIII	2.0	1.0	20	6.00
XIV	2.0	1.0	30	6.12
XV	2.0	1.0	35	6.07
XVI	2.0	1.0	40	6.01
XVII	2.0	1.0	45	6.01
XVIII	3.5	1.0	25	4.56

These results are considered vital as the cobb value as well as filler retention and drainage time change with variation in pH values of the systems. Though the cobb value improves (18.4 to 16.7 g/m^2) marginally on increasing alum dosing from 2 to 3.5%, the filler retention decreases from 56.4% to 53.5%. At pH of 5 (alum content of 2.5%), the filler retention is 59.2% but the cobb value is highest of all the sets (21.3 g/m^2). The drainage time marginally improves at pH of 4.5 to 9.6 second in stead of 10.1 sec. in II i.e. pH of 6. The changes in cobb values with alum content are shown in **Fig.1** along with that of reverse sizing **(Table-3).** The filler retention values with

Table-2

Cobb, ash and drainage time in normal sizing on varying alum content with talc

Set No.	Cobb (g/m^2)	Ash (%)	Drainage time (Sec.)
I	No size	15.70	9.80
II	18.4	14.10	10.13
III	21.3	14.80	10.05
IV	17.8	13.45	10.30
V	16.7	13.37	9.58

respect to alum content during sizing are presented in Fig.2 for both normal and reverse sizing. In normal sizing, the abrupt rise of cobb value to 21.3 g/m^2 at pH 5.16 from 4.81 and then again reduction to 18.4 g/m^2 is indicative of the narrow range where normal sizing practice is possible. In reverse sizing, the change of cobb value with pH is systematic in form of a canopy. What is exceptional for reverse sizing than in normal sizing (Fig.1). The alum consumption in reverse sizing is also compared to normal sizing as the pH is on the higher side in case of reverse sizing. Thus better sizing property with reduced alum consumption is possible with reverse sizing.

In **Fig.2** the filler retention Vs alum content is plotted for reverse sizing and normal sizing. Here also the reverse sizing shows enhanced filler retention property compared to normal sizing. With 2.5% of alum content, ~61% of filler retention occurs while in normal sizing it is 59.2%. The ash contents in Table-2 for normal sizing are given while

Table-3

Cobb, ash and drainage time in reverse sizing on varying alum content with talc

Set No.	Cobb (g/m^2)	Ash (%)	Drainage time (Sec.)
VI	16.7	15.9	9.95
VII	18.2	15.24	9.63
VIII	17.5	14.17	10.10
IX	16.2	13.3	8.59

in Table-3, ash contents of reverse sizing are tabulated.

The variation, in drainage time for normal (Table-2) and reverse sizing (Table-3) are in similar range (9-10 sec.). It may be inferred therefore that difference between normal and reverse sizing is exhibited in the water resistance property of the fibres essentially.

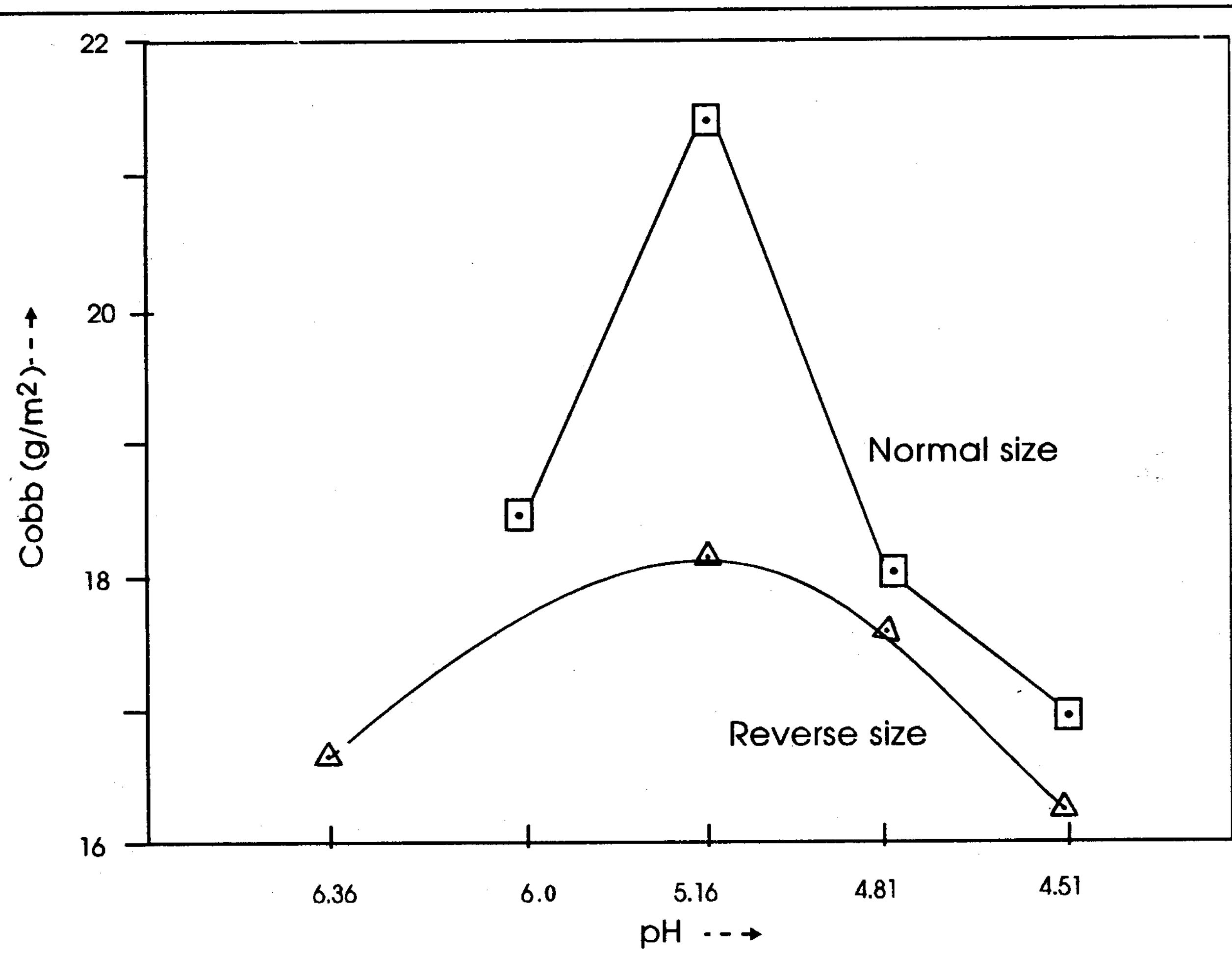

Fig.1. Cobb values at different stock pH in normal and reverse sizing.

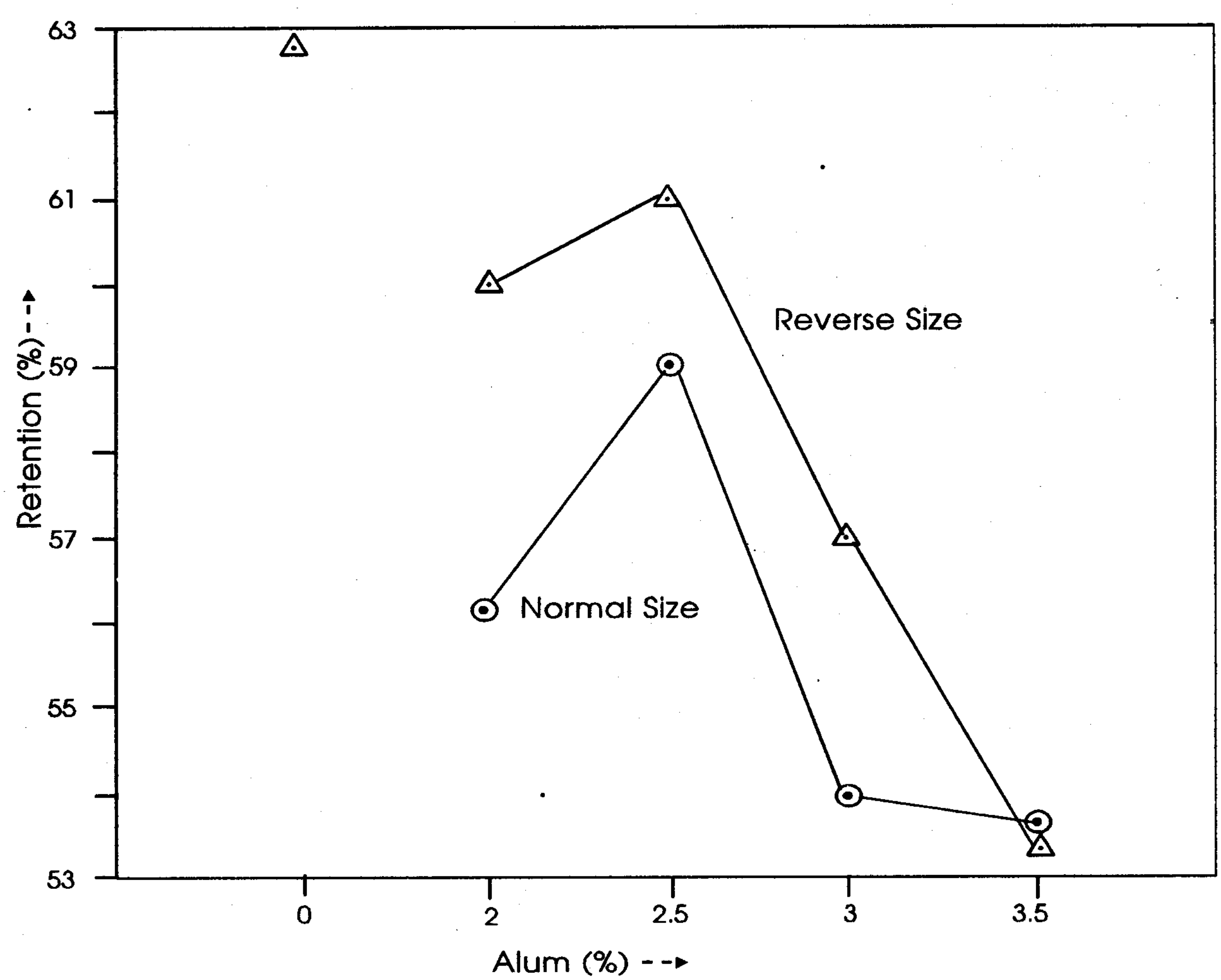

Fig.2. Filler retention on alum variation in normal and reverse sizing.

The optical and surface properties in normal sizing on varying alum content are presented in **Table-4.** It is of high manufacturing interest to see that at 2% of alum addition the brightness value is 74.2% El which is reduced to 70.3% with 3.5% of alum, i.e. 3.9% El drop.. The opacity value of hand sheet with 3.5% of alum is however higher than that of 2% alum addition. The smoothness value also marginally improves (from 80 ml/min to 70 ml/min) on increasing the alum dosing from 2 to 3.5%. Correspondingly the porosity increases to 160 ml/min at 3.5% alum dosing to 120 ml/min at 2% of alum dosing. Depending upon the end product property requirement therefore alum dosing should be controlled. However, brightness drop being ~4% El on increasing alum dosing from 2 to 3.5%, it may be recommended to have stock preparation strategy for lower alum dosing. This will automatically be appreciated economically with cost reduction output.

Comparison of these results with those of reverse sizing in **Table-5** will show that variations in properties are practically negligible on increasing the alum content from 2 to 3.5%; the brightness is 73.6-73.3% El, opacity 89.7-88.8%, smoothness 65-75 ml/min and porosity 130-160 ml/min. While at 3.5% alum addition, the brightness in reverse sizing is

Table-4

Optical and surface properties in normal sizing on varying alum content with talc

Set No.	Brightness (% El)	Opacity (%)	Smoothness (ml/min)	porosity (ml/min)
I	73.5	89.0	75	140
II	74.2	89.2	80	120
iii	71.8	89.4	65	120
iv	73.7	89.8	75	145
v	70.3	92.2	70	160

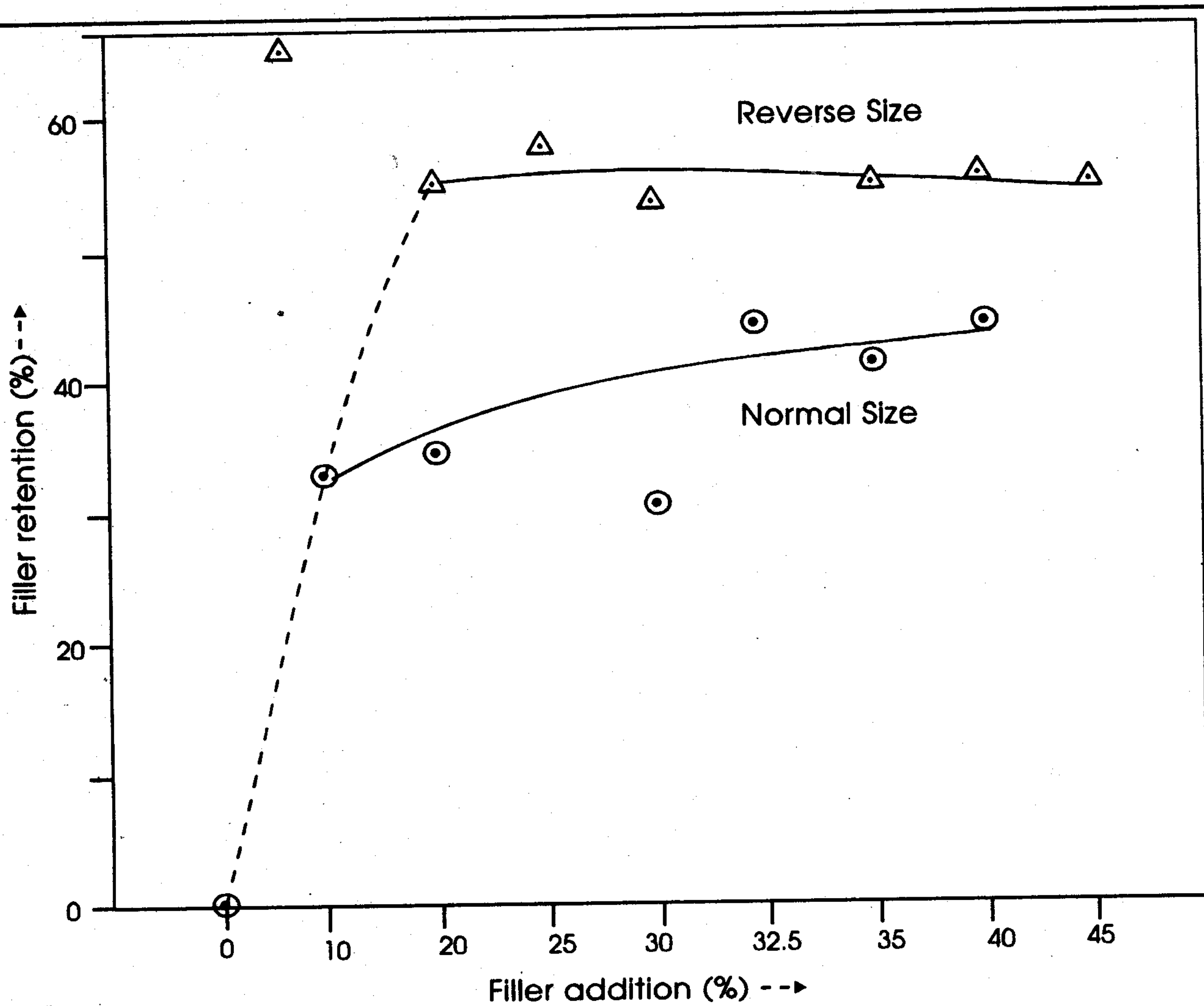

Fig.3. Filler retention vs filler addition in normal and reverse sizing.

73.3% El instead of 70.3% El in normal sizing, it is marginally (by 0.6% El) lesser in reverse sizing than in normal sizing at 2% of alum dosing but opacity and smoothness are marginally higher in reverse sizing than in normal sizing. The fact that the variation in brightness property at varying pH is minimum in reverse sizing, it allows more flexibility in manufacturing process and thus preference for reverse sizing can be desirable from these properties also. In reverse sizing also alum content can be managed at 2%.

Table-5

Optical and surface properties in reverse sizing on varying alum content with talc

Set No.	Brightness (% El)	Opacity (%)	Smoothness (ml/min)	porosity (ml/min)
VI	73.6	89.7	65	130
VII	73.6	89.7	70	145
VIII	73.7	89.7	75	160
IX	73.3	88.8	65	150

The strength properties of normal and reverse

Table-6

Strength properties in normal sizing on varying alum content with talc

Set No.	Bulk (cc/g)	Tear factor	Burst factor	Breaking length (m)	Double fold (no.)
I	1.50	45.9	29.5	4860	9
II	1.49	45.6	30.1	4760	10
III	1.51	46.8	28.6	4655	7
IV	1.54	45.8	27.1	4685	7
V	1.67	46.8	29.8	4820	6

Table-7					
Strength properties in reverse sizing on varying alum content with talc					
Set No.	**Bulk (cc/g)**	**Tear factor**	**Burst factor**	**Breaking length (m)**	**Double fold (no.)**
VI	1.54	46.6	29.3	4610	5
VII	1.52	46.6	28.4	4415	7
VIII	1.54	45.3	26.7	4275	6
IX	1.55	48.3	26.6	4255	7

sized hand sheets are shown in **Table-6** and 7 respectively at alum variation of 2 to 3.5%. Tear, burst factors and double fold in both the hand sheets are practically same but the breaking length values in Table-6 are marginally higher than in Table-7 i.e. with reverse sizing.

As reduction in rosin consumption is of high commercial interest in paper manufacturing, experiments have been conducted at rosin dosing of 0.6 (Set X), 0.8 (Set XI) and 1.2 (Set XII) with fixed alum content for which the cobb, ash and drainage properties are given in **Table-8,** optical and surface properties in **Table-9** and strength properties in **Table-10.** In Table-8, it is surprising to find that in hand sheet prepared with 1.2% of rosin, the cobb value is very poor. At 0.6% of rosin also there is no sizing and only at 0.8% rosin, cobb value of 22 g/m^2 is obtained. In hand sheet with 0.6% rosin, the ash content has gone upto 18.2% which is much higher than in others. Further work is in progress

Table-8			
Cobb, ash and drainage time in reverse sizing on varying alum content with talc			
Set No.	**Cobb (g/m^2)**	**Ash (%)**	**Drainage time (Sec.)**
X	No size	18.18	11.0
XI	22.0	14.08	11.0
XII	No size	13.82	12.0

Table-9				
Optical and surface properties in reverse sizing on varying alum content with talc				
Set No.	**Brightness (% El)**	**Opacity (%)**	**Smoothness (ml/min)**	**porosity (ml/min)**
X	70.0	91.0	80	145
XI	71.7	89.3	80	150
XII	71.3	91.6	65	115

Table-10					
Strength properties in reverse sizing on varying rosin content with talc					
Set No.	**Bulk (cc/g)**	**Tear factor**	**Burst factor**	**Breaking length (m)**	**Double fold (no.)**
X	1.52	45.8	29.0	4305	6
XI	1.50	45.5	28.5	4610	7
XII	1.49	46.5	27.1	4730	8

to define the rosin consumption pattern for optimum water resistance property. The optical, surface (Table-9) and strength properties (Table-10) of hand sheets on varying rosin contents are also not appreciable and therefore rosin dosing of 0.8 or rather 1% is recommended at alum dosing of 2% in reverse sizing. These experiments have not been tried in normal sizing.

In the sets XIII to XVII **(Table 11-13)** the alum dosing has been fixed to 2%, rosin to 1% and variation in filler content has been made at addition level of 20, 30, 35, 40 and 45% in reverse sizing. Here also results of experiments on normal sizing have not been reported. The cobb values increase with increase in filler content and at 45% of filler addition, no sizing was observed. The gradual deterioration in water resistance property with increase in ash content can be infered from **Fig.-4.** The cobb value upto 31.5 g/m^2, obtained for 35% of filler addition can be the

Table-11				
Cobb, ash and drainage time in reverse sizing on varying talc addition level				
Set No.	**Cobb (g/m^2)**	**Ash (%)**	**Retention (%)**	**Drainage time (Sec.)**
XIII	17.6	11.28	56.4	9.00
XIV	21.8	16.13	53.7	9.00
XV	31.5	18.60	53.1	9.00
XVI	62.8	20.96	52.4	9.00
XVII	No size	22.28	49.5	9.00

Table-12				
Optical and surface properties in reverse sizing on varying talc addition level				
Set No.	**Brightness (% El)**	**Opacity (%)**	**Smoothness (ml/min)**	**porosity (ml/min)**
XIII	76.2	87.5	60	135
XIV	73.2	89.3	70	145
XV	73.5	88.9	75	170
XVI	73.0	89.4	75	185
XVII	75.1	90.5	80	180

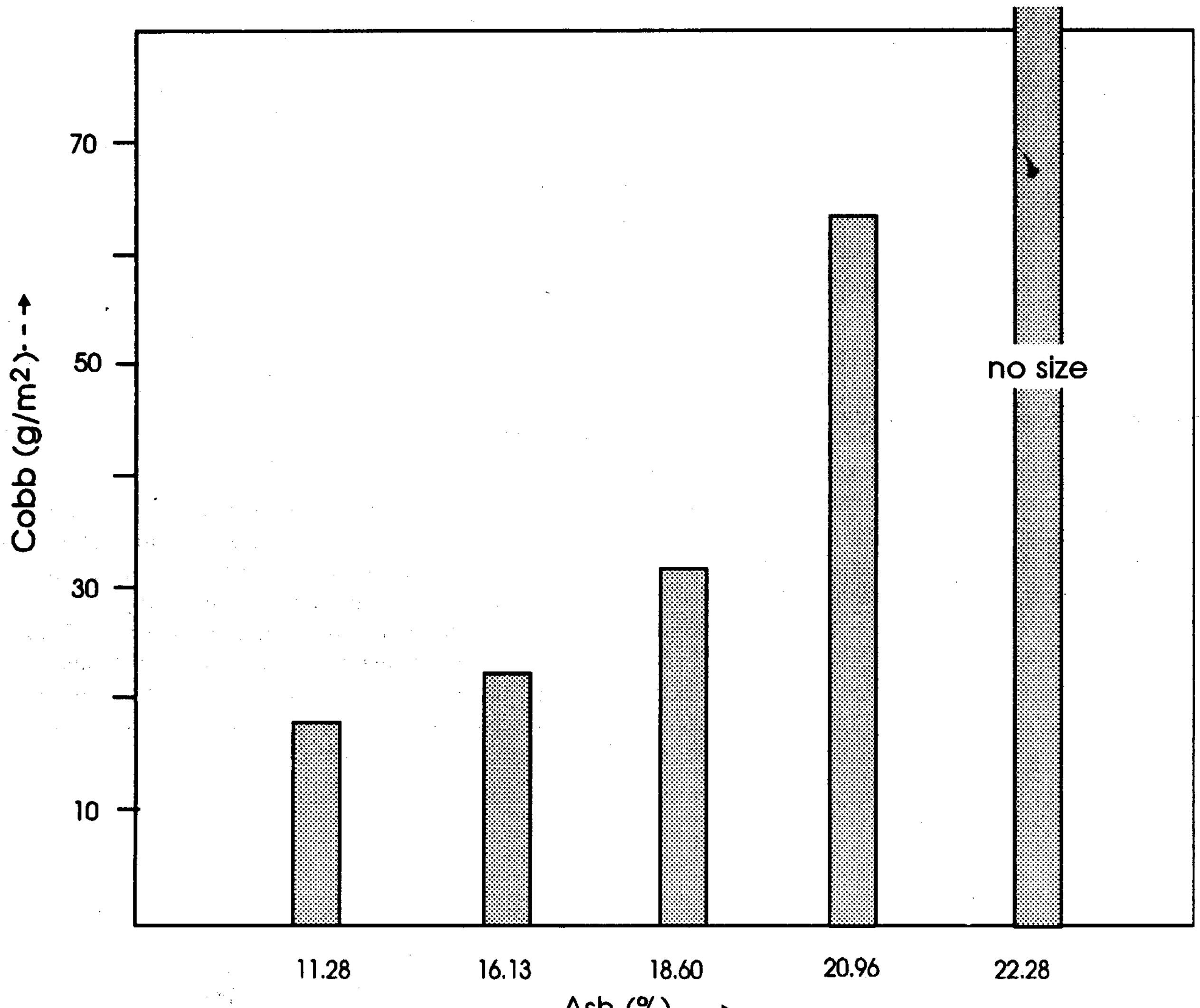

Fig.4. Ash content vs Cobb values.

recommended level. The ash content value of 16.1% at 30% and 18.6% at 35% of filler addition are also attractive; however the % retention with 20% addition level is higher (56.4%) than at other addition levels (53.7 at 30% and 53.1 at 35%). The drainage time remains constant at 9 sec. at all addition levels.

Table-13

Strength properties in reverse sizing on varying talc addition level

Set No.	Bulk (cc/g)	Tear factor	Burst factor	Breaking length (m)	Double fold (no.)
XIII	1.50	45.5	33.5	5115	10
XIV	1.52	45.8	27.5	4525	6
XV	1.52	42.6	26.5	4415	5
XVI	1.50	43.5	25.8	4090	5
XVII	1.51	41.1	25.2	4200	4

The optical and surface properties of these sets, presented in **Table-12** indicate that the high brightness value of 76.2% El in set XIII corresponding to 20% filler addition, is of only interest compared to all earlier brightness values. However, the opacity value is reduced to 87.5% here. The opacity, smoothness and porosity have not changed much.

The strength properties at 20% addition level are comparatively higher than in other sets. Deterioration in strength properties with increase in filler content is already an established fact (16).

It can be seen in the results discussed above that in set no. (Table-1), II, VI and XII-XVII, the pH in the stock is 6.0-6.4. In the neutral sizing, theoritically the pH should be at ~7 but pH 6.0-6.4 is also near to neutral sizing. By reducing the alum content and

Table-14

Analysis of process water used

Set No.	Properties		Water-A	Water-B
1.	pH		7.72	6.78
2.	Conductivity	(μmho)	120	200
3.	Ca	(ppm)	121	243
4.	Mg	(ppm)	25	275
5.	Fe	(ppm)	0.6	1.5
6.	Na	(ppm)	15	23
7.	K	(ppm)	6	6

with normal rosin dosing of 1%, sizing nearer to neutral stage, can be accomplished.

Apart from alum and rosin contents, the water quality also plays important role in governing the sizing efficiency. Two qualities of water have been employed (**Table-14**) in the stock preparation A and B (**Table-15**). B contains higher amount of salt than in A. The results of hand sheets prepared with A and B will show that the hand sheet with water having lower metal contents, has higher sizing efficiency; i.e. cobb value of 16.3 g/m² instead of 20.3 g/m² in B. Coincidently, brightness, opacity, smoothness, porosity, strength properties and ash content all are better in hand sheets prepared from water with lower hardness than that of higher hardness. In **Table-16**, the analysis of metals in back water of blank and talc are given. The pH is increased from 6.45 to 6.99

Table-15

Properties of hand sheets prepared using different water

Properties		Water-A	Water-B
Cobb	(g/m²)	16.3	20.3
Brightness	(% El)	77.4	75.9
Opacity	(%)	91.1	90.6
Smoothness	(ml/min)	130	150
Porosity	(ml/min)	390	450
Bulk	(cc/g)	1.51	1.57
Tear factor		45.7	46.8
Burst factor		23.7	22.3
Breaking length	(m)	3615	3465
Double fold	(no.)	5	4
Drainage time	(sec.)	8.11	7.51
Ash	(%)	12.05	11.68

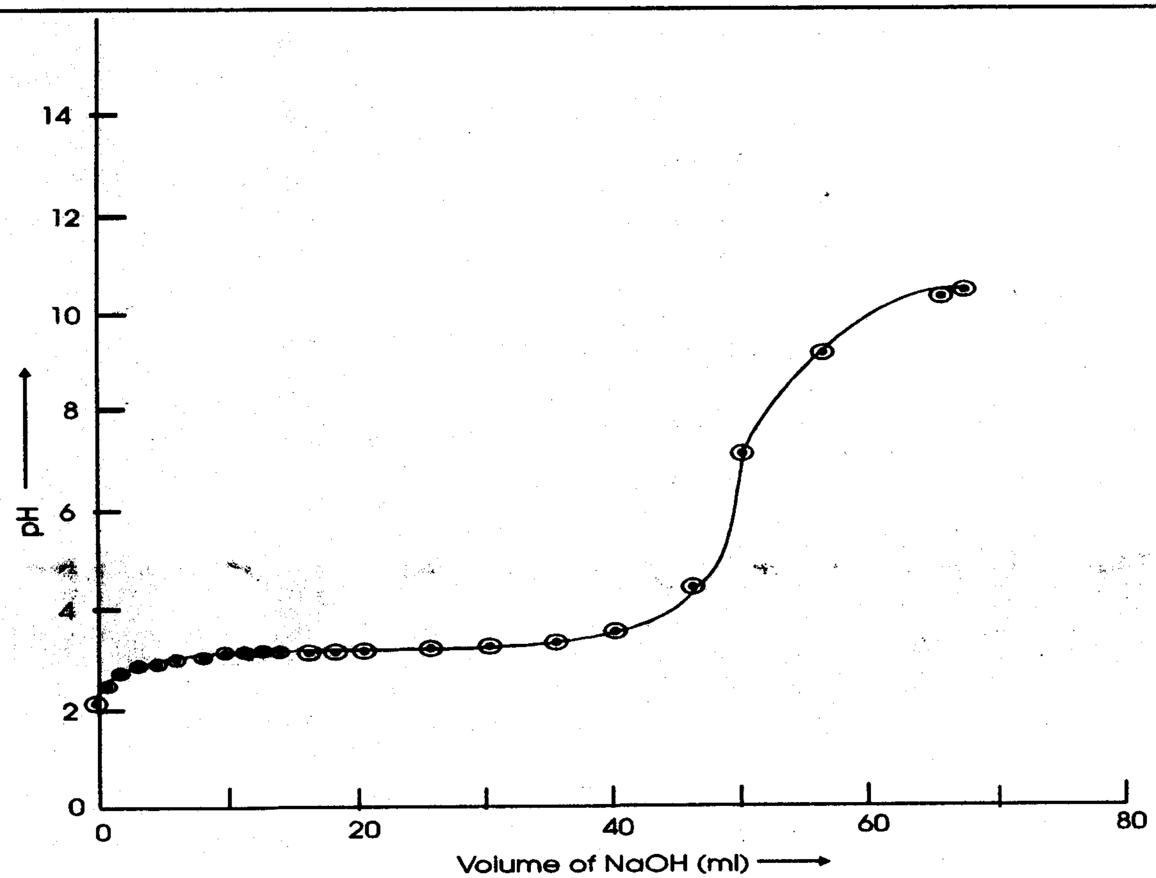

Fig.5. Neutralization curve of alum.

Table-16				
Analysis of back water				
S. No.	Properties		Blank	Talc
1.	pH		6.45	6.99
2.	Conductivity	(μmho)	150	160
3.	Ca	(ppm)	164	223
4.	Mg	(ppm)	75	87
5.	Fe	(ppm)	1.9	3.2
6.	Na	(ppm)	23	15
7.	K	(ppm)	8	5

when talc is incorporated. Talc is known to be neutral (6). Ca and Mg are found to be marginally higher in the back water with talc. As these are alkaline metals, the pH increase may be because of Ca and Mg, present in free form in talc. Fe is also found to be slightly more in the back water with talc but Na and K are present in reduced amounts.

Variation in alum content accompanies change in pH as shown in **Fig.5** where the pH has varied from 2 to 10 on gradual addition of NaOH to alum. The derivatives d(pH)/dv shown in **Fig.6** are quite prominent at 5 pH values namely 2.43, 2.84, 5.07, 7.49 and 8.57. These pH values are attributed (17) to the following 5 reactions.

$Al\ (H_2O)_6^{3+} + H_2O \Longleftrightarrow \{Al\ (OH)\ (H_2O)_5\}^{2+} + H^+$ ...(i)

$Al\ (H_2O)_6^{3+} + SO_4^{--} \Longleftrightarrow \{Al\ (SO)_4 (H_2O)_4\} + H^+ + H_2O$ ...(ii)

$\{Al\ (OH)\ (H_2O)_5\}^{2+} + H_2O \Longleftrightarrow \{Al\ (OH)_2\ (H_2O)_4\}^{1+} + H^+$ ...(iii)

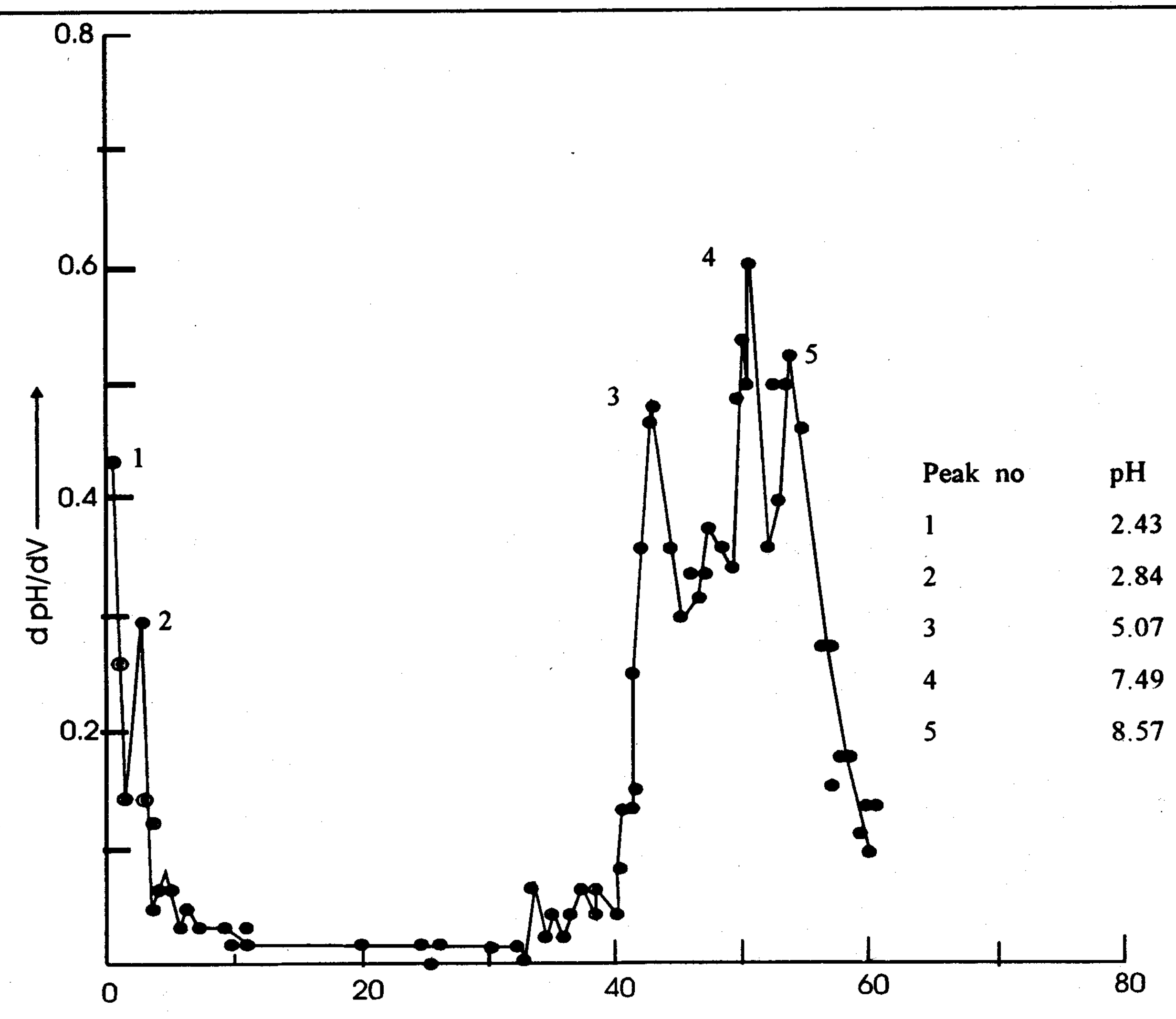

Fig.6. Hydrolysis of alum at different pH.

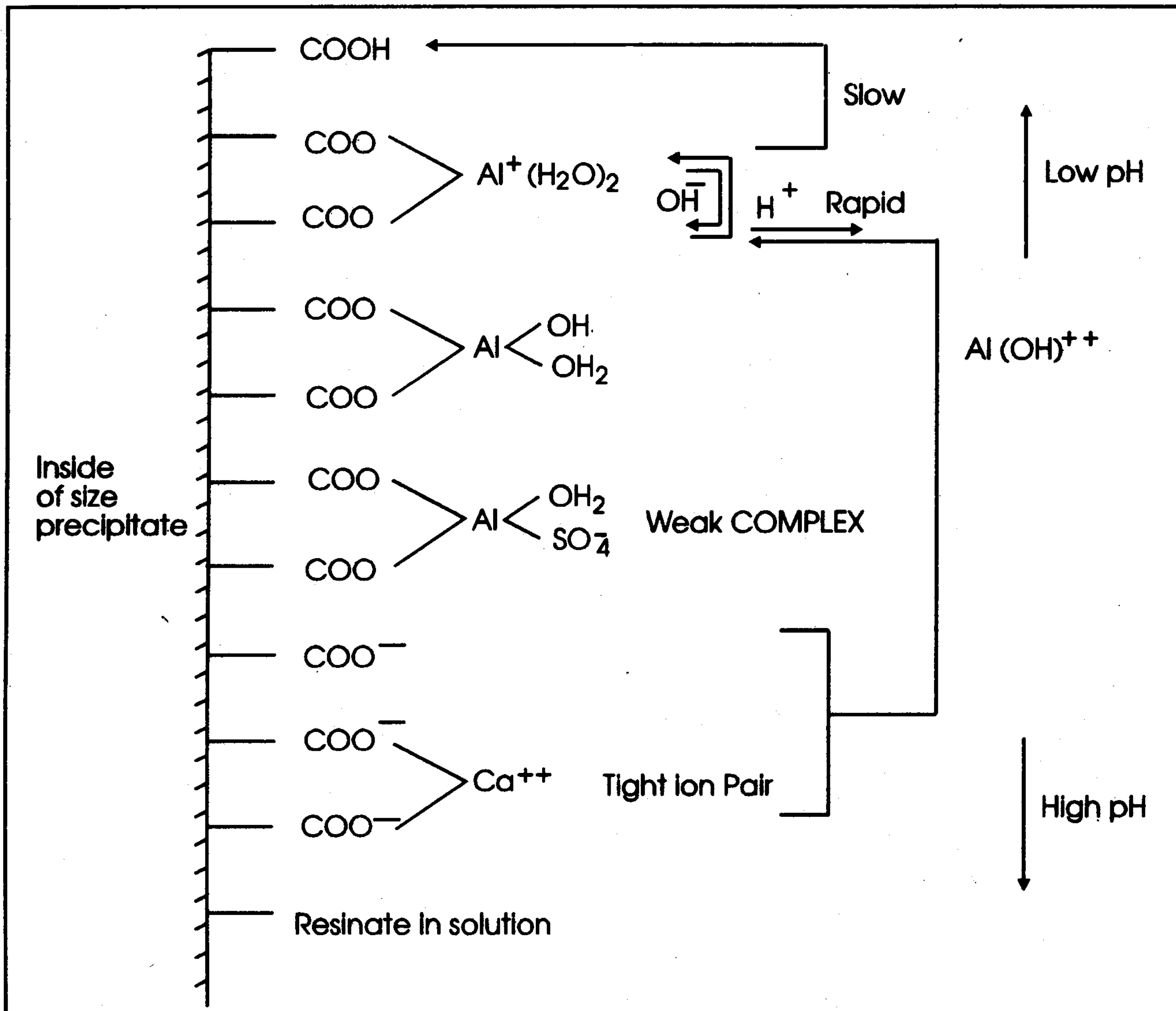

Fig.7. Mechanism of interaction of Cellulose and alum at different pH.

$\{Al\ (OH)_2\ (H_2O)_4\}^{1+} + H_2O \Longleftrightarrow \{Al\ (OH)_3\ (H_2O)_3\}^0 + H^+$ ...(iv)

$\{Al\ (OH)_3\ (H_2O)_3\}^0 + H_2O \Longleftrightarrow \{Al\ (OH)_4\ (H_2O)_2\}^{1-} + H^+$ ...(v)

In the present work, reaction (iii) should come into play where Al^{2+}, Al^{1+} or Al rather than Al^{3+} exist. The mechanism at different pH hase rightly been shown (18) in Fig.7.

Sizing can be accomplished only when both alum and rosin (1) are present, where formation of Al-rosin precipitate takes place.

Formation of Al-rosin hydrophobes and level of water resistance property imparted to the pulp or paper can be summed up to be governed by all the factors above namely:

(1) mode of sizing : Normal or Reverse

(2) Alum content

(3) Rosin content

(4) pH

(5) Water quality

(6) Filler : Nature and percentage

(7) Fibre used.

The stock preparation strategy has thus to be planned according to all the 7 factors.

Each industry should prepare its stock preparation strategy for obtaining optimum efficiency after thoroughly analysing the feed water and alum quality along with the derivative of rosin used and pulp quality. Validity of reverse sizing and reduction in alum use to 2%, for optimum sizing efficiency need not be applicable to all mills.

CONCLUSION

Acid sizing with alum and rosin in normal and reverse modes result in significant difference in sizing and filler retention efficiencies and to some extent in other properties also. The cobb value in normal sizing is higher than in reverse sizing. The filler retention value is higher in reverse sizing than that in normal sizing at same alum percentage. The optimum stock preparation efficiency has been found in reverse sizing with alum content of 2-2.5% and rosin content of 1% at 25% addition level of talc. In the acid sizing, pH of 4.5 is maintained but with 2% alum and 1% rosin, sizing can be made efficiently nearer to neutral pH i.e. at 6 to 6.4. Water having low level of metals imparts better sizing efficiency than water with higher metal contents.

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