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G. Venkoba Rao^a; N. V. S. R. Murthy^a; P. V. Annam Raju^a; G. S. R. P. Sauna^a

^a The A.P. Paper Mills Limited, Rajahmundry, Andhra Pradesh, INDIA

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EFFECT OF PULP EXTRACTIVES
ON SIZING

G. Venkoba Rao, N.V.S.R. Murthy,
P.V. Annam Raju & G.S.R.P. Sarma

The A.P. Paper Mills Limited,
Rajahmundry : 533 105,
Andhra Pradesh, INDIA.

ABSTRACT

The effect of specific extractive components of bamboo (*Dendrocalamus strictus*) and tropical mixed hardwoods (TMHS) kraft pulps on sizing has been studied. It was found that the removal of the extractive components by diethyl ether improves sizing substantially, which may be attributable to the presence of oleic acid and its derivatives in the extractives. To substantiate this, the effect of added oleic acid and methyl oleate on sizing has also been studied. The possible mechanism of action of these compounds has also been postulated.

INTRODUCTION

In a recent review on the chemistry of rosin sizing¹ it has been pointed out that compounds such as fatty alcohols, unsaturated fatty acids, pitch dispersants and defoamers reduce hydrophobic nature of the size film and thereby adversely affect the sizing. However it is to be pointed out here, that there is no mention about the specific compounds and the extent to which these adversely affect sizing. A literature survey also revealed that not much work is on record on the effect of pulp components except hemicelluloses and inorganic components on sizing^{2,3}. As components

like unsaturated fatty acids, for example, linoleic and oleic acids form the major part of the pulp extractives, especially those from hardwoods^{4,5}, we have initiated our studies on the effect of extractive components on sizing. We present in this communication the results of our studies on the sizing of bamboo (*Dendrocalamus strictus*) and tropical mixed hardwoods (TMHWS) kraft unbleached pulps, especially the effect of pulp extractives.

RESULTS AND DISCUSSION

The beaten bamboo and the TMHWS unbleached pulps were subjected to diethyl ether extraction. The ether extractives ranged from 0.4% to 0.6% for bamboo and 0.7% and 1.0% for TMHWS. Handsheets were made from both unextracted and extracted pulps adding the same quantity of rosin size (0.8% on O.D. pulp basis) in all cases, maintaining the same stock pH 5.0 with the addition of alum. N-grade rosin of acid number 165 was used to prepare the rosin soap size. The handsheets were dried on the L&W laboratory sheet dryer under the same conditions. Sizing values were determined using the Thiocyanate Flotation Method (TAPPI-UM429). The results of the study are presented in Table 1. All the sizing values are reported in seconds. Reproducibility of the test is within 10%.

It is evident from the results that the removal of extractive components by diethyl ether improved sizing considerably for both the bamboo and TMHWS pulps. A chromatographic study of these ether extractives showed the presence of oleic acid and its esters in the extractives of both bamboo and TMHWS pulps. Hence, the improvement in sizing may be attributed to the removal of oleic acid and its esters by diethyl ether.

To further confirm the detrimental effect of oleic acid on sizing, different dosages of oleic acid were added, and sizing was studied. We are also reporting for the first time in literature the effect of added ester of

TABLE-1

Effect of Ether Extraction on Sizing:

Set No	Bamboo				Tropical Mixed Hardwood			
	A		B		A		B	
	Alum %	Sizing Sec.	Alum %	Sizing Sec.	Alum %	Sizing Sec.	Alum %	Sizing Sec.
1.	4.2	106	3.5	182	5.1	118	4.1	160
2.	4.2	100	3.7	129	4.7	109	3.5	138
3.	4.0	108	3.1	161	4.7	100	4.1	121

Basis weight = $102 \pm 2 \text{ g/m}^2$

A = Unextracted pulp ; B = Extracted pulp

unsaturated fatty acids, viz., methyloleate on sizing. The order of addition of chemical was additive, rosin and alum to get the stock pH 5.0. The results are tabulated in Table-2.

From the perusal of the results, the following facts emerge:

1. Addition of oleic acid and methyloleate considerably decrease sizing.
2. The effect is more marked in the case of methyloleate than in the case of free acid.

The observation that the ester as well as free oleic acid reduce sizing is quite revealing. This suggests the formation of a complex between oleic acid and also its esters with the aluminium compounds. Most probably these complexes may be more stable than aluminium rosinate which are responsible for the sizing. The fact that even ester is also having adverse effect

TABLE-2

Effect of Addition of Oleic acid and Its Ester on Sizing:

S. Particu- No lars	A		B		C		D	
	Alum %	Siz- ing Sec.	Alum %	Siz- ing Sec.	Alum %	Siz- ing Sec.	Alum %	Siz- ing Sec.
1. Blank	2.5	100	5.1	88	5.1	109	4.1	121
2. <u>Oleic acid</u>								
a. 0.1%	2.9	93	5.3	64	5.4	105	4.9	82
b. 0.2%	2.9	80	5.9	44	5.6	93	5.0	27
c. 0.3%	2.9	60	5.9	37	5.9	61	5.0	17
3. <u>Methyl- oleate</u>								
a. 0.1%	3.0	90	5.3	61	5.6	105	5.1	34
b. 0.2%	3.1	75	6.1	28	5.9	71	5.1	16
c. 0.3%	3.0	55	6.3	12	6.1	41	5.3	6

Basis weight = $102 \pm 2 \text{ g/m}^2$

A, B & C = Unextracted bamboo pulps

D = Extracted TMHWS pulp

indicates that the oleic acid does not react with aluminium compounds to form a simple salt but acts as a coordinating ligand in the complex formed. Such complexes can be formed between esters such as methyl-oleate and aluminium compounds because as ligands both oleic acid and its esters have almost the same effect. It is pertinent to point out here that organo aluminium compounds with olefines as ligands in complexes have been reported in literature and the structure of such complexes in which there is an interaction between the double bond and the aluminium have been confirmed by I.R and N.M.R. spectroscopy^{6,7}. The very

TABLE-3

Effect of Alum Dosage on Sizing of Oleic acid and Methyloleate added Pulp:

Set No	Alum dosage %	Stock pH	Blank	Sizing values in Seconds	
				Oleic acid 0.2%	Methyloleate 0.2%
1.	2.76	5.5	80	34	17
2.	3.73	5.0	86	49	40
3.	6.21	4.5	73	43	38

Basis weight = $102 \pm 2 \text{ g/m}^2$.

fact that the higher consumption of alum to attain the same stock pH, vide Table-2, in the case of oleic acid and its ester added pulps, and lower consumption of alum in the case of extracted pulps, vide Table-1 lends further support to our proposal. However, we would like to add here that this is only one of the many possible ways through which the fatty acids and their derivatives affect sizing.

As these extractive components tie up part of aluminium of alum added, we have also investigated the effects of different dosages of alum on sizing of bamboo pulp in the presence of oleic acid and methyloleate. The order of addition followed was additive, rosin and alum. The results of the study are presented in Table-3.

It is seen from the data, that increased dosage of alum no doubt increases the sizing, but not to the level of sizing observed in the absence of oleic acid and its ester. This may most probably be due to the fact that our experiments have been conducted at a

stock pH 5.0 and considerable increase in the alum dosage resulted in the stock pH dropping to a lower level at which the efficiency of sizing decreases.

Further work is in progress by us on the nature of the complexes formed between aluminum compounds and oleic acid derivatives.

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