PROJECT REPORT FORM

PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 4
DATE 1/7/44 Typed 1/12/44
NOTE BOOK see end of report
PAGE " TO "
SIGNED John W. Swanson
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Further Experiments with Waring Blendor Beating and The Effects of Locust Bean Gum Addition.

Introduction:

Data presented in Report No. 2 of this project indicated that considerable increases in tearing resistance could be obtained simultaneously with increases in bursting strength when a Waring Blendor was used as a beater. Such characteristics are very desirable from a papermaking standpoint since it is the usual occurrence for the tearing resistance to sharply decrease with increase in bursting strength. The unusual properties were not due entirely to addition of locust bean gum because further experiments showed that the pulp alone gave similar tear increases. Therefore it seemed desirable to further investigate this type of beating and the effect of locust bean gum upon the properties in question.

It is well known in the paper industry that most pulps increase in tearing resistance during the very first part of the beating cycle but thereafter a sharp decrease becomes evident. It is believed that the latter phenomenon may be due primarily to a shortening of the fiber length and that the Waring Blendor which presumably might not cut the fiber appreciably does give a unique type of beating action. In talking this matter over with Dr. Rowland and Mr. Wells of the Institute staff it was learned that some information on Waring Blendor beating was available. (See File on Ronald Trist.)This material was examined and found to be quite brief. Since our results seemed interesting enough we decided to persue the investigation a little further.

Work Done:

1. Two pulps, Weyerhaeuser bleached sulfite and Duracel bleached kraft were beaten for various intervals in the Waring Blendor and the Valley beater.

2. Sheets made from these pulps were compared as to bursting and tearing strengths.

3. The effect of locust bean gum on one of the beaten pulps was studied to some extent.

Experimental:

Beating Procedure at 1.5% consistency

Ten grams of the pulp (O. D. basis) were placed in a Waring Blendor and 714 ml. of water were added. The pulp was allowed to soak for five minutes and then the beater was turned on low speed for the exact number of minutes desired. The pulp was diluted to 2000 ml. (0.5%) and made into 1.5 g. handsheets on a Valley mold in the customary manner.

In the experiments where locust bean gum was added to the pulp this was done by first heating 0.1 g. of the gum (1% on pulp), in about 50 ml. of water to 80° C. and then adding the dispersion to the pulp two minutes before the end of the beating time. The pulp was then diluted as before and made into handsheets.

Beating Procedure at 3.0% Consistency

Twenty grams of pulp (O.D. basis) were placed in a Waring Blendor and 667 ml. of water were added. The mixture was allowed to soak for five minutes and then the beater was turned on high speed for an exact number of minutes. The pulp was diluted to 4000 ml. and made into handsheets as before.

Attempts to beat the pulp at 3% consistency with the low speed were unsuccessful because the pulp did not mix adequately.

Results and Discussion

The data on the beating of Duracel bleached kraft at 1.5 and 3.0% consistencies in the Waring Blendor and in the Valley beater are given respectively in Tables I, II, and III. The burst-tear factors are plotted against beating time in Figure 1.

The burst-tear factor is a value obtained by addition of the bursting strength per 100 pounds to the tear factor multiplied by 100. The bursting strength, of course, continues to increase with degree of beating but the tearing resistance (tear factor) only increases during the very first part of the beating cycle and thereafter decreases regularly. This characteristic of the tear value may be the result of a number of factors, among them being the type of beating action. Thus, in the curves of Figure 1 the maximum height of the curve gives to a certain extent a relative measure of the ability of the beaters to develop

a combination of bursting and tearing strength in pulps.

The data for Duracel bleached kraft indicate that Waring Blendor beating develops somewhat greater pulp strength than the Valley beater. Beating in the Blendor at high speed and higher consistency (3%) gave about the same maximum value, the only apparent difference being a more rapid development to the maximum.

The data on the beating of Weyerhaeuser bleached sulfite are in Tables IV and V and for one per cent locust bean gum addition in Table VI. The burst-tear factors are plotted in Figure 1 and from these it appears that the Waring Blendor possesses no significant advantage over the Valley beater for this sulfite pulp. The addition of one per cent of locust bean gum during the beating cycle showed that the gum neither increased nor decreased the tear value of the resulting sheet of paper. Rather it appears that the gum supplements the hydration effects of the beating action.

The work as a whole seems to indicate that the Waring Blendor might possess some advantage as a beater for hard pulps such as kraft but no discernible advantage for softer pulps.

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jw-sfbm

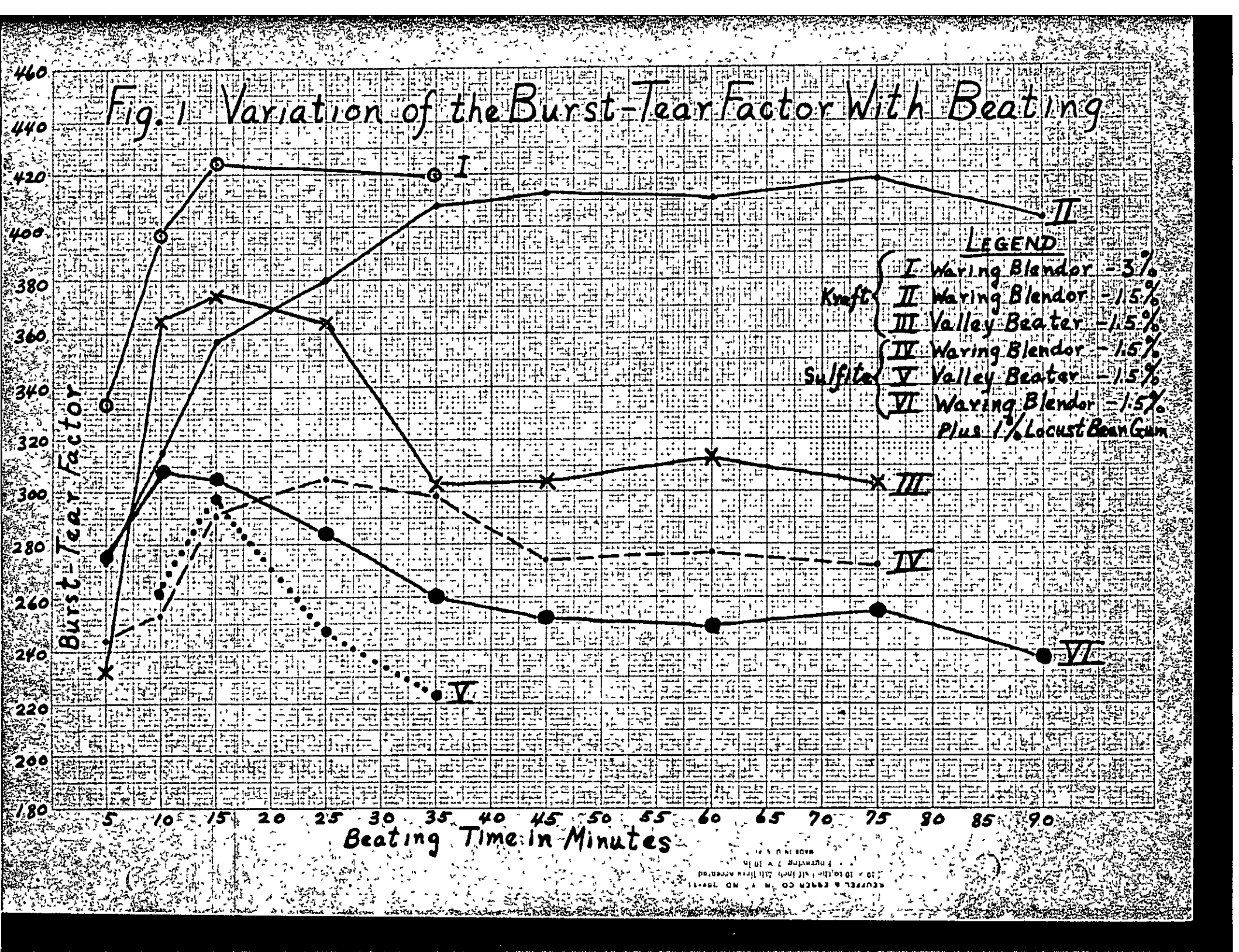
Fig. 1 Variation of the Burst-Tear Factor With Beating
Burst-Tear Factor
Beating Time in Minutes
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
I
II
III
IV
V
VI
LEGEND
Kraft
I Waring Blendor -3%
II Waring Blendor -1.5%
III Valley Beater -1.5%
Sulfite
IV Waring Blendor -1.5%
V Valley Beater -1.5%
VI Waring Blendor -1.5%
Plus 1% Locust Bean Gum

TABLE I

VARIATION OF BURST AND TEAR DURING BEATING OF DURACEL BLEACHED KRAFT IN THE WARING BLENDOR
Consistency = 1.5%

Beating Time (minutes)	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Bursting Strength (Mullen) Pts./100#	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	S.R. Freeness of Pulp	File No.
5	48.4	0.0057	8.5	12.9	27	119	2.46	273	850	110489
10	47.4	0.0053	9.0	16.3	34	133	2.81	315	845	110490
15	47.8	0.0053	9.0	21.4	45	149	3.12	357	840	110491
25	48.4	0.0052	9.5	27.9	58	156	3.22	380	---	110588
35**	48.4	0.0050	9.5	32.7	68	190	3.93	461	830* ---	110589
45	46.5	0.0049	9.5	34.8	75	157	3.38	413	815	110693
60	48.2	0.0049	10.0	39.0	81	159	3.30	411	810	110694
75	48.0	0.0049	10.0	41.8	87	159	3.31	418	790	110695
90	46.4	0.0043	11.0	44.2	95	143	3.08	403	775	110734
** Check on 35 minute beating time										
35	49.0	0.0050	10.0	34.7	71	164	3.35	406	820	110761
Effect of one per cent Locust Bean Gum addition to 45 minute beating.										
45	47.9	0.0048	10.0	52.4	109	143	2.99	408	---	110762

* Freeness at 30 minutes beating time

TABLE II

VARIATION OF BURST AND TEAR DURING BEATING IN THE WARING BLENDOR AT 3% CONSISTENCY

Stock - Duracel Bleached Kraft

Beating Time (minutes)	S. R. Freeness	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Pts./100#	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	File No.
5*	---	47.0	0.0058	8.0	9.8	21	81	1.72	193	110801
5	---	47.1	0.0051	9.0	20.3	43	137	2.91	334	110802
10	825	47.2	0.0049	9.5	28.5	60	159	3.37	397	110803
15	815	48.2	0.0051	9.5	30.2	63	174	3.61	424	110804
35	720	49.3	0.0049	10.0	51.8	105	155	3.14	419	111342

* Used low Waring Blendor speed which gave poor circulation
All others at high speed.

TABLE III

THE VARIATION OF BURST AND TEAR DURING BEATING OF DURACEL BLEACHED KRAFT IN THE VALLEY BEATER*

Beating Time (minutes)	S. R. Freeness	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Bursting Strength (Mullen) Pts./100#	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	File No.
5	850	48.7	0.0056	8.5	14.0	29	99	2.03	232	110826
10	850	49.7	0.0053	9.5	226	45	159	3.20	365	110827
15	850	44.9	0.0046	10.0	28.0	62	140	3.12	374	110828
25	830	47.7	0.0046	10.5	43.3	91	130	2.73	364	110829
35	820	47.2	0.0042	11.5	53.9	114	89	1.89	303	110830
45	800	47.8	0.0042	11.5	59.4	124	86	1.80	304	110831
60	765	48.4	0.0041	12.0	65.2	135	86	1.78	313	110832
75	705	47.4	0.0040	12.0	67.9	143	76	1.60	303	110833

* Consistency 1.5%
4500 g. on bed plate

TABLE IV

VARIATION OF BURST AND TEAR DURING BEATING OF WEYERHAEUSER BLEACHED SULFITE IN THE WARING BLENDOR

Consistency 1.5%

Beating Time (minutes)	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Pts/100#	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	File No.
5	48.5	--	--	12.1	25	106	2.19	244	110585
10	47.0	--	--	16.1	34	103	2.19	253	110585
15	47.0	--	--	18.9	40	118	2.51	291	110585
25	46.4	0.0045	10.5	25.5	55	116	2.50	305	110753
35	45.1	0.0043	10.5	29.0	64	106	2.35	299	110754
45	46.2	0.0043	10.5	31.3	68	95	2.06	274	110755
60	45.7	0.0043	10.5	34.9	76	92	2.01	277	110756
75	45.5	0.0042	11.0	36.1	79	88	1.93	272	110757

TABLE V

VARIATION OF BURST AND TEAR DURING BEATING OF WEYERHAEUSER BLEACHED SULFITE IN THE VALLEY BEATER
Consistency 1.5%

Beating Time (minutes)	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Pts./100#	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	File No.
5	50.0	0.0053	9.5	10.5	21	*	--	--	111504
10	46.5	0.0047	10.0	15.0	32	107	2.30	262	111505
15	46.8	0.0045	10.5	20.9	45	118	2.52	297	111506
25	47.6	0.0043	11.0	32.5	68	85	1.79	247	111507
35	47.5	0.0041	11.5	38.2	80	68	1.43	223	111508

* No good tears

TABLE VI

VARIATION OF BURST AND TEAR DURING BEATING UPON ADDITION OF ONE PER CENT OF COOKED LOCUST BEAN GUM

Stock - Weyerhaeuser Bleached Sulfite
Beater - Waring Blendor

Beating Time (minutes)	Basis Weight 25x40/500	Caliper inch	Apparent Density	Bursting Strength (Mullen) Pts.	Pts./100#	Per Cent Increase in Burst*	Elmendorf Tear g./sheet	Tear Factor	Burst-Tear Factor	File No.
5	48.6	0.0051	9.5	19.3	41	64.0	113	2.33	274	110866
10	48.2	0.0049	10.0	27.3	57	67.7	121	2.51	308	110867
15	47.4	0.0048	10.0	31.7	67	67.5	113	2.38	305	110868
25	46.5	0.0045	10.5	38.2	82	49.1	94	2.02	284	110869
35	47.0	0.0045	10.5	40.5	86	34.4	82	1.74	260	110870
45	46.7	0.0043	11.0	42.6	91	33.8	75	1.61	252	110871
60	46.4	0.0042	11.0	45.7	98	29.0	70	1.51	249	110872
75	46.5	0.0042	11.0	45.8	98	24.1	73	1.57	255	110873
90	45.3	0.0042	11.0	44.6	97	--	64	1.40	237	110874

* Per cent increase over blank at same beating time.
See Table IV for corresponding blank sheet.

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PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 11
DATE July 28, 1944. (typed 7/31/44)
NOTE BOOK 573
PAGE 59-64, 66- TO 81, 111-113
SIGNED John W. Swanson
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AN EVALUATION OF SEVERAL BORAX-SODIUM HYPOCHLORITE CONVERTED MUCILAGES AS CLAY COATING ADHESIVES

Introduction:

Previous work on Project 969 (Report 1) has shown that converted mannogalactan mucilages are strong adhesives for pigment coatings. It was also found that a limited amount of wet scrub resistance could be obtained by incorporation of a small amount of buffered borax solution. These experiments were made with converted products having little possibility of commercial manufacture. A method of conversion has now been devised which may possibly be commercially feasible. This is the borax-sodium hypochlorite technique. Several member mills have already expressed their interest in converted mucilages of this type. Therefore, it became desirable to evaluate as coating adhesives some of the promising products made by the new method.

Experimental:

Work Done

1. Several types of converted mucilages were evaluated in coating colors--these included converted G4-2, G44 and locust bean gums.

2. The coatings were examined for Denison wax pick test and visual smoothness. Two coatings were tested for K and N ink absorption and compared with starch coatings.

Procedure

Since many of the converted products varied considerably in ash and moisture contents all evaluations were made on an oven dry-ash free basis for the mucilage. After several experiments, the following procedure was adopted.

12 g. of converted mucilage (O.D. and ash free).
240 ml. water.
Glacial acetic acid to pH 5.0-5.5.

The mixture was heated to 80° C. with stirring and allowed to cool to about 40° C. The pH was then adjusted to pH 6.0-6.5 with dilute alkali and added to the following clay slip:

100 G. HT clay
50-60 ml. water
1.5 ml. 10% sodium tetraphosphate (Quadrafos)

After thorough mixing, the coating mixture was screened through a 100 mesh sieve and used to make drew downs with a 0.0015 inch bar.

Results and Discussion:

The experiments with converted G4-2 mucilages showed that this material is unsuitable as a coating adhesive. Coatings made with these products were not only very rough, presumably because of the non-dispersible seed coat present, but also the pick value was very low. (See Table I) At first it was believed that the roughness was due entirely to agglomerated clay particles produced by the salts present in the converted mucilage. However, an experiment with an acid hydrolyzed G4-2 (G11-556) which had a very low ash content also gave a rough coating. When converted locust bean gums were used, smooth coatings were obtained. In order to show that the G4-2 mucilage was responsible for the roughness, separate coatings were made with the cooked mucilage and a clay slip. The mucilage coating was very rough while the clay coating was very smooth. Examination of the mucilage coating with a low power microscope indicated that most of the roughness was due to the seed coat present in the G4-2 mucilage. However, numerous craters were also evident and these were the result of undispersed particles of mucilage which had been highly swollen while the film was wet but had shrunk upon drying. This was evident in finished coatings as tiny transparent spots.

Two samples of converted guar G44 were evaluated. (This mucilage has the seed coat removed and is much improved over G4-2.) Sample R25225 (General Mills code number) was difficult to disperse both before and after conversion and as a result, coatings made with the converted product were rough and unsuitable. Sample R25545, however, dispersed quite well and gave very good coatings from the standpoints of both smoothness and adhesive strength. Twelve per cent of this mucilage based on the weight of the clay, gave average wax pick test values of 5A. This converted mucilage is therefore equivalent to casein in adhesive strength.

The experiments were made at a relatively low coating solids content because the mucilages were only moderately converted and possessed viscosities too high for coating at higher solids content. Further experi-

TABLE I

CHARACTERISTICS OF THE COATING COLORS AND COATED SHEETS

Code No. of Coating	Mucilage Used	Type of Mucilage	Per Cent Mucilage on Clay	Apparent Viscosity of Color	Per Cent Solids Applied to Sheet	Denison Wax Test Max.	Min.	Av.	Remarks on Appearance of Coatings
C59-1-573	G55-573	G4-2	12	medium	30		poor		Very rough and pitted
C59-2-573	G11-556*	G4-2	12	medium	30		poor		Very rough
C60-1-573	G133-431*	locust bean gum	12	medium	30	-	-	4A	Smooth
C60-2-573	G57-573 G55-573	G4-2	12	medium	30		poor		Very rough
C61-573	G17-573	locust bean gum	12	medium	30	-	-	5A	Smooth
C67-1-573	G62-573	locust bean gum	12	Thick	33		poor	2A	Smooth
C67-2-573	G62-573	locust bean gum	12	medium	30	6A	5A	5A	Smooth
C71-573	G63-573	G44 R25225	12	medium	25	6A	5A	5A	Rough and pitted
C79-1-573	G74-573	G44 R25545	12	medium	25	6A	5A	5A	Smooth
C79-2-573	G74-573	G44 R25545	10	medium	25	4A	3A	3A	Smooth
C81-1-573	G80-573	G44 R25545	12	medium	27.6	5A	4A	5A	Smooth
C81-2-573	G80-573	G44 R25545	12	thinner	25	5A	4A	5A	Smooth
C111-573**	G74-573	G44 R25545	12	very thick	25	2A-	2A	2A-	Smooth

* These are alcohol acid converted mucilages used for comparison purposes.

** Added about 30% urea formaldehyde resin on weight of mucilage.

TABLE II

RELATIVE INK ABSORPTION VALUES FOR
MUCILAGE AND STARCH COATINGS

File No.	Designation	Adhesive Used	Per Cent Adhesive on Clay	K and N Ink Absorption Average Reflectance %		
				Ro Original	Ro Inked	Difference
113483	C79-573	Mucilage G74-573	10	75.5	43.5	32.0
113484	C79-573	Mucilage G74-573	12	75.0	44.1	30.9
113485	C48-557	Starch	18	80.1	36.6	43.5
113487	Champion * International Paper Company	Starch	22	70.4	43.5	26.9
113488	C19-1-557	Starch	22.5	78.7	39.6	39.1

* Machine-finished, calendered.
All others not calendered.

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PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 10
DATE June 19, 1944
NOTE BOOK 555 573
PAGE 150 TO 6-22, 23-46
SIGNED John W. Swanson
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Bleaching of Flame Tree Mucilage

Introduction

The mannogalactan mucilage obtained from the flame tree seed (Delonix regia) is a particularly potent adhesive for application to the paper industry. The principal objection to using the mucilage at the present time is that the dark seed coat cannot be completely milled out. Therefore, the product cannot be used in high grade papers because of the many dark specks retained by the sheet. All attempts, so far, to effect a separation of mucilage and seed coat have failed. Therefore, it was decided that bleaching should be tried with a borax solution as a suspension medium. (See Report 9 on the borax technique). Preliminary test tube experiments showed the possibility of doing this and several further experiments were made.

The importance of this work lies in the fact that it makes available to the paper industry a cheap potent mucilage suitable for practically all types of paper.

Experimental

Work Done:

1. Flame tree mucilage was suspended in borax solution and bleached with various quantities of sodium hypochlorite.
2. Those products found to be suitable from a speck standpoint were evaluated as beater adhesives after cooking.
3. Several of the more highly bleached products were also evaluated as cold water soluble beater adhesives.
4. Attempts were made to bleach the mucilage by means of gaseous chlorine and nitrogen dioxide

Bleaching Procedure

60 g. flame tree mucilage (through 60 mesh)
600 ml. water
12 g. borax

The borax was dissolved in the water and the mucilage added with stirring. The mixture was stirred for 15 minutes at room temperature and was then filtered (with difficulty) on a fritted glass Buchner funnel. The product was washed once with water and the excess removed by suction. The wet pad of mucilage weighed 217.5 g. and was then separated into three 72.5 g. samples and each suspended in 100 ml. of water. Various quantities of sodium hypochlorite solution were added and the mixture stirred occasionally for several hours until the available chlorine was nearly consumed. Those samples which contained an insufficient amount of chlorine to completely bleach the dark specks were used for further experiments by adding more sodium hypochlorite solution. After bleaching, the products were filtered off, washed with water and air dried.

A second series of experiments was made which differed from the first only in that the borax washed mucilage was resuspended in fresh 3% borax solution for the bleaching procedure. It was thought that a stronger borax solution might effect a saving of chlorine necessary for bleaching. Both series of experiments are summarized in Table I. A control was made by stirring 10 g. of the flame tree mucilage in 100 ml. of 2% borax solution for 45 minutes followed by filtration and washing with water. Yield 8.7 g.

The mucilages were cooked at 2% concentration in water acidulated with HCl to pH = 5.5. The temperature was raised to 80-85° C. and held for 20 minutes.

Results and Discussion

In the first experiments on the bleaching of flame tree mucilage it was found that a considerable quantity of the colored material could be removed by a preliminary washing with borax solution. This effected a considerable saving in the amount of chlorine necessary to bleach the mucilage. The data in Table I indicate that at least 3% of available chlorine is necessary for bleaching of the dark specks present in the mucilage. Perhaps improvements in the preliminary extraction procedure will further reduce the chlorine necessary. Three percent of chlorine gave a product practically free of specks having only a faint yellow color. Increasing percentages of chlorine gave products of increasing brightness

and with 7 to 15% of chlorine pure white mucilages were obtained. These larger quantities of chlorine are unnecessary from a speck standpoint and they were used in these experiments only to determine the effect on cold water dispersibility. The 15 hour bleaching period is also unnecessary since only about one hour is needed for consumption of the major part of the chlorine. Resuspension of the washed mucilage in 3% borax solution instead of water did not decrease the minimum amount of chlorine necessary for bleaching.

The beater evaluation data for the bleached mucilages are presented in Tables II and III. The cooked mucilages at 1.5% addition to the pulp gave very good increases in bursting strength and folding endurance. These increases are as good as those obtained from guar G4-2 mucilage at 1.5% addition to the pulp. It appears that the degree of bleaching up to 10% chlorine does not alter the strength qualities appreciably. At 15% chlorine there was a noticeable decrease in burst and fold.

Addition of the bleached mucilages to the beater as dry powders gave only about 30-50% of the strength attainable by cooking the mucilage prior to pulp addition. This indicates that moderate bleaching did not appreciably increase the cold water dispersibility. That product which had been treated with 15% of available chlorine gave the highest burst and fold increases.

Bleaching with Gaseous Chlorine and Nitrogen Dioxide

Several preliminary attempts to bleach flame tree mucilage by gaseous chlorine and nitrogen dioxide have been made. Neither gas will bleach the mucilage at its normal moisture content (about 7-10% H_2O). It is necessary to increase the moisture in the mucilage to about 15-25% before the bleaching will occur. However, even at this moisture content the bleached product retains a rather deep yellow to orange color which does not disappear. Furthermore, absorption of the gas makes the product strongly acidic thereby enabling continuous acid hydrolysis to occur. Neutralization with ammonia leaves a considerable quantity of ammonium chloride which is also acidic. Some success has been attained by giving the mucilage a preliminary borax extraction followed by passage of the gas through the wet product in amounts insufficient to make the mixture acidic. This procedure probably holds no advantage over bleaching in the aqueous borax solution.

Bleaching of flame tree mucilage during the cooking procedure has been tried to a limited extent. It was found that about 5% of chlorine was necessary to bleach the specks since the extra coloring matter had not been removed by extraction.

It is probable that the borax suspension technique of bleaching could be accomplished at a cost of about one cent per pound of mucilage.

jws/vk

TABLE I

A Summary of the Bleaching Data of Flame Tree Mucilage

Code No.	Per Cent Available Chlorine Added on Mucilage	Time in Hours	Percentage Yield of Original Mucilage	Appearance of Product	Relative Viscosity at 1% 30° C.*
G7-1-573	0.5	2	-	Many specks	-
G7-2-573	1.0	2.5	-	Many specks	-
G7-3-573	2.0	3.0	-	Some specks	-
G7-4-573	2.5	5.0	-	Some specks	-
G7-5-573	3.0	5.0	82.6	Very few specks of light yellow color	21.1
G7-6-573	4.0	4.5	82.6	No visible specks	18.6
G7-7-573	5.0	5.0	82.6	" " "	16.1
		Following Bleached in 3% Borax Solution			
G8-1-573	0.5	3	-	Many specks	-
G8-2-573	1.0	15	-	Many specks	-
G8-3-573	2.0	15	-	Some specks	-
G8-4-573	3.0	15	-	No specks	-
G9-5-573	7.0	16	84.0	No specks White color	-
G9-6-573	10.0	16	82.6	Pure white	-
G9-7-573	15.0	16	80.1	Pure white	-

* Unbleached control 25.1

Table II

Beater Evaluation of Cooked Bleached Flame Tree Mucilages. 1.5% Mucilage on Pulp, Freeness 770, 2% Rosin, 4.5% Alum

File No.	Code No.	Per Cent Chlorine for Bleach	Basis Weight 25x40/500	Bursting Strength Points	Bursting Strength Pts./100 lbs.	Per Cent Increase in Burst	MIT Fold	Per Cent Increase in Fold	Gurley Porosity Sec./100 cc.	Elmendorf Tear g./sheet	Tear Factor
112980	Blank	-	47.0	28.8	61	-	103	-	15	76	1.62
112984	Control	0	47.4	40.6	86	41.0	299	190	16	56	1.18
112981	G7-5-573	3	46.5	38.8	83	36.1	318	208	19	50	1.12
112982	G7-6-573	4	47.2	40.3	86	41.0	298	189	18	54	1.14
112983	G7-6-573*	4	47.3	39.7	84	37.7	293	184	18	55	1.16
112987	Blank	-	47.5	28.1	59	-	57	-	19	78	1.64
112986	G7-7-573	5	46.9	40.8	87	47.5	289	407	19	55	1.17
113053	G9-5-573	7	46.3	37.3	81	37.3	302	446	17	57	1.23
113054	G9-6-573	10	47.3	38.7	82	39.0	319	460	18	61	1.29
113055	G9-7-573	15	46.7	38.4	82	39.0	212	272	18	62	1.33

* Cooked at pH = 5.5

Table III

Evaluation of Bleached Flame Tree Mucilages Added Dry to Beater

113221	Blank	-	48.3	28.6	59	-	38	-	25	80	1.66
113222	G7-6-573	4	48.2	32.1	67	13.5	63	65.8	30	71	1.47
113223	G7-7-573	5	48.6	32.3	66	11.8	62	63.2	26	72	1.48
113224	G9-5-573	7	48.6	31.3	64	8.5	94	147.0	22	68	1.40
113225	G9-6-573	10	47.7	32.0	67	13.5	80	110.0	20	64	1.34
113226	G9-7-573	15	47.8	34.5	72	22.0	137	260.0	23	63	1.32

PROJECT REPORT FORM

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Dr. Rowland
Mr. Swanson

PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 9
DATE June 1, 1944 (typed 6-12-44)
NOTE BOOK 556 573
PAGE 14 to 140 ~~10~~ 10 to 40
SIGNED John W. Swanson

John W. Swanson

THE CONVERSION OF MANNOGALACTAN MUCILAGES IN AQUEOUS BORAX SOLUTIONS

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THE CONVERSION OF MANNOGALACTAN MUCILAGES IN AQUEOUS BORAX SOLUTIONS

Introduction:

The matter of a suitable conversion medium for thinning down the viscosity of mannogalactan mucilages has been a considerable impediment to the progress on this problem. The mucilages hydrate readily in water thereby making it difficult and expensive to isolate the converted products. Alcohols and other organic materials in which the products do not hydrate appreciably are expensive and often unsuitable because of reactivity with the converting agent. These factors have been explained in greater detail in previous reports.

The search for a suitable conversion medium has led to the use of aqueous borax solutions. The work of this report indicates that it is entirely feasible to convert mannogalactans suspended in a water solution of borax. This procedure is simply an application of the property of mannogalactans to form a water insoluble gel in the presence of borax. In this case, the small particles of mucilage do not dissolve because the borax solution presumably surrounds each particle with a layer of the borax gel, thereby, preventing the penetration of a sufficient amount of water to disperse the mucilage.

This report covers some exploratory work upon the conversion of locust bean gum and guar G4-2 by means of sodium hypochlorite in a borax solution. Locust bean gum was used most frequently because of its greater purity and uniformity. At the present time, however, relatively pure guar products have become available and the experimental data obtained from the locust bean gum oxidations have been found to be applicable to this guar with minor changes.

The conversion of mannogalactans in aqueous borax solution is not limited to sodium hypochlorite. It is reasonable to expect that many of the alkaline oxidizing agents used for converting starches may be employed. Sodium peroxide has been tried with success and experiments with other compounds will be investigated as time permits.

Experimental:

Work Done:

Information upon the following points pertinent to this method of converting has been obtained.

1. The possibilities of conversion in borax media and limitations thereof.
2. The relative degree of hydration of the mucilage in various concentrations of borax.

3. The effect of concentration of borax solution upon the speed of conversion, yield and ash content of the converted product.
4. The effects of impurities in the mucilage such as protein and seed coat upon the rate of conversion.
5. Methods of protein removal and purification of mucilages.
6. The quantity of chlorine necessary for conversion of the mucilage.
7. The effect of alkali concentration upon the rate of conversion.
8. The possibilities of these converted mucilages as tubsize adhesives.
9. The possibilities of these products as cold water soluble beater adhesives.

General Conversion Procedure:

17 g. Borax
500 ml. water
50 g. Locust bean gum
91 ml. NaOCl (6.5% Cl_2 and 3.1 N in NaOH)

The borax was dissolved in water and the gum was added to the solution with stirring. The sodium hypochlorite solution was then added and the reaction allowed to proceed with continued stirring. Usually a 6 degree rise in temperature was noted. At the desired time, the mixture was filtered off on a Büchner funnel, washed once with water and air dried. Variations in this procedure are noted in Table II where a summary of the conditions of each conversion is presented. For minute details of individual conversions the notebook should be consulted. The Code No. of each product represents the page and notebook number.

TABLE I

SUMMARY OF PROPERTIES OF LOCUST BEAN GUM TREATED WITH VARIOUS CONCENTRATIONS OF BORAX SOLUTION

Conc. of Borax Per cent	Volume of Hydrated Gum after 24 hrs.	Yield of Product grams	Ash Per cent O.D. basis	H_2O Per cent	O.D. Ash free Yield	Per cent Yield of Manno-galactan
3.4	37	4.7	7.33	15.3	3.64	86.3
2.72	37	4.4	6.82	11.8	3.58	84.8
2.04	40	4.5	5.44	10.7	3.77	89.1
1.36	40	4.3	4.21	10.4	3.68	87.2
0.68	47	4.2	2.41	8.6	3.74	88.6
0.34	54	4.1	1.5	9.2	3.66	86.8
0.17	63	3.9	0.84	9.7	3.48	82.5

Conversion of the Series G72-556 to G78-556.

52 g. Borax
3000 ml. water
1500 ml. NaOCl — 1400 ml. of 2.7 % Cl_2
400 g. Locust bean gum — 100 ml. of 6.5 % Cl_2

The ingredients were mixed in the above order in a 5-liter 3-neck flask fitted with a thermometer, a mercury sealed stirrer and a delivery tube for collection of evolved gases by water displacement. Upon addition of the locust bean gum the temperature increased from 25.0 to 32.5° C. and about 750 ml. of a colorless gas were evolved and collected. Samples of the converting mixture were removed from time to time by siphoning off aliquots. These were filtered and the products washed with 500 ml. of water and air dried. Five samples were obtained varying in conversion time from 6 to 96 hours. The filtrate in each case was analyzed for chlorine and sodium hydroxide. Glycerine was added just prior to determination of the latter property since boric acid is a strong acid only in the presence of a neutral polyhydroxy compound. A summary of the properties of the products may be found in Table III.

The gas evolved during the first hour of the reaction was insoluble in water, neutral, colorless, had a faint odor of bleach liquor, gave a weak test for CO_2, was very unreactive, and appeared to be principally nitrogen. Magnesium metal was burned in a bottle of the gas and when this was dissolved in water an odor of ammonia was noticed. A determination of the density of the gas gave a value of 1.28 - that of nitrogen is 1.25.

Alkaline Extraction for Removal of Protein.

After several preliminary experiments it was found that protein material present in the raw mucilages seriously interfered with the conversion of the mannogalactan. Attempts were made to remove a considerable part of the protein by alkaline extraction. This led to the adoption of the following tentative extraction procedure.

12.8 g. borax
20.0 g. sodium carbonate
500.0 ml. water
50. g. mannogalactan gum.

The borax and sodium carbonate were dissolved in the water and the gum added with stirring. The mixture was stirred for one hour at room temperature and the gum filtered off and resuspended in 500 ml. of water. After a few moments the gum was filtered off and the excess water drawn off. This product was then resuspended in borax solution (of the desired concentration) and converted as before with sodium hypochlorite solution. The products possessing the code numbers G120-556 and beyond were each given this preliminary alkaline extraction prior to conversion. Extraction with 3% borax alone at room temperature was also tried but this procedure gave products of higher nitrogen content and so it was not used. Further work upon an optimum extraction method has given a still better procedure but this was not used on the products of this report.

Results and Discussion:

Preliminary Investigation of the Behavior of Locust Bean Gum in Borax Solutions.

Test tube experiments with both locust bean gum and guar G4-2 demonstrated quite clearly that mannogalactans can be quite readily converted with sodium hypochlorite solution. This led to a more careful study of the procedure which, thus far, has pointed out a number of factors which influence the conversion.

One of the first factors investigated was the permissable range of borax concentration which could be employed from the standpoint of mucilage hydration and solubility. This was done by suspending 5 g. (4.22 g. O.D. ash free) of locust bean gum in 100 ml. of the desired concentration of borax solution. The degree of swelling in milliliters was observed after

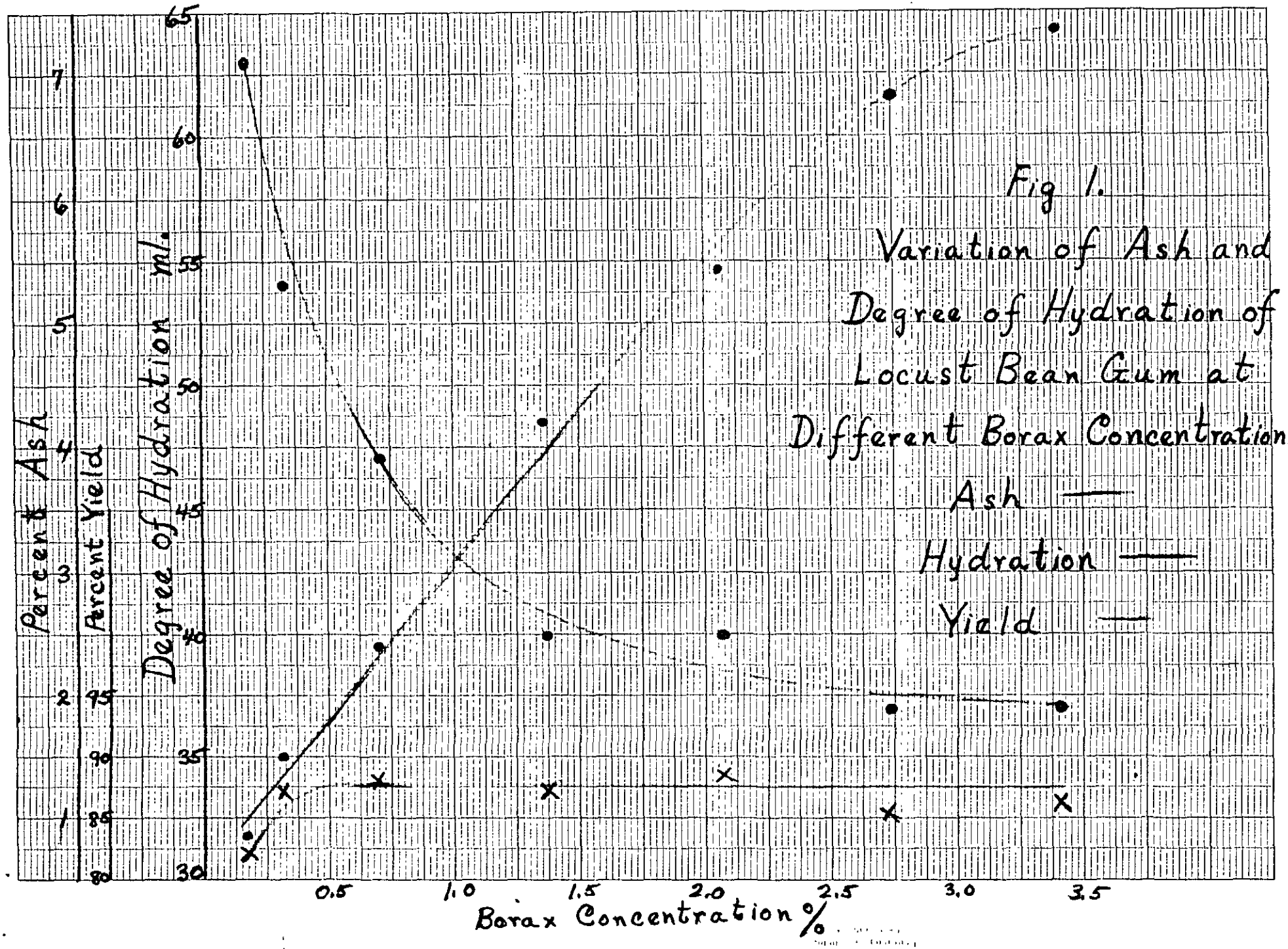


Fig 1.
Variation of Ash and Degree of Hydration of Locust Bean Gum at Different Borax Concentrations
Ash —
Hydration ——
Yield — —

standing 24 hours. The gums were then filtered off and yields determined. The data are presented in Table I and are plotted in Fig. 1. The ash content increased steadily with borax concentration and there seemed to be some tendency for the moisture content to vary similarly. The degree of hydration or swelling was greatest in the lower concentrations of borax and decreased to approach an almost constant value from 2.0-3.5% borax. The percentage yield of recovered mannogalactan was approximately constant (86%) down to 0.3 per cent borax concentration - then a significantly greater amount was lost through solubility. Subsequent experiments have shown that the average yield for a moderately converted mucilage in one to two per cent borax is about 80-85%. This seems rather low upon first examination but it is now known that 6-7 per cent of the raw locust bean gum is protein material, which is soluble in the alkaline medium. Correction for this would bring the yield of mannogalactan up to about 90 per cent. The remaining ten per cent of the mucilage remains unaccounted for. It is possible that this fraction does not form an insoluble complex with borax and is therefore leached out. Perhaps extraction with borax may furnish a better means of fractionation of the various mannogalactan polymers for fundamental studies. One of the most important factors made apparent from these data was that the mucilage may be quite highly swollen without a significant loss in yield. The importance of this lies in the probable heterogeneity of the reaction on particles of mucilage which are not highly swollen. This will be discussed more fully in a subsequent section.

Preliminary Conversions of Locust Bean Gum.

The first attempts to convert 50 g. samples of locust bean gum with sodium hypochlorite solution encountered several puzzling phenomena. When the hypochlorite and gum were mixed a very rapid reaction occurred during which a considerable quantity of a gas was liberated. Starch-iodine tests of the converting mixture gave strongly positive results for chlorine during the first part of the reaction but as the oxidation proceeded the test became less distinct. At about 3-1/2 hours it became negative. This behavior indicated that the available chlorine had been consumed. However, further investigation proved that this was not the case since a considerable quantity of chlorine was found by titration to be present even after 96 hours reaction time. Further experiments indicated that about 80% of the available chlorine was consumed during the first one-half hour of the reaction. The remaining 20% of chlorine was consumed at a slower rate. Also, it was noted that products oxidized for shorter periods of time possessed considerably higher viscosities than those oxidized for longer periods. However, the additional decrease in viscosity caused by the action of the last 20% of the available chlorine was found to be considerably dependent upon the borax concentration and amount of alkali present in the mixture. In other words, it was found that at a definite borax concentration the more sodium hydroxide present the greater the reduction in viscosity. Also lower borax concentrations yielded products having lower viscosities, thereby indicating that the more highly swollen mucilage particles were attacked to a greater extent or perhaps more readily than particles swollen to a lesser extent. See Table II G18-556 to G65-556. It was believed for a time that the viscosity decrease which occurred in the later part of the reaction might be due to air stirred into

the mixture during the long conversion time. An experiment (G111-1-556 and G111-2-556) was made by oxidizing a double batch of mucilage for two hours after which time it was separated into two batches. One half was allowed to continue in the normal manner and air was bubbled through the other for 22 hours. A comparison of the viscosities showed that dissolved air did not appreciably affect the degree of conversion.

A series of converted products (G72-556 to G78-556) were next made by oxidizing a 400 g. batch of locust bean gum and removing samples from time to time. The rate of chlorine consumption and changes in alkali concentration were followed throughout the reaction period of 96 hours. The gases evolved during the first hour of the reaction were collected and later analyzed. The data are given in Table III and are plotted in Fig. 2. The viscostiy of the products decreased rapidly during the first six hours of the reaction but thereafter at a much slower rate, presumably because of the much lower concentration of available chlorine.

The variation in ratio of sodium hydroxide to chlorine present was one of the important findings of this experiment. It was found that the ratio increased sharply during the first ten hours of reaction and thereafter slowly decreased. This may account for the disappearance of the starch-iodine test while chlorine was still present.

Since there was an excess of sodium hydroxide present in the sodium hypochlorite solution it is to be expected that in a purely oxidative type of reaction the ratio of residual sodium hydroxide to residual chlorine should continue to increase with time. The curve in Fig. 2 which illustrates changes in the ratio shows the expected increase during the first hours of conversion but it then attains a maximum and thereafter slowly declines. This seems to indicate that some type of acidic group which neutralizes the excess sodium hydroxide is formed during the reaction. Two possible explanations may be made -

(a) the protein may react with the hypochlorite to form an acidic compound or

(b) uronic acid groups may be formed on the mannogalactan chain.

Some evidence has been obtained for the latter reaction. The filtrates from each of the above converted products were mixed with two volumes of acetone and allowed to stand overnight. This gave in each case about 2.3 g. of a carbohydrate product which was rich in uronic acids. These samples did not possess a reducing value with Fehling's solution but a small amount of a blue precipitate formed. Tests for uronic acid on locust bean gum and the converted mucilage G30-556 gave 1.21% and 1.38% carbon dioxide respectively. It is planned when time permits to analyze the filtrate soluble material quantitatively for carbon dioxide, mannose and galactose. This may lead to a better interpretation of reaction mechanics.

TABLE II

A SUMMARY OF CONVERTING CONDITIONS AND PROPERTIES OF THE CONVERTED MUCILAGES

Code No.	Mucilage Used	Per Cent Borax in Medium during Conversion	Per Cent available Chlorine on Gum	Approximate pH of the Medium	Time of Conversion in Hours	Air dry Yield Grams	Moisture content per cent	Ash per cent O. D.	True Yield Oven dry and Ash free Grams	True Yield Oven dry and Ash free per cent	Relative Viscosity 1% 30°C.	Remarks	
G18-556	Locust Bean Gum	2.8	12.0	12+ *	16	52.1	19.4	15.2	34.1	80.8	222.1		
G19-556	" " "	2.8	12.0	12+	4	52.6	23.4	10.3	34.9	82.8	261.1		
G30-556	" " "	1.12	12.0	12+	54	46.0	14.4	9.62	34.9	82.8	5.9		
G31-556	" " "	2.8	12.0	9.+ **	54	46.7	15.4	9.1	35.3	83.8	296.8	Added 9.3ml. Con.HCl	after NaOCl
G31-556	Extracted 15g. with 400ml. water one hour air dried					12.9	8.3	2.63	11.5	100.0	273.3	Extracted to reduce	ash content
G32-556	Locust Bean Gum	2.8	12.0	12+	54	45.6	12.8	9.91	35.2	83.5	132.3		
G51-556	" " "	1.12	12.0	12+	72	47.7	18.4	8.73	34.8	82.5	5.2	This was a double	size batch
G65-556	" " "	1.12	12.0	9.+ **	20	41.7	9.5	5.35	35.5	84.2	91.8	1% $CoCl_2 6H_2O$ added	as catalyst
G72-556 - G78-556	See Table III.												
G114-8-556	Locust Bean Gum	1.57	22.0	12+ ***	6.0	14.9	12.0	7.38	--	--	1.68	Two Stage Chlorination	
G120-556	" " "	1.57	11.0	12+ ***	5.5	29.0	11.2	6.27	--	--	15.7	Had previous Alkaline	Extraction
G125-556	" " "	1.57	11.0	12+ ***	5.5	27.3	13.9	6.73	--	--	23.8	Same as G120-556	but $CrCl_3$ a
G131-556	" " "	1.57	11.0	14 ($\frac{3}{NaOH}$)	5.5	33.2	14.0	11.2	--	--	3.9	Oxidation in strong	(3N) alkali
G10-573	" " "	1.57	11.0	7.2	2.0	--	--	--	--	--	--	Gum hydrated too	much (disca
G17-573	" " "	1.57	11.0	7.7	2.0	48.2	21.5	8.91	33.6	79.6	6.8	Buffered at pH = 7.7	
G58-556 G4-2		1.12	12.0	12+ *	43.0	41.5	9.4	5.54	34.8	76.3	9.26		
G59-556 G4-2		1.12	12.0	8.+ **	42.0	41.7	9.0	4.63	36.0	78.9	64.6		
G90-7-556 G4-2		1.57	22.0	12+ ***	3.0	13.5	9.4	4.49	--	--	25.7	Two Stage Chlorination	
G111-1-556 G4-2		1.3	11.0 + air	12+ ***	24.0	32.5	8.2	4.43	28.4	68.2	54.3	Air bubbled through	for 22 hour
G111-2-556 G4-2		1.3	11.0	12+ ***	24.0	40.0	10.4	4.13	34.2		50.7		

* NaOCl Used was 6.5% Cl_2 and 3.7 N NaOH.
** " " " 2.7% Cl_2 " 0.97 N NaOH.
*** " " " 7.4% Cl_2 " 2.7 N NaOH.

TABLE III

A SUMMARY OF CONVERSION CONDITIONS AND PROPERTIES OF CONVERTED LOCUST

Bean Gums G72-556 to G78-556.

Borax Concentration 1.15%
Available Chlorine (on gum) at beginning 11%

Code No.	Conversion Time in Hours	Weight of air dried sample	Analysis of Filtrate Basis - Original total Total Chlorine grams	Total NaOH grams	Ratio NaOH Chlorine	Analysis of Sample Moisture %	Ash %	Relative Viscosity 1% 30° C.	Weight of Sample from filtrate. grams
--	0	0	43.7	53.5	1.22	--	--	about 1000	--
--	1	0	3.98	5.63	1.42	--	--	--	--
G72-556	6	76.7	1.68	4.14	2.46	13.7	4.87	195.0	2.293
G73-556	24	77.3	1.10	2.70	2.46	15.45	4.94	--	2.367
G76-556	48	77.5	0.91	2.16	2.38	15.4	4.64	--	2.605
G77-556	72	58.1	0.79	1.80	2.38	13.9	4.62	152.0	2.484
G78-556	96	63.5	0.75	1.62	2.16	14.8	4.67	143.0	2.384
Total		353.1							12.133

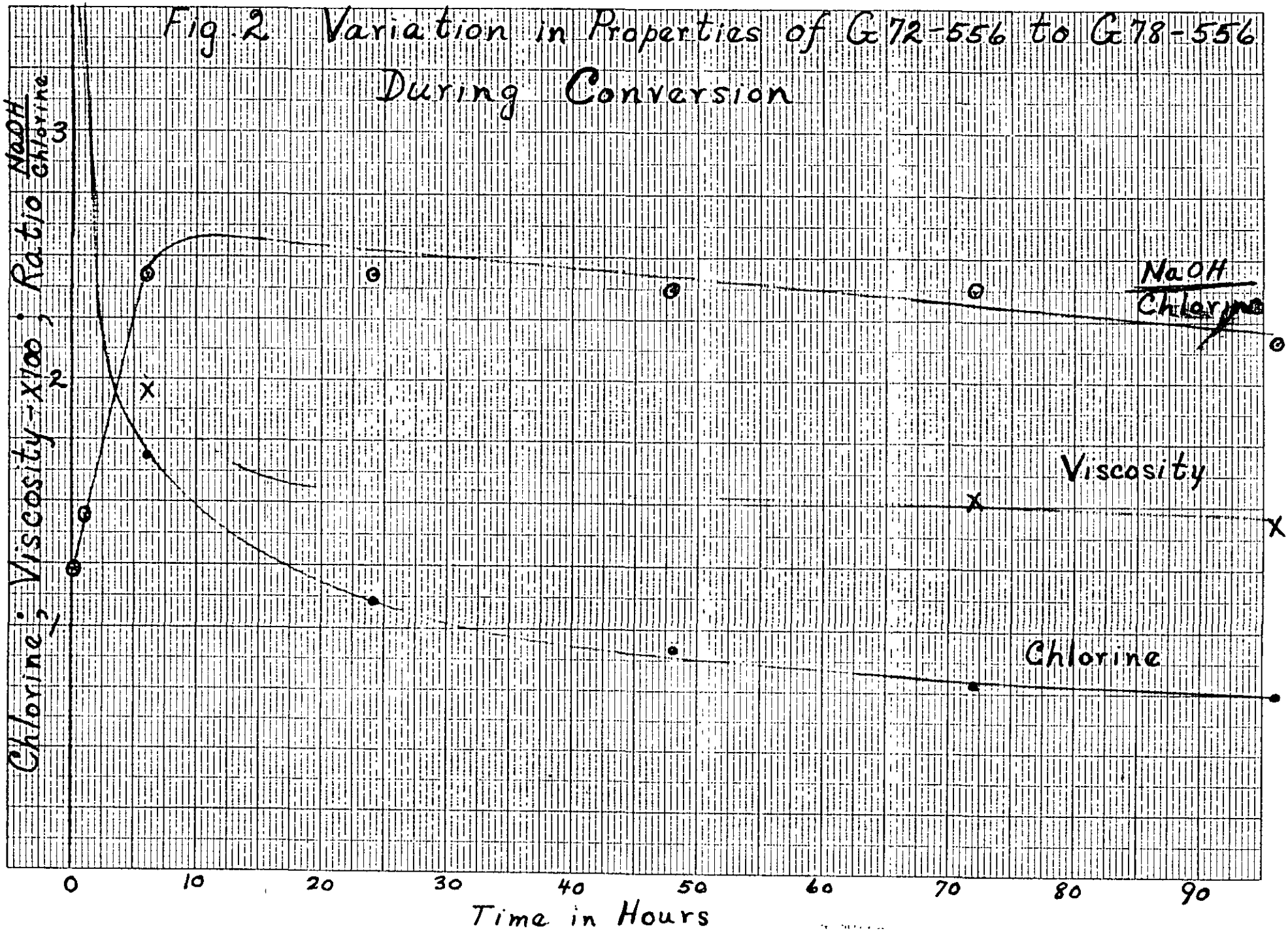


Fig. 2 Variation in Properties of G 72-556 to G 78-556
During Conversion
Chlorine, Viscosity ÷ 100, Ratio NaOH / Chlorine
Chlorine
Viscosity
NaOH / Chlorine
0
10
20
30
40
50
60
70
80
90
Time in Hours

The Effect of the Protein Content of the Mucilage on the Conversion Reaction.

The gas evolved during the initial part of the conversion of products G72-556 to G78-556 was collected by water displacement. About 750 ml. were obtained. Tests upon the gas indicated that a mere trace of CO_2 was present and that the remainder was nitrogen. Presumably this resulted from the oxidation of protein material in the mucilage. However, this is unusual because ammonia, an aldehyde and carbon dioxide are usually obtained by oxidation of protein.

Several experiments were made to determine the possible influence of the nitrogen or protein content of the mucilage on the chlorine consumption. Two two-stage conversions were made, one with locust bean gum and the other with guar G4-2. The conversions were started with 11% of available chlorine and at 105 minutes an additional 11% of chlorine was added. The rate of chlorine consumption was determined by titration of available chlorine at various intervals. The conversions were labelled G90-556 for G4-2 and G114-556 for locust bean gum. These experiments were followed by converting products which had been first extracted with a solution of borax and sodium carbonate to remove some of the protein. The data are given in Table IV and are plotted in Fig. 3

The curves of Fig. 3 indicate that the conversion reaction is quite dependent upon the amount of protein present in the raw mucilage. It required about 13% of chlorine to change the rate of oxidation of locust bean gum but about 20% for the G4-2 mucilage which had a somewhat higher protein content and considerable seed coat material. (For protein multiply nitrogen x 6.25). When the raw gums were previously extracted with alkali to remove some of the protein a much different curve resulted. Only about 5% of chlorine was then required to change the rate of oxidation. It is believed that the reaction of sodium hypochlorite with protein is much more rapid than with mannogalactan. Thus, when the reaction begins both protein and mannogalactan are oxidized but the reaction with protein is so much more rapid that as long as a significant amount of protein remains, the gum, relatively speaking, is only slightly attacked. Only after the protein has been oxidized does the attack take place principally upon the gum. Therefore, it appears that impurities in the raw mucilages will certainly play a significant role in conversion and it would seem to be advantageous to remove as much of the protein as possible. Since the present G4-2 mucilage varies considerably in protein content from batch to batch (See Table V) and contains nearly 20% of inert seed coat material, which no doubt consumes chlorine too, much of the work thus far has been done with locust bean gum. Recently, however, General Mills Inc. has produced a fairly uniform guar G44 mucilage essentially free from seed coat. Several trial conversions of this mucilage have been quite successful.

TABLE IV

COMPARATIVE DATA ON THE RATE OF CHLORINE CONSUMPTION
UNDER VARIOUS EXPERIMENTAL CONDITIONS

G90-556 Guar
Not Alkaline Extracted
Nitrogen = 1.16%

Conversion Time in Minutes	Total grams Chlorine present
0	5.5
15	0.75
45	0.63
90	0.53
105 added more NaOCl	6.03
110	1.62
115	1.42
135	0.90
150	0.78
180	0.68

G114-556 Locust Bean Gum
Not Alkaline Extracted
Nitrogen = 1.07%

Conversion Time in Minutes	Total grams Chlorine present
0	5.6
5	2.1
25	1.05
60	0.75
95	0.65
105 added more NaOCl	6.10
115	5.14
120	5.00
135	4.60
190	4.11
360	2.70

G120-556 Locust Bean Gum
Alkalaine Extracted
Nitrogen = 0.56%

Conversion Time in Minutes	Total grams Chlorine present
0	5.55
10	3.62
20	3.04
45	2.60
120	2.08
330	1.50

G125-556 Locust Bean Gum
Alkaline Extracted

Conversion Time in Minutes	Total grams Chlorine present
0	5.57
10	3.54
25	2.93
45	2.67
65	2.39
70 added 2 ml. 1% $CrCl_3.xH_2O$	--
75	2.20
110	2.06
200	1.77
330	1.55

TABLE IV (continued)

COMPARATIVE DATA ON THE RATE OF CHLORINE CONSUMPTION
UNDER VARIOUS EXPERIMENTAL CONDITIONS

G131-556 Locust Bean Gum
Alkaline Extracted (Reaction in 3N NaOH)

Conversion Time in Minutes	Total grams Chlorine present
0	5.66
10	3.12
25	2.51
60	2.11
120	1.82
200	1.52
330	1.23

G17-573 Locust Bean Gum
Alkaline Extracted (Reaction at pH = 7.7)

Conversion Time in Minutes	Total grams Chlorine present
0	5.6
3	3.36
14	2.28
30	1.74
60	1.22
120	0.84

G55-573 Guar G4-2
Alkaline Extracted
Nitrogen = 0.37%

Conversion Time in Minutes	Total grams Chlorine present
0	5.5
20	2.8
60	2.43
180	1.77
330	1.28
390	1.11

G10-573 Locust Bean Gum
Alkaline Extracted (Reaction at pH = 7.2)

Conversion Time in Minutes	Total grams Chlorine present
0	5.6
12	1.94
24	1.48
120	0.53

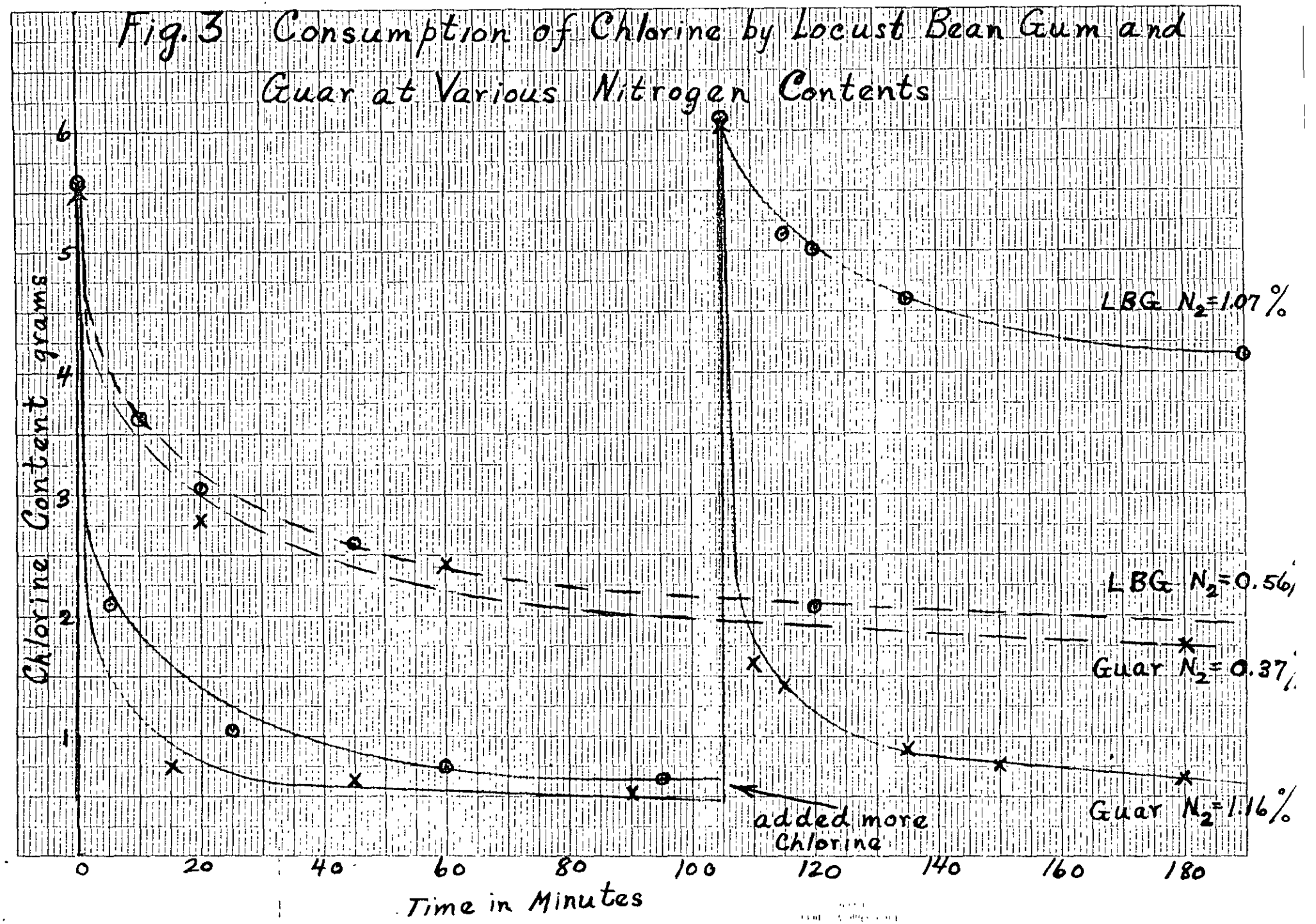
G57-573 Guar G4-2
Alkaline Extracted
Reaction at pH = 7.5

Conversion Time in minutes	Total grams Chlorine present
0	5.5
30	1.37

G63-573 Guar G44
Alkaline Extracted
Reaction at pH = 12

Conversion Time in Minutes	Total grams Chlorine present
0	5.5
15	2.67
60	2.01
100	1.55
180	1.22
300	0.57
360	0.40

Fig. 3 Consumption of Chlorine by Locust Bean Gum and Guar at Various Nitrogen Contents



Extraction of Protein

The best method of extracting the protein material from the mucilage has not as yet been devised. Several methods have been tried using the residual nitrogen content as a measure of effectiveness. Locust bean gum which had been extracted for one hour with a 3% borax solution had a higher nitrogen content than when it had been extracted with a solution 2.5% in borax and 4% in sodium carbonate. Therefore, in most cases the latter procedure was used for protein removal prior to conversion.

TABLE V

PROTEIN CONTENT OF VARIOUS MUCILAGES

File No.	Code No.	Extraction Procedure	Moisture %	Ash %	Nitrogen * %	Protein % 6.25
112251	Raw Locust Bean Gum	none	13.01	0.86	1.07	6.69
113141	Locust Bean Gum G34-1-573	One hour with Borax and Na_2CO_3 Room Temp.	15.30	9.29	0.56	3.50
113142	Locust Bean Gum G34-2-573	One hour with Borax Solution Room Temp.	14.66	3.96	0.63	3.94
113165	Locust Bean Gum G17-573	Converted Extracted Gum in Borax Solution	21.01	8.85	0.20	1.25
112668	G4-2 - 3/3/44 G4-2	none	8.26	1.82	1.16	7.25
112669	G116-556 G4-2	One hour with Borax and Na_2CO_3	12.24	6.39	0.51	3.18
113166	G58-556 G4-2	Converted in Borax and Strong NaOH	9.87	5.86	0.21	1.31
113167	G59-556	Converted in Borax and Weak NaOH	8.88	4.86	0.12	0.75
112193	G4 Old G4-2	none	--	--	0.69	4.32
112194	12/10/43 New G4-2	none	--	--	0.89	5.56
112195	2/4/44 G4-2	none	--	--	2.44	15.25
112647	Neenah Paper Co. G4-2	none	6.60	--	2.61	16.30
112648	Gilbert Paper Co. G4-2	none	6.24	--	1.55	9.68
112920	4/7/44 G44	none	6.11	1.97	0.98	6.12
112919	4/6/44	none	5.60	1.41	1.10	6.87
113288	G4-2	0.5 hour in 3% Borax at 50°C	9.70	3.69	0.37	2.30

*Nitrogen on O.D. basis and where data are available it is also on ash free basis.

Subsequent to the experiments of this report a better extraction procedure was devised and has been used in recent conversions. It was found that extraction of the mucilage for 0.5 hour in 3% borax solution at 50° C. yielded a product of lower nitrogen content than the above preferred method. It should be mentioned that this method still removes only about 65% of the protein. Further experiments will no doubt result in procedures giving more complete removal. On the other hand, it is possible that a certain amount of residual protein may be desirable during the conversion to bear the strongly degradative effects which are present during the first part of the reaction when the hypochlorite is more concentrated. It must be mentioned, however, that the lower the protein content prior to conversion the less chlorine will be required to convert the mannogalactan to a desired viscosity. Interestingly enough, even the converted products contain appreciable amounts of nitrogen (0.1-0.2%). This may or may not be proteinaceous in character. It is believed that this nitrogen may be present in the skin substance which surrounds each mucilage cell. A further study of this substance has been planned.

The Effect of Alkali Concentration and pH on the Rate of Conversion.

Several conversions of both guar and locust bean gum have been carried out at different pH to investigate, in a preliminary way, the effect on the rapidity of the reaction. It has been found that the oxidation is greatly affected by the pH or alkali concentration. The data on rate of chlorine consumption are given in Table IV. They are also plotted in Figures 4 and 5 where the rates of chlorine reaction are plotted against time. The shapes of the curves indicate that pH must be a significant factor in the rate of reaction. Thus, using as a basis the time necessary for locust bean gum (Fig.4) to utilize 3.5 g. or 64% of the available chlorine present, it may be seen that at pH = 12 about 160 minutes were required while in 3N NaOH 70 minutes were necessary. The most rapid reactions took place at pH = 7.7 (22 minutes), and pH = 7.2 (12 minutes). Similar reaction times were observed for two cases of guar mucilage (Fig. 5). A guar G44 oxidation (G63-573) proceeded more rapidly at pH = 12 than did G4-2. At present this can not be explained adequately. However it should be mentioned that the differences in the two curves are not the results of experimental error. Curves of any one mucilage can be reproduced quite closely.

A thorough interpretation of the reaction mechanics involved at different pH must wait until we have obtained more conclusive data. However, a logical interpretation can be made by analogy from information available upon the sodium hypochlorite oxidation of cellulose. This will give us somewhat of a working hypothesis upon which to plan further experiments. It is well known that bleaching of cellulose takes place most rapidly in a neutral medium and that as the pH increases so does the necessary reaction time. The greater reactivity near the neutral point is explained on the knowledge that two types of oxidant - hypochlorite ion and hypochlorous acid - are present under these conditions. As the pH increases less hypochlorous acid is present

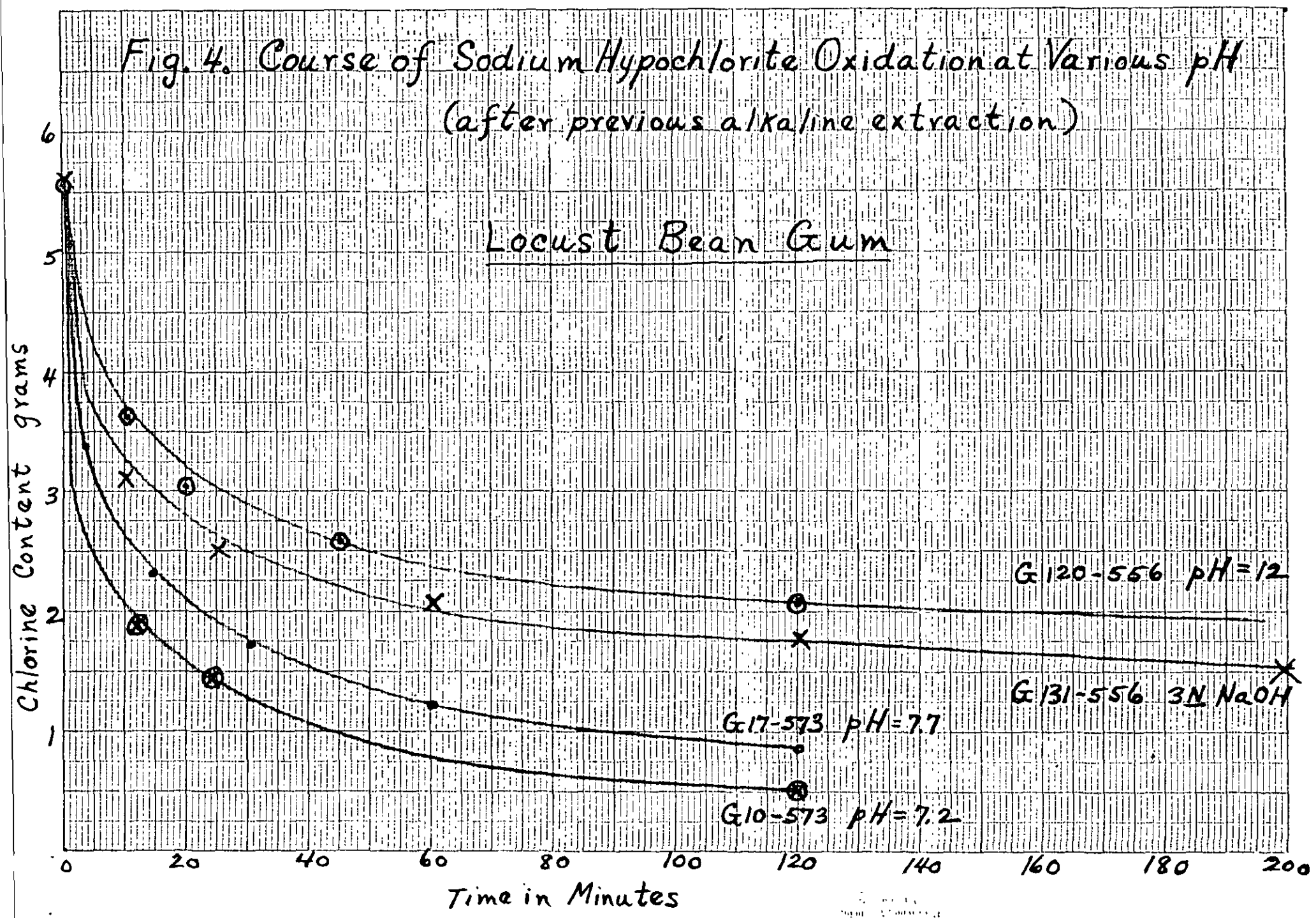


Fig. 4. Course of Sodium Hypochlorite Oxidation at Various pH
(after previous alkaline extraction)
Locust Bean Gum
Chlorine Content grams
Time in Minutes
G 120-566 pH = 12
G 131-556 3N NaOH
G 17-573 pH = 7.7
G 10-573 pH = 7.2
0
20
40
60
80
100
120
140
160
180
200
1
2
3
4
5
6

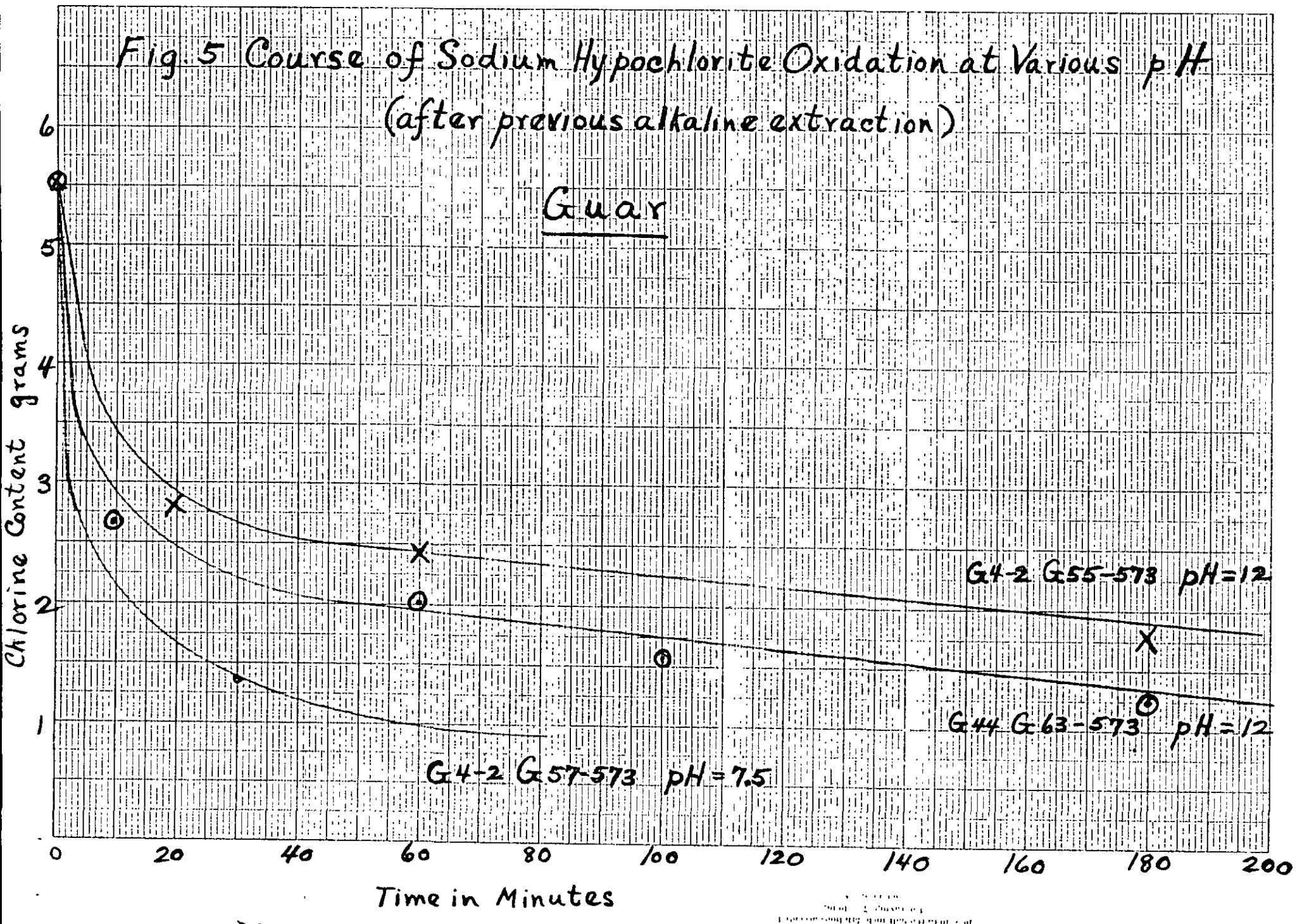


Fig 5 Course of Sodium Hypochlorite Oxidation at Various pH
(after previous alkaline extraction)
Guar
Chlorine Content grams
Time in Minutes
G4-2 G55-573 pH=12
G44 G63-573 pH=12
G4-2 G57-573 pH=7.5
0
20
40
60
80
100
120
140
160
180
200
1
2
3
4
5
6

and oxidation becomes slower. This same interpretation should hold true with oxidation of mannogalactans and an additional factor - that of swelling near a neutral pH - should enable better penetration of the oxidizing agent and promote the reaction. Again referring to cellulose, as the alkalinity is further increased to the range of very strong alkali, i.e. 3N NaOH, very rapid oxidation occurrs. This is explained by the mercerizing action of the alkali on the cellulose which enables the oxidizing agent to penetrate the structure more easily. A similar interpretation might be made for the more rapid oxidation of mannogalactan in 3N NaOH. (See G131-556 in Fig. 4).

Due care must be exercised during reactions carried out at lower pH values. The mannogalactan must, of course, remain insoluble in the conversion medium and therefore the pH must not be allowed to come too close to the neutral point for there, solubilization begins immediately. Boric acid has no insolubilizing action on the mucilage. Since sodium hypochlorite solutions characteristically produce HCl during their reaction, the alkalinity decreases and if an insufficient quantity is present the pH will fall rapidly toward the neutral point. Therefore, when carrying out oxidations at pH close to the neutral point the mixture must be watched very closely and either a strongly buffered medium must be used or occasional additions of alkali must be made. High alkali concentrations, insofar as we have investigated, do not cause an appreciable solubilization above that taking place at mildly alkaline pH.

It is possible that the optimum type of conversion would be one in which the initial pH is high enough so that the final pH would end at about 7.5. This would enable the first part of the reaction to proceed rapidly under alkaline conditions because of the high concentration of sodium hypochlorite. The latter part of the reaction would also proceed rapidly because of low pH and the swelling of the mannogalactan. This would give the shortest time of conversion and highest economy of chlorine.

The Evaluation of the Converted Mucilages as Tubsize Adhesives.

Several of the converted locust bean and guar gums were used as tubsize adhesives at one per cent concentration and 50° C. on a 100 per cent rag stock. The tubsize solutions were made up by cooking the converted gums in water containing enough acid to bring the pH to about 5.5. The amount of acid necessary varied with the ash content of the converted gum. Some variations in temperature and percentage of application were also made. The low concentration of tubsize solution was used for two reasons (a) some of the products were too viscous to be used at higher concentrations and (b) it was believed that outstanding adhesive characteristics would be more evident.

The converted locust bean gum products appear to be particularly outstanding tubsize adhesives. (See Table VI). At one per cent concentration the optimal converted gums gave burst increases of 30-35% and fold increases of 50-80%. Of course, the most viscous mucilages in several cases gave somewhat lower strength increases but this may be attributed to less penetration of the sheet during tubsizing. Strength increases of the above

magnitude are realized with starches only at much higher concentrations. Typical data for two starches, Superfilm No. 4 at 3% and Satin Hercules at 5% concentration are given in Table VI.

Tubsizing with a one percent solution of the mucilage does not show the maximum strength qualities attainable because insufficient mucilage is picked up or absorbed to form a continuous film on the fibers of the sheet. Measurement of the amount of mucilage picked up during tubbing was made by weighing the paper before and after entering the tub. The concentration of solution being known (1%), the mucilage remaining in the sheet could be calculated from the weight of the wet sheet. By this method it was found that only 0.4% of mucilage was applied to the sheet. An experiment was made to show the effect of a more continuous film coverage of the fiber. One sheet was tubsized with a solution containing one per cent of a converted starch and a second sheet was tubsized with a 3 per cent solution of the same starch. The former solution gave a 39.4% increase in burst and the latter a 26.7% increase. An experiment at higher concentration of mucilage alone was made with gum G51-556. Although this product was not particularly outstanding when used as a one per cent tubsize, at 3.5% it gave a 45.6% increase in burst and a 140% increase in both directions of folding endurance. These values are scarcely attainable with starch at any concentration or temperature of application on this sheet conditioned at 50% relative humidity and 73° F.

The converted guar mucilages (Table VII) did not show tubsize characteristics as good as the locust bean gums. This was primarily due to the large amount of impurities present, principally seed coat. Therefore the actual concentration of mucilage was about 0.8% rather than one per cent - a difference sufficient to account for the lower strength values. No doubt if the solutions had been made up on the basis of mannogalactan present they would have equalled locust bean gum products.

An Evaluation of Some of the Converted Products as Cold Water Soluble Beater Adhesives.

One of the ultimate goals of the application of mucilages to the paper industry is to make a product which is cold water soluble. This means a product that can be added to a beater in the form of a dry powder and be expected to fully disperse during the period of beating. During some experiments it appeared that the oxidized mucilages dissolved rather easily in cold acidified water and might possibly serve the purpose as a dry addition beater adhesive.

TABLE VI

TUBSIZE CHARACTERISTICS OF THE LOCUST BEAN GUMS CHLORINATED IN A BORAX MEDIUM

File No.	Code No.	Tubsize Conditions: Per cent Solids	Tubsize Conditions: Temperature °C.	Relative Viscosity at 1% 30°C.	Basis Weight 17x22/500 lb.	Caliper - inch	Bursting Strength: Points	Bursting Strength: Pts./100#	Per cent Increase in Burst	M I T Fold: In	M I T Fold: Across	Per cent Increase in Fold: In	Per cent Increase in Fold: Across	Gurley Porosity Sec/100 cc.	Elmendorf Tear g./sheet: In	Elmendorf Tear g./sheet: Across	Schopper Tensile lb./inch: In	Schopper Tensile lb./inch: Across
	Average Blank	--	--	--	18.7	0.0033	29.9	160	--	217	57	--	--	225	92	102	26.0	13.0
112070	G18-556	1.0	50	222.	19.9	0.0039	39.9	201	25.6	347	100	60.0	75.4	302	102	107	--	--
112071	G19-556	1.0	50	261.	19.7	0.0038	40.4	205	28.1	297	98	36.9	72.0	294	100	111	--	--
112072	G19-556	1.0	61	261.	19.7	0.0039	40.6	206	28.8	285	123	32.3	116.	300	99	113	--	--
112135	G30-556	1.0	50	5.9	18.8	0.0039	38.0	202	26.2	321	90	52.6	57.9	188	94	108	--	--
112137	G31-556	1.0	50	296.8	19.0	0.0039	37.2	196	22.5	321	90	52.6	57.9	230	93	111	--	--
112139	G32-556	1.0	50	132	19.2	0.0039	39.9	208	30.0	395	83	77.4	45.6	230	98	110	--	--
112198	G51-556	1.0	50	5.2	19.6	0.0039	38.4	196	22.5	290	80	33.6	40.4	197	95	116	--	--
112200	G51-556	3.5	50	26.0 (2%)	19.5	0.0039	45.5	233	45.6	526	142	142.	149.	332	92	105	--	--
112540	G65-556	1.0	50	91.8	19.2	0.0039	41.1	214	33.8	421	82	94.1	43.8	234	90	103	--	--
112541	G72-556	1.0	60	195.0	19.3	0.0039	39.5	205	28.1	409	86	88.5	50.9	257	92	106	--	--
112543	G77-556	1.0	60	152.0	19.3	0.0038	40.0	207	29.4	407	98	87.6	72.0	256	95	109	--	--
112544	G78-556	1.0	60	143.0	19.3	0.0038	40.3	209	30.6	369	96	70.1	68.4	238	93	110	--	--
112766	G114-8-556	1.0	50	1.68	19.3	0.0038	36.3	188	17.5	324	72	49.4	26.4	171	93	105	27.5	13.6
112767	G120-556	1.0	50	15.7	19.0	0.0038	40.8	215	34.4	354	88	63.2	54.4	207	92	103	29.2	14.2
112769	G125-556	1.0	50	23.8	19.1	0.0038	38.9	204	27.5	366	88	68.7	54.4	221	90	101	29.4	14.0
112812	G131-556	1.0	50	3.9	18.9	0.0037	40.7	215	34.4	395	81	82.1	42.1	188	92	103	29.0	14.2
113079	G17-573	1.0	50	6.8	19.0	0.0040	39.7	209	30.6	413	93	90.3	63.2	193	94	106	--	--
112815	1% G30-556+G51-556 + 2% Superfilm No. 4	3.0	50	8.85	19.0	0.0038	42.3	223	39.4	397	86	83.0	50.9	206	88	104	30.1	14.5
112816	Superfilm No. 4	3.0	50	1.63 (2%)	19.1	0.0038	38.7	203	26.9	379	83	74.7	45.6	174	92	100	28.7	14.2
111614	Satin Hercules	5.0	50	1.60 (2%)	20.7	0.0041	42.4	205	28.1	429	122	97.8	114.0	249	97	107	31.7	14.6

Note: All sheets conditioned at 50% Relative Humidity and 73° F.

Several divergent types of converted mucilage were evaluated in this way. One per cent of the converted gums (O. D. and ash free) were added to the beater early in the beating cycle along with 2% of rosin and 4.5% of alum. For comparison the same mucilages were also cooked and added to the pulp.

The data are in Table VIII. It appears that two of the earliest converted products (G19-556 and G30-556) are fairly good cold water beater adhesives but, the remainder of the products do not disperse very well under these conditions. The reason for the G19 and G30 products dispersing more completely is not at present explainable. Certain differences in conversion procedure may account for it. These products were the only ones of the group which were not alkaline extracted to remove the protein prior to conversion and they were washed with borax solution following their conversion. It was unfortunate that not enough sample of G30-556 was available to evaluate it after cooking. However, the strength values, particularly the burst, are sufficiently high to commend the product without this comparison.

Raw locust bean gum, which had been treated with strong alkali, has the property of dispersing quite readily in cold acidulated water. It was believed that this method might possibly be a better way of making a cold water soluble mucilage. The gum (G27-573 Table VIII) was made by treating locust bean gum with 50% sodium hydroxide for 5 hours at room temperature. It is evident from the data that this product was not readily soluble in the white water of the beater. However, it dissolves readily when a water suspension is acidified with hydrochloric or acetic acids. It is possible that the alum may have interfered with the beater dispersion. This same factor may have influenced the results obtained with the oxidized mucilages.

TABLE VII

TUBSIZE CHARACTERISTICS OF G4-2 GUMS CHLORINATED IN A BORAX MEDIUM

File No.	Code No.	Tubsize Conditions: Per cent Solids	Tubsize Conditions: Temperature °C.	Relative Viscosity at 1% 30°C.	Basis Weight 17x22/500	Caliper - inch	Bursting Points	Strength Pts./100#	Per cent Increase in Burst	MIT Fold: In	MIT Fold: Across	Per cent Increase in Fold: In	Per cent Increase in Fold: Across	Gurley Porosity Sec./100cc.	Elmendorf Tear G./Sheet: In	Elmendorf Tear G./Sheet: Across	Schopper Tensile lb/inch: In	Schopper Tensile lb/inch: Across
	Average Blank	--	--	--	18.7	0.0033	29.9	160	--	217	57	--	--	225	92	102	26.0	13.0
112355	G58-556	1	50	9.26	19.3	0.0040	38.4	199	24.4	230	62	6.0	8.8	181	95	107	--	--
112353	G59-556	1	50	64.6	19.2	0.0040	37.8	197	23.1	327	56	50.7	--	194	95	108	--	--
112762	G90-556	1	50	25.7	19.0	0.0038	36.8	194	21.2	252	67	16.1	17.5	199	93	104	28.3	13.4
112763	G111-1-556	1	50	54.3	19.2	0.0038	35.3	184	15.0	267	58	23.0	1.7	195	102	106	27.3	13.2
112764	G111-2-556	1	50	50.7	19.3	0.0038	36.8	191	19.4	234	61	7.8	7.0	189	94	115	27.6	13.0

TABLE VIII

BEATER EVALUATION OF SOME OF THE CONVERTED LOCUST BEAN GUMS

One Per cent Addition – Rosin size 2%; Freeness 720. Alum 4.5%.

File No.	Code No.	Manner of adding gum to pulp	Basis Weight 25x40/500	Caliper - inch	Apparent Density	Bursting Strength Points	Bursting Strength Pts./100#	Per cent Increase in Burst	MIT Fold	Per cent Increase in Fold	Thwing Formation	Gurley Porosity Sec./100cc.	Elmendorf Tear g./sheet	Tear Factor	Schopper Tensile lb/inch
Average Blank for dry addition			46.5	0.0043	11.0	24.6	53	--	56	--	--	24	80	1.72	14.8
Average Blank for cooked addition			47.2	0.0043	11.0	26.9	57	--	73	--	--	23	81	1.70	14.1
112133	G19-556	Dry powder	46.4	0.0043	11.0	40.1	86	62.3	271	384	44.4	14	65	1.40	19.4
113250	G19-556	Cooked	49.9	0.0044	11.0	45.1	90	58.0	353	384	--	31	53	1.06	23.7
112134	G30-556	Dry powder	46.3	0.0044	10.5	40.3	87	64.1	268	379	43.0	13	64	1.38	18.1
		Insufficient sample for cooked addition													
113144	G131-556	Dry powder	48.3	0.0043	11.5	33.7	70	32.1	214	282	--	41	61	1.26	19.8
113239	G131-556	Cooked	47.0	0.0043	11.0	40.3	86	50.9	451	518	--	26	57	1.21	18.8
113143	G17-573	Dry powder	48.2	0.0042	11.5	35.1	73	37.8	269	381	--	26	58	1.20	20.3
113241	G17-573	Cooked	48.3	0 0044	11.0	42.0	87	52.6	467	540	--	25	58	1.20	20.2
113145	G27-573	Dry powder	48.5	0.0043	11.0	31.8	66	24.6	272	384	--	39	62	1.28	18.2
113251	G27-573	Cooked	48.9	0.0044	11.0	42.7	87	52.6	418	473	--	24	52	1.06	24.1
110035	Raw locust bean gum	Dry powder	48.3	0.0043	11.0	42.1	87	52.6	343	370	40.9	18	58	1.20	21.3

Note: All sheets were conditioned at 50% Relative Humidity and 73° F.

The Problem of Cold Water Solubility

Microscopic examinations of the behavior of mucilages in the presence of acids and alkalis have been made. It was observed that strong alkali has no apparent swelling or dispersive action on the mucilage cells but strong acids cause instantaneous dispersion of the mucilage. Apparently the membrane surrounding each mucilage cell is of a selective type and is permeable to acids but impermeable to alkalis. This phenomenon should be further investigated. It may possibly be a type of anomalous osmosis or a Donnan equilibrium in which the mucilage is acting as a group of negatively charged micelles within the cell wall which is impermeable to the micelles but permeable to the ions of the acid on the outside.

It is now believed that the problem of cold water solubility is not one of making the mucilage soluble, it is one of making the cell wall easily ruptured or soluble in cold water.

A Discussion of Possible Limitations of the Conversion Method.

Conversion of mannogalactans in borax solution at room temperature perhaps cannot be carried out to give products of extremely low viscosity such as might be required for high solids coating work. There seems to be a general trend that the greater the degree of conversion the higher the concentration of borax necessary for formation of the insoluble gel. It seems reasonable to expect that at any definite borax concentration there would be a degree of conversion beyond which the yield would decrease rapidly because of solubilization. This has been noted at low borax concentrations (0.5-1.0%) with products which have been converted only to a medium extent. The use of a saturated solution of borax at room temperature (3.5%) will of course make more highly converted products possible. But even at 3.5% concentration a limit should be expected. At this point it might be advantageous to convert at a higher temperature where a more concentrated solution of borax may be obtained: for example, 10.5% at 50° C. This would be an advantage only on the condition that the increased borax concentration had a greater effect on insolubilization than the higher temperature had on solubilization. Conversions of this type would have to be made at a fairly high pH since it is believed that lowering the pH of conversion is equivalent to decreasing the effective borax concentration. This should be more fully investigated. Possibly, reactions at higher temperatures would be more rapid but they might also give a more heterogeneous type of conversion.

The subject of the residual ash content of the converted mucilages may be important in certain applications such as coating. It would be a definite advantage to remove the ash entirely from the finished product but no feasible method of doing so is known at the present time. A considerable amount of the ash can be extracted from the mucilage by suspending for a time

in water and following by filtration. The ash on one product was lowered from 9.1% to 2.6% by this method without any loss in mannogalactan. This product was not highly converted and it is to be expected that a significant loss of carbohydrate would occurr with products of low viscosity. Further work should be done upon this subject. One of the noticeable results of lowering the ash content is that the products dry to an extremely hard material which is powdered with difficulty. These materials do not disperse quite as well in cold acidulated water as do those which dry to easily powdered gums.

The Economics of the Conversion.

The present method of converting the mucilage probably is not the optimum. Much work remains to be done and without doubt this will improve the procedure from both an economical angle and a more desirable final product. However, the following rough approximation of the cost of the materials for the present conversion will be made.

For a 1000 pound conversion the following chemicals would be necessary.

200 lbs. chlorine per $0.0175	=	$3.50
300 lbs. borax per $0.021	= $6.30 (Use at least 3 times)	= 2.10
260 lbs. caustic soda per $0.023	=	5.98
	Total per 1000 lbs. =	$11.58

Labor and power facilities would depend largely upon the plant conditions. The borax extraction solution can be used at least three times, perhaps more, and when the protein content has been built up it can be recovered by acidification. It is probable that the final cost of conversion would be under two cents per pound.

It should be mentioned that the above quantity of chlorine represents 20 per cent on the weight of the mucilage. In making up the sodium hypochlorite solution one half of the chlorine always forms inert chloride ions and is therefore wasted. From this it is apparent that whatever can be done to reduce the available chlorine necessary for conversion would in reality mean a saving of twice that quantity of chlorine.

Suggestions for Further Work.

The following investigations should be undertaken with guar G44 mucilage.

1. Optimum method for extraction of protein. These variables should be noted:
   a. Borax concentration
   b. Temperature
   c. Time of extraction
   d. Addition of sodium carbonate

e. Yield of mucilage
f. Ease of filtration

2. The behavior of mucilage in various concentrations of borax at room temperature. (This has been done for locust bean gum). Then extend the study to higher temperatures.

3. The behavior of mucilage in various concentrations of borax at different pH. (Compare with 2.)

4. Study the conversion of mucilage with sodium hypochlorite at various pH both at room temperature and then elevated temperatures.

5. Study possibilities of converting over a definite pH range such as might occur in a normal conversion reaction.

6. Evaluate the suitable products as tubsizes at concentrations from 3-8 per cent. Also as coating adhesives.

7. Conversion of larger batches (25 lbs.) by the optimum procedure for mill trials as tubsize and coating adhesives.

8. Study the effect of conversion upon the mucilage cell membrane.

9. Study the effects of swelling agents such as acids and salts on mucilage cell membrane.

10. Study the products recovered from the filtrate of conversion mixture.

11. A study of other alkaline converting agents should be made including sodium peroxide, sodium perborate, hydrogen peroxide, potassium permanganate etc.

12. Further attempts should be made to study enzyme conversion of mucilages.

Summary

1. It has been found that aqueous solutions of borax give suitable media for sodium hypochlorite conversion of mannogalactans.

2. The behavior of mucilages in various concentrations of borax was studied. It was found that pronounced swelling took place in the lower concentrations of borax. (0.17 - 1.75%) but the yield decreased appreciably only below 0.34% borax. The ash content increased steadily with borax concentration.

3. Preliminary conversions in 2.8% borax solution indicated that certain impurities were present which interfered with the conversion of the carbohydrate. The principal impurity was found to be protein.

4. The effect of the protein content of the mucilage on the conversion reaction was studied and it was found that the protein utilized the available chlorine at a more rapid rate than did the mucilage. Decreasing the protein content by alkaline extraction of the mucilage gave more efficient conversions.

5. The optimum method of extraction of protein has not thus far been determined but extraction with 2.5% borax and 4% sodium carbonate removed more protein than 3% borax alone.

6. The protein content of guar G4-2 varied considerably from sample to sample so most of the subsequent work was done with locust bean gum.

7. The effect of the alkali concentration and pH during conversion was investigated to a limited extent. It was found that the reaction proceeded much more rapidly at lower pH (7.2-7.7) than at pH = 12. Very strong alkali (3N NaOH) also increased the rate of reaction.

8. The converted locust bean gum mucilages were used as tubsizes and found to be several times superior to converted starches.

9. Some of the mucilages were evaluated as cold water soluble beater adhesives. Two of the earlier products were good in this respect but later products were only mediocre.

10. It is believed that the problem of making the mucilages cold water soluble is not one of making the carbohydrate soluble but one of making the cell membrane easily ruptured or soluble in cold water.

11. It has been found that strong alkalis do not cause appreciable swelling of the mucilages cells but strong acids cause instantaneous dispersion.

12. The possible limitations of the method of converting were discussed. The degree of conversion may be limited by the solubility of the converted products in borax solutions of definite concentration.

13. It is believed that the converted product could be made by the present method at a cost under two cents per pound.

14. An outline of further work was presented.

jws/leh

PROJECT REPORT FORM

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REPORT NO.
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Dr. Wise

REPORT ON THE MUCILAGE FROM ILES MANNANE
(Also termed Iles Iles; "Hollandia" etc.)

A sample of the crude sample marked Hollandia "high viscosity" was obtained from the colloid group. The ground powder was sifted into boiling water, the mixture heated for 10-15 minutes, cooled, and centrifuged. The nearly colorless, aqueous dispersion was decanted sharply from the residue and precipitated by means of ethanol. The "fibrous" precipitate was triturated successively with ethanol, acetone, and finally with ether. It was drained off on mercerized broadcloth after each trituration and squeezed free from solvent. The material was finally air-dried. At the same time smaller amounts of a "flocculent" mucilage were obtained. This could best be washed in the centrifuge, and this was also washed successively with the above mentioned solvents. The mixture of fibrous and flocculent material was used in orienting experiments. Later, a somewhat larger sample of purified (fibrous) iles mucilage was isolated by a similar procedure, the only variant being omission of the acetone trituration. Only alcohol and ether were used in the dehydration in this case.

The mucilage evidently gives the same type of borax-gel test as that given by the mannogalactans (e.g. locust bean gum). Physically it also resembled the latter. However, it is chemically very different. The cold suspension of iles mucilage in water gives a deep blue coloration with iodine solution. This is not given by the mannogalactans.

Hydrolysis of the air-dried mucilage with 1% sulfuric acid showed (from a study of the hydrolysis-time curve) that the hydrolysis was virtually complete in 12 1/2 hours. Thus, 150 mg. of air-dried mucilage (139.7 mg. oven dry) yielded (by the Munson-Walker Method) 141 mg. reducing sugars (calculated as glucose) after 12 1/2 hours.

The neutralized hydrolyzate contained mannose (identified as the phenylhydrazone, m.p. 194.5-195.5° uncorr.). The filtrate from a quantitative mannose determination on heating, yielded a voluminous precipitate of phenyl-glucosazone, m 207-208° uncorr.). When hydrolyzed for very brief periods with HCl, the iles mucilage failed to respond to the Seliwanoff test for d-fructose, whereas under identical conditions inulin gave a characteristic deep red pigment, soluble in amyl alcohol. Evidently fructosans are absent from the iles gum.

Another 500 mg. sample of the iles mucilage was hydrolyzed with 2% HNO_3 for several hours, and then carried through the mucic acid determination for galactose. At the end of two days in the refrigerator, the HNO_3 acid solution showed only a faint cloudiness, but no weighable precipitate was obtained. This indicates the absence of galactose and galacturonic acid in more than traces. The absence of galactose was confirmed by quantitative differential fermentations of the neutralized iles (H_2SO_4) hydrolyzate. When the hydrolyzate corresponding to 100 mg. of air-dried mucilage was fermented by organism (N.R.R.L.) No. 379, the Munson-Walker reducing value was 36.2 mg. Cu_2O. When fermented with organism (N.R.R.L.) No. 966 in a parallel experiment, the final reducing value was 35.8 mg. Cu_2O. These values are identical (within the experimental error), and clearly indicate the absence of galactose.

A proximate summative analysis of the mucilage (o.d.) follows:

% anhydromannose	41%
% anhydroglucose (calculated from Munson-Walker reducing values)	48.6%
% uronic anhydride	3.6%
% pentosans (uncorrected for hexosans or uronic anhydride)	1.76%
% ash	0.53%

The above values for anhydroglucose and pentosans are given with reservations, but it is apparent that the mucilage contains largely mannose and glucose groups. How these exist in the mucilage is problematical. The glucose may emanate from starch or from a true mannoglucan or, possibly, from a mixture of either type of polymer.

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CONVERSION OF MANNO GALACTANS DURING THE COOKING PROCEDURE BY MEANS OF HYPOCHLORITE SOLUTIONS

INTRODUCTION

The ultimate goal in conversion of manno galactan mucilages is to make a marketable product which has been converted to the desired degree before shipment. Progress along this line is being made but the variables have not been sufficiently worked out to permit large-scale conversions. In the meantime, the cooperating paper mills are receiving G4-2 mucilage in order to evaluate it prior to the time of the new planting of Guar seed. Some of these mills will perhaps want to evaluate the G4-2 in coating colors and as a tub-sizing adhesive. Therefore, these experiments were made to investigate the possibility of converting small amounts in the paper mill for experimental purposes. Several experimental variables were investigated. Inasmuch as a commercial G4-2 was not available when these experiments were initiated, two other manno galactans were used to study the essential features of the method of conversion, these were locust bean gum and honey locust bean gum.

Attempts were made to study another point in connection with conversion. It should be recalled that under certain conditions, conversions in which certain other substances are concomitantly oxidized with the principal carbohydrate give a superior type of converted adhesive. This was mentioned in Report 5 where a dichromate converted locust bean gum made in the presence of oxalic acid gave much higher strength qualities than other types of conversions. Some experiments of this type were attempted with hypochlorite oxidation.

EXPERIMENTAL

GENERAL CONVERSION PROCEDURE

20 g. Manno galactan gum
83.4 ml. of 2.5% Bleach liquor
297 ml. of water

The water and bleach liquor were mixed in a three neck flask fitted with a steam injector, stirrer, and thermometer. The gum was then

added carefully with stirring and the mixture heated with steam to 50° C. in 5 minutes and held at this temperature for 30-35 minutes. The mixture became very thick and gradually thinned out. The converted product was then cooked by raising the temperature to 90° C. during 20 minutes and holding there for 5 minutes. It was then diluted to 2% gum solids, the relative viscosity determined at 30° C. and if found to be suitable it was used as a tubsize at 50° C.

Lesser quantities of bleach liquor were used for some experiments. In these cases the volume of liquid medium was maintained constant by variation of the volume of water added. There were also variations in the acidity and alkalinity during conversion. These characteristics were brought about by the addition of various quantities of acid or alkali.

Several experiments were made with sodium hypochlorite solution in place of bleach liquor. The procedure in this case was essentially the same.

RESULTS AND DISCUSSION

The conversion variables and resultant viscosities are summarized in Table I. The tub-size characteristics are in Table II and handsheet data of G97-530, G99-530, and G100-1-530 are in Table III.

The honey locust bean conversions with calcium hypochlorite solution may be summarized by saying that it appears that the lower the degree of conversion, the better the strength properties. Any alteration in procedure which gave a lower relative viscosity seemed to give a product of lower strength. On the other hand, it appears that perhaps the converting agent itself was to blame. It is evident that the locust bean conversion made with calcium hypochlorite also gave low strength values as tub sizes. Honey locust bean gum converted more easily with calcium hypochlorite than did locust bean gum. The explanation of this difference may lie in the method of preparation of the mucilage. The locust bean gum is essentially neutral and contains a considerable amount of protein. The honey locust bean gum was strongly alkaline and it is probable that most of the protein had been extracted under these conditions. It has been found in another series of experiments that residual protein in mucilages is oxidized much more rapidly than the manno galactan. In mucilages which contained considerable amounts of protein, a much greater quantity of chlorine was necessary to convert to a definite viscosity. A preliminary alkaline extraction of these mucilages markedly decreased the amount of chlorine

necessary to attain a given viscosity. The greater difficulty of conversion of locust bean gum may probably be explained on this basis. The addition of enough acid to bring the pH to about 5-6 gave a more efficient conversion of locust bean gum but the product did not possess very good strength quality.

The addition of methyl alcohol to the chlorination mixture as a product undergoing concomitant oxidation gave a product of poor strength quality but oxalic acid under these conditions increased the strength of product somewhat.

The use of sodium hypochlorite instead of calcium hypochlorite gave products possessing better strength qualities on the whole. Neutral media made by adjusting with hydrochloric and oxalic acids gave more rapid and more efficient conversions as shown by viscosity data. Conversions of locust bean gum with sodium hypochlorite at room temperature gave products which compared well with those made at 50° C.

In conclusion, it appears that a reasonably fluid converted locust bean gum can be made by converting with 10% of available chlorine in the form of sodium hypochlorite in a medium made about neutral with hydrochloric or oxalic acid.

jws/hmf

TABLE I

SUMMARY OF CONVERSION VARIABLES AND RELATIVE VISCOSITIES OF THE CONVERTED GUMS

Code No.	Gum Used	Converting Agent	% Converting Agent	Remarks	Relative Viscosity 2% and 30°C.	% Conc. as Tube Size*
G97-530	Honey Locust Bean Gum R21876	Calcium Hypochlorite	10		2.96	2
G99-530	R21876	Calcium Hypochlorite	8		5.86	2
G100-1-530	R21876	Calcium Hypochlorite	5		45.0	2
G100-2-530	R21876	Calcium Hypochlorite	5	Conversion made at 90°C. instead of 50°C.	73.9	Discarded
G104-530	Honey Locust Bean Gum R21880	Calcium Hypochlorite	10		3.28	2
G106-530	R21880	Calcium Hypochlorite	10	Added 2.5 ml. N NaOH	40.2	2
G107-1-530	R21880	Calcium Hypochlorite	10	Made neutral with HCl	2.28	2
G107-2-530	R21880	Calcium Hypochlorite	10		3.72	5
G108-530	R22525	Calcium Hypochlorite	10		3.22	5
G109-530	R22525	Calcium Hypochlorite	10	Lumped up, discarded	-	-
G110-530	R22525	Calcium Hypochlorite	10	Added 10% superfilm No. 4	2.80	5
G129-530	Honey Locust Gum from Neenah Paper Co.	Calcium Hypochlorite	10	Added 12 ml. 0.958 N HCl pH = 4-5	-	2
			Locust Bean Gum			
G103-530	Locust Bean Gum	Calcium Hypochlorite	10	Very thick, discarded	-	-
G131-530	Locust Bean Gum	Calcium Hypochlorite	10	Added 12 ml. N HCl pH = 5-6	1.55	4.5
G132-530	Locust Bean Gum	Calcium Hypochlorite	10	Added 12 ml. N HCl pH = 6 and 2 ml. CH_3OH	2.06	2.
G133-530	Locust Bean Gum	Calcium Hypochlorite	10	Added 12 ml. N HCl pH = 5-6 and 5 ml. CH_3OH.	-	2
G111-530	Locust Bean Gum	Calcium Hypochlorite	10	Added 10 ml. N oxalic acid	4.43	2
G112-530	Locust Bean Gum	Sodium Hypochlorite	7.4	Added 10 ml. N oxalic acid	31.2	2
G115-1-530	Locust Bean Gum	Sodium Hypochlorite	7.4	Added 77.7 ml. N oxalic acid - pH = 4-5	Thick, discarded	-
G115-2-530	Locust Bean Gum	Sodium Hypochlorite	10.	Added 10 ml. N oxalic acid and 40.8 ml. 0.96 N HCl	7.93	2
G117-1-530	Locust Bean Gum	Sodium Hypochlorite	10	Added 40.8 ml. 0.96 N HCl no oxalic acid pH = 7	15.3	2
G117-2-530	Locust Bean Gum	Sodium Hypochlorite	10	Added 40.8 ml. 0.96 N HCl pH = 5-6 and 20 ml. N oxalic acid	7.38	2
G119-530	Locust Bean Gum	Sodium Hypochlorite	10	Added 40.8 ml. 0.96 N HCl pH = 6 and 30 ml. N oxalic acid	22.2	2
			Converted at Room Temperature (26.0-28°C.)			
G53-530	Locust Bean Gum	Sodium Hypochlorite	10	28°C. for 55 minutes.	5.02	2
G55-530	Locust Bean Gum	Sodium Hypochlorite	10	Added 108 ml. 0.1 N HCl, held at 26°C. for 35 minutes	8.30	2
G57-530	Locust Bean Gum	Sodium Hypochlorite	10	Added 200 ml. 0.1 N HCl, held at 26.5°C. for 50 minutes	7.70	2

* See Table II for Tube Size Properties.

TABLE II

TUB SIZE CHARACTERISTICS OF THE HYPOCHLORITE CONVERTED HONEY LOCUST AND LOCUST BEAN GUMS

A. Honey Locust Bean Gum

File No.	Code No	Relative Viscosity 2% and 30°C.	% Solids in Tube Size	Basis Weight 17x22/500	Caliper -inch	Bursting Strength Points	Points/100#	% Increase in Burst	M.I.T. Fold In	Across	% Increase Fold In	Across	Ink Penetration Wire	Felt	Pick Test Wire	Felt	Elmendorf Tear g./sheet In	Across	Tensile lb./inch In	Across	Stretch % In	Across	Porosity Sec./100
Average	Blank	-	-	18.9	0.0031	30.6	162	-	235	66	-	-	22	24	16A	16A	90	100	26.0	12.0	2.8	6.8	240
111262	G97-530	2.96	2	19.7	0.0038	37.1	188	16.0	312	85	45.6	28.8	33	41	18A	16A	89	99	28.8	13.5	3.7	9.1	153
111263	G99-530	5.86	2	19.7	0.0038	39.0	198	22.2	436	102	85.6	54.6	29	30	18A	16A	93	95	29.2	13.9	4.0	8.6	173
111265	G100-1-530	45.0	2	19.4	0.0038	39.9	206	27.2	474	118	102.	78.8	30	31	18A	16A	90	97	30.4	14.0	3.6	9.2	200
111300	G104-530	3.22	2	19.7	0.0039	38.5	195	20.4	346	101	47.3	53.1	34	36	20A	18A	93	100	29.0	13.7	3.7	8.9	212
111316	G106-530	40.2	2	19.9	0.0037	41.5	209	29.0	453	108	92.9	63.7	32	33	23A	20A	91	98	30.4	14.3	3.9	9.4	295
111302	G107-1-530	2.28	2	19.7	0.0039	36.8	187	15.4	396	100	68.5	51.6	29	38	18A	18A	91	103	29.5	13.5	3.9	9.3	208
111304	G107-2-530	3.72	5	20.5	0.0040	42.9	209	29.0	734	136	222.	106.	33	40	23A	20A	90	93	31.1	15.1	4.4	9.6	301
111305	G108-530	3.22	5	20.6	0.0040	41.4	201	24.1	424	126	80.4	91.	30	43	23A	18A	89	92	30.2	14.8	4.2	9.5	262
111307	G110-530	2.8	5	19.9	0.0040	41.2	207	27.8	514	129	118.	95.5	33	35	23A	20A	93	100	31.4	14.7	4.1	8.7	261
111515	G129-530	-	2	20.1	0.0040	37.4	186	14.8	350	75	49.	13.6	-	-	-	-	89	105	-	-	-	-	-

B. Tube Size Characteristics of Locust Bean Gum Conversions

111515	G131-530	4.5	4.5	20.4	0.0041	38.9	191	17.9	349	103	48.6	56.1	-	-	-	-	84	100	-	-	-	-	-
111518	G132-530	2.06	2.	20.0	0.0040	37.8	189	16.7	339	78	44.3	18.2	-	-	-	-	88	102	-	-	-	-	-
111519	G133-530	-	2	20.2	0.0040	37.7	187	15.4	353	91	50.3	37.9	-	-	-	-	90	104	-	-	-	-	-
111318	G111-530	4.43	2	19.6	0.0038	39.0	199	22.8	408	111	74.1	68.2	23	31	23A	18A	91	99	29.4	14.0	3.6	9.2	217
111319	G112-530	31.2	2	20.0	0.0038	40.6	203	25.3	396	108	68.6	63.7	34	41	23A	20A	95	110	30.9	14.1	4.3	8.9	280
111354	G115-2-530	7.93	2	19.8	0.0039	41.9	212	30.9	461	105	96.3	59.1	29	32	23A	20A	99	106	30.4	14.2	4.5	9.9	250
111356	G117-1-530	15.3	2	19.9	0.0040	42.3	213	31.5	417	123	77.5	86.4	30	36	23A	18A	94	102	29.8	14.1	4.7	9.4	260
111357	G117-2-530	7.38	2	20.1	0.0040	41.6	207	27.8	441	126	87.8	91.0	26	45	23A	18A	96	104	29.6	14.0	4.7	9.2	280
111359	G119-530	22.2	2	19.9	0.0039	42.4	213	31.5	367	110	56.2	66.7	23	50	23A	18A	93	106	29.9	14.2	4.8	9.4	274
111065	G53-530	5.02	2	19.2	0.0039	40.7	212	30.9	416	122	77.1	84.9	-	-	-	-	90	101	-	-	-	-	-
111079	G55-530	8.30	2	19.3	0.0039	41.0	212	30.9	382	100	62.6	51.6	24	28	20A	16A	95	100	29.1	14.2	3.8	8.6	206
111081	G57-530	7.70	2	19.3	0.0039	40.8	211	30.2	431	111	83.4	6.82	22	29	18A	18A	92	100	30.1	14.0	3.8	8.8	201

TABLE III

HANDSHEET CHARACTERISTICS OF THREE CONVERTED HONEY LOCUST BEAN GUMS
ONE PER CENT ADDITION

Gum Used	Basis Weight 25x40/500	Bursting Strength Points	Points/100#	% Increase in Burst	M.I.T. Fold	% Increase in Fold	Thwing Formation	Elmendorf Tear g./ Sheet	Tear Factor
Blank	44.8	14.2	32	-	7	-	27.9	112	2.50
G97-530	44.3	17.8	40	25.0	21	200	31.9	109	2.46
G99-530	41.9	18.1	43	34.4	26	272	35.0	95	2.27
G100-1-530	42.2	21.5	51	59.4	28	300	39.3	94	2.23

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CONVERSION OF LOCUST BEAN GUM BY MEANS OF HYPOCHLORITE SOLUTIONS

Introduction

The conversion of mannogalactans must be accomplished in a somewhat different manner than that used for starch since the mucilages are soluble in cold water and hydrate much more rapidly. It is necessary to use a conversion medium in which hydration of the mucilage will be held at a definite minimum. Certain alcohols, ethers and other organic solvents may serve as suitable conversion media but a further requirement--non-reactivity with the converting agent--must be recognized. This factor eliminates the possible use of many of the alcohols, esters and ketones since they react with hypochlorites. Tertiary alcohols, ethers and certain chlorinated solvents might be found suitable. The experiments of this report were conducted in tertiary butyl alcohol and butyl ether. These substances are, relatively speaking, non-reactive with hypochlorite solutions and served quite well as reaction media. Subsequent to these and other experiments to be reported, it has been found that hypochlorite conversion of mannogalactans can be carried out in aqueous borax solutions. These experiments will be reported in the near future.

EXPERIMENTAL:

Conversion of the G 119-506 Series of Locust Bean Gums

Ten grams of locust bean gum were placed in a 250 ml. glass stoppered flask and a mixture of 10-45 ml. of a commercial sodium hypochlorite solution (5-22% available chlorine on gum) and 65 ml. of t-butyl alcohol were added with vigorous shaking. The flasks were stoppered and allowed to stand at room temperature for twenty-two hours. The gums were then filtered off, washed with absolute alcohol and air dried. Those samples containing larger amounts of sodium hypochlorite were somewhat more highly hydrated because of the increase in aqueous phase. All samples possessed some unused available chlorine.

Conversion of the G 132-506 Series of Locust Bean Gums

This series of gums was converted with calcium base bleach liquor possessing 5.8% available chlorine. Twenty grams of locust bean gum were placed in four flasks and then temporary emulsions of 130 ml. of t-butyl alcohol and 10-40 ml. of bleach liquor and water were added with vigorous shaking. The amount of water mixed with the bleach liquor depended upon the quantity of available chlorine desired in the sample. Thus, the first sample contained 40 ml. of bleach liquor and no additional water, the second contained 30 ml. of bleach liquor and 10 ml. of water, the third sample 20 ml. of bleach and 20 ml. of water, etc., thereby keeping the total amount of aqueous phase and thus the degree of hydration the same in each case. After mixing the flasks were stoppered and allowed to stand at room temperature for 16 hours. Considerable swelling took place in all samples and a yellow color was present which increased with chlorine content. The butyl alcohol was decanted off on a funnel and gum mixed with 95% ethyl alcohol, filtered, washed with alcohol and air dried.

Conversion of G 154-506 Series of Locust Bean Gums

Twenty grams of locust bean gum were placed in a flask and then an emulsion of 20 or 40 ml. of sodium hypochlorite (5.3% available chlorine) and 130 ml. of butyl ether was poured onto the gum with shaking. The emulsion was stabilized to some extent, temporarily, by two drops of soap solution. After 16 hours the products were filtered off and washed with ether. The one containing 40 ml. of sodium hypochlorite was more highly swollen and it was necessary to partially dehydrate it with 95% alcohol before air drying.

Conversion of G 80-530 Series of Locust Bean Gums

This series of gums combined some of the better parts of previous procedures and a more complete study was made of the products. The chlorine content was held constant in this series and the degree of alkalinity of the sodium hypochlorite solution was varied.

G 80-1-530

Forty grams of locust bean gum were added to a mixture of 53.3ml. of NaOCl (7.6% Cl_2 and 3.4 N in NaOH), 62.2 ml. of water and 250 ml. of butyl ether. After vigorous stirring the mixture was allowed to stand at room temperature.

G 81-2-530

This product was similar to the above with the exception that 31.1 ml. of water and 31.1 ml. of 0.958 N HCl were used to reduce the alkalinity. In this case one-half of the excess NaOH was neutralized. Other reagents were the same.

G 81-3-530

Ingredients for this conversion differed only in that 62.2 ml. of 0.958 N HCl were added instead of water. This amount of acid neutralized all NaOH in excess of the ratio necessary for stabilization of the NaOCl. This product was white whereas the previous products were a distinct orange color.

After standing overnight at room temperature the products were filtered off, dehydrated with a small amount of alcohol and air dried.

The relative cold water solubility of the three converted gums above was determined as follows:

One gram samples of the air dried gums were stirred gently in a beaker with 100 ml. of distilled water for exactly 10 minutes. The undissolved part was then centrigued off and an aliquot of the supernatant liquor weighed out and evaporated to dryness. The results are given in Table I.

Determinations of other properties of the converted gums were made according to procedures explained in previous reports. The Reducing Value was determined by the method of Farley and Nixon, "Ind. Eng. Chem. Anal. Ed.", 13, 616 (1941).

Results and Discussion

The converted gums were evaluated both in the beater by dry addition and as tubsizes at one per cent concentration and 50° C. The relative viscosities, moistures and reducing values were determined for most of the gums. The data are presented in Tables I, II, and III.

TABLE I

A SUMMARY OF CONVERTING CONDITIONS AND PROPERTIES OF THE CONVERTED GUMS

Code No.	Converting Agent	Per Cent Chlorine on gum	Converting Medium	Time of Conversion Hours	Moisture %	Ash %	Reducing Value mgcu/g	Relative Viscosity at 1% and 30° C.	Relative Solubility in water at 22° C.
G 119-1-506	Commercial NaOCl	5.0	t-butyl alcohol	22	16.5	-	-	54.4	-
G 119-2-506	"	10.0	"	22	18.1	-	-	6.14	-
G 119-3-506	"	15.0	"	22	18.4	-	-	2.6	-
G 119-4-506	"	22.0	"	22	18.1	-	-	1.67	-
G 132-1-506	Calcium Bleach liquor	11.6	"	16	17.3	-	10.7	84.0	-
G 132-2-506	"	8.7	"	16	17.1	-	8.92	63.9	-
G 132-3-506	"	5.8	"	16	15.9	-	8.65	68.2	-
G 132-4-506	"	2.9	"	16	14.5	-	12.0	145.0	-
G 154-1-506	NaOCl	10.5	Butyl ether	16	16.2	-	62.6	1.51	-
G 154-2-506	"	5.2	"	16	15.3	-	28.3	8.04	-
G 80-1-530	Strong alkaline NaOCl	10.0	"	16	8.4	10.7	78.8	2.14	75.2
G 81-2-530	Mildly alkaline NaOCl	10.0	"	16	8.4	8.7	59.2	2.75	68.3
G 81-3-530	Neutral NaOCl	10.0	"	16	8.8	7.85	43.1	33.1	55.7

TABLE II

HANDSHEET CHARACTERISTICS OF THE HYPOCHLORITE CONVERTED GUMS AT 1% DRY ADDITION TO BEATER PULP CONSISTENCY DURING BEATING ABOUT 1.6%; FREENESS 720

File No.	Converted Gum Used	Relative Appearance of Stained Sheet	Per Cent Chlorine Used in Converting	Basic Weight 25x40/500	Caliper Inch	Apparent Density	Bursting Strength (Mullen) Points	Pts/100#	Per Cent Increase In Burst	MIT Fold	Per Cent Increase in Fold	Thwing Formation	Porosity sec/100 cc.	Elmendorf Tear g./sheet	Tear Factor	Tensile lb./inch
110974	Blank	no specks	-	47.9	0.0044	11.0	23.7	57	-	43	-	47.1	11	83	1.73	15.0
110975	G 119-1-506	many specks	5	47.6	0.0043	11.0	39.1	82	43.8	183	326	47.5	12	65	1.37	17.9
110976	G 119-2-506	a few specks	10	47.8	0.0043	11.0	37.7	79	38.6	233	442	49.4	12	67	1.40	19.1
110977	G 119-3-506	very few specks	15	48.6	0.0044	11.0	38.2	79	38.6	230	435	47.9	14	68	1.40	18.2
110978	G 119-4-506	no specks	22	47.6	0.0042	11.5	35.1	74	29.8	137	216	46.2	14	69	1.45	19.5
110924	G 154-1-506	no specks	10.5	48.3	0.0044	11.0	31.7	66	19.8	74	72.	47.8	7	76	1.57	15.9
110925	G 154-2-506	a few specks	5.5	47.9	0.0042	11.5	33.0	69	21.1	145	237	49.1	11	74	1.54	16.9
110904	Blank	no specks	-	47.6	0.0043	11.0	29.8	63	-	80	-	44.7	10	77	1.62	16.1
110905	G-132-1-506	a few specks	11.6	47.5	0.0043	11.0	38.8	82	30.2	364	355	49.0	10	71	1.49	19.7
110906	G 132-2-506	a few specks	8.7	48.2	0.0044	11.0	38.8	80	27.0	247	209	48.5	12	75	1.56	18.9
110907	G 132-3-506	many specks	5.8	47.5	0.0042	11.5	37.1	78	23.8	196	145	46.2	11	76	1.60	18.1
110908	G 132-4-506	very many specks	2.9	47.1	0.0043	11.0	32.7	69	4.7	175	118	49.0	9	75	1.59	16.4
111226	Blank	no specks	-	48.2	0.0043	11.0	26.1	54	-	62	-	50.0	7	92	1.91	14.7
111227	G 80-1-530	very few specks	10.0	50.7	0.0046	11.0	35.8	71	31.5	150	142	49.8	11	80	1.58	20.0
111228	G 81-2-530	very few specks	10.0	47.6	0.0042	11.5	35.3	74	37.0	218	252	50.0	8	72	1.51	17.2
111229	G 81-3-530	many specks	10.0	48.2	0.0043	11.0	37.8	78	44.4	297	389	50.3	8	68	1.41	19.1

TABL III

TUBSIZE CHARACTERISTICS OF THE HYPOCHLORITE CONVERTED GUMS AT 1% CONCENTRATION AND 50° C. 100% RA STOCK

File No.	Converted Gum Used	Chlorine Conc. % on Gum	Relative Viscosity 1% 30° C.	Basic Weight 17x22/500	Caliper -inch	Bursting Strength Points	Pts/100#	Per Cent Increase in Burst	M.I.T. Fold In	Across	Per Cent Increase Fold In	Across	Ink Penetration Wire	Felt	Pick Test Wire	Felt	Elmendorf Tear g./sheet In	Across	Tensile lb/inch In	Across	Stretch % In	Across	Porosity sec/100cc.
Average	Blank	-	-	18.9	0.0031	30.6	162	-	235	66	-	-	22	24	16A	16A	90	100	26.0	12.0	2.8	6.8	240
111068	G 119-1-506	5.0	54.4	19.1	0.0040	39.1	205	26.5	307	83	56.2	25.8	22	24	18A	16A	89	102	29.4	13.8	3.6	9.0	245
111069	G 119-2-506	10.0	6.14	19.1	0.0039	40.5	212	30.9	424	91	80.5	37.9	21	20	20A	16A	88	100	29.0	13.7	3.6	8.3	210
111070	G 119-3-506	15.0	2.61	19.1	0.0039	38.4	201	24.1	305	95	29.8	44.0	19	20	16A	16A	92	102	28.2	13.6	3.7	8.6	190
111071	G 119-4-506	22.0	1.67	19.1	0.0040	36.8	193	19.1	290	92	23.4	39.4	20	24	16A	16A	94	107	28.2	13.4	3.6	8.7	176
111058	G 132-1-506	11.6	84.0	19.2	0.0040	37.9	197	21.6	433	90	84.4	36.4	17	23	16A	13A	91	107	29.1	13.2	3.6	8.1	224
111059	G 132-2-506	8.7	63.9	19.1	0.0040	36.4	191	17.9	306	77	30.2	16.7	23	25	16A	14A	97	104	28.3	12.9	3.5	8.3	229
111060	G 132-3-506	5.8	68.2	19.0	0.0040	36.6	193	19.1	332	82	41.3	24.2	23	25	16A	13A	92	103	28.9	13.0	3.5	8.5	234
111061	G 132-4-506	2.9	145.0	19.0	0.0040	36.8	194	19.8	401	86	70.8	30.3	15	18	16A	14A	98	105	28.0	12.8	3.5	8.1	245
111056	G 154-1-506	10.5	1.51	19.2	0.0040	37.9	197	21.6	328	100	41.3	51.5	19	20	16A	14A	93	97	28.2	13.2	3.6	8.1	169
111055	G 154-2-506	5.2	8.04	19.0	0.0040	38.5	203	25.3	355	109	51.1	65.2	21	24	18A	14A	90	100	29.0	13.1	3.6	8.3	218
111201	G 80-1-530	10.0	2.14	19.4	0.0038	37.3	192	18.5	289	89	23.0	34.9	29	43	18A	14A	96	106	28.4	13.2	3.9	8.2	186
111203	G 81-2-530	10.0	2.75	19.3	0.0039	38.4	199	22.8	416	108	77.1	63.7	27	40	18A	16A	97	102	29.0	13.2	3.6	8.0	193
111205	G 81-3-530	10.0	33.1	19.2	0.0039	38.3	199	22.8	254	94	8.1	42.4	46	51	16A	16A	93	103	29.0	13.8	3.8	8.8	235

Conversion Conditions

It appears from the data of Table I that sodium and calcium hypochlorite quite readily attack the carbohydrate chains and cause conversion. The sodium hypochlorite gave a greater degree of conversion per amount of available chlorine than did calcium hypochlorite. This is shown by the relative viscosity and reducing values under the two conditions. It should be pointed out however that the degree of hydration varied in the G 119-506 series of gums since the amount of aqueous phase was increased with increasing amounts of chlorine. In the G 132-506 series the amount of aqueous phase was held constant. In the last series (G 80-530 to G 81-530) the aqueous phase and amount of chlorine were held the same and the alkalinity of the mixture was varied by addition of definite amounts of acid. These experiments showed that strongly alkaline sodium hypochlorite was more efficient as a converting agent than weakly alkaline or neutral hypochlorite. This is shown by the reducing values and relative viscosities of the products and, more significantly, by the relative cold water solubility. The latter property showed that as the degree of alkalinity increased the cold water solubility increased. Thus, the most highly alkaline medium gave a product 75.2% soluble in ten minutes, whereas, the neutral medium gave a product only 55.7% soluble in the same time.

Evaluation of the Converted Products in the Beater

The products were added to the beater as a dry powder and thus strength improvements were dependent upon two factors (1) the actual amount of the gum which dissolved during the beating procedure and (2) the intrinsic adhesive strength of the dissolved gum. The first factor was measured relatively by staining the handsheet to determine the amount of undispersed gum. The second factor was measured by the strength characteristics of the handsheet. The data of Table II appear to support the following statements:

1. The use of sodium hypochlorite as the converting agent gave series of gums (G 119-506, G 154-506 and G 80-81-530) which showed the best strength characteristics with the products of lowest degree of conversion in spite of the fact that these gums were not dispersed to as great an extent as the more highly converted products of the series.

2. The use of calcium hypochlorite as the converting agent gave products (Series G 132-506) which showed increased evidence of strength with the increase in degree of conversion.

The apparent contrasts between the two converting agents cannot be fully explained at present but it should be pointed out that the series of gums converted with calcium hypochlorite show much less divergence of chemical and physical properties than do the sodium hypochlorite converted gums (See Table I).

Evaluation of the Converted Products as Tubsizes

Trends, similar to those mentioned above under beater evaluation, are also noticeable when the products were used as tubsizes. However, there seems to be less contrast between the two converting agents.

The strength values principally burst and fold, are not particularly high in the sense of the ultimate strength which can be achieved with a 100% rag stock. But, when it is realized that only a 1% tubsize solution was used with a very high roll-nip pressure these values may appear to be rather exceptional especially when compared with starch.

Further Work:

This work has clearly demonstrated that locust bean gum can be converted by means of hypochlorite solutions. The use of organic solvents as reaction media would not be a serious handicap since they could be recovered. However, further work on conversion by this particular method has not been planned for the near future because a somewhat more promising aqueous method of conversion has been devised.

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PROJECT REPORT FORM

PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 6
DATE January 3, 1944 (Typed 1/17/4
NOTE BOOK 530
PAGE See Below. TO
SIGNED John W. Swanson

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SOME PRELIMINARY EXPERIMENTS ON ENZYME CONVERSION

OF LOCUST BEAN GUM.

Introduction:

Paper mills which now enzyme convert their own starches for tub and calender sizing probably would desire to do the same thing with the mucilages when they become generally available. Therefore, it seemes desirable to have some information on enzyme conversion of mannogalactan mucilages. This report is concerned with several attempts to utilize commercial starch converting enzymes for conversion of locust bean gum and the demonstration of the possibility of conversion by means of an enzyme mixture obtained from sprouted Guar seed. The work with the commercial enzymes was done by Mr. Fronmuller and is included in this report in order to give a complete picture of the work to date.

The Literature:

A survey of the literature disclosed that some work has been done on the action of enzymes upon certain mucilages of the mannogalactan type. None of this work was done with common commercial enzymes but it gave certain leads which have proved helpful.

Tagliani (4) states that malt extracts and animal "ferments" caused no rapid decomposition of locust bean gum solutions but upon standing several days a gradual alteration in homogeneity was observed which be believed indicated that a partial activation of a proenzyme had taken place.

Karrer (2) mentions that the enzyme from Helix pomatia (a species of snail) hydrolyzes the carbohydrate of the locust bean to mannose and galactose. Also mannan splitting enzymes may be found in numerous plants such as locust bean gum, the seeds of Indigo, Lucern, Klee, many leguminosae, dates, orchids, and certain molds.

Abderhalden (1) states that the mannogalactans present in numerous plants

serve as reserve materials and are produced by the enzymes of these plants which are summarized as Seminase. These enzymes may also be found in the mold fungi (Aspergillus niger and Aspergillus fuscus) and in barley malt. Konjak mannan and a mannogalactan containing mucilage from Hydrangea paniculata are dissolved and hydrolyzed by Bacterium mesentericus vulgatus.

Waksman and Davison (5) state that seminase converts mannogalactans to mannose and galactose. The optimal temperature of this enzyme (mixture) is 35-40° C. and the optimal reaction takes place in weakly acidic media. It is formed abundantly by various plants such as leguminosae, barley, rye, and orchids. Also mentioned was a closely related enzyme called Carubinase which digest the polysaccharide of Ceratonia siliqua (locust bean gum) and produces d-mannose and a small amount of galactose.

Lew and Gortner (3) found that Emulsin and Saliva had no effect upon locust bean gum sols but Takadiastase caused an appreciable hydrolysis upon standing overnight. The product possessed 87% of the theoretical reducing value but only 1.21% of the mannose had been hydrolyzed off. No definite conclusions were made since the constituents of the Takadiastase were unknown.

Results and Discussion:

Conversion of Locust Bean Gum with Commercial Starch Enzymes.

Attempts to convert locust bean gum with commercial enzymes such as Takadiastase, Clarase, Enzyme 1275 (Takamine) and Diastafor L were unsuccessful. Mr. Fronmuller stated that he believed some conversion had taken place with Clarase and Takadiastase under acidic conditions but, in view of the relatively large amounts of HCl present (pH = 1-2.0) during the cooking procedure there is little doubt that the reduction in viscosity was primarily the effect of acidic and not enzymic hydrolysis. Furthermore, when a higher pH was present (pH = 4.5) very little reduction in viscosity was noted. Therefore, it is believed that the sheets tubsized by Mr. Fronmuller with Clarase and Takadiastase converted locust bean gum (Table I) in reality represent sheets tubsized with acid converted products. It appears reasonable to assume from this work that starch saccharifying enzymes do not readily attack mannogalactans under the conditions used in these experiments.

Conversion of Locust Bean Gum with an Extract of Sprouted Guar Seed.

Enzymes mentioned in the literature survey of this report and other hemicellulases, cytases etc. were not obtainable from the Takamine Enzyme Laboratories. It was decided, therefore, that perhaps a suitable enzyme mixture could be obtained from some of the manno-galactan containing seeds. Several species of seed were sprouted (Guar Cyamopsis tetragonolola; Flame tree Deloria regia; and Tara Caesalpinia spinosa). The Guar seed appeared to be the most promising from the standpoint of rapidity of sprouting and these were dried and extracted as explained in the experimental section of this report.

The extract was first shown to contain active enzymes by test tube experiments with cooked locust bean gum. A comparison at various intervals of the relative viscosities of gum solutions with and without the extract showed that a very rapid hydrolysis occurred in the presence of the extract. Following this experiment a larger quantity of gum was converted with the extract and used as a tubsize. See G61-530 in Table I. Further experiments with the enzyme extract have shown that preliminary dispersion of the locust bean gum at 65° C. and cooling to 35-40° C. enables the enzymes to act upon the mucilage much more rapidly. One further product was used as a tubsize and the data are in Table I. See G76-2-530. A comparison of the tubsize characteristics of these products shows that the one with the higher relative viscosity (G61-530) was better in most respects than the product with the lower viscosity.

Attempts to fractionate the extract by alcohol precipitation and thereby concentrate the enzymes have so far met with only partial success. A product was obtained which possessed some enzyme activity but the reaction was considerably slower than with the original extract. This product redispersed in water only with difficulty which may partially account for the slower action but it is well known that contact with dehydrating agents such as acetone and alcohol seriously impairs the activity of certain types of enzymes. This may well be one of those enzymes.

Further work with this enzyme mixture might involve the following:

1. Attempts to concentrate the enzyme by the following methods:

    a. Vacuum distillation of the water
    b. Precipitation of the enzyme by salts such as ammonium sulfate followed by redispersion and electrodialysis.

c. Adsorption of the enzymes from solution by starch or some other appropriate adsorbant.

2. A study of the concentrated products including, optimal concentration of enzyme and pH of conversion.

(Table I, See page 5)

Experimental:

Attempted Conversions of Locust Bean Gum with Takadiastase.

G13-1-530*

200 g. water
10 g. gum
0.1 g. Takadiastase (Park Davis).

The mucilage and enzyme were mixed and then added to the water with stirring. Steam was then injected and the temperature was maintained at 40° C. for 30 minutes, and at 60° C. for 20 minutes. Then the temperature was raised to 95° C. in 8 minutes and maintained for 8 minutes. At 80° C. some thinning was noticed but it was not sufficient to warrant use of the final mixture as a tubsize.

G18-2-530

This conversion was similar to G13-1-530 with the exception that 300 ml. of water were used and that after the 20 minute period at 60° C., one ml. of conc. hydrochloric acid was added. The temperature was then raised to 95° C. in 17 minutes and held for 8 minutes. The relative viscosity was measured at 30° C. and 2.5% concentration and found to be 8.3. The addition of the acid gave a mixture of very low pH and it is probable that this mixture was acid hydrolyzed rather then enzyme hydrolyzed.

G19-530

This conversion was similar to the above G18-2-530 mixture with the exception that one drop of concentrated hydrochloric acid was

* The number refers to page, position and notebook number.

TABLE I

TUB SIZE CHARACTERISTICS OF THE ENZYME CONVERTED LOCUST BEAN GUMS AT 2% CONCENTRATION AND 50° C.

File No.	Gum used and Enzyme	Ph of Gum sol. During Cook	Relative Viscosity of gum at 30°-30°C.	Basis Weight 17x22/500	Caliper -inch	Bursting Strength (Mullen) Pts.	Bursting Strength (Mullen) Pts. per 100 lb.	% Increase In Burst
	Blank			18.9	0.0032	30.6	162	--
111022	G42-530 (Clarase	1-2.0	3.1	19.3	--	37.3	193	19.1
111089	G61-530 (Guer)	7.0	11.7	19.2	0.0038	40.1	209	29.0
111207	G76-2-530 (Guar	7.0	8.7	19.4	0.0039	39.2	202	24.7
110686	Blank for 110887			21.0	0.0040	23.5	112	--
110887	G18-2-530 (Takadiastase)	1-2.0	3.3(2.5%)	21.5	0.0042	31.2	145	29.4

	MIT Fold		Increase In fold		Gurley Porosity	Ink Penetration Seconds		Pick Test (Denison waxes)		Elmendorf Tear		Schopper Tensile lb./inch		Stretch,	
	In	Across	In	Across	Sec/100cc.	Wire	Felt	Wire	Felt	In	Across	In	Across	In	Across
	235	66	--		240	21	25	19A	14A	88	100	25.5	12.3	2.6	7.1
	404	89	71.9	34.9	--	--		--		94	95	--		--	
	439	111	86.8	68.2	201	20	25	23A	18A	92	101	30.2	14.5	3.9	9.6
	294	97	25.1	47.0	195	23	25	23A	18A	93	100	29.7	14.8	3.8	8.7
	55	19	--		74	219	228	11A	10A	53	58	26.9	11.9	1.9	4.7
	144	26	162.	36.8	74	167	198	18A	11A	56	62	22.3	11.2	2.8	6.2

added at the beginning. The viscosity did not decrease very rapidly and at the end of the 20 minute heating at 60° C. four drops of conc. hydrochloric acid were added. The mixture was then heated to 95° C. as before. At 2.4% gum concentration the mixture was very viscous and unsuitable for tubsizing purposes.

G34-1-530

25 g. Locust bean gum
475 g. water
0.25 g. Taka diastase

The gum and water were mixed in the cooker and the enzyme was added. The temperature was raised to 40° C. and then to 51° C. during a 30 minute period. After raising the temperature to 65° during 10 minutes and holding there for 15 minutes no thinning out was noticed. The temperature was then raised to 95° C. and held there for several minutes but no thinning occurred.

G34-2-530

This conversion was similar to G34-1-530 as to constituents but no immediate heating was applied. The mixture was stirred for about one-half hour and then allowed to stand at room temperature overnight. The temperature was raised to 40° C. and held for 30 minutes, then to 60° C. in 15 minutes and held for 15 minutes and then to 90° C. in 13 minutes and held for 15 minutes. It was then noted that the solution was very viscous and unsuitable for tubsizing purposes.

An Attempted Conversion of Locust Bean Gum with Clarase Enzyme.

G42-530

250 g. water (tap)
10 g. gum
0.1 g. Clarase enzyme
2.4 g. conc. HCl (37%)

The water was adjusted to pH of 4.5 with dil. HCl and the gum and enzyme mixed in. Then the temperature was maintained at 40° C. for

30 minutes, raised to 60° C. in 10 minutes and held at 60° C. for 20 minutes. The acid was then added and the temperature raised to 90° C. in 10 minutes and held there for 30 minutes. At 80° C. a rapid decrease in viscosity was noted and the mixture became quite fluid. The pH being very low was adjusted to 5 with dilute NaOH and then the mixture was used as a tubsize at 2% concentration and 50° C. on a sulfite bond stock. The results are in Table I. It is believed that this product was essentially acid converted rather than enzyme converted.

Enzyme Acid Conversion of Locust Bean Gum with Enzyme 1275.

G43-530

250 g. water
10 g. gum
0.1 g. Enzyme 1275 (Takamine)

The above constituents were mixed after adjusting the pH of the water to 4.5. No appreicable conversion took place during 30 minutes at 40° C. and 30 minutes at 60° C. The gel was then cooled to 40° C. and 9.9 g. of Enzyme 1275 in 25 ml. water were added and the mixture allowed to stand overnight. Then the temperature was raised to 50° C., held for one hour, and then raised to 95° C. for 20 minutes. A slight decrease in viscosity was evident.

An Attempted Conversion of Locust Bean Gum with Diastafor L Enzyme.

G43-1-530

No conversion took place with this enzyme in 48 hours at 1% enzyme concentration.

G71-1-530

An attempt to convert locust bean gum and a Guar mucilage G4 R-22603 with large quantities of precipitated Taka diastase caused some reduction in the viscosity. The relative viscosities at 2% and 30° C. were 38 and 45 respectively.

Preparation of an Enzyme Mixture from Sprouted Guar Seed.

Five grams of Guar seed (Cyamopsis tetragonolola) were moistened in a crystallizing dish with a wet pulp mixture containing a few drops of toluene. The dish was covered and placed in an oven at 40° C. for three days. The sprouted seeds were then air dried under an electric fan at room temperature. The dried seeds were placed in a mortar with a small amount of sand and water and ground to a fine mixture. More water was added from time to time and filtered off on a fritted glass crucible. The insoluble material was washed thoroughly and the filtrate (30 ml.) was placed in a test tube. Further batches of sprouted seed were treated similarly.

Conversion of Locust Bean Gum with the Enzyme Mixture Isolated from Guar Seed. (Test tube Experiment)

A 0.4% despersion of locust bean gum was made and cooled to room temperature. Ten ml. samples of this solution were added to each of two test tubes. To the first tube 5 ml. of distilled water were added; to the second 5 ml. of the enzyme mixture. Immediately 10 ml. of these mixtures were placed in separate viscometers and the viscosity determined. The following values were obtained.

Tube No. 1 water and gum after 3 minutes Rv = 3.31
Tube No. 1 water and gum after overnight Rv = 6.34

Tube No. 2 gum and Enzyme after 3 minutes Rv = 1.35
Tube No. 2 gum and Enzyme after overnight Rv = 1.06

Conversion of Locust Bean Gum with the Enzyme Mixture Obtained from Sprouted Guar Seed.

G61-530

20 g. gum
355 ml. water

The water and gum were mixed and heated to 60° C. and allowed to cool to 35° C. with occasional stirring. Then 25 ml. of the liquid enzyme mixture from sprouted Guar seed were added and thoroughly stirred into the mixture. After allowing to stand with occasional stirring for four hours at 30-35° C. steam was injected at such a rate that the

temperature was raised to 94° C. in 17 minutes. The temperature was held at 90-94° C. for 5 minutes and then the mixture was diluted to 2% gum concentration and used as a tubsize at 50° C. on a 100% rag stock. Appreciable conversion had taken place with this enzyme mixture as shown by a relative viscosity of 11.7 at 2% solids and 30° C. After standing overnight the viscosity fell to 7.5 indicating that perhaps the enzyme had not been completely inactivated by the heating for 5 minutes at 90-94° C.

Isolation of a Product Thought to be an Enzyme from the Extract of Sprouted Guar Seed.

One gram of dried sprouted Guar Seeds was ground as before and the filtrate (15 ml.) collected. The filtrate was centrifuged and decanted from the residue. Then 49 ml. of absolute ethyl alcohol were added to the centrifugate, the precipitate allowed to settle and the supernatant layer decanted. The precipitate was washed with fresh alcohol, centrifuged out and vacuum dried at room temperature over P_2O_5. The material thus obtained weighed 0.04444 g. and possessed a gray color and sharp peppery odor.

A 0.4% locust bean gum dispersion was made and 20 ml. placed in each of two test tubes. To the first tube one ml. of water was added and to the second 1 ml. of a solution of the above enzyme preparation (1 ml. = 0.1 mg. or 0.12% on the gum). These mixtures were then placed in viscometers at 30° C. and the relative viscosities were determined as follows:

1. Water + locust bean gum	Relative Viscosity
3 minutes	32.6
10 minutes	32.6
16 hours	27.2
2. 0.12% Enzyme + locust bean gum	
3 minutes	25.2
10 minutes	21.4
16 hours	2.24

Conversion of Locust Bean Gum with the Alcohol Precipitated Guar Enzyme Preparation.

Twenty grams of locust bean gum were mixed with 480 ml. of water and stirred to a stiff paste. A 0.044 g. (0.22%) sample of the enzyme preparation made from the Guar seeds was dissolved (with difficulty) in 10 ml. of water and added to the gum mixture. The temperature was raised to 40° C. and held there for one hour. Some thinning out occurred but not sufficient to warrent cooking for tubsizing purposes. The mixture was allowed to stand at room temperature for 43 hours after which it was quite thin. The mixture was discarded because of the long conversion period necessary.

Conversion of Locust Bean Gum with Guar Enzyme Extracted from Five Grams of Seed.

G76-1-530

Twenty grams of gum were mixed with 550 ml. of water and the extract from 5 grams of sprouted Guar seed was added. The temperature was then raised to 35° C. for 30 minutes whereupon thinning out seemed to occur. The temperature was then raised to 93° C. during 25 minutes and held there for 5 minutes. Heating seemed to cause considerable thickening in this case. At 2% and 30° C. the mixture possessed a relative viscosity of 42.8.

Conversion of Locust Bean Gum after Dispersing at 65° C.

G76-2-530

Twenty grams of locust bean gum were mixed with 550 ml. of water and heated with stirring to 65° C. and then cooled to 36° C. The enzyme extract from 5 g. of sprouted Guar seeds was added and the conversion allowed to proceed for 2 hours at 36° C. Noticeable thinning occurred in one half hour. The temperature was then raised to 93° C. held for 3 minutes and the mixture diluted to 2% and used as a tubsize at 50° C. The relative viscosity at 2% and 30° C. was 3.73.

An Attempted Alcohol Fractionation of the Enzyme Mixture of Sprouted Guar Seed.

Five grams of air dried sprouted Guar seed were ground with

water and sand and filtered through a coarse glass filter crucible. The insoluble residue was washed with successive portions of water and filtered. The filtrate was centrifuged and decanted from the residue. Volume 134 ml. Successive 30 ml. portions of absolute ethyl alcohol were then added to the centrifugate followed by periods of standing to allow flocculation. Precipitates formed at 47.3% and 74.5% alcohol concentrations, the first being quite dark in color and the second gfay. The precipitated materials were in turn centrifuged off, washed with absolute alcohol and vacuum dried at room temperature.

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