Study Of Modified Rosin Sizing Using Sulfonated Cashewnut Shell Liquid (CNSL) As An Additive

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ABSTRACT

New materials are continually being suggested or patented for sizing of paper. Most of them never reach commercial production, but some have found a place in special applications. The paper maker wishes to manufacture the grades under neutral or alkaline conditions, thereby ruling out the effective use of alum, which is necessary in sizing with rosin. To find these needs a group of chemical compounds, best described as reactive sizes, have displaced a significant fraction of the rosin size used in the paper industry. Reactive sizes are often called synthetic sizes in contrast to rosin sizes considered to be natural products. This study is based on the fact that cellulose fibers in water behave as polyanions and bear a negative electrical charge. As a result, the fibers have the ability to bind cations. Studies of ion-exchange properties of pulp suggest that acidic groups such as sulphonic, phenolic and carboxylic are responsible for cation exchange. Secondly, most of the synthetic size molecules consist of a long, usually straight, hydrocarbon chain (hydrophobic portion) in contrast to the fused ring character of rosin acids. These important points in chemistry led us to use sulfonated CNSL along with rosin as modified rosin size and study the effects on sizing of paper. The sulfonated CNSL molecule contains both phenolic as well as sulphonic groups plus a hydrophobic hydrocarbon [-$C_{15}H_{29}$] side chain. The molecule has surface acting properties and most importantly, it is obtained from natural resources.

KEYWORDS *Rosin sizing, sulfonated CNSL, ion exchange, Dispersed Rosin (DR), fortified rosin.*

Introduction

Sizing refers to a process of obtaining or imparting resistance to penetration of liquid such as water, juice, milk etc. in paper or paper board. Since cellulose fibers are hydrophilic in nature and paper structure is porous, it absorbs large amount of water. Sizing helps to control rate and extent of liquid penetration[1]. The two principal sizing processes are internal sizing and external sizing. Internal sizing is a process where suitable sizing agents are added to papermaking stock and precipitated upon the fiber for the purpose of controlling the penetration of liquid on to the final dry paper or paper board. External sizing or surface sizing involves the application of film forming substance like starch, gum, polymers to already formed paper or paper board to control porosity and to improve printing and strength properties[2]. Three types of internal sizing employed in papermaking are

Acid sizing at pH of 4 to 4.5
Neutral sizing at pH of 6 to 6.5
Alkaline sizing at pH of 7 to 8.2

In acid sizing and neutral sizing, rosin is used as sizing material while in alkaline sizing; synthetic chemicals like alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are employed. It has been accepted that an effective sizing agent must fulfill the following criteria[3,4].

1. The size must be evenly distributed through the paper.
2. The size must be oriented onto the cellulose fibers in order to optimize its hydrophobicity.
3. The spacing between size molecules on the fiber must be such that water is effectively repelled.

Fortified rosin size

Fortified rosin is free rosin which has been fortified with a synthetic resin[5]. Fortified rosin sizes are made by reacting maleic anhydride or other dienophiles with rosin to increase the number of carboxylic groups. Fortified rosins are more efficient than regular size, and generally lower dose is required. In some cases, the reduced consumption[6] more than offsets the higher cost of fortified rosin.

Dispersion sizes

Contain almost 100% free rosin which is collidally stabilized and supplied to paper mills at about 40% solids. The dispersion sizes represent a significant advance in sizing technology which has offered the industry several benefits; more sizing per kg of rosin used, broader pH range for sizing, improved drainage, improved paper strength and no need for emulsification equipment. The basis of these benefits lies primarily in the different surface-chemical behavior of dispersion size.

Mechanism of acid sizing

In acid sizing, paper is sized with rosin and alum at pH around 4 to 4.5. A soap size is fully solubalized and highly anionic. Most of the rosin reacts with alum as soon as it is added to paper stock in aqueous suspension to form size precipitate (aluminium resinate). This positively charged precipitate gets attached to negatively charged fiber. Thus, size is retained on the fiber. In the last step of sizing when the sheet is

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passed on to the drier, the precipitate melts and flows on fiber surface. The rosin which consists of hydrophobic and hydrophilic group rearranges itself with the help of Al^{+3} ions in such a way that highly repellent rosin group orients outside the fiber and hydrophilic end orients towards the fiber. Alum also acts as a retention aid which increases the size efficiency. Alum dissociates into sulfate and Al^{+3} ions. This further reacts with water to form aluminum hydrate and H+ ions. These H^{+} ions reduce pH to acidic condition.

Mechanism of neutral sizing

In neutral condition, the concentration of H^{+} ions will be reduced resulting in more anionic fiber which will have greater attraction force towards the cationic size precipitate and increase the efficiency of size. An effective rosin size at neutral pH consists of dispersed rosin which is stable and chemically reactive at pH around 7, aluminium ion Al^{+3} source, with sufficient cationic charge for bonding with retention aids like polyacryl amides to help in retention of size, fillers and fines. The neutral pH gives more permanency, reduced corrosion and good strength properties.

Sulfonated CNSL is prepared by sulfonating commercial CNSL with concentrated sulfuric acid[7]. It is a buff colored emulsion soapy to touch and smell. It is sparingly soluble in water with good surface active properties. It is mainly used as a penetrating aid in Kraft pulping and deinking processes.

Experimental

The fortified rosin samples were collected from Biokraft Organics Pvt. Ltd., Bangalore and tested for sizing in the laboratory.

Preparation of acid size

i) **Rosin I** N grade rosin was mixed with sulfuric acid at 175 °C, few minutes retention was given to it. Maleic anhydride was then added at same temperature and retained for few minutes. To the resultant mixture ethyl glycol was added at 130 °C and retained for 30 minutes. Further caustic was added for desired saponification and pH was adjusted to 9.0. Finally it was diluted with water to bring the total solids to 50%.

ii) **Rosin II** To the prepared Rosin I added filler urea to get ratio of 50:50

iii) **Rosin III** To the prepared Rosin I added filler urea to get ratio of 45:55

iv) **Rosin IV** To the prepared Rosin I added filler urea to get ratio of 40:60

Preparation of neutral size dispersed rosin

i) **Mill dispersed rosin** Was collected from West Coast Paper Mills Ltd., which was supplied by Arjun Chemicals.

ii) **Dispersed rosin (DR) -I-** Rosin I (TS of 48% and pH of 9.0) was mixed with sulfonated CNSL (TS of 48% and pH of 4.0) in the ratio of 2:1. An emulsion of DR- I was obtained with TS of 48% and pH of 7.5

iii) **Dispersed rosin (DR) -II-** Rosin II (TS of 54% and pH of 9.5) was mixed with sulfonated CNSL (TS of 48% and pH of 4.0) in the ratio of 95% rosin II and 5% of sulfonated CNSL. An emulsion of DR- II was obtained with TS of 45% and pH of 7.2

All the sizes were tested according to TAPPI standards and the properties are listed in table 1

Table 1- Properties of acid and neutral sizes

Properties	Mill Rosin	Rosin I	Rosin II	Rosin III	Rosin IV	Mill DR	DR –I	DR-II
Total solids (%)	50	48	54	47	48	38	48	45
pH	9.5	9.0	9.5	9.2	10.5	4.0	7.5	7.2
Total rosin (%)	32.0	63.4	40.2	38.4	40.9	47.1	25.2	58.8
Free rosin (%)	4.0	22.2	6.0	5.0	11.5	49.1	67.8	18.1

Table 2- Comparison of rosin I and II with mill rosin

Particulars	Mill rosin			Rosin I				Rosin II			
Charge (%)	0.8	1.0	1.2	0.8	1.0	1.2	1.5	0.8	1.0	1.2	1.5
Cobb (g/m^2)	19.2	19.5	16.2	21.6	17.2	16.8	16.0	20.1	19.3	19.5	17.7
Sizing (sec)	19	21	22	13	16	18	20	13	16	17	20
GSM of sheet	61	61	61	59	60	61	61	61	59	60	61
Bursting strength (kg/cm^2)	2.1	2.3	2.2	2.05	2.06	2.02	2.0	2.25	2.3	2.1	2.15
Burst factor	34.4	37.7	36	34.7	34.3	33.1	32.7	36.8	38.8	35	35.2
Tearing resistance (g_f)	5	4	4	4	5	5	5	5	4	4	4
Tear factor	32.7	26.2	26.2	27.1	33.3	32.7	32.7	32.7	27.1	26.6	26.6
Double fold	7	6	5	7	6	6	6	6	5	7	6

Table 3- Comparison of rosin III and IV with mill rosin

Particulars	Mill rosin			Rosin III				Rosin IV			
Charge (%)	0.8	1.0	1.2	0.8	1.0	1.2	1.5	0.8	1.0	1.2	1.5
Cobb (g/m^2)	19.2	19.5	16.2	19.7	18.7	17.7	16.6	26.6	24.6	22.3	21
Sizing (sec)	19	21	22	10	11	16	14	10	11	12	13
GSM of sheet	61	61	61	60	59	60	61	60	59	60	61
Bursting strength (kg/cm^2)	2.1	2.3	2.2	2.4	2.4	2.3	2.4	2.1	2	2.1	2.1
Burst factor	34.4	37.7	36	40.4	40.6	38.3	39.3	35	34.9	35.5	35.5
Tearing resistance (g_f)	5	4	4	4	5	4	4	4	5	4	4
Tear factor	32.7	26.2	26.2	26.6	33.8	26.6	26.2	26.6	33.8	27.1	26.6
Double fold	7	6	5	7	6	6	6	4	5	4	4

Table 4- Comparison of DR I and DR II with mill dispersed rosin (at 35 ^{0}SR and pH 6.5)

Particulars	Mill dispersed rosin				DR –I					DR –II			
Charge (%)	0.8	1.0	1.2	1.5	1.2	1.5	2.3	2.5	3.0	1.2	1.8	2.5	3.5
Cobb (g/m^2)	21.7	18.9	18.1	17.6	22	21.7	22.4	22.4	21.9	21.6	19.2	17.1	16.7
Sizing (sec)	19	22	24	28	11	13	12	12	13	18	23	27	28
GSM of sheet	61	60	59	61	60	62	59	61	61	60	60	61	61
Bursting strength (kg/cm^2)	1.8	1.7	1.8	2	2.1	2	2.0	1.8	1.8	2.1	2.1	2.2	2.2
Burst factor	29.5	28.3	30.5	32.7	36	32.2	33.8	29.5	29.5	35.0	35.0	36.1	36.1
Tearing resistance (g_f)	3	4	4	5	4	4	5	4	4	5	5	6	5
Tear factor	19.7	26.6	27.1	32.7	26.6	25.8	33.8	26.2	26.2	33.3	33.3	39.3	32.7
Double fold	3	3	4	3	3	2	3	3	3	3	3	4	4

Table 5 -Comparison of DR I and DR II with mill dispersed rosin (at 40 ^{0}SR and pH 6.5)

Particulars	Mill dispersed rosin				DR -I				DR –II			
Charge (%)	0.8	1.0	1.2	1.5	1.8	2.0	2.5	3.0	0.8	1.3	1.8	2.5
Cobb (g/m^2)	20.9	17.7	18.1	17.6	19.62	17.48	17	15.0	23.3	21.7	18.8	16.6
Sizing (sec)	18	24	24	28	19	21	27	33	14	18	25	28
GSM of sheet	60	60	59	61	60	60	61	61	60	60	61	61
Bursting strength (kg/cm^2)	2.3	2.3	2.4	2.4	1.8	1.8	1.8	1.8	2.2	2.3	2.4	2.3
Burst factor	38.3	38.3	39.3	39.3	30.0	30.0	29.5	29.5	36.6	38.3	39.3	37.7
Tearing resistance (g_f)	5	5	6	5	4	3	4	4	5	5	5	6
Tear factor	33.3	33.3	39.3	32.7	26.6	20.0	19.7	26.2	33.3	33.3	32.7	39.3
Double fold	3	4	3	4	3	3	3	3	3	3	4	4

Sizing experiments

Mixed hard wood pulp was collected from a Paper Mill, and beaten in lab valley beater to 35 ^{0}SR according to TAPPI standard T 200. The stock was diluted to 0.25% consistency and different dosages of rosin size were added. Then pH was adjusted to 4.5 using 20 g/l alum solution. Talc 10% was added using 20 g/l talc slurry. Paper sheets of 60 gsm were made on British Hand sheet making machine according to TAPPI standard T 205. Sheets were air dried and tested for sizing, Cobb and different strength properties according to TAPPI standards. In neutral sizing, the same procedure was followed except that pH was adjusted to 6.5 using 20 g/l alum solution. Few sets were prepared using 40 ^{0}SR beaten pulp to test the effect of freeness on retention. All the results are tabulated in the tables above.

Results And Disscussions

- Cobb values are found in the range of 16-17 g/m^2 for rosin I, II, III at 1.5% charge and for mill dispersed rosin at 1.2% charge. Comparatively high values are observed for rosin IV at these charges. Cobb values are in the range of 16 to 22 g/m^{2}for mill dispersed rosin and DR II, at charge ranging between 0.8 to 1.5% and 1.2 to 3.5% respectively, where as DR I gave high Cobb values. When ^{0}SR is increased from 35 to 40, decrease in Cobb is observed for DR I indicating improvement in size.

- Highest size value of 22 sec is observed for mill rosin at 1.2% charge. Size value 20 sec is observed for rosin I and II at 1.5% charge. Size values decreased for both rosin III and IV. Mill dispersed rosin and DR II gave same size value i.e. 28 sec at 1.5% and 3.5% charge respectively, but for DR I it is found to be low. With increase in ^{0}SR from 35 to 40 a good increase in Cobb value is observed for DR I at 3% charge, indicating improvement in size.

- Burst factors are quite comparable ranging between 33 to 40 for rosin I, II, III, IV and mill rosin. Rosin III is found to give higher value of burst factor among all the rosin samples. With increase in ^{0}SR, increase in burst factor values is observed for mill dispersed rosin and DR II. But the same decreases for DR I indicating decrease in strength properties.

- Tear factor ranges from 26 to 34 for rosin I, II, III, IV and mill rosin. With increase in ^{0}SR increase in tear factor values is observed for mill dispersed rosin and DR II but the same decreases for DR I indicating decrease in strength properties.

- Over all rosin I, II, III have shown better results than rosin IV. 1-1.2% charge is found to be optimum. Sizing with rosin I, II and III have given same results as that of Mill rosin. DR I and DR II are to be used in higher dosages. 2.5% of DR I has given comparable results of sizing with mill dispersed rosin at 40 ^{0}SR but strength properties are lower. When ^{0}SR is increased from 35 to 40, Cobb has decreased and sizing has improved, but there is no improvement in strength properties as observed with mill rosin. DR II has given comparable results with mill dispersed rosin at 35 ^{0}SR as well as 40 ^{0}SR.

- Sulfonated CNSL is obtained by sulfonation of commercial CNSL (cardanol). Sulfonated CNSL mainly contains cardanol sulfonate with little quantity of cardol sulfonate. These compounds contain sulfonic and phenolic groups which increase the ion-exchange properties of pulp[8] and thus help in improving sizing properties. Sulfonated CNSL is a surface active agent with good dispersing properties, thus it disperses rosin properly in emulsion form. These properties help in the reduction of rosin consumption.

Conclusion

This research work offers a vital opportunity to explore the use of sulfonated CNSL as a supportive chemical in neutral rosin sizing. Sulfonated CNSL is a surface active agent obtained from natural resources and is biodegradable. Therefore its use is eco friendly. Apart from this it has antifungal and antibacterial properties. This supports its use as wet end additive, so sulfonated CNSL is useful as an additive in neutral rosin sizing.

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