Effective Sizing of Waste Paper Containing Calcium Carbonate with Rosin and Alum System

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ABSTRACT

Paper mills in India use different types of waste paper in the production of various paper grades ranging from cultural to packaging. The waste papers of foreign origin are generally neutral sized containing substantial amount of Calcium carbonate as filler. Recycling of such type of papers give problem in sizing with rosin soap and alum under acidic conditions. The present studies indicated that such paper could be suitably sized by using dispersed fortified rosin at pH 6.2. The pH can be controlled by using either alum or Poly aluminium Chloride (PAC) or by the mixture of both. PAC did not show advantage over alum up to pH 6.2 however it was more effective at higher pH levels. Premixing of dispersed rosin size with alum prior to addition to the stock gave better sizing than separate addition. Addition of cationic starch gave improvement in the sizing with dispersed rosin where as not much effect was observed for rosin soap size. The rosin-alum system may not match the performance of common neutral sizes under all conditions; however, it gives a viable alternative to raise the wet end pH close to neutral level. Plackett Burman statistical evaluation of different process variables on sizing indicated that more effective variables were Sizing dose > Stock temperature > filler amount > cationic starch.

INTRODUCTION

All over the world, the trend of using recycled fibers for papermaking is increasing. Recycled fiber has become an important element in pulp and paper business. The key driving force for the utilization of recycled fibers has traditionally been economics. In India, paper industry is rapidly shifting towards paper making from raw materials other than wood. The agricultural residues and wastepaper have emerged as two main alternatives to the forest based raw materials. Today about 63% of paper mills in India are using waste paper as raw material and it accounts for 31% of total paper production. The supplies of waste paper in India are from eastern countries, Middle East and USA. One of the major problems with the imported papers is that these are

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generally alkaline/neutral sized containing substantial amount of $CaCO_3$ as filler. Recycling of waste paper containing $CaCO_3$ therefore tends to give problems in acid process owing to the decomposition of $CaCO_3$. This decomposition results in accumulation of sparingly soluble gypsum (calcium sulphate) and calcium hardness in the white water, with the liberation of carbon dioxide.

The $CaCO_3$ filled papers when repulped and sized with Rosin soap/alum under acidic pH condition give problems like severe pH swings, excessive alum and size consumption, loss of filler, high deposit problem, foaming, etc in the system. To overcome these problems it is advisable to size such paper at neutral or close to neutral pH. The reactive sizes available are alkyl ketene dimmers (AKD) and alkenyl succinic anhydrides (ASA). However, it is well-known that sizing with synthetic sizes becomes more difficult and uneconomical when the proportion of "trash" and detrimental substances are sufficient in paper pulp [1]. It is generally considered that the concentration of trash material increases with pH. In an acid system, alum act as a remedy to bind or coagulate un wanted components while, in alkaline systems containing $CaCO_3$, pH depression to the "alum level" would not be acceptable. Keeping all these in view the development of close to neutral pH with rosin is being preferred now a days.

In the present investigations different ways of sizing the waste paper containing $CaCO_3$ have been studied with the objective of making properly sized paper. Different process variables like amount of dispersed rosin size, Alum PAC ratio, amount of cationic starch, filler amount, residual hypo, stock temperature and mode of mixing which affect the paper sizing have also been studied using Plackett Burman statistical model.

RESULTS AND DISCUSSION

Sizing with fortified rosin soap size and dispersed fortified rosin size were tried for waste paper containing $CaCO_3$ and without $CaCO_3$. The sizing response of these is shown in Fig. 1 There is a marked difference in sizing response between wastepaper containing no $CaCO_3$ and waste paper containing $CaCO_3$ with rosin soap size/alum at 4.5 pH. At this pH, with Rosin soap size, wastepaper containing no $CaCO_3$ develops a good sizing while waste paper containing $CaCO_3$ shows poor sizing. At the same pH, when sizing was carried out with Dispersed rosin size, sizing response for both types of pulps improved in comparison to Rosin soap sizing and the difference in sizing response between wastepaper containing no $CaCO_3$ and waste paper containing $CaCO_3$ also narrows down. However the decomposition of filler to the extent of 40% was observed at this pH. When pH was increased to 6.2, Dispersed rosin size shows effective sizing with both wastepapers. Also the loss of $CaCO_3$ was relatively lessened (6%) at this pH.

Dispersed rosin showed relatively more improvement in sizing than rosin soap with the increment in size dosage (Fig. 2). Fig. 3 illustrates the effect of stock pH on the degree of sizing on waste paper containing $CaCO_3$, with rosin soap / alum and dispersed rosin / alum systems. At the pH range 4 to 6.2 dispersed rosin acid/ alum system shows effective sizing. However rosin soap/alum system fails to give effective sizing above pH value of 5.0. The effective sizing at 4.2 to 5.0 pH, is probably due to the highest charge density of alum at this pH [2].

MECHANISM OF SIZING

These observations can be explained on the basis of sizing mechanism of Dispersed rosin and Rosin soap. Soap size reacts with alum as soon as it is added to the paper stock. Both electro static bonding and co-ordinate bonding participate in this reaction, which obviously results in a strong bond complex as illustrated in Fig. 4. Since alum is able to form ionic and co-ordinate bonds with rosin only at acidic pH, sizing with soap size has to be developed in the low pH region [2].

On the other hand, dispersed rosin size consists of rosin acid droplets, which have considerable surface areas. Therefore, its retention is a consequence of colloid and surface chemistry. Dispersed rosin does not react readily with alum to form an aluminium resinate. The alum acts as a bridge between the negatively charged fibre and, the negatively charged rosin micelle Fig. 5.

The most significant property of the dispersed size is its reduced reactivity to form rasinate as it enters the paper machine water system. Soap sizes cannot be used in $CaCO_3$ systems as they quickly exchange their sodium ions to form resinate and Ca++ion, which in turn interferes with size. The presence of Ca++ion would compete with alum and form calcium soap which is reported to reduce sizing [3].

Fig. 1 Sizing of waste paper with rosin soap and dispersed rosin at different pH

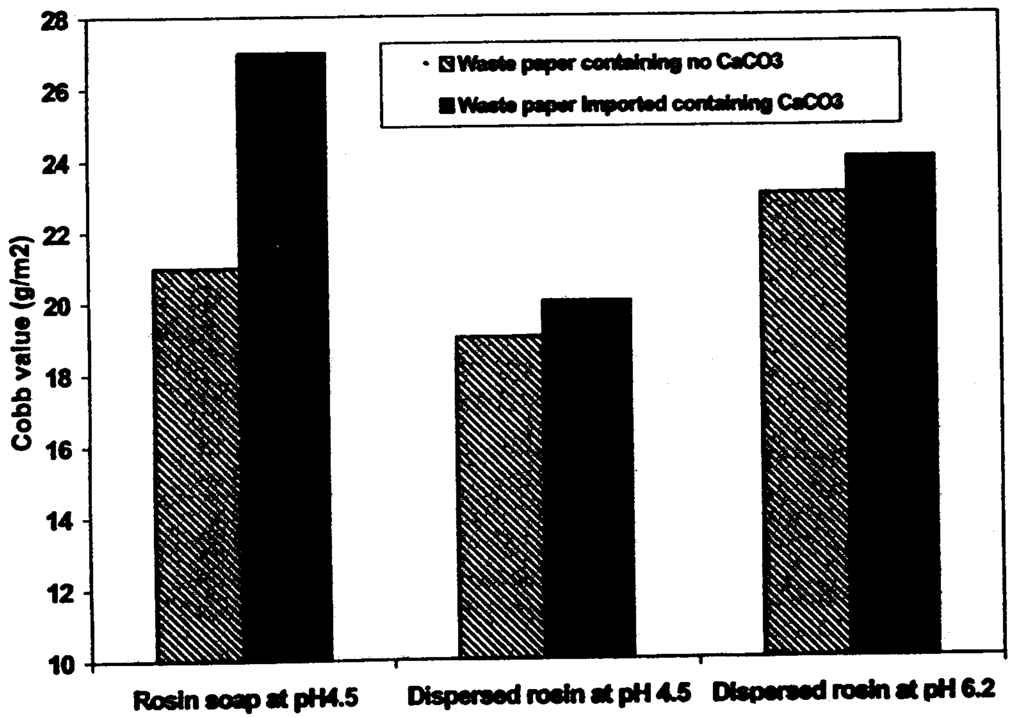
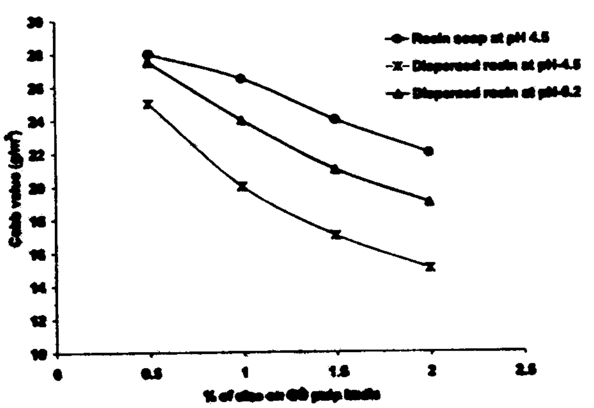


Fig.2 Effect of size dosage on sizing on cobb value at different pH level



Many researchers have described the strong reactivity of alum with cellulosic fibre at higher pH. Alum hydrolyses as pH increases to form colloidal aluminium aggregates [4] which can help to retain the size due to their strong surface activity. As pH increases, aluminium species, have higher adsorption on fibres [5-8], which is no doubt beneficial to sizing.

In a rosin - alum system rosin in either its free acid or soap form will react with alum to give the aluminium ester products which create hydrophobicity. In the case of soap rosin size under acidic conditions, most of the rosin reacts rapidly with alum in solution to give the aluminium ester. In case of dispersed rosin size the reaction of rosin acid and alum does not proceed in solution, but occurs on the fibre surfaces in the drier section. The dispersed rosin size particles are relatively free to migrate during the drying process, throughout the paper web. However, as the paper temperature increases on its movement over the drying cyclinders, the heat creates a sintering process where the rosin particles melt and distribute uniformly over the surface area of the fibres to form the aluminium resinate [9]

ADDITION OF PAC

Addition of PAC in place of alum did not show much difference in sizing improvement upto pH value of 6.2. At pH higher than 6.2 PAC showed better effect indicating that addition of PAC will be required at higher pH (Fig. 6). Different modes of

Fig.3 Effect of pH on sizing with rosin soap and dispersed rosin

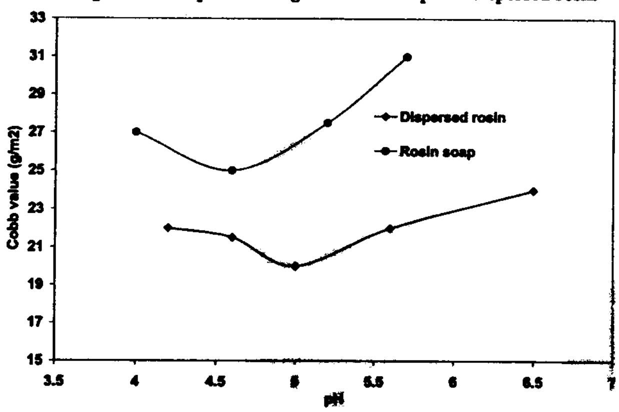
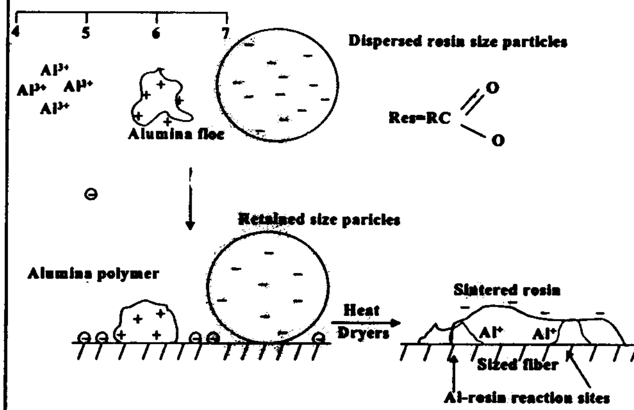
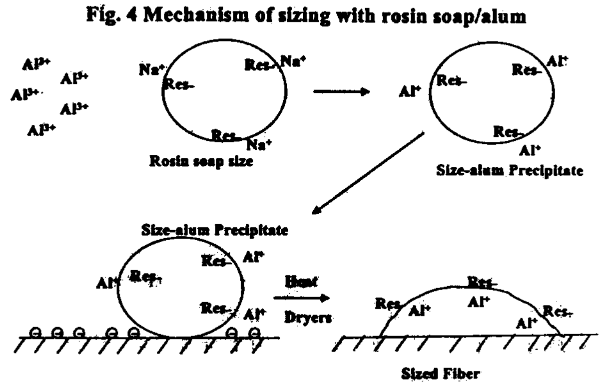


Fig. 5 Mechanism of sizing with dispersed rosin/alum



addition of alum and PAC play an important role on the sizing efficiency especially at neutral pH. Two modes of mixing were tried. One separate i.e. rosin size followed by alum/PAC, another pre-mixing in which alum/PAC was mixed with rosin size and then the mixture of these two was mixed to the thick stock. An improvement in the cobb value of hand sheets was observed when rosin size and alum/PAC were pre-mixed as shown in Fig. 6. Pre-Mixing allows interaction in an environment where the cationic charge of alum/PAC is higher than it would be in the elevated pH stock. Hence, a higher degree of reactivity is achieved with available rosin leading to increased retention and sizing. Premixing of Dispersed rosin and alum/PAC and addition to thick stock allows the formation of the discrete aluminium/size particles immediately in the presence of the fibre.

Fig. 4 Mechanism of sizing with rosin soap/alum

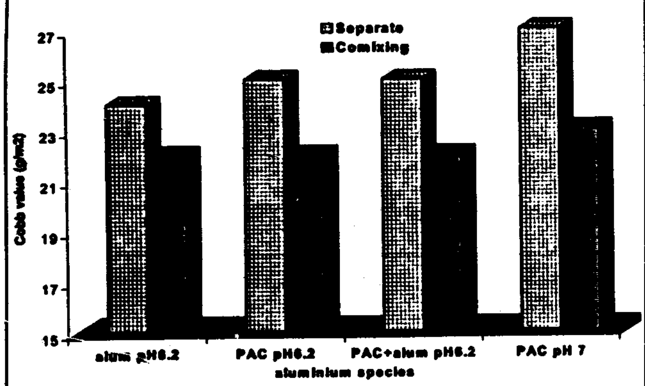


This minimizes any opportunity for polyanions or cations to interfere in the case of waste paper containing CaCO.

ADDITION OF CATIONIC STARCH IN SIZING

The addition of cationic starch in the stock further improves the sizing response in case of dispersed rosin. Since dispersed rosin sizes, are the dispersion of free rosin acids, which have considerable surface areas. Therefore, its retention is a consequence of colloid and surface chemistry and is facilitated by conventional retention aids like cationic starch, which can bridge between surfaces. Cationic starch being a high molecular weight polyelectrolyte, creates electrostatically assisted multiple bond that helps to anchor the dispersed size particle. This also assures good attachment under high shear. Fig. 7 shows the effect of cationic starch on sizing efficiency of two types of rosin sizes. With the addition of 0.5% of cationic starch, the cobb value decreases in case of dispersed rosin size. The decrease in the cobb value is more at 6.2 pH that at 4.5 pH for dispersed rosin size. By adding cationic starch and premixing of alum & dispersed rosin sizing can be improved further. Rosin soap sizes on other hand did not show such improvment in sizing on the addition of cationic starch. This suggests that cationic starch is more suitable for sizing with dispersed rosin sizes for neutral application. An added feature of cationic starch is that it also functions as the retention aid for fines and filler, improving first pass retention.

Fig.6 Effect of mode of addition on cobb value



EFFECT OF DIFFERENT PROCESS VARIABLES ON SIZING

Since paper making stock is the complex mixture of fibers, fiber fines, fillers, sizing chemicals retention aids, slimicides etc. it was decided to check the effect of selected seven process variables on sizing of waste paper. The relative effect of seven process variables on imported waste paper pulp (with $CaCO_3$) has been studied using a Plackett-Burman statistical design.

PLACKETT-BURMAN DESIGN

In this type of experimental design [10], two levels of each variable were selected as given in Table-I.

The high (+) and low (-) levels are chosen far enough apart to expect as significant response in sizing properties, but not so remote from normal stock preparation conditions which are usually practiced in mill. The assumption made was that with in the restricted range of each variable, the response is essentially linear.

Table-II shows the combination of sizing conditions for waste paper pulp containing $CaCO_3$ used in the experimental setup.

The sizing degree of hand sheets, evaluated by Cobb and contact angle are given in Table-III

Fig.7 Effect of addition of cationic starch on cobb value

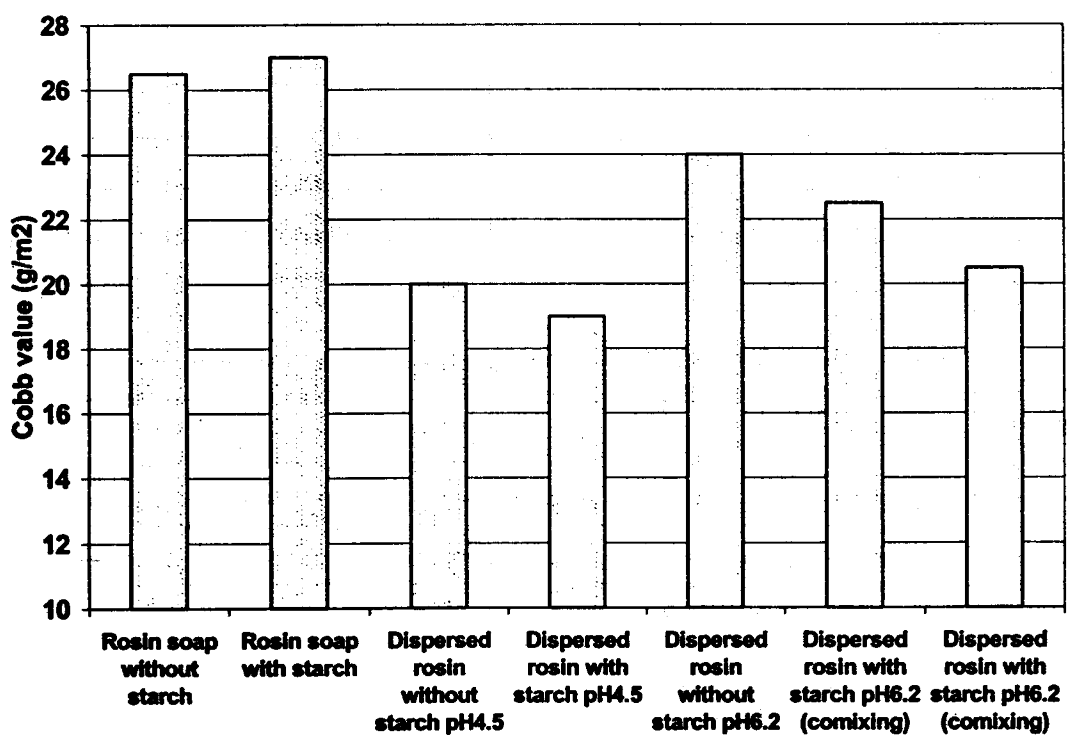


Table-I

S.No.	Process Variables	Process Variable Conditions	
		Low level (-)	High levle (+)
A	Dispersed rosin size (%)	1	2
B	Alum/PAC ratio	1:0	1:1
C	Cationic starch (%)	0.2	1
D	Filler amount (%)	10	30
E	Residual Hypo (%)	0	0.5
F	Stock Temperature (°C)	20	50
G	Mode of Mixing	Seperately mixed	Pre-mixed

Table-II Sizing conditions used in accordance to Plackett - Burman design

Experiment No.	A	B	C	D	E	F	G
1	+	+	+	-	+	-	-
2	-	+	+	+	-	+	-
3	-	-	+	+	+	-	+
4	+	-	_	+	+	+	-
5	-	+	-	-	+	+	+
6	+	-	+	-	-	+	+
7	+	+	-	+	-	-	+
8	_	-	-	-	-	-	-

Table-III Cobb & Contact angle values for different experiments

Experiment No.	1	2	3	4	5	6	7	8
Cobb Value (g/m²)	19	52	42	47.4	48.7	21.4	23.5	41.4
Contact Angle °	109°	53°	72°	68°	61°	101°	96°	76°

The relative ranking as process variable was evaluated and the results were recorded in Table-IV

The results indicated that the variables mainly affecting the cobb value and contact angle of handsheets are the amount of dispersed rosin size, stock temperature and the amount of filler added. The main effect of -18.2 means that when the amount

Table-IV Main effect of Process variables of sizing and their relative ranking

S.No.	Process Variables	Cobb Value	Contact angle
A.	Amount of dispersed rosin size	-18.2 (1)	+27.75 (1)
B.	Alum/PAC ratio	-2.25 (7)	+0.25(7)
C.	Amount of cationic starch	-6.65 (4)	+8.75 (4)
D	Amount of filler	+ 8.6 (3)	-14.75 (3)
E.	Residual Hypo	+ 4.7 (6)	- 3.75 (6)
F.	Stock Temperature	+ 10.9 (2)	-17.25 (2)
G.	Mode of mixing	- 6.05 (5)	+5.75 (5)
* Figures in parenthesis are the rank number.			

Table-V Most Influential Process Variables for Sizing of waste paper

Property	Process variables	Main effect as % of mean
	1. Amount of dispersed rosin size	- 49.32%
Cobb value (g/m^2)	2. Stock Temperature	+ 29.54%
	3. Amount of filler	+ 23.3%
	4. Cationic starch	- 18.02%
	1. Amount of dispersed rosin size	+ 34.96%
Contact angle (^{0})	2. Stock Temperature	- 21.73%
	3. Amount of filler	- 18.58%
	4. Cationic starch	+ 11.02%

of size increased from low level (1%) to high level (2%). there is a decrease in cobb value (as indicated by-ve sign) which implies that sizing improves with addition of dispersed rosin size. This is in accordance to our earlier findings in studying the effect of rosin size dosage on sizing performance. Similarly. the value of 10.9 for process variable. stock temperature indicates that when stock temperature increases from its low level (20°C) to higher level (50°C). the cobb value increases (as indicated by +ve singn). which implies that sizing falls drastically wth the rise in stock temperature. Same is the case with other variables. The relative rank of effectiveness of different process variables remains same when sizing of paper was checked by contact angle method, although the sign got reversed. The sign reversal is due to the fact that increase in contact angle values indicates sizing improvment

RELATIVE EFFECT OF MAJOR PROCESS VARIABLES

Table-V shows the major influential process variables and their effect on sizing property of waste paper. The effect here has been expressed as a percentage of the mean values of cobb values. This immediately demonstrates that when sizing was checked by cobb value, amount of dispersed rosin and stock temperature were particularly sensitive. Similarly amount of filler is more sensitive than amount of cationic starch.

EXPERIMENTAL

The waste paper pulp used for the above experiments was procured from a mill based on waste paper as raw material. The pulp contained 20% $CaCO_3$ filler. The pulp was sized with Rosin soap/Dispersed rosin. The dispersed rosin used was white emulsion, fortified anionic in nature having pH 6. Rosin soap used was fortified, anionic in nature having pH value of 8.5. Handsheets were made on Rapid Kothen sheet former according to the ISO standard method TO6/565N706. The hand sheets were conditioned at temperature 27± 1°C and 65 ±2% relative humidity prior to testing. Cobb value was tested as per standard Tappi Method 441om-90 and contact angle measured as per standard Scan method P18:66

CONCLUSIONS

- Dispersed fortified rosin and alum can be used as a sizing system for making paper from waste paper containing $CaCO_3$. This system has significant advantages over common acid sizing system using rosin soap and alum & is operable over a wide range of pH.
- Sizing of waste paper containing $CaCO_3$ can be done more effectively using dispersed fortified rosin rather than rosin soap.
- Dispersed rosin works effectively at pH range 4.5 to 6.2. At 4.5 pH the decomposition of $CaCO_3$ to the level of 40% was observed where at it was only 6% at pH levels of 6.2
- PAC in place of alum did not show much advantage up to pH level of 6.2, however going to higher pH 7.0 addition of PAC was found to be useful.
- Premixing of dispersed rosin with alum/PAC showed better sizing than normal practice of separate addition.
- Addition of cationic starch produced better effect in sizing dispersed rosin at 6.2 pH than acidic sizing.
- The process variables which affect sizing in descending order were found to be Sizing dose > Stock temperature > filler amount > cationic starch.

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REFERENCES

1. Leo Neimo, Papermaking Chemistry, Finish Paper Engineers Association and Tappi press, p. 177 (1999).
2. Juntai Liu, 'Paper Technology', (6), 20 (1993).
3. Anthony R. Colasurdo, Neutral/Alkaline papermaking short course 1990 p. 71.
4. Bottero, J.-Y. and Fiessinger, F: Nordic pulp and paper research Journal: (2) 81 (1989).
5. Arnson, T.R.: Notes of 1987 TAPPI Sizing short Course: p. 31
6. Edward Strazdin 'Mechanistic aspect of rosin sizing' TAPPI Journal, 60 (10), 102 (1977)
7. Edward Strazdin TAPPI Journal, 64 (1), 31 (1981).
8. J. Marton, F.L. Kurrjle, "Retention of rosin size' Canada Pulp and Paper Journal of Science, Vol. 13, No. 1 Jan 1987
9. Lovat MacGregor, David Howie.: Paper Technology (7), 27 (1998)
10. R.D. Cardwell and S.B. Cundall, Appita Vol. 29, No. 5, March 1976