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The Effect of Galacto-Mannans on Handsheets Made From Softwood, Hardwood or Rag Pulps

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SUMMARY

Some published information reports that galacto-mannans, when used as strength producing beater additives, do not effect significant strength increases in hardwood pulps. In order to investigate this problem further, six pulps covering a wide range of pulping processes and chemical compositions, were evaluated before and after the addition of locust bean gum, a galacto-mannan, to the pulp.

The results obtained indicate that galacto-mannans do favorably affect the strength properties of hardwood pulps. Substantial increases in bursting strength, tensile strength and folding endurance were noted for all the hardwood pulps employed, as well as for a rag pulp. These strength increases were caused by very low concentrations of locust bean gum, making their use economically feasible.

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INTRODUCTION

Beating and refining are mechanical processes of preparing pulp fibers for paper manufacture. Specifically, beating and refining cause the fibers to imbibe water and to swell, roughen the fiber surface and split tiny strands called fibrils from the fiber. This action gives the ultimate sheet of paper increased strength due to the large area made available for bonding by swelling and fibrilation (1).

For years, papermakers have sought ways to impart these desirable characteristics, namely, improved fiber bonding and increased strength, to pulp fibers by treatment with chemicals, rather than by mechanical treatment as in beating and refining. A portion of the appreciable cost of power to operate refining equipment could thus be saved, and several undesirable features of beaten stock could be reduced. Excessively beaten stock has a tendency to shrink to a large extent upon drying, to become more translucent, less compressible and less oil receptive than slightly refined fibers (1).

It has been suggested (2, 3), that if a hydrophilic compound could be adsorbed on the cellulose molecule by some of the hydroxyl groups, the fiber would more readily take up water and swell. The fiber structure would be opened up by the hydrophilic colloids, and the compounds' water loving nature would cause further swelling. A group of compounds known as galacto-mannans has been found which seems to work as postulated above. Gruenhut (3) thinks that the linear galacto-mannan mole-

cule aligns itself along the cellulose molecule and is adsorbed on the fiber, held fast by hydrogen bonds, which she thinks are mainly responsible for the gum-fiber attraction.

PROPERTIES OF GALACTO-MANNANS

Galacto-mannans are branched polysaccharides of high molecular weight (those most frequently encountered range from 220,000 to 310,000 (4, 5)), usually classified with the natural gums. Some hemicelluloses found in wood are probably similar in structure. The gums, which are hydrophilic, give the appearance of being water soluble, but actually form a colloidal dispersion. The water solutions are highly viscous or mucilageonous (6). Dilute mineral acids, heavy metal salts and oxidizing agents tend to lower the viscosity of galacto-mannan solutions, while alkalies generally increase it. Most salts and electrolytes have little effect on viscosity, but in concentrated solutions may cause precipitation of the gum. Control of pH is said not to be important, nor does heat seem to have much effect on viscosity.

In the solid state, galacto-mannans are amorphous and will not crystallize out of solution. With alkaline earth metals, adsorption complexes are formed. The gums give a neutral reaction in water, but, upon standing, will turn acidic. Their charge in water is negative (3).

As mentioned, galacto-mannans are branched polysaccharides which appear to be associated with plant life processes. The molecule is actually a linear chain of d-mannose units linked B-glycosidically through the 1 and 4 carbons. Attached to some of the d-mannose units through a 1, 6 glycosidic linkage are d-galactose groups. The frequency with which the galactose units appear varies with the plant

source of the gum.

As a typical example of a galacto-mannan, the structure of a part of the locust bean gum molecule is presented as described by Deull and Neukom (5).

Locust Bean Gum (Ceratonia Siliqua)

average molecular weight - 310,000
average D.P. - 1500

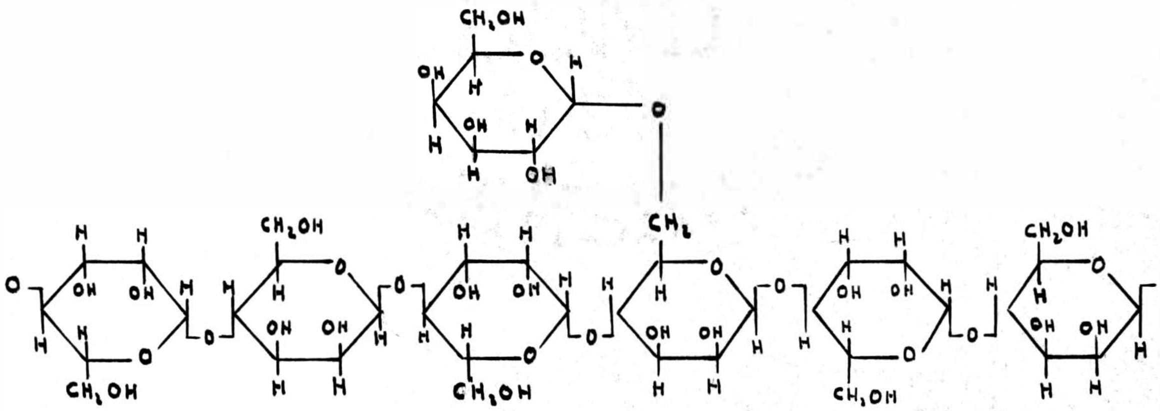

Fig. 1

The structure of the molecule probably partially explains the viscosity of the compound's solutions (7, 4). The branching galactose units increase mechanical entanglement, and three dimensional structures are formed which have huge areas of hydrophilic groups exposed. The associated water molecules are thus partially immobilized, and the result is a viscous solution. In addition, the high molecular weight undoubtedly plays an important part.

Although not the only galacto-mannan used in the paper industry, locust bean gum is one of the more important ones. Guar gum is also extensively used, especially since it is grown in the United States, while locust bean gum must be imported from southern Europe and the Mediterranean area. These two gums are the best known of the commer-

cial gums of this group, but galacto-mannans also may be obtained from such sources as alfalfa seed, sweet clover and the endosperms of other leguminous plants (7).

SOME EFFECTS OF GALACTO-MANNANS ON PULP

Upon addition to the beater or headbox of the papermachine, galacto-mannans produce many effects in softwood or coniferous pulps. In low concentrations (0.5 per cent based on the weight of the fiber) galacto-mannans give the pulp high strength increases in 70 per cent less beating time, in some cases (1). It has been reported (1, 4, 8, 9) that appreciable burst, tensile, tear and fold strength improvements are noted as well as an improvement in sheet formation, while a high freeness level is maintained.

Leech(10) thinks that a beater adhesive, such as a galacto-mannan, increases pulp strength properties by affecting one or more of the following factors: (1) The strength of the fibers, (2) the strength of the bonds, (3) the number of bonds, and (4) the distribution of fibers and bonds (formation). Furthermore, he determined the extent to which locust bean gum influenced each of these factors. His results are presented in Table I.

Table I

Effect of Locust Bean Gum on some Factors Influencing Pulp Strength

Strength increases due to:	Contribution %
Increased bonded area	15
Improved formation	25
Increased bonding strength	60
Increased fiber strength	0

This worker attributes the great increase in bonding strength to the flexibility of the gum-cellulose bonds, which are not so rigidly held in the crystalline fiber structure as cellulose-cellulose bonds.

An interesting technique for estimating the value of strength producing additives has been devised by Davison, Putnam, Mashburn and Ware (11). By plotting the values for one strength property of paper as abscissa against the values for another strength property as ordinate, a "beating curve" is obtained. The best results occur when tearing resistance is plotted against burst or tensile strength. By comparing the curves of pulp sheets made with and without internal additives at the same tear-burst or tear-tensile ratios, the "property disproportionation values, or those values which are unique for sheets made with internal additives" can be calculated.

Although the strength improvements caused by galacto-mannans with softwood pulps are quite substantial, some reports (1, 8, 9) indicate that such strength increases do not occur when a 100 per cent hardwood, or deciduous furnish is used. This problem will be investigated further in this thesis.

Very little has been reported on the reason for the failure of galacto-mannans with hardwood pulps. Swanson (1) did some work on the subject, using locust bean gum with coniferous and deciduous sulphite pulps. Some of his findings are tabulated in Table II.

Table II

Effect of Locust Bean Gum on Coniferous and Deciduous Sulphite Pulps

	per cent gum	Schopper-Riegler freeness (ml.)	Mullen	tear	fold	tensile
100% coniferous Sulphite pulp	0.0	750	25.5	60	42	14.3
	0.5	685	27.9	71	80	16.7
	1.0	639	34.3	44	188	16.8
	3.0	568	37.6	45	167	18.5
	5.0	638	40.8	51	253	18.2
	10.0	548	39.8	41	392	18.5
100% deciduous sulphite pulp	0.0	770	8.0	19	0	2.2
	0.5	680	8.1	19	0	2.6
	1.0	730	8.2	20	0	2.7
	3.0	663	8.1	19	0	3.3
	5.0	680	8.4	20	0	3.1
	10.0	619	8.3	19	0	3.6

Obviously, the above data do not show any significant strength increases in the case of the hardwood pulp. However, Swanson found that 10 to 45 per cent of the furnish could be made up of hardwood pulp and the strength of the paper maintained using three per cent gum based on the fiber weight.

Hamilton (9) and Casey (8) also mentioned the fact that hardwood pulps do not increase in strength upon the addition of a galacto-mannan.

MANNANS AND PULP STRENGTH

A comparison of the chemical composition of a typical hardwood with that of a typical softwood may give some indication of the reason for the reported ineffectiveness of galacto-mannans with hardwood pulps. Sutermeister (12) gives such a comparison.

Table III

Chemical Composition of Typical Woods

Component	Jack pine (%)	Birch (%)
Lignin	28.4	22.1
Cellulose (Cross & Bevan)	52.2	44.9
Pentosans	10.7	21.2
Mannans	5.5	0.2
Acetyl	1.5	3.2
Methoxyl	1.7	1.4
Uronic acids	3.6	4.8
Ash	0.3	0.4

One of the obvious differences between the two woods is in the mannan content. Stamm and Harris (13) also showed that the amount of mannan in hardwoods is almost negligible.

More light was shed on the problem by Jonas and Rieth (14) who showed that pulps similar in chemical composition except for mannan content, had different strength properties. High mannan content pulps showed higher burst and tensile strength than pulps containing little or no mannan. In addition, Khinchin (15) in the U.S.S.R. presented a theory that the swelling properties of softwoods in water may be due to the presence of mannans. He believed that the mannans found in softwoods were more easily hydrated than the pentosans (xylan) which were found in both hardwoods and softwoods. This would explain the greater swelling of softwood fibers in water. The theory has not been substantiated by anyone else, however (16).

Thompson, Swanson and Wise (17),when studying the effect of hemi-

cellulose as beater additives, found that the softwood hemicelluloses (black spruce and Douglas fir) were much more effective in producing strength than those from aspen, a hardwood. These workers attributed the success of softwood hemicelluloses as beater additives to their higher hexosan content, consisting chiefly of mannan. When two hemicellulose fractions from spruce wood, one containing seven per cent and the other twenty-two per cent mannan, were added to a beater furnish, the one with the higher mannan content was more effective as a beater adhesive.

It was found that the degree to which strength properties of the pulp were improved using either hemicelluloses high in mannans, or using locust bean gum was about the same (17).

Whether the reported inability of galacto-mannans to increase the strength properties of hardwood pulps is due to the lower mannan content of this type of fiber, will be investigated in this thesis.

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EXPERIMENTAL DESIGN

In order to determine whether the reported inability of galacto-mannans to effect strength increases in hardwood pulps is due to their low mannan content, or to some other factor, a variety of pulps will be tested. Locust bean gum will be the galacto-mannan used in this work, with the following pulps:

I. Bleached Swedish acid sulphite -- mainly birch

II. Natchez Supercell bleached kraft-- southern hardwoods

III. Seagull bleached soda-- mainly poplar

IV. Badger bleached acid sulphite-- mainly poplar

V. Natchez bleached kraft-- southern pines

VI. Bleached rag --- Lee Paper Company, Vicksburg, Michigan

It is readily seen that a good range of mannan contents is covered, namely, from a high level for coniferous pulp to complete absence in rag pulp, and that a variety of pulping processes is represented.

Sheets will be made from these pulps at both a rather high and an intermediate freeness level, and at varying concentrations of locust bean gum. The sheets will be tested for bursting strength, tensile strength, tearing resistance and folding endurance.

EXPERIMENTAL PROCEDURES

Cooking of Gum

A fresh batch of locust bean gum solution was prepared before each day's experiments in the following manner: The gum was dispersed in cold distilled water and diluted to 1% concentration (based on the air dry gum weight). This dispersion was brought to 200 F in a steam bath and held at that temperature for 45 minutes, with constant stirring. To terminate the cooking period, the dispersion was diluted to

0.5% concentration with cold distilled water.

Stock preparation

It was hoped at the start of the experimental work to evaluate each pulp after five minutes beating, and also after beating to 425 ml Canadian Standard freeness. However, the Badger acid sulphite pulp was found to have a freeness too low to permit this procedure. Therefore, the original plan was modified somewhat. After ten minutes initial disintegration, all the pulps were circulated for five minutes in a 1 1/2 pound Valley laboratory beater at 1.57% consistency and approximately 23 C, without weights. Then, 5500 grams were added to the lever of the beater, and the pulps beaten for five minutes at 500 plus/minus 10 rpm.

Approximately 8000 ml of stock was withdrawn from the beater, and used for forming handsheets. The remaining pulp was beaten until 425 ml freeness was attained, in the cases of all pulps excepting the Badger acid sulphite, whose initial freeness was too low to permit this procedure. The high freeness range sample of this exception was merely disintegrated for ten minutes and then evaluated.

Pulps in the high freeness range, from 558 to 712 ml, were labelled "series A", whereas pulps in the intermediate range, from 383 to 433 ml, were designated as "series B" pulps. Freeness values and beating periods for each pulp may be found in Table IV.

Sheet Forming

Four sets of seven 8"x8" sheets each were formed on a Noble and Wood sheet machine from each pulp sample, containing 0.0%, 0.25%, 0.50%, and 1.0% locust bean gum (based on the oven dry fiber weight). The only

exception was in the case of the rag pulp sample which had been beaten five minutes. Formation was not good enough with this rather long fibered sample to warrant testing.

Evaluation of handsheets

All eleven sets of sheets were evaluated in the same manner. After conditioning at 50% relative humidity and 73 F for at least six hours, the sheets were subjected to these physical tests: Bursting strength, tensile strength, tearing resistance, folding endurance, caliper and moisture content. From these values were calculated the burst factor, breaking length (tensile strength) and tear factor, which corrected the original quantities for weight and moisture differences. Also, the apparent specific volumes of the sheets were calculated.

Table V shows these calculated results. Furthermore, the per cent strength increases caused by the varying galacto-mannan concentrations are presented, based on control tests for sheets without locust bean gum. Figures 2 and 3 in the appendix show the per cent increases graphically for the burst and tensile factors.

DISCUSSION OF RESULTS

Burst factor

Significant increases were noted in the burst factor for all the pulps used in the experimentation. As may be seen from Table II, in the series A pulps (i.e. high freeness pulps) the percentage increase caused by the use of locust bean gum was greater for every hardwood pulp than the percentage increase for the particular grade of softwood kraft pulp used. This condition was also observed in the series B pulps (intermediate range), with the exception of the Swedish acid sulphite, which was only slightly lower percentage-wise than the softwood kraft.

Breaking length

In this case the series A hardwood pulps again showed substantial strength increases, although not always as much as the softwood kraft. The series B hardwood and rag pulps all showed per cent strength increases equal to, or greater than, the kraft softwood.

Tear factor

The results of this test varied greatly. There was generally a decrease in tearing resistance, as would be expected. Two series A pulps exhibited substantial increases however, a condition similar to that commonly encountered at the beginning of a pulp evaluation by the beater method.

Folding endurance

Rather spectacular results were obtained in folding endurance in terms of per cent increases. As much as 275% increases were observed. The series A hardwood pulps, came close, but did not exceed the increases observed for the kraft softwood. In series B, all the hardwood and rag pulps showed increases far greater than the softwood pulp used.

Basis weights and apparent specific volumes of the sheets were not affected significantly by the addition of locust bean gum to the pulp.

CONCLUSIONS

Contrary to some published information, the data obtained in this thesis show that galacto-mannans do favorably affect the strength properties of hardwood pulps. It is also indicated that these favorable effects are not governed by the mannan content of the pulp being used, nor by the pulping process used. The former is most dramatically

demonstrated by the rag pulp, which is practically all cellulose. This pulp shows good affinity for galacto-mannans. Consistent, substantial increases in bursting strength, tensile strength and folding endurance can be attributed to the presence of galacto-mannans in the sheet.

Conclusions based upon per cent increases in strength can be slightly misleading, since the strength values for the control tests, (i.e. those without gum), are much lower for hardwood pulps than for softwood pulps. Hence, a given numerical increase in strength would appear as a higher percentage increase with the originally weaker hardwood pulp than with the stronger softwood pulp. Inspection of the original test values obtained and reported in Table V will show, however, that good strength increases were caused by galacto-mannans in every hardwood and rag pulp used.

These results indicate that galacto-mannans can be used effectively with hardwood and rag pulps. Low concentrations of locust bean gum produce considerable strength increases in these types of pulp. Thus, the use of galacto-mannans with hardwood pulps seems to be just as feasible, economically, as their use with softwood pulps.

Table IV

Beating Times and Canadian Standard Freenesses

Identification	Type of Pulp	Beating Time (min)	Canadian Standard Freeness
I A	Bleached Swedish Acid Sulphite - Birch	5	603
II A	Bleached Natchez Kraft - Hardwood	5	674
III A	Bleached Seagull Soda - Hardwood	5	567
IV A	Bleached Badger Acid Sulphite - Poplar	0	558
V A	Bleached Natchez Kraft - Pine	5	712
VI A	Bleached Lee Rag	5	623
I B	Bleached Swedish Acid Sulphite - Birch	15	426
II B	Bleached Natchez Kraft - Hardwood	10	418
III B	Bleached Seagull Soda - Hardwood	11	423
IV B	Bleached Badger Acid Sulphite - Poplar	5	383
V B	Bleached Natchez Kraft - Pine	20	433
VI B	Bleached Lee Rag	20	429

Table V

Tabulation of Results

Table V

Tabulation of Results

Identification	Canadian Standard Freeness	% Locust Bean Gum	Sheet Weight	Apparent Specific Volume	Burst Factor	Breaking Length (M) (Tensile Strength)	Tear Factor	Folding Endurance	% Increase Burst Factor	% Increase Breaking Length	% Increase Tear Factor	% Increase Folding Endurance
I A	603	0.00	59.53	.0226	15.40	3558.9	70.9	3.6				
		0.25	61.57	.0219	20.04	3683.6	70.2	6.8	30.10	3.51	-1.00	89.0
		0.50	62.23	.0216	20.28	4033.3	69.4	5.3	31.70	13.34	-2.12	47.0
		1.00	62.51	.0219	20.36	4063.6	77.8	8.6	32.30	14.20	9.75	139.0
II A	674	0.00	62.06	.0247	8.44	2338.9	64.45	1.0				
		0.25	65.12	.0240	9.99	2698.0	76.17	2.6	18.40	15.48	18.22	160.0
		0.50	65.35	.0247	11.40	2609.8	78.35	2.8	35.10	11.60	21.60	180.0
		1.00	62.16	.0244	11.25	2607.6	83.91	2.8	33.30	11.50	30.20	180.0
III A	567	0.00	60.63	.0209	9.22	2399.0	52.78	1.0				
		0.25	61.31	.0215	11.70	2767.0	55.64	2.4	27.20	15.38	5.45	140.0
		0.50	59.90	.0214	12.38	2963.4	53.42	2.0	34.70	23.45	1.26	100.0
		1.00	62.23	.0211	13.90	3197.5	55.69	2.8	52.50	33.30	5.52	180.6
IV A	558	0.00	65.01	.0205	13.19	2963.1	39.37	3.2				
		0.25	75.67	.0185	17.84	3320.9	45.80	6.6	35.30	12.06	16.34	106.2
		0.50	74.81	.0185	18.65	3609.7	49.19	8.2	41.50	21.82	24.95	156.2
		1.00	74.22	.0189	20.32	3683.2	48.85	11.0	54.10	24.30	24.10	244.0
V A	712	0.00	60.28	.0231	29.80	4274.1	192.0	47.4				
		0.25	61.82	.0225	32.47	5013.9	207.1	174.0	8.95	17.30	7.85	267.0
		0.50	60.24	.0230	33.40	4859.2	185.0	143.0	12.10	13.70	-3.65	202.0
		1.00	59.74	.0228	36.72	4920.2	172.3	149.0	23.21	15.13	-10.26	213.0
VI A	623	0.00	-	-	-	-	-	-	-	-	-	
		0.25	-	-	-	-	-	-	-	-	-	-
		0.50	-	-	-	-	-	-	-	-	-	-
		1.00	-	-	-	-	-	-	-	-	-	-
I B	426	0.00	60.80	.0201	41.28	6863.7	69.47	154.0				
		0.25	61.28	.0191	43.42	7007.0	64.23	228.0	5.19	2.09	-7.55	48.0
		0.50	60.75	.0192	44.32	7516.4	64.79	257.0	7.36	9.49	-6.75	66.9
		1.00	62.87	.0190	44.28	8128.8	62.61	310.0	7.27	18.41	-9.90	101.0
II B	418	0.00	62.84	.0208	28.70	4658.2	85.04	36.0				
		0.25	61.12	.0211	31.52	5392.9	80.10	63.8	9.80	15.71	-5.81	77.3
		0.50	63.07	.0203	33.27	5096.7	77.60	51.0	15.91	9.41	- 8.75	41.7
		1.00	63.66	.0203	33.68	5567.2	77.90	75.6	17.32	19.41	-8.30	110.0
III B	423	0.00	62.96	.0208	28.70	4658.2	60.27	10.0				
		0.25	61.13	.0200	25.19	5095.2	57.60	11.2	25.50	15.85	-4.45	12.0
		0.50	64.69	.0192	26.41	4730.6	66.78	21.0	31.60	7.58	10.81	110.0
		1.00	60.31	.0208	26.46	4863.6	59.27	18.4	31.75	10.62	-1.66	84.0
IV B	383	0.00	61.31	.0196	20.52	4493.3	34.97	9.8				
		0.25	62.59	.0194	22.97	4831.4	32.36	25.6	11.95	7.53	-7.46	161.2
		0.50	63.40	.0191	23.23	4912.8	35.30	33.2	13.21	9.32	0.95	238.8
		1.00	61.04	.0195	24.65	5320.7	38.43	32.2	20.12	18.42	9.90	228.5
V B	433	0.00	58.47	.0194	52.66	7582.0	114.90	857.4				
		0.25	60.75	.0192	56.07	8233.3	107.10	1050.6	6.47	8.6	-6.80	22.6
		0.50	59.01	.0198	55.37	8383.7	102.10	915.0	5.14	10.60	-11.15	6.7
		1.00	60.38	.0193	57.56	8711.6	98.13	956.2	9.30	14.89	-14.60	11.5
VI B	429	0.00	59.10	.0230	19.93	2394.6	213.90	20.8				
		0.25	59.27	.0229	23.55	3489.8	221.40	35.4	18.15	45.70	3.51	70.2
		0.50	60.95	.0226	25.72	3731.0	243.1	53.6	29.00	55.75	13.66	156.6
		1.00	62.28	.0231	29.80	4253.4	227.6	77.4	49.50	77.50	6.41	272.1

BURST FACTOR ~ % INCREASE

FIGURE 2

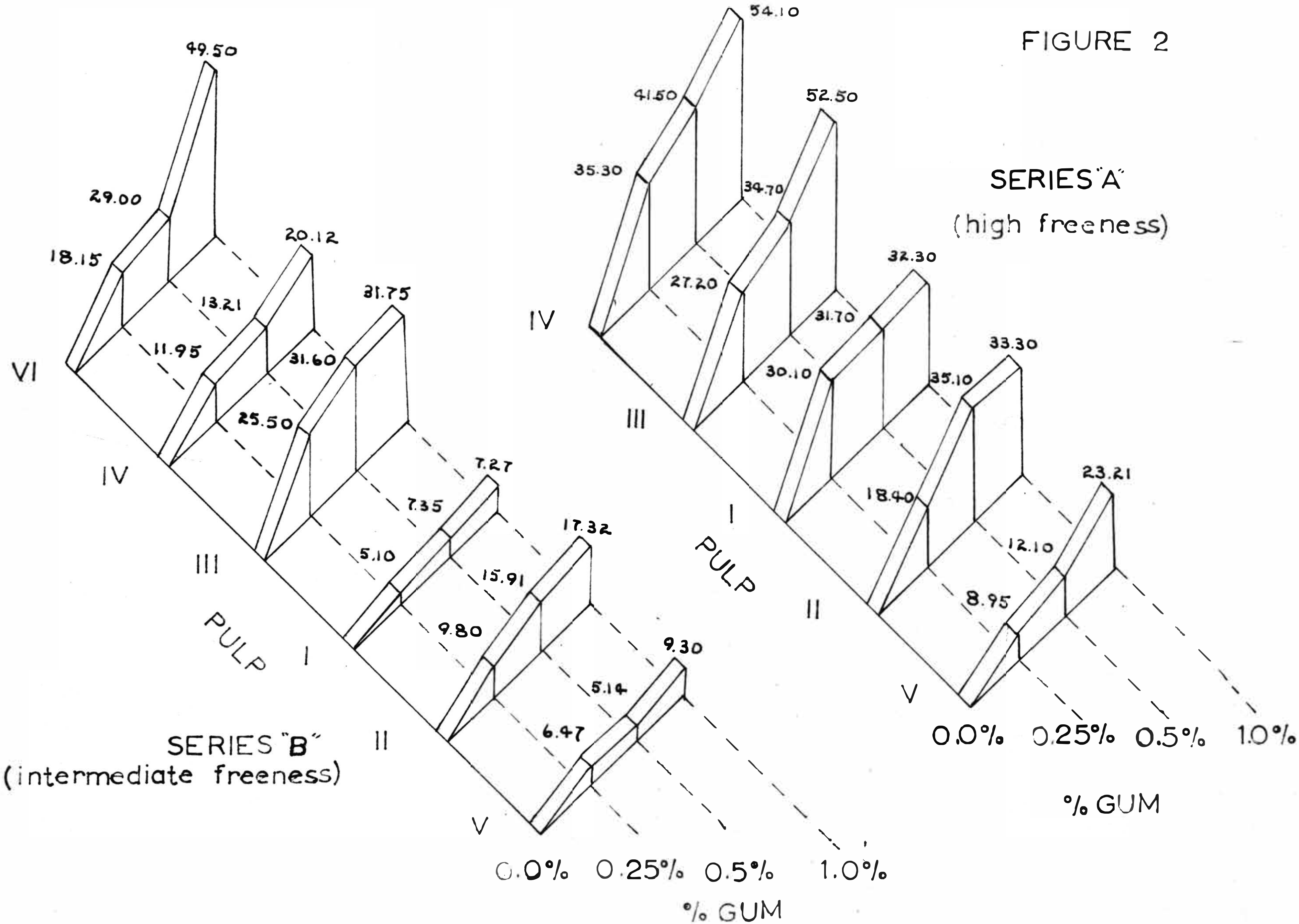

FIGURE 3
BREAKING LENGTH ~ % INCREASE