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Project Reports

# PROJECT REPORT FORM

PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 23
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NOTE BOOK 669
PAGE 13 TO 22
27, 31 TO 34
SIGNED John W Swanson
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## PREPARATION OF ALLYL GUAR

### INTRODUCTION

Considerable interest has been shown recently in allyl derivatives of carbohydrates because of their unique film forming and adhesive properties. These new products promise to become very important in the resin, varnish, and paint fields. As prepared, they are soluble in most organic solvents but upon exposure to air, heat, certain chemical agents, or infrared and ultraviolet light a cross linkage oxidation and polymerization occurs which leaves a very inert product of high gloss, good abrasion resistance etc. One of the very interesting materials for making allyl products is starch. The similarity of guar mucilage to starch, in so far as polymolecularity is concerned. led to some preliminary experiments to prepare an allyl guar mannogalactan product and study some of its properties.

### EXPERIMENTAL

The method used for allylation of guar was patterned after that used for starch as published by Nichols, Smith and Yanovsky, in Ind. Eng. Chem., 37, 201(1945). These investigators proceeded through the acetate derivative, simultaneously saponifying and etherifying with alkali and allyl bromide or chloride.

### PURIFICATION OF GUAR G4-L

Thirty grams of oil-free guar G4-L were dispersed in a total of 3 liters of distilled water in a Waring blendor and then cooked with direct steam. The temperature was raised to 95° C. and held there for 20 minutes.

The viscous mixture was supercentrifuged and cooled to 35° C. and slowly added to 8 liters of vigorously stirred cold 94% ethyl alcohol. The precipitated mannogalactan was collected by decantation and filtration through cloth and then treated with fresh 95% ethyl alcohol, twice more with absolute ethanol and finally with absolute ether. The product was then sucked dry at the filter and placed in a sample bottle. Yield: 80%.

ACETYLATION OF GUAR MANNOGALACTAN

Twenty grams (o. d.) of the purified guar were weighed out and placed in a one liter 3-neck flask fitted with a condenser and a mercury sealed stirrer. Three hundred fifty milliliters of pyridine (17.5 parts) and 284 ml. of acetic anhydride (14.2 parts) were added. The flask was placed in an oil bath at 105-110° C. and the contents stirred for 20 hours. A $CaCl_2$ tube was attached to the condenser to prevent the entrance of moisture. The mixture became very viscous and darkened somewhat during the reaction time. After 20 hours the mixture was cooled and poured into about 7 volumes of 94% ethyl alcohol in a Waring blendor. The precipitated acetate was filtered off on a fritted glass funnel with suction and then washed twice with fresh alcohol in a Waring blendor and finally mixed with 95% alcohol and allowed to stand overnight. The product was washed once more, filtered and vacuum dried over $CaCl_2$ for 48 hours. Yield: 35 g. practically quantitative. Acetyl content by method of Genung and Mallatt [Ind. Eng. Chem. Anal Ed., 13, 369(1941)] 43.8, 43.7% calculated for triacetate $C_6H_7O_5(OCCH_3)_3$ 44.8%.

PREPARATION OF GUAR ALLYL MANNOGALACTAN

Two grams of guar acetate were dissolved in 45 g. of acetone and mixed with 45 g. of 50% NaOH and 45 ml. of allyl chloride. The mixture was sealed in a stainless steel bomb and heated with continuous rotation for 11-21 hours at 80° C. The bomb was cooled, the contents transferred into a 500 ml. distilling flask and the volatile matter steam distilled during 15 minutes. The gummy yellow-brown residue was washed with distilled water until free of alkali which lightened the color considerably. The gum was extracted with acetone and the solution was poured into 8 volumes of water. In the pure water the gum formed a colloidal solution which was only slowly flocced by sodium chloride but rapidly flocced by small amounts of $Al_2(SO_4)_3$. The entire batch was flocculated with alum and the gum collected by centrifuging. It was necessary to store the product under water or in solution in a pure organic solvent to help prevent oxidation and polymerization. Products stored under water for a few days usually developed an organic solvent insoluble layer of gum. None of the products made thus far have been analyzed for allyl value because of partial insolubility.

DISCUSSION OF THE PRODUCT

The allyl mannogalactan prepared above is soluble in most organic solvents such as acetone, alcohol etc., but insoluble in aliphatic hydrocarbons. The allyl content is probably about 2 allyl groups per hexose unit as shown by solubility characteristics.

A solution of the allyl product in acetone was evaporated on glass and also painted onto a birch panel. The film on the glass after drying

overnight and oven tresting at 90° C. for 48 hours was quite insoluble and nonswelling in water and organic solvents. Upon removing the film from the glass it was found to be somewhat brittle. The film on the birch panel after oven heating overnight and standing for a week in the air became very insoluble in water and showed very little effect on treatment with acetone, ether and alcohol. It also showed fairly good abrasion resistance.

FURTHER WORK

When time permits further investigations of this product should be made by someone experienced in testing resins and plastics.

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## DEXTRINIZATION OF MANNOGALACTAN MUCILAGES

II Guar Mucilages G4-5 and G4-L, Tara G7-6, and Flame Tree G9.

### INTRODUCTION

In report No. 18 of this project it was shown that a very good tubsizing adhesive could be made by heating locust bean gum at various temperatures in the presence of small amounts of acid. The work of this report is an extension of this method of conversion to guar, tara, and flame tree mucilages.

### EXPERIMENTAL

The dextrinization equipment and methods of incorporating and measuring the hydrochloric acid catalyst were described in report No. 18 and need not be repeated here. Two other acidic catalysts were tried during the present series of experiments and these were added to the mucilage by somewhat different procedures.

### PROCEDURE FOR ADDITION OF CHLORINE AS A CATALYST

A one liter suction flask was fitted with a 10 cm. fritted glass Büchner type funnel and dry chlorine was passed into the flask to displace the air. One hundred fifty grams of G4-L mucilage were placed in the funnel and chlorine gas was passed upward through the mass for various times.

The amount of active acid present in the mucilage was determined by dispersing a 5.00 g. sample in 495 ml. of distilled water in a Waring Blendor

for one minute. One hundred grams of this solution was treated with an excess of standard NaOH and the mixture heated to boiling. After cooling the sample was back titrated to pH 6.35 using a pH meter.

PROCEDURE FOR ADDITION OF ACETIC ACID AS A CATALYST

A two liter Pyrex reagent bottle was fitted internally with two flanges made of glass rod fastened by means of scotch tape. These flanges served to agitate the dry mucilage during the subsequent rotation. One hundred fifty grams of G4-5 mucilage were placed in the bottle and the bottle was attached to a ball mill rotating mechanism which was tipped upward at an angle of about 15-20°. Six 3/4-inch porcelain balls were added and rotation begun. Nine and one half grams of glacial acetic acid were sprayed into the rotating mucilage from an atomizer giving a mixture containing 6.33% of acid. After rotation for 0.5 hour to remove any caking and small lumps the sample was dextrinized, as shown in Table I.

TABLE I

DEXTRINIZATION DATA

| Code No. | Kind of Mucilage | Ml. of conc. HCl used | Time of add. HCl to $H_2SO_4$ in sec. | % HCl on mucilage | Dextrinization Temp. °C. | Dextrinization Time, hrs. | Relative viscosity 1% & 30°C | Volume centrifuged solids from 50 ml of 1% | Color of dextrin |
|---|---|---|---|---|---|---|---|---|---|
| G38-669 | G4-5 | 1.5 | 283 | 0.116 | 143 | 3 | 7.25 | | light brown |
| | | | | | 143 | 7 | 4.27 | | brown |
| | | | | | 143 | 10.25 | 3.18 | | brown |
| | | | | | 143 | 13.25 | 2.59 | 3.75 | brown |
| | | | | | 143 | 16 | 2.20 | 3.0 | brown |
| | | | | | 143 | 19 | 2.19 | 3.0 | brown |
| G44-669 | G4-5 | 3.0 | 555 | 0.584 | 143 | 2 | 1.18 | 1.5 | brown |
| | | | | | 143 | 3 | 1.09 | 1.25 | brown |
| G48-669 | G4-5 | 0.0 | — | 0.000 | 25 | — | 572.0 | | |
| | | | | | 140 | 6 | 3.36 | | light brown |
| | | | | | 140 | 21.5 | 2.68 | 4.0 | brown |
| G49-669 | G4-5 | 1.5 | 293 | 0.141 | 140 | 12 | 1.82 | | brown |
| G50-669 | G4-L | 1.5 | 285 | 0.266 | 25 | 16 | 115.6 | | light tan |
| | | | | 0.266 | 25 | 40 | 83.5 | | |
| | | | | | 125-137 | 0.5 | 1.45 | 2.0 | tan |
| G56-669 | G4-L | 0.5 | 100 | 0.070 | 25 | 16 | 626.0 | | |
| | | | | | 143 | 2 | 18.6 | 3.0 | tan |
| | | | | | 143 | 4 | 10.2 | | tan |
| | | | | | 143 | 7 | 5.5 | | tan |
| | | | | | 143 | 9 | 4.68 | 3.0 | |
| | | | | | 143 | 12 | 3.73 | 3.5 | |
| | | | | | 143 | 15 | 3.0 | 3.0 | light brown |
| G63-669 | G4-L | 0.0 | — | | 143 | 3 | 34.5 | 4.5 | |
| | | | | | 143 | 6 | 13.9 | 4.5 | |

TABLE I (continued)

DEXTRINIZATION DATA

| Code No. | Kind of mucilage | Ml. of conc. HCl used | Time of add. HCl to $H_2SO_4$ in sec. | % HCl on mucilage | Dextrinization Temp. °C. | Dextrinization Time, hrs. | Relative viscosity 1% & 30°C | Vol. centrifuged solids from 50 ml of 1% | Apparent percentage of sugar | Color of dextrin |
|---|---|---|---|---|---|---|---|---|---|---|
| G63-669 (cont) | G4-L | | | | 143 | 9 | — | — | 0.67 | tan |
| | | | | | 143 | 12 | 10.8 | 4.0 | 0.67 | |
| | | | | | 143 | 15 | 11.6 | 4.0 | 0.82 | |
| | | | | | 143 | 18 | 10.1 | 4.0 | | tan |
| | | | | | 143 | 21 | 9.2 | 4.0 | | light brown |
| | | | | | 143 | 27.75 | 6.3 | 4.0 | — | |
| | | | | | 143 | 33.5 | 4.7 | 3.5 | | light brown |
| G81-669 | G4-5 | 0.0 | — | | 140 | 4.0 | 12.1 | — | 0.96 | tan |
| | | | | | 140 | 8 | 3.5 | — | 1.10 | light brown |
| | | | | | 140 | 12 | 3.4 | | 1.38 | |
| | | | | | 140 | 16 | 4.0 | | 1.61 | |
| | | | | | 140 | 20 | 3.4 | | 1.64 | brown |
| | | | | | 140 | 24 | 3.1 | | 1.58 | brown |
| G87-669 | G4-5 | 3.0 | 575 | 0.237 | — | — | — | — | — | |
| G88-669 | G4-5 | 3.0 | 570 | 0.233 | 105 | 5 | 25.1 | | | tan |
| | | | | | 105 | 14.25 | 9.3 | 3.5 | | |
| | | | | | 105 | 20 | 6.3 | | | |
| | | | | | 105 | 26.5 | 5.4 | | | |
| | | | | | 105 | 48 | 2.93 | | | brown |
| G91-669 | G4-5 | 3.0 | 575 | 0.217 | 85 | 20.5 | 49.7 | | | |
| | | | | | 85 | 88 | 18.4 | | | light brown |
| G98-669 | G4-5 | 7.5 | 1050 | 0.863 | 25 | 24 | 54.6 | | | tan |
| | | | | | 85 | 14 | 1.13 | | | tan |

TABLE I (continued)

DEXTRINIZATION DATA

| Code No. | Kind of mucilage used | Ml. of conc. HCl used | Time of add. HCl to $H_2SO_4$ in sec. | %HCl on mucilage | Dextrinization Temp. °C. | Dextrinization Time, Hrs. | Relative viscosity 1% & 30°C | Color of dextrin |
|---|---|---|---|---|---|---|---|---|
| G101-669 | G4-5 | 0.0 | — | | 180-187 | 1 | 1.27 | brown |
| G104-669 | G4-5 | 0.0 | — | | 120-170 | 1.25 | 4.54 | brown |
| G105-669 | G4-5 | 0.0 | — | | 120-172 | 1.5 | 9.7 * | light brown |
| G106-669 | G4-5 | 0.0 | — | | 120-180 | 1.83 | 2.73 | light brown |
| G118-669 | G4-5 | 0.0 | — | | 158 | 3.75 | 2.27 | brown |
| G135-669 | G4-5 | 0.0 | — | | 100-155 | 2.5 | | |
| | | | | | 100-158 | 4.75 | 2.6 | brown |
| | | | | | 100-157 | 7 | 2.06 | brown |
| G138-669 | G4-L | 0.0 | — | | 100-160 | 4.25 | 4.85 | |
| | | | | | 100-157 | 8 | 4.25 | |
| | | | | | 100-160 | 20 | 2.4 | dark brown |
| G139-669 | G4-L | chlorine | 300 | 0.097** | 100-136 | 15 | 1.09 | brown |
| G141-669 | G4-L | chlorine | 300 | 0.116** | 100-137 | 3.5 | 1.4 | tan |
| G143-669 | G4-L | chlorine | 60 | 0.139 | 121 | 14 | 1.85 | light brown |
| G157-669 | G4-5 | HAc | — | 6.33 | 100 | 0.5 | 304.0 | |
| | | | | | 100 | 3 | 15.8 | |
| | | | | | 100 | 5 | 11.6 | |
| | | | | | 100 | 11.5 | 6.1 | brown |
| G6-690 | Tara G7-6 | none | | — | 120-148 | 6.25 | 7.9 | dark brown |
| | | | | | 120-153 | 8.75 | 4.7 | |
| | | | | | 120-155 | 10.5 | 3.3 | dark brown |
| G15-690 | Flame Tree G9 | none | | — | 140 | 5 | 1.8 | brown |
| G16-690 | Flame Tree G9 | none | | — | 120-154 | 3 | 2.8 | brown |
| G19-690 | Honey locust gum | none | | alkaline | 120-150 | 3 | too high | dark brown |
| G24-690 | Locust bean gum | none | | — | 120-148 | 3.5 | 150.4 | |
| | | | | | 120-154 | 21.25 | 2.36 | dark brown |

* Not evenly heated, caked up in bottle

** Values in error because some chlorine volatilized during determination

COOKING OF MUCILAGES FOR VISCOSITY MEASUREMENTS

Two and one-half grams of the mucilage were slurried in 175 ml. of $H_2O$ in a tared beaker. Steam was injected to 87° C. and the temperature was held at 85-87° C. for 10 minutes. The mixture was stirred for 10 minutes longer while cooling, diluted to 1% concentration and the relative viscosity was determined at 30° C. in a modified Ostwald viscometer.

COOKING OF MUCILAGES FOR TUBSIZING

Fifteen grams of the dextrinized mucilage were slurried in 250 ml. of water in a tared beaker and heated by means of direct steam to 87° C. The mixture was held at 85-87° C. for 10 minutes and stirred 10 minutes more while cooling when it was diluted to the desired concentration and used as a tubsize in the usual manner on the laboratory size press.

METHOD OF DETERMINATION OF APPARENT SUGAR IN THE DEXTRINIZED MUCILAGE

A modified Somogyi micromethod was used for determination of the apparent sugar. The copper reagent had the following composition:

| | |
|---|---|
| $CuSO_4 \cdot 5H_2O$ | 7.5 g/liter |
| $KNaC_4H_4O_6 \cdot 4H_2O$ | 25.0 g |
| $Na_2CO_3$ | 25.0 g |
| $NaHCO_3$ | 20.0 g |
| KI | 5.0 g |
| $KIO_3$ | 0.535 g accurate. |

The chemicals were dissolved in the order given in 850 ml. of distilled water. The $KIO_3$ was dissolved separately and added to the solution quantitatively. Two liters of solution were made up at one time and the bottle fitted with a siphon and soda-lime tube.

The sample consisted of 5 ml. of the agitated one per cent mucilage solution used for the viscosity measurements. A 50-minute heating period

in the boiling water bath was used. This period had been determined in previous mucilage experiments (see report No. 17).

DEXTRINIZATION TEMPERATURES

When large samples of mucilage (150-300 g) were dextrinized the temperature of dextrinization was difficult to attain rapidly. This was due to both the bottle and mucilage being cool and cooling of the oven while making the necessary connections to the bottle. For these reasons the dextrinization temperature was not a rigidly controlled factor but was a temperature range. For temperatures above 125° C. the time of dextrinization was started when the thermometer inside the bottle reached 125° C. About 30 minutes were generally required for the temperature to rise from 125°C. to 143°C.

RESULTS AND DISCUSSION

The dextrinization data are presented in Table I and several typical curves are given in Figure 1. From these it may be readily seen that guar mucilage is dextrinized in a manner similar to locust bean gum.

The viscosity of the final product of dextrinization depends upon four factors:- temperature, time, acid concentration, and purity of the original mucilage. High temperature alone was found to rapidly reduce the viscosity of guar mucilage but this almost invariably gave a dark brown product. Starting with a somewhat purer product such as G4-L resulted in a somewhat lighter color but the product was still dark enough to noticeably lower the brightness of a sheet. Increased acid concentrations enabled the use of lower dextrinization temperatures as well as a shorter time but the acid for the most part remained in the final sample and continued to

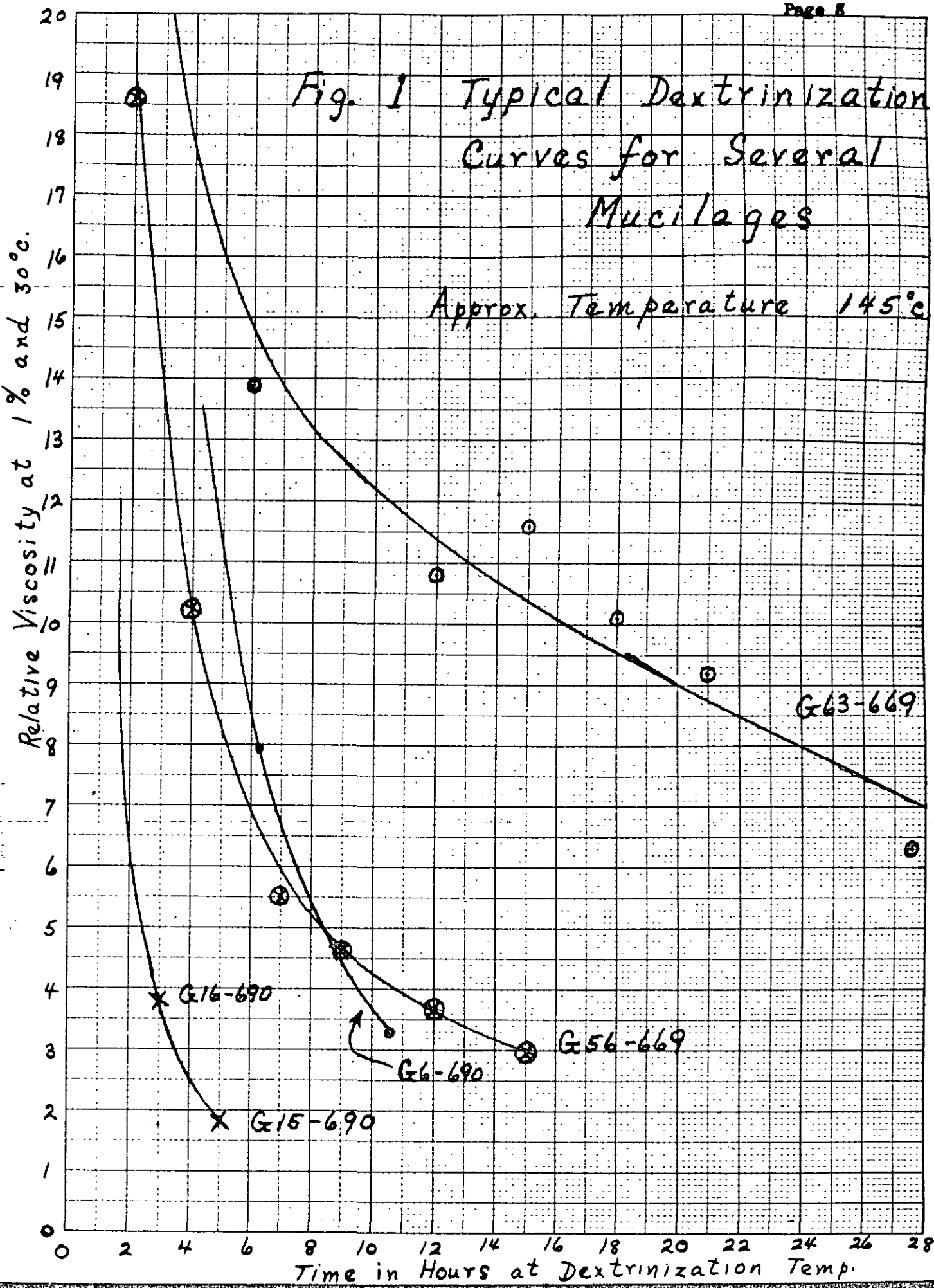


Fig. 1 Typical Dextrinization Curves for Several Mucilages
Approx. Temperature 145°c
Relative Viscosity at 1% and 30°c.
Time in Hours at Dextrinization Temp.
G63-669
G56-669
G6-690
G16-690
G15-690
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28

slowly convert the mucilage. It is believed that acid concentrations in the neighborhood of 0.1 to 0.15% may cause no detrimental effect in this respect but 0.2 to 0.3% is probably an excessive amount to leave in the final product. When higher conversion temperatures were used it seemed reasonable to expect that a considerable part of the HCl used in these experiments would be volatilized. However, it was found that the acidity of the dextrinized products had increased. Analyses of several dextrins are given in Table II.

TABLE II

EFFECT OF HEATING ON THE ACID CONTENT OF DEXTRINIZED MUCILAGE

| Converted mucilage | Dextrinization conditions | | Acid % |
|---|---|---|---|
| | Temp. °C. | Time, hrs. | |
| G38-669 (G4-5) | 25 | — | 0.116 |
| | 143 | 19 | 0.246 |
| G48-669 (G4-5) | 25 | — | 0.000 |
| | 140 | 21.5 | 0.194 |
| G50-669 (G4-L) | 25 | — | 0.266 |
| | 125-137 | 0.5 | 0.252 |
| G56-669 (G4-L) | 25 | — | 0.070 |
| | 143 | 15 | 0.116 |
| G91-669 (G4-5) | 25 | — | 0.217 |
| | 85 | 20.5 | 0.252 |
| Guar germ flour | 25 | — | 0.000 |
| | 160 | 2.5 | 0.000 |
| | 160 | 46.5 | trace |

Whether the HCl volatilized or not is unknown but it may easily be seen that even the acid concentration of G4-L is increased. This may possibly be the result of protein breakdown, oxidation of the mucilage by air, or breakdown of fatty acid materials present in these mucilages. A sample of guar germ flour was heated at 160° C. for various lengths of time but failed to develop any significant amount of titratable acidity.

The use of chlorine gas as an acidic catalyst did not give a product of lighter color than straight HCl. Otherwise this catalyst functioned similarly to HCl.

EVALUATION OF THE TUBSIZE QUALITIES OF THE DEXTRINIZED MUCILAGES

In order to use the converted mucilages as tubsizes the relative viscosity at 1% had to be 4.0 or below. Certain products having higher viscosities than this were evaluated but these could not be expected to enter commercial use for this purpose. The data are presented in Table III where it is apparent that fairly outstanding tubsize adhesives can be made from guar mucilage when the product is in the proper viscosity range. In Figure 2 the percentage increase in bursting strength imparted by a 4.0% tubsize solution is plotted against the relative viscosity. Locust bean gum samples G151-654 (Report No. 18) are also plotted and the result seems to indicate that the lower the viscosity the poorer is the tubsizing adhesive strength. The guar dextrin samples are quite erratic but if sufficient tests were made to make the data statistically valid it is believed that the same conclusion would result. It is also apparent from the data presented that tara mucilage G6-690, flame tree mucilage G15- and G16-690, and locust bean gum mucilages G151-654, G16- and G24-690 are, despite their greater percentage of impurities, all somewhat superior to guar mucilage. A similar conclusion has been empirically made for other methods of conversion and it begins to appear that guar mucilage may be the poorest source of mannogalactan for conversion purposes. Because so little is known about the chemical structure of the mannogalactans these differences cannot be accounted for at the present time. Perhaps when our methylation work is further along we can proceed to convert guar mucilage more intelligently.

TABLE III

SIZE CHARACTERISTICS OF THE DEXTRINIZED MUCILAGES
100% rag stock

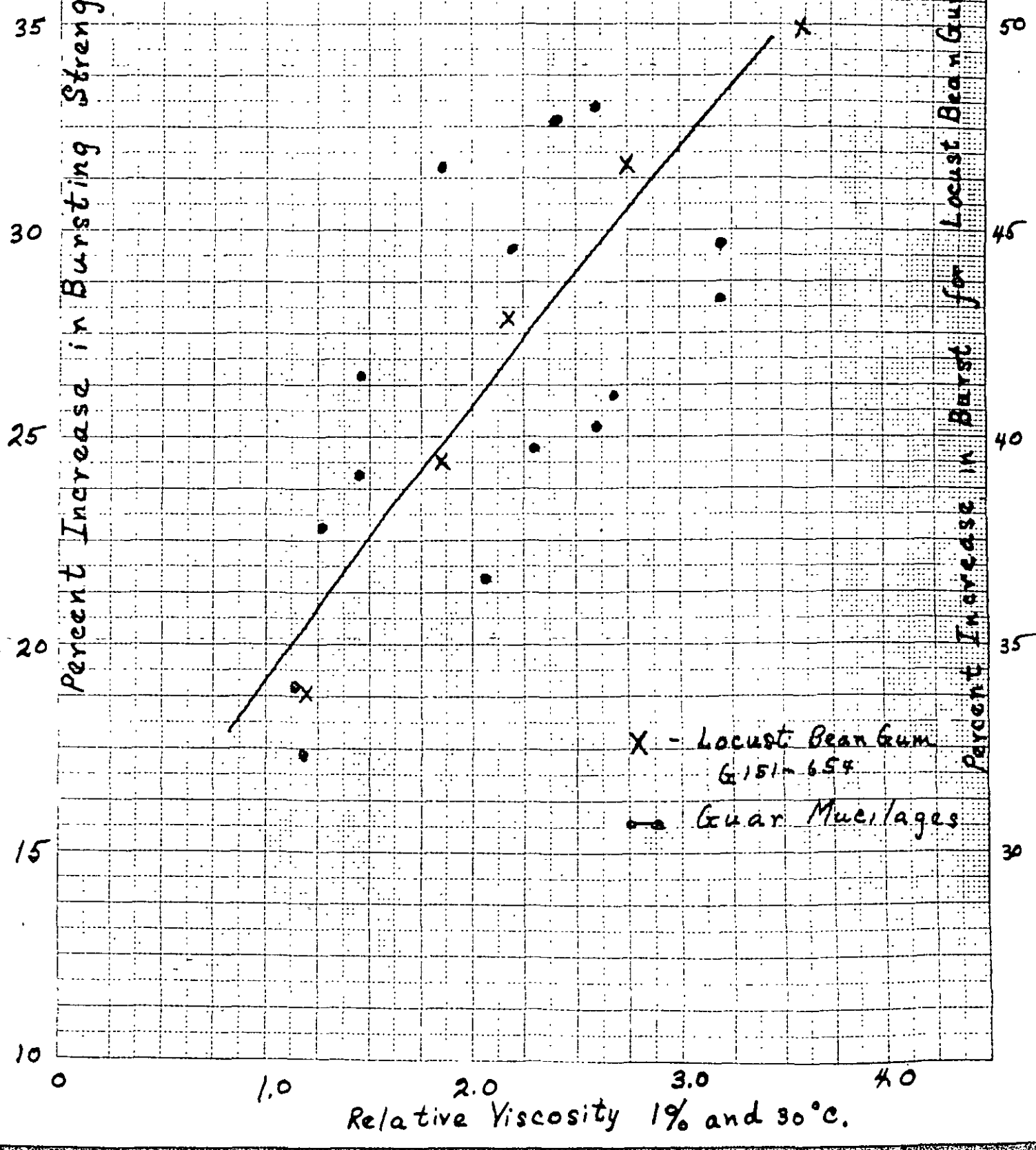
| IPC File No. | Code No. | Relative viscosity 1% & 30°C | Concentration % | Temp. of tubsize °C. | Basis wt. 17 x 22/500 | Caliper -inch | Bursting Strength Points | Bursting Strength Pts/100 lbs | % Increase in burst | MIT Fold In | MIT Fold Across | Gurley porosity sec/100 cc | Elmendorf Tear g/sheet In | Elmendorf Tear g/sheet Across | Brightness % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Blank | — | — | — | 19.3 | 0.0034 | 31.2 | 162 | — | 226 | 61 | 181 | 90 | 100 | 79.1 |
| 121798 | 038-669 | 4.27 | 2.0 | 60 | 19.3 | 0.0039 | 38.1 | 197 | 21.6 | 313 | 70 | 204 | 92 | 111 | 76.2 |
| 121799 | 038-669 | 3.18 | 4.0 | 59 | 19.6 | 0.0039 | 41.1 | 210 | 29.6 | 362 | 95 | 284 | 92 | 105 | 73.3 |
| 121800 | 038-669 | 3.18 | 2.0 | 58 | 19.3 | 0.0039 | 37.4 | 194 | 19.7 | 281 | 66 | 189 | 92 | 104 | 76.4 |
| 121844 | 038-669 | 2.59 | 4.0 | 62 | 19.3 | 0.0039 | 41.6 | 216 | 33.3 | 409 | 85 | 247 | 88 | 107 | 72.9 |
| 121845 | 038-669 | 2.59 | 2.0 | 61 | 19.2 | 0.0039 | 38.6 | 201 | 24.1 | 298 | 70 | 181 | 93 | 113 | 75.3 |
| 121846 | 038-669 | 2.20 | 4.0 | 62 | 19.5 | 0.0040 | 41.0 | 210 | 29.6 | 374 | 82 | 235 | 93 | 106 | 73.6 |
| 121847 | 038-669 | 2.20 | 2.0 | 58 | 19.5 | 0.0040 | 38.6 | 195 | 19.8 | 273 | 63 | 180 | 97 | 109 | 76.1 |
| 121848 | 044-669 | 1.18 | 4.0 | 60 | 19.7 | 0.0040 | 37.5 | 190 | 17.3 | 265 | 73 | 157 | 93 | 102 | 75.6 |
| 121849 | 044-669 | 1.18 | 2.0 | 58 | 19.6 | 0.0040 | 37.3 | 190 | 17.3 | 205 | 63 | 145 | 92 | 109 | 76.6 |
| 121884 | 044-669 | 1.09 | 7.0 | 61 | 19.6 | 0.0039 | 40.3 | 206 | 27.2 | 421 | 99 | 155 | 92 | 98 | 72.3 |
| 121885 | 048-669 | 2.68 | 4.0 | 56 | 19.3 | 0.0039 | 39.4 | 204 | 25.9 | 400 | 91 | 211 | 92 | 96 | 72.8 |
| 121886 | 048-669 | 2.68 | 2.0 | 61 | 19.6 | 0.0040 | 37.0 | 189 | 16.7 | 309 | 74 | 175 | 96 | 101 | 76.0 |
| 121918 | 049-669 | 1.82 | 5.0 | 60 | 19.8 | 0.0040 | 42.2 | 213 | 31.5 | 399 | 89 | 223 | 91 | 108 | 72.5 |
| 121919 | 049-669 | 1.82 | 2.0 | 59 | 19.5 | 0.0040 | 37.8 | 194 | 19.7 | 231 | 62 | 164 | 92 | 107 | 75.3 |
| 121920 | 050-669 | 1.45 | 4.0 | 61 | 19.9 | 0.0040 | 40.7 | 205 | 26.6 | 318 | 92 | 172 | 94 | 104 | 77.4 |
| 121921 | 050-669 | 1.45 | 2.0 | 59 | 19.6 | 0.0040 | 37.2 | 190 | 17.3 | 239 | 74 | 154 | 94 | 106 | 77.9 |
| 121926 | 056-669 | 10.2 | 2.0 | 56 | 19.5 | 0.0040 | 39.6 | 203 | 25.3 | 292 | 78 | 203 | 93 | 105 | 77.8 |
| 122257 | 063-669 | 10.8 | 2.0 | 63 | 20.0 | 0.0041 | 39.4 | 197 | 21.6 | 321 | 84 | 152 | 101 | 112 | 76.8 |
| 122258 | 063-669 | 4.7 | 2.0 | 62 | 19.8 | 0.0040 | 38.6 | 195 | 20.4 | 310 | 73 | 140 | 97 | 113 | 76.9 |
| 122208 | 081-669 | 12.1 | 2.0 | 58 | 19.9 | 0.0040 | 38.2 | 192 | 18.5 | 328 | 74 | 147 | 96 | 101 | 76.8 |
| 122207 | 081-669 | 3.5 | 2.0 | 59 | 19.7 | 0.0040 | 36.3 | 184 | 13.6 | 303 | 75 | 135 | 98 | 114 | 76.6 |
| 122209 | 081-669 | 3.4 | 2.0 | 61 | 19.5 | 0.0040 | 37.2 | 191 | 17.9 | 333 | 62 | 131 | 98 | 105 | 76.0 |
| 122146 | 098-669 | 1.13 | 8.0 | 62 | 19.8 | 0.0041 | 39.6 | 201 | 24.1 | 357 | 88 | 144 | 92 | 104 | 77.1 |
| 122147 | 098-669 | 1.13 | 4.0 | 59 | 19.5 | 0.0040 | 37.8 | 194 | 19.7 | 379 | 82 | 134 | 90 | 101 | 77.7 |
| 122148 | 0101-669 | 1.27 | 8.0 | 61 | 19.7 | 0.0040 | 42.1 | 214 | 32.1 | 465 | 99 | 157 | 92 | 101 | 70.9 |
| 122149 | 0101-669 | 1.27 | 4.0 | 61 | 19.6 | 0.0040 | 39.1 | 199 | 22.8 | 275 | 76 | 150 | 95 | 105 | 74.1 |
| 122150 | 0104-669 | 4.54 | 2.0 | 60 | 19.7 | 0.0040 | 40.4 | 205 | 26.6 | 349 | 88 | 154 | 90 | 110 | 77.1 |
| 122442 | 0135-669 | 2.6 | 4.0 | 62 | 19.6 | 0.0039 | 39.8 | 203 | 25.3 | 258 | 82 | 196 | 86 | 95 | 73.8 |
| 122443 | 0135-669 | 2.6 | 2.0 | 61 | 19.6 | 0.0040 | 37.1 | 189 | 16.7 | 245 | 74 | 163 | 94 | 106 | 76.6 |

TABLE III (cont.)

TUBSIZE CHARACTERISTICS OF THE DEXTRINIZED MUCILAGES
100% rag stock

| IPO File No. | Code No. | Relative viscosity 1% & 30°C | Concentration % | Temp. of tubsize °C. | Basis wt. 17 x 22/500 | Caliper -inch | Bursting Strength Points | Bursting Strength Pts/100 lbs | % Increase in burst | MIT Fold In | MIT Fold Across | Gurley porosity sec/100 cc | Elmendorf Tear g/sheet In | Elmendorf Tear g/sheet Across | Brightness % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 122444 | 0135-669 | 2.06 | 4.0 | 57 | 19.7 | 0.0040 | 38.8 | 197 | 21.6 | 291 | 87 | 200 | 100 | 105 | 74.8 |
| 122445 | 0135-669 | 2.06 | 2.0 | 59 | 19.5 | 0.0040 | 35.0 | 179 | 10.5 | 236 | 80 | 163 | 92 | 106 | 76.2 |
| 122446 | 0139-669 | 1.09 | 8.0 | 60 | 20.1 | 0.0040 | 39.5 | 197 | 21.6 | 284 | 86 | 164 | 94 | 100 | 73.1 |
| 122364 | 0118-669 | 2.27 | 4.0 | 63 | 19.5 | 0.0040 | 39.3 | 202 | 24.7 | 299 | 76 | 205 | 93 | 107 | 75.5 |
| 122365 | 0118-669 | 2.27 | 2.0 | 60 | 19.5 | 0.0040 | 36.4 | 187 | 15.4 | 262 | 60 | 181 | 93 | 108 | 76.7 |
| 122454 | 0138-669 | 2.4 | 4.0 | 59 | 18.8 | 0.0040 | 40.5 | 215 | 32.7 | 446 | 95 | 241 | 96 | 101 | 73.4 |
| 122455 | 0138-669 | 2.4 | 2.0 | 57 | 18.5 | 0.0040 | 38.8 | 210 | 29.6 | 236 | 93 | 184 | 97 | 105 | 75.6 |
| 123109 | 0141-669 | 1.4 | 4.0 | 61 | 20.0 | 0.0040 | 40.1 | 201 | 24.1 | 406 | 87 | 158 | 92 | 107 | 77.0 |
| 123110 | 0141-669 | 1.4 | 2.0 | 60 | 19.8 | 0.0040 | 38.0 | 192 | 18.5 | 324 | 77 | 154 | 93 | 105 | 77.8 |
| 123107 | 0143-669 | 1.85 | 4.0 | 63 | 19.9 | 0.0040 | 42.4 | 213 | 31.5 | 548 | 113 | 181 | 93 | 105 | 76.8 |
| 123108 | 0143-669 | 1.85 | 2.0 | 59 | 19.8 | 0.0040 | 39.4 | 199 | 22.8 | 361 | 91 | 158 | 95 | 107 | 77.6 |
| 123111 | 0157-669 | 6.1 | 3.0 | 62 | 19.6 | 0.0040 | 42.2 | 215 | 32.7 | 388 | 105 | 225 | 96 | 106 | 75.5 |
| 123112 | 0157-669 | 6.1 | 2.0 | 60 | 19.7 | 0.0040 | 38.9 | 197 | 21.6 | 328 | 74 | 182 | 96 | 104 | 75.8 |
| 123176 | 06-690 | 4.7 | 3.0 | 60 | 19.9 | 0.0038 | 42.8 | 215 | 32.7 | 365 | 82 | 308 | 98 | 112 | 70.9 |
| 123177 | 06-690 | 4.7 | 2.0 | 62 | 19.8 | 0.0038 | 41.3 | 209 | 29.0 | 296 | 64 | 231 | 95 | 111 | 73.9 |
| 123178 | 06-690 | 3.3 | 4.0 | 60 | 19.8 | 0.0039 | 43.6 | 220 | 35.8 | 539 | 84 | 374 | 97 | 105 | 69.0 |
| 123179 | 06-690 | 3.3 | 2.0 | 59 | 19.6 | 0.0039 | 39.3 | 201 | 24.1 | 253 | 85 | 211 | 97 | 109 | 73.6 |
| 123291 | 015-690 | 1.8 | 6.0 | 56 | 19.7 | 0.0040 | 44.7 | 227 | 40.2 | 539 | 119 | 328 | 91 | 96 | 67.0 |
| 123292 | 015-690 | 1.8 | 4.0 | 56 | 19.7 | 0.0040 | 42.3 | 215 | 32.7 | 404 | 102 | 260 | 90 | 101 | 70.8 |
| 123293 | 016-690 | 2.8 | 4.0 | 60 | 19.3 | 0.0040 | 42.6 | 221 | 36.4 | 577 | 105 | 302 | 91 | 101 | 71.8 |
| 123294 | 016-690 | 2.8 | 2.0 | 50 | 19.4 | 0.0040 | 40.2 | 207 | 27.8 | 333 | 99 | 194 | 93 | 101 | 75.2 |
| | 024-690 | 2.38 | 4.0 | 62 | 19.6 | 0.0040 | 44.1 | 225 | 38.9 | 439 | 115 | 286 | 89 | 94 | — |
| | 024-690 | 2.38 | 2.0 | 59 | 19.4 | 0.0040 | 38.8 | 200 | 23.4 | 272 | 89 | 196 | 92 | 102 | — |

# Fig. 2 Relationship Between Viscosity and Bursting Strength. 4% Tubsize



The mechanism of the dextrinization of guar mucilage should be studied more fundamentally. For example it is possible if not probable that the galactosides and mannosides in the mucilage chain may be connected by different linkages. Thus, the mannosides may be joined by $\beta$-linkages and the galactosides by $\alpha$-linkages. Under such conditions it might be expected that the $\alpha$-linkages would hydrolyze much faster than the $\beta$-linkages giving essentially a mannan dextrin. It is obvious that the reverse case might predominate in another type of mucilage giving a galactoside dextrin. Furthermore, the way in which the chains are constructed--the pattern of distribution of mannose and galactose--would greatly influence the adhesive strength of the dextrin obtained.

The hot water solubility of guar mucilage is progressively decreased to a constant value upon dextrinization at 150° C. This is shown in Table IV and Figure 3. In these experiments oven-dry G4-L was heated in closed weighing bottles in an oven at 150° C. The solubility was determined by cooking by the method used for viscosity determinations and 25 g. aliquots were evaporated to dryness. It may be fortuitous that the solubility becomes constant at approximately 57%--the percentage of mannose in guar--but this should be investigated. Attempts to determine the galactose in the soluble part of the 9 hour sample in Table IV by the method of Wise and Appling [Ind. Eng. Chem., 16, 28(1944)] gave a value of 4.0% while a mannose determination gave 50.4%. An untreated sample of guar mucilage gave a similar set of values which is at present unexplainable. It is believed that the unpurified mucilage may contain a material which acts as a nutrient for the yeast organism which does not attack galactose or which slows down the other organism in some way thereby causing failure of the method. This is being investigated further.

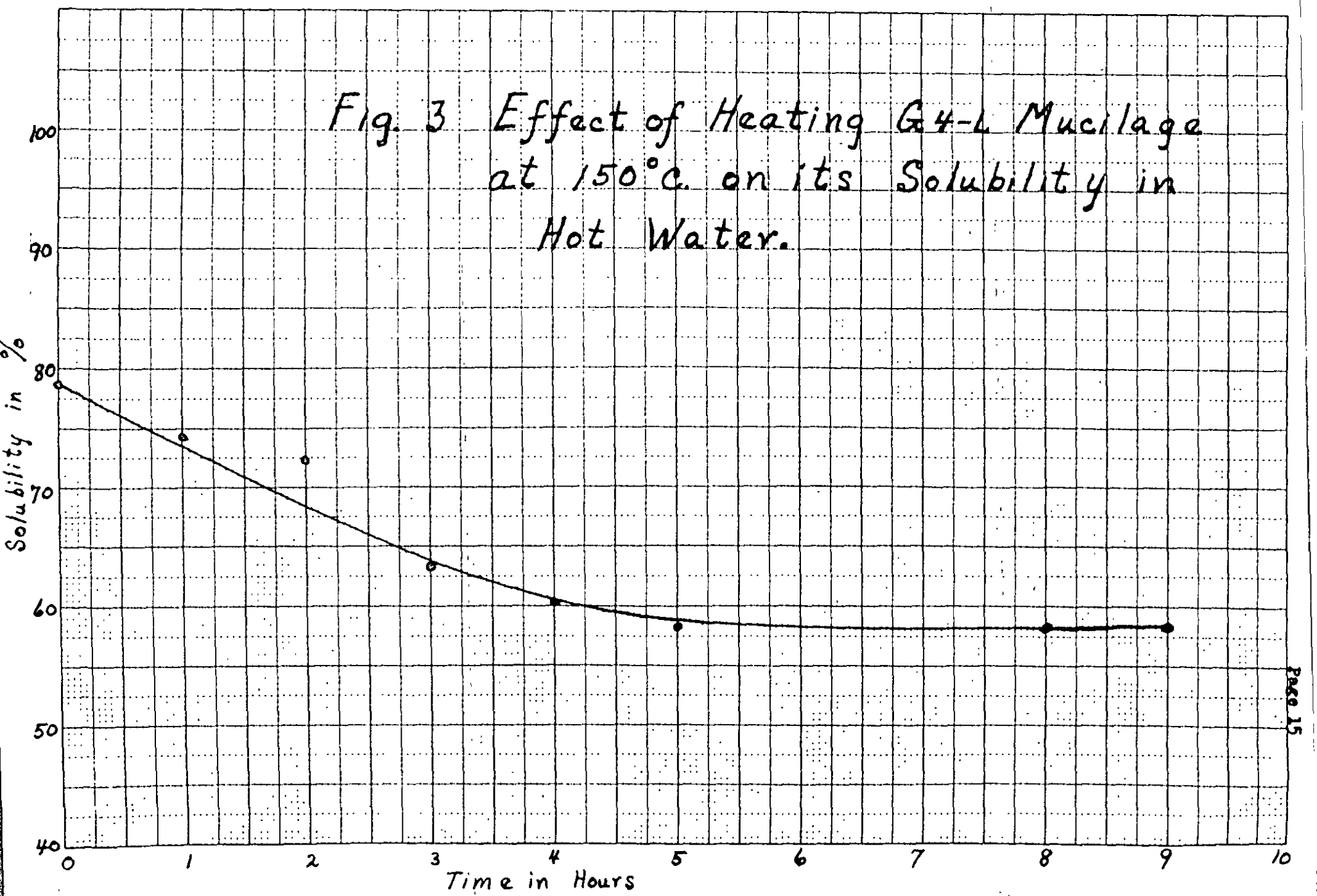


Fig. 3 Effect of Heating G4-L Mucilage at 150°C. on its Solubility in Hot Water.
Solubility in %
100
90
80
70
60
50
40
0
1
2
3
4
5
6
7
8
9
10
Time in Hours

TABLE IV

EFFECT OF HEATING G4-L MUCILAGE AT 150° C. ON SOLUBILITY AND VISCOSITY

| Time in hours, Heated at 150° C. | Solubility in % | Viscosity at 1% & 30° C. Before Centrifuging | Viscosity at 1% & 30° C. After Centrifuging |
|---|---|---|---|
| 0.0 | 78.5 | too viscous | |
| 1.0 | 74.4 | too viscous | |
| 2.0 | 72.4 | 92.5 | 83.0 |
| 3.0 | 63.2 | 16.8 | 14.4 |
| 4.0 | 60.4 | 9.55 | 7.37 |
| 5.0 | 58.4 | 6.41 | 5.58 |
| 9.0 | 57.7 | 3.60 | 3.22 |

The percentage of apparent sugar in a few dextrins was determined by a modified Somogyi method in order to obtain an idea of the magnitude of chemical degradation. It is interesting to note that the amount of reducing material seemed to reach a constant value in the case of G4-5 mucilage G81-669. This property of the dextrins might be profitably studied further.

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PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 21
DATE April 23, 1946
NOTE BOOK 654 and *
PAGE 126 TO 130
SIGNED John W. Swanson
John W. Swanson

Experiments with a Bentonite-Mannogalactan Mucilage Complex and its Effect on the Ash Content of Handsheets

Introduction: Some months ago during a discussion of mucilage problems with several representatives of General Mills Inc. it was mentioned that small amounts of mannogalactan mucilages clarified or flocced bentonite dispersions. This was tried later in the laboratory where it was learned that as little as two drops of 0.5% guar mucilage would completely flocc 50 ml. of a 0.5% bentonite dispersion. This phenomenon seemed very interesting for the following reasons:

1. It is unusual to find two highly hydrated colloids having like charges which coagulate or flocc when mixed.
2. A new type of complex addition product between the bentonite lattice and the mucilage appears to be formed which may be similar to the borax-mucilage complex.
3. The complex formation may not be limited to bentonite alone but may form with the more hydrous fractions of many clays used as filling materials. Furthermore, this complex formation might account for the poorer results obtained in some mills because part of the mucilage was inactivated by reaction with certain hydrous mineral species in the filler.
4. The complex may retain some of the adhesive properties of the mucilage and become useful as a means of increasing the ash content of a sheet of paper. Fine fibers would also be retained more completely under these conditions.
5. A possible analytical tool for mannogalactan mucilages might be developed.

This report is concerned with several preliminary experiments with the phenomenon. Flocculation tests in graduated cylinders were made with locust bean gum mucilage and this was followed by a study of the effects of bentonite-guar mucilage mixtures on the ash and strength properties of handsheets.

Experimental:

Preliminary Flocculing Experiments with Locust Bean Gum.

a. Bentonite dispersion

Ten grams of Wyoming bentonite were added to a 2 liter flask and wetted with 30 ml. of 95% ethyl alcohol. The mixture was diluted with water to 2 liters accompanied by shaking.

b. Locust Bean Gum.

Cook A.

Ten grams of locust bean gum were suspended in about 1500 ml. of water and direct steam injected until the temperature reached 85° C. The mixture was then diluted to 0.5% concentration and placed in two 2 liter flasks and autoclaved for 25 minutes at 120° C. The flasks were weighed, the concentration again adjusted to 0.5% with sterile water and the solution was poured into sterile 125 ml. flasks and sealed with rubber stoppers. The viscosity of this mucilage solution was somewhat below normal because of the longer time taken to raise the temperature to 85° C. which allowed the natural enzymes to act longer. After sterilization, however, the viscosity remained constant for several months provided the seal was not broken.

Cook B.

Two and one half grams of locust bean gum were slurried in 350 ml. of water and steam injected to raise the temperature to 90° C. After holding at 85-90° C. for 10 minutes the mixture was diluted to 0.5% gum concentration and used.

c. The Flocculing Experiments

One hundred ml. of the bentonite dispersion was added to each of several 100 ml. graduated cylinders. The desired number of drops of

mucilage was then added to each cylinder from an eye dropper and followed by immediate shaking. The mixture was allowed to flocc and the flocc volume recorded at various intervals. This procedure was used for the first A and B sets recorded in Table I but it was believed that air bubbles may have become entrapped with this method of mixing. Therefore, subsequent experiments were made by gently stirring the bentonite and mucilage in a beaker and carefully transferring the mixture to the graduated cylinder.

One hundred drops of the mucilage solution weighed 8.3 g. which gave a weight per drop of 0.083 g. The mucilage percentages in Table I were calculated from this value.

The effect of the concentration of mucilage when added to the bentonite dispersion may be seen from the data of Table II. In these experiments the same total quantity of mucilage was added to the bentonite but different concentrations were used.

In Table III the effect of the length of time taken to add the mucilage to the bentonite dispersion was studied at one concentration.

Experiments with the Bentonite-Mucilage Complex in Handsheets

a. Beating of Pulp.

Three hundred sixty grams (O. D. basis) of Weyerhaeuser bleached sulfite pulp were slushed in the Valley beater with 23 liters of water for 5 minutes and then beaten for 51 minutes with 5500 g. on the bedplate. Shopper Riegler freeness 570 and 625, consistency 1.5%.

TABLE I

The Effect of Locust Bean Gum on the Floc Volume of a Bentonite Dispersion

| Mucilage Used Cook | Mucilage Added: Number of drops 0.5% | Conc. on Bentonite % | Conc. % of Solution | Floc Volume cc. at Time in Hours: 1 | 2 | 3 | 4 | 16 | 18 | 21 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Hours | | | | | | |
| A | 10 | 0.83 | 0.00415 | 0 | | | | 5 | 5 | |
| | 20 | 1.66 | 0.0083 | | | | | 17 | 16 | |
| | 40 | 3.32 | 0.0166 | 100 | | | | 40 | 38 | |
| | 80 | 6.65 | 0.0332 | 105 | | | | 86 | 83 | |
| B | 10 | 0.83 | 0.00415 | 55 | | | | 24 | 23 | |
| | 20 | 1.66 | 0.0083 | 88 | | | | 34 | 32 | |
| | 40 | 3.32 | 0.0166 | 95 | | | | 41 | 40 | |
| | 80 | 6.65 | 0.0332 | 98 | | | | 43 | 42 | |
| B. | 0 | 0 | 0 | | 0 | 0 | 0 | | | 0.5 |
| | 1 | 0.08 | 0.000415 | | 0 | 0 | 0 | | | 1.0 |
| | 3 | 0.25 | 0.00124 | | 1 | 2 | 2 | | | 4.0 |
| | 5 | 0.41 | 0.00207 | | 3 | 4 | 4 | | | 6.0 |
| | 10 | 0.83 | 0.00415 | | 18 | 18 | 13 | | | 14.0 |
| | 20 | 1.66 | 0.0083 | | 52 | 48 | 44 | | | 28.0 |
| | 40 | 3.32 | 0.0166 | | 96 | 91 | 85 | | | 45.0 |
| | 80 | 6.65 | 0.0332 | | 99 | 91 | 82 | | | 56.0 |
| | 160 | 13.3 | 0.0664 | | 92 | 89 | 76 | | | 52.0 |
| | 200 | 16.6 | 0.083 | | | | | | | 55.0 |

TABLE II

Effect of Mucilage Concentration When Added to the Bentonite

| | Conc. Mucilage % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| B | 0.25 | 20 | 0.83 | 0.00415 | 16 | 15 | 14 | 11 |
| | 0.125 | 40 | 0.83 | 0.00415 | 6 | 8 | 9 | 12 |
| | 0.05 | 100 | 0.83 | 0.00415 | 5 | 6 | 6 | 7 |

TABLE III

Effect of Time of Adding Mucilage to the Bentonite

| | B Time to Add Gum in Seconds | | | | 20 Hours |
|---|---|---|---|---|---|
| B | 180 | 20 | 1.66 | 0.0083 | 31 |
| | 15 | 20 | 1.66 | 0.0083 | 28 |
| | 7 | 20 | 1.66 | 0.0083 | 30 |

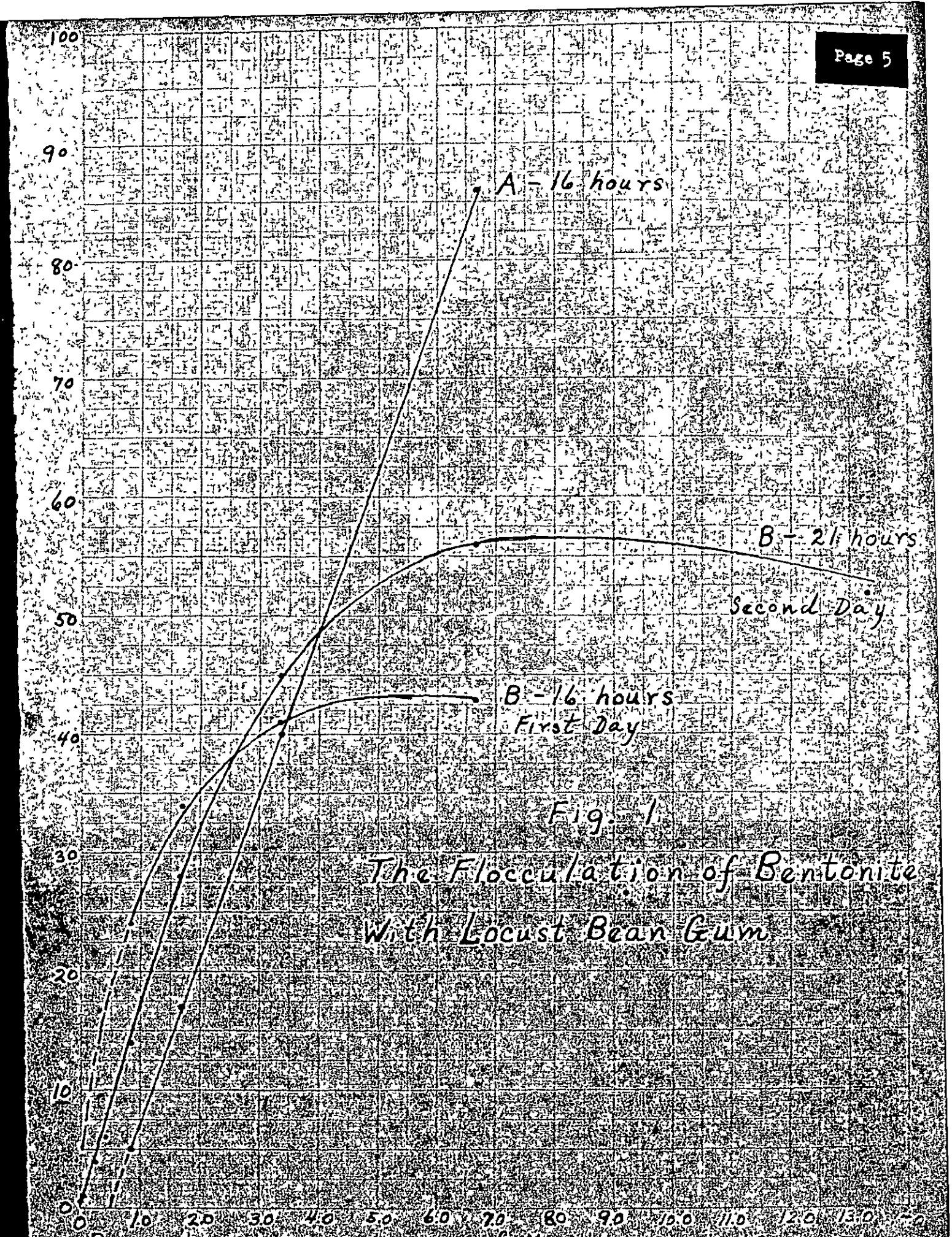


Fig. 1.

The Flocculation of Bentonite With Locust Bean Gum

Cooking the Guar Mucilage

Ten grams of guar G4-5 mucilage were slurried in 1500 ml. of 0.25% borax solution and heated to 87° C. with direct steam. Then 67 ml. of 0.3 N HCL were added and the temperature was held at 85-87° C. for 10 minutes with continued stirring. After cooling the concentration was adjusted to 0.5%.

Making the Handsheets.

The first series of handsheets in Table IV were made somewhat differently than the later sets.

Thirty grams of the beaten pulp were measured out into a pail and 30 g. of bentonite which had been previously wetted first with 30 ml. of 95% alcohol and then with 250 ml. of water was added and stirred for 5 minutes until the lumps dispersed. Then 30 g. of the mucilage solution (1.5% on the fiber) were added with vigorous stirring. After 5 minutes the mixture was diluted to 0.5% fiber consistency and 12 handsheets (1.5 g. each) were made in the regular manner. The following sets of sheets were made in addition to the above: (a) a blank with 1.5% of mucilage in which the bentonite was omitted (b) a set in which the bentonite but no mucilage was added and (c) a set in which the mucilage was not added until the stock containing the bentonite had been diluted to 0.5% consistency.

All of the remaining sets of sheets were made by the following procedure except where certain constituents were left out for comparative purposes. Thirty grams of pulp (O. D. basis) were measured out in a

## TABLE IV

### Handsheet Characteristics with Mucilage-Bentonite Mixtures

| Gum Added % | Bentonite Added % | Basis Weight 25 x 40/ 500 | Caliper inch | Bursting Strength Points | Bursting Strength Points 100 lbs. | MIT Fold | Gurley Porosity Sec./100 cc. | Elmendorf Tear g/sheet | Tear Factor | Ash % |
|---|---|---|---|---|---|---|---|---|---|---|
| **Preliminary Experiments Freeness 570** | | | | | | | | | | |
| 1.5 | none | 46.7 | 0.0042 | 47.9 | 103 | | | 45 | 0.96 | 0.3 |
| 0.0 | 100 | 46.7 | 0.0051 | 14.5 | 31 | | | 76 | 1.63 | 8.7 |
| 1.5 | 100 | 42.4 | 0.0043 | 14.0 | 33 | | | 56 | 1.32 | 20.1 |
| 1.5* | 100 | 42.0 | 0.0043 | 21.6 | 51 | | | 58 | 1.38 | 20.0 |
| **Control Experiments no Rosin or Alum Freeness 625** | | | | | | | | | | |
| Blank | none | 51.5 | 0.0040 | 34.7 | 67 | 254 | 52 | 52 | 1.01 | 0.39 |
| 0.75 | none | 52.8 | 0.0040 | 43.3 | 82 | 494 | 68 | 49 | 0.93 | 0.28 |
| 1.5 | none | 51.9 | 0.0040 | 43.5 | 84 | 447 | 71 | 45 | 0.87 | 0.2 |
| 2.0 | none | 52.0 | 0.0040 | 42.6 | 82 | 511 | 70 | 44 | 0.85 | 0.18 |
| 3.0 | none | 52.6 | 0.0040 | 49.9 | 95 | 483 | 95 | 42 | 0.80 | 0.3 |
| 5.0 | none | 52.6 | 0.0040 | 48.5 | 92 | 599 | 106 | 41 | 0.78 | 0.4 |
| **Control Experiments with 2% Rosin and 4.5% Alum** | | | | | | | | | | |
| Blank | none | 52.9 | 0.0040 | 35.2 | 66.5 | 305 | 55 | 60 | 1.13 | 0.6 |
| 0.75 | none | 54.1 | 0.0041 | 44.9 | 83 | 450 | 65 | 51 | 0.94 | 0.5 |
| 1.5 | none | 52.9 | 0.0040 | 42.7 | 81 | 421 | 68 | 45 | 0.85 | 0.5 |
| 2.0 | none | 53.5 | 0.0041 | 38.5 | 72 | 417 | 74 | 45 | 0.84 | 0.7 |
| 3.0 | none | 54.1 | 0.0041 | 48.4 | 90 | 494 | 97 | 46 | 0.85 | 0.5 |
| 5.0 | none | 53.1 | 0.0041 | 49.8 | 94 | 668 | 94 | 42 | 0.79 | 0.6 |
| **Mucilage-Bentonite Experiments no Rosin or Alum** | | | | | | | | | | |
| 0.0 | 100 | 44.8 | 0.0044 | 22.1 | 49 | 29 | 53 | 76 | 1.70 | 5.3 |
| 0.75 | 100 | 42.7 | 0.0039 | 17.2 | 40 | 15 | 147 | 55 | 1.29 | 11.0 |
| 1.5 | 100 | 42.1 | 0.0039 | 16.0 | 38 | 12 | 238 | 62 | 1.47 | 15.1 |
| 2.0 | 100 | 40.1 | 0.0035 | 13.7 | 34 | 9 | 334 | 53 | 1.32 | 21.5 |
| 3.0 | 50 | 41.4 | 0.0036 | 19.7 | 48 | 29 | 350 | 53 | 1.28 | 16.0 |
| 5.0 | 50 | 41.4 | 0.0033 | 21.4 | 52 | 39 | 420 | 44 | 1.06 | 19.5 |
| **Mucilage-Bentonite Experiments with 2% Rosin and 4.5% Alum** | | | | | | | | | | |
| 0.0 | 100 | 44.9 | 0.0041 | 18.7 | 42 | 12 | 65 | 75 | 1.67 | 5.7 |
| 0.75 | 100 | 42.9 | 0.0040 | 15.6 | 36 | 10 | 148 | 61 | 1.42 | 10.8 |
| 1.5 | 100 | 42.8 | 0.0039 | 14.3 | 33 | 7 | 244 | 54 | 1.26 | 15.5 |
| 2.0 | 100 | 43.1 | 0.0038 | 14.3 | 33 | 7 | 312 | 50 | 1.16 | 20.2 |
| 3.0 | 50 | 44.6 | 0.0039 | 20.0 | 45 | 25 | 392 | 49 | 1.10 | 18.1 |
| 5.0 | 50 | 44.0 | 0.0036 | 21.0 | 48 | 49 | 412 | 47 | 1.07 | 17.5 |

* The mucilage for this and the following sets of sheets was added to the diluted (0.5%) stock.

graduated cylinder and 30 grams of bentonite added with stirring. The mixture was diluted to 0.5% fiber consistency and then the desired quantity of cooked guar mucilage added with stirring. Then 2% of rosin size (based on fiber) was added with 5 minutes stirring followed by 4.5% of alum and another 5 minute stirring period. The sheets were made as before except that sufficient N $H_2SO_4$ was added to the sheet mold to maintain the pH at 4.5 - 5.0 in all furnishes containing rosin and alum.

With 3 and 5% of mucilage it was necessary to lower the bentonite addition to 50% on the weight of the fiber because drainage was exceedingly slow.

Results and Discussion:

The Flocculation Experiments

From an inspection of Table I and Figure 1 it may be seen that the type of floc and completeness of flocculation is dependent upon the amount of mucilage added to the bentonite dispersion. Mucilage A gave a straight line relationship when flocculation volume was plotted against the percentage concentration of mucilage on the bentonite. This was not the case with mucilage B but after standing for a day there was a tendency toward the straight line relationship at lower concentrations. This difference in mucilages A and B cannot be accounted for at present but it may be related to the degree of dispersion, the viscosity and the state of degradation of the mucilage. Further work should be done on this phenomenon. It would appear that an analytical tool for mucilage might possibly develop from such studies. The concentration

of the mucilage at the time of addition to the bentonite seemed to make considerable difference in the flocculation volume but a wide variation of the time taken to add 20 drops of 0.5% mucilage did not seem to have any pronounced effect.

The Handsheet Experiments

In the first series of experiments of Table IV the marked ability of the bentonite-mucilage complex to increase the ash content of handsheets was quite apparent. The addition of 100% of bentonite on the weight of fiber gave an ash content of 8.7% and when 1.5% of mucilage was added the ash increased to 20.1%. The interesting point about this data was the strength properties of the sheets. The sheet containing 20.1% ash had a bursting strength equivalent to the sheet containing 8.7% ash. The addition of the mucilage to the stock after dilution to 0.5% fiber consistency made an even greater improvement in bursting strength. For this reason subsequent sheets were made in this manner.

The basis weight of the sheets containing bentonite and mucilage were unaccountably low, which may prevent strict comperison of the strength properties with the blank and the controls. However it is believed that the B. and M. sheets may be compared with one another with valid results.

Several other interesting points are indicated from the data of Table IV. (1) At the Schopper-Riegler freeness 625 less bentonite was retained by the fiber alone than at freeness 570 and the addition

of rosin and alum did not increase this value. Since bentonite is flocculated by alum solutions it seems unusual that greater retention did not result. (2) With 3% G4-5 mucilage and 50% bentonite the ash content increased from 5.3% ash for the blank to 16.0% ash and the bursting strength was the same. With 5% G4-5 and 50% bentonite the ash became 19.5% and the burst value was greater than that of the control. It was necessary to use 50% bentonite with the higher mucilage concentrations (3 and 5%) in order to form the sheets which drained very slowly and had rather poor formation. The very high Gurley porosity values show indirectly just how slow these furnishes really were.

Further work:

It is believed that this method of loading may impart some unique properties to the sheet and further work is being done. The large quantities of bentonite used in these experiments have served to show the feasibility of a high ash content in this rather light weight sheet. Future experiments will be made from the other direction starting with smaller additions of bentonite and working toward the higher values. It is likely that a significant part of the mucilage is taken up by the excess bentonite and thereby at least partially inactivated. Therefore, experiments made with lower amounts of bentonite should give a better insight into how much strength can be gained per unit of mucilage and ash added.

Further work should also be done with mixtures of bentonite and other fillers provided the bentonite complex manifests an advantage over straight beater clay-mucilage mixtures.

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# PROJECT REPORT FORM

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Dr. Rowland
Mr. Swanson

PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 20
DATE April 8, 1946
NOTE BOOK 669
PAGE 110 TO 118
SIGNED John W. Swanson
John W. Swanson

SOME EXPERIMENTS WITH THE EFFECTS OF GUAR MUCILAGE ON DOUGLAS FIR PULP

INTRODUCTION:

The principle difficulty encountered in substituting Douglas fir kraft pulp for hemlock which is becoming scarce is in developing sufficient bursting strength. Douglas fir gives a long fiber which has plenty of tearing resistance when made into a sheet but the maximum bursting strength falls considerably short of that of hemlock and certain other pulps. It was believed that guar mucilage might possibly supplement this strength deficiency. This report is concerned with several preliminary experiments made to determine the effectiveness of guar G4-5 on this pulp.

EXPERIMENTAL:

The pulp used was a commercially produced sample obtained from the Crown Zellerback Corporation in the form of wet lap. Our sample, taken from the large skid in the pulp laboratory, contained an average of 53.5 % moisture.

Beating of Pulps A and B. Three hundred sixty grams (O.D. basis) of the wet lap were slushed for 5 minutes with 22,625 ml. of water in a valley beater. Then a weight of 5500 g. was placed on the bedplate and the pulp was beaten for 5 minutes. The weight was removed and the stock slushed while 10.5 liters were removed and designated as Pulp A. (Schopper Riegler freeness 870). The remainder of the stock was then

beaten for an additional 25 minutes and designated as Pulp B. (S. R. freeness 800). These pulps were used for making the blanks and the samples to which cooked G4-5 mucilage was added.

Beating of Pulps A and B with Dry G4-5 Mucilage. The procedure was similar to that above except that after the first 5 minutes slushing period the appropriate quantity of dry G4-5 mucilage was added to make 0.5, 1.0 or 2.0% on the O. D. weight of fiber present. A and B pulps were removed after the appropriate beating intervals.

Beating of Pulp for Freeness 480. The procedure was similar to that used for Pulps A and B made for evaluation of cooked mucilage except the pulp was beaten for 2 hours. S. R. Freeness 480. This degree of beating was evaluated only with cooked mucilage.

Procedure for Cooking G4-5 Mucilage. Five grams of G4-5 were slurried in 300 ml. of 0.25% borax solution and this mixture was heated with direct steam to 87° c. for 5 minutes. After stirring for 10 minutes while cooling, the mixture was diluted to 0.5% concentration for use.

PREPARATION OF HANDSHEETS

Blank. Twenty-five grams (O. D.) of stock (1460 ml.) were diluted to 0.5% consistency and eight 1.5 g. handsheets were made in a valley sheet mold using 4 stirring strokes and a 35 second interval of standing before forming the sheet. The sheets were pressed and dried in the usual manner.

Sheets Containing Cooked G4-5 Mucilage. The procedure was similar to that for the blank but the appropriate quantity of 0.5% mucilage solution was added to the pulp and stirred in for 5 minutes before dilution to 0.5% pulp consistency. Sets of sheets were made at 0.5, 1.0, and 2.0% of G4-5 mucilage based on the weight of O. D. fiber.

Sheets Containing Dry G4-5 Mucilage. An aliquot of the appropriate stock which had been beaten in the presence of the dry added mucilage was measured out and diluted to 0.5% consistency. The sheets were made as above.

Sheets Made with No Standing Time in Mold. The above sets of sheets were all made with a 35 second interval of standing after stirring but prior to formation of the sheets. This was done to emphasize the formation improving effects of the guar mucilage. At freeness 480 however, two sets of sheets, a blank and one containing 2% cooked mucilage, were made witnout a standing time.

RESULTS AND DISCUSSION

The data are presented in Table I where it is quite apparent that guar mucilage does build strength in this Douglas fir pulp. The experiments, thus far, have not produced a sheet of quite the desired bursting strength when compared with hemlock pulp. According to data obtained by the pulp lab for hemlock pulp a bursting strength of about 148 points per 100 lbs. is desired. It is believed that further experiments might reach this value with the fir pulp.

TABLE I

THE EFFECTS OF G4-5 MUCILAGE ON THE STRENGTH PROPERTIES OF DOUGLAS FIR PULP

| G4-5 Added Percent | Freeness S. R. | Basis Weight 25x40/500 | Caliper Inches | Bursting Strength Points | Bursting Strength Points 100 lbs. | M.I.T. Fold | Gurley Porosity Sec./100c. | Elmendorf Tear g/sheet | Tear Factor | Taber "Initial" Stiffness Units | Thwing Formation Units | Schopper Tensile lb/inch |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Dry Addition of Mucilage** | | | | | | | | | | | | |
| Blank | 870 | 50.6 | 0.0075 | 12.7 | 25 | 7 | 0 | 111 | 2.19 | 3.1 | 14.5 | 7.9 |
| 0.5 | | 46.3 | 0.0072 | 15.4 | 33 | 11 | 0 | 123 | 2.66 | 2.7 | 14.7 | 8.5 |
| 1.0 | | 48.9 | 0.0073 | 17.7 | 36 | 12 | 0 | 132 | 2.70 | 3.0 | 14.8 | 9.3 |
| 2.0 | | 48.3 | 0.0070 | 19.7 | 41 | 21 | 0 | 127 | 2.63 | 3.0 | 15.1 | 9.4 |
| Blank | 800 | 48.5 | 0.0053 | 39.7 | 82 | 539 | 7 | 127 | 2.60 | 2.8 | 11.8 | 20.3 |
| 0.5 | | 48.1 | 0.0052 | 44.9 | 93 | 589 | 6 | 117 | 2.43 | 2.2 | 14.2 | 21.6 |
| 1.0 | | 51.2 | 0.0052 | 54.9 | 107 | 578 | 6 | 113 | 2.21 | 2.6 | 15.1 | 23.5 |
| 2.0 | | 46.5 | 0.0050 | 44.7 | 96 | 600 | 4 | 93 | 2.00 | 2.2 | 15.1 | 21.3 |
| **Cooked Addition of Mucilage** | | | | | | | | | | | | |
| 0.5 | 870 | 49.7 | 0.0069 | 17.8 | 36 | 19 | 0 | 127 | 2.56 | 4.3 | 15.5 | 9.5 |
| 1.0 | | 49.0 | 0.0070 | 19.5 | 40 | 19 | 0 | 129 | 2.63 | 3.2 | 15.6 | 10.3 |
| 2.0 | | 47.0 | 0.0069 | 19.6 | 42 | 26 | 0 | 138 | 2.94 | 3.2 | 16.0 | 10.4 |
| 0.5 | 800 | 47.8 | 0.0054 | 50.2 | 105 | 726 | 7 | 97 | 2.03 | 2.2 | 13.8 | 21.0 |
| 1.0 | | 47.9 | 0.0053 | 52.3 | 109 | 712 | 7 | 102 | 2.13 | 2.2 | 13.7 | 22.1 |
| 2.0 | | 48.4 | 0.0053 | 52.6 | 109 | 732 | 8 | 101 | 2.09 | 2.4 | 14.3 | 23.0 |
| Blank | 480 | 47.3 | 0.0046 | 48.5 | 103 | 1100 | 84 | 97 | 2.05 | 1.9 | 13.3 | 24.2 |
| 0.5 | | 46.9 | 0.0045 | 57.1 | 122 | 967 | 87 | 87 | 1.86 | 1.9 | 14.8 | 27.5 |
| 1.0 | | 46.3 | 0.0044 | 61.0 | 132 | 1140 | 82 | 81 | 1.75 | 1.9 | 15.2 | 27.5 |
| 2.0 | | 48.0 | 0.0047 | 63.5 | 132 | 1060 | 87 | 83 | 1.73 | 2.1 | 15.4 | 27.4 |
| **Sheets Made With No Standing Time in Sheet Mold** | | | | | | | | | | | | |
| Blank | 480 | 48.0 | 0.0048 | 52.8 | 110 | 882 | 81 | 93 | 1.94 | 2.1 | 15.5 | 25.2 |
| 2.0 | | 48.5 | 0.0045 | 66.5 | 137 | 874 | 91 | 88 | 1.81 | 2.0 | 17.6 | 29.2 |

Note: All sheets conditioned at 50% R. H and 73°F.

The formation values seem to be somewhat erratic, showing little improvement with added guar mucilage. This is probably the result of the technique used. The 35 second interval prior to forming the sheet is undoubtedly too long for this extraordinarily long fibered stock. The sets of sheets made with practically no interval in the sheet mold after stirring showed a decided formation improvement when guar mucilage was present.

JWS/EG

# PROJECT REPORT FORM

PROJECT NO. 210
COOPERATOR Institute
REPORT NO. 19
DATE March 26, 1946
NOTE BOOK 654
PAGE 96-97, 122 TO 123, 128-129
SIGNED John W. Swanson
John W. Swanson

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## INCREASING THE WET STRENGTH OF PAPER BY ADDITION OF BORAX AND MAGNESIUM METABORATE TO A FURNISH CONTAINING GUAR MUCILAGE

Introduction: Mannogalactan mucilages would probably find wider use in the improvement of wet strength in papers if a simple method of setting up the borate gel could be devised. Heretofore, it has been necessary to apply the borate solution in a secondary operation such as spraying, modified size pressing, or running the solution onto a modified dandy roll. Each of these operations possesses disadvantages sufficient to discourage the use of mucilage for wet strength. The work of this report is concerned with several preliminary experiments on methods of setting up wet strength properties by addition of borates to the furnish prior to sheet formation.

Experimental:

Magnesium Metaborate

A. Twenty-five grams of borax was dissolved in 333 ml. of water and warmed to 50° C.

B. Thirteen grams of $MgCl_2 \cdot 6H_2O$ was dissolved in 16.6 ml. of water and the solution was added to A. A precipitate of $Mg(BO_2)_2 \cdot 2H_2O$ formed which amounted to 2% of the total weight present.

Beating of Pulp

Three hundred sixty grams (O.D. basis) of Weyerhaeuser bleached sulfite pulp was beaten in a Valley beater with 4500 g. (plus 1000 g. balance weight) on the bed plate to an average Schopper Riegler freeness of 520.

Cooking of G4-5 Mucilage

Two and one-half grams of G4-5 was added with stirring to 250 ml. of 0.25% borax solution and the mixture heated with direct steam to 87° C. Dilute HCl (12.5 ml. of 0.3N) was added to a pH of 4-5. The temperature was held at about 85° C. for 10 minutes before diluting to 0.5% mucilage concentration for use.

Making the Sheets

Thirty grams of pulp (O.D. basis) were measured out at 1.4% consistency and 90 g. of 0.5% G4-5 mucilage (1.5% on pulp) was added with vigorous stirring. After 5 minutes the appropriate quantity of magnesium metaborate suspension was added to give the desired percentage based on the fiber. The mixture was diluted to 0.5% pulp consistency and seven 1.5 g. sheets were made in the regular manner.

In those experiments in which borax alone was added to the stock containing mucilage, the borax was first dissolved in water and then added to the stock. All pH values in the sheet mold were in the range 9.35-10.0.

A set of control sheets was made with 1.5% mucilage. After drying, some of these sheets were dipped in 1% borax solution and redried.

Results and Discussion

The data are presented in Table I where it may be seen that small amounts of magnesium metaborate and borax, 5-15%, did not produce a noticeable wet tensile strength. One hundred percent of borax on the weight of fiber still did not show improvement but simultaneous addition of 100% of magnesium metaborate and 100% of borax about equalled the wet tensile strength developed in the borax dipped control sheets.

It appears that the amount of borate necessary to develop the wet tensile might be economically prohibitive but further experiments with this method should be made before a definite conclusion is reached. The use of NaOH or $Na_2CO_3$ along with borax and magnesium metaborate may intensify the effect and enable much smaller quantities to be used.

jws/fer

TABLE I

EFFECT OF VARIOUS QUANTITIES OF BORAX AND MAGNESIUM METAPORATE
ON THE WET STRENGTH DEVELOPED WITH GUAR MUCILAGE
(1.5% GH-5 on fiber)

| Institute File No. | Magnesium Metaborate % on fiber | Borax, % on fiber | Basis Weight 25x40/500 | Bursting Strength, Mullen | | Schopper Tensile | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Points | Pt. per 100 lb. | Dry lb./inch | Wet* lb./inch | Ratio (Wet/Dry) % |
| 120899 | 0.0 | 0.0 | 47.3 | 53.1 | 112 | 25.5 | 1.3 | 5.1 |
| 121339 | 0.0 | Borax dipped | 48.2 | 53.8 | 112 | 23.9 | 3.4 | 14.2 |
| 120900 | 2.00 | 0.0 | 46.0 | 51.2 | 111 | 25.3 | 1.0 | 4.0 |
| 120901 | 5.0 | 0.0 | 46.4 | 50.7 | 109 | 23.3 | 1.0 | 4.3 |
| 121133 | 100. | 0.0 | 46.3 | 52.7 | 114 | 24.8 | 2.4 | 9.7 |
| 120902 | 0.0 | 5.0 | 26.2 | 59.5 | 107 | 24.6 | 1.1 | 4.5 |
| 120903 | 0.0 | 15.0 | 47.2 | 51.0 | 108 | 25.2 | 1.0 | 4.0 |
| 121134 | 0.0 | 100. | 47.8 | 48.3 | 101 | 23.5 | 1.0 | 4.3 |
| 121338 | 100. | 100. | 42.7 | 46.6 | 109 | 24.0 | 3.1 | 12.9 |

* A 1 to 1-1/2 inch portion of each specimen was thoroughly wetted with water by means of an atomizer. All tests were started 15 seconds after the strip was wetted.

All conditioned at 50% R H., 73° F.

# PROJECT REPORT FORM

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COOPERATOR Institute
REPORT NO. 18
DATE January 16, 1946
NOTE BOOK 654
PAGE 140 TO 160
SIGNED John W. Swanson
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Dextrinization of Mannogalactan Mucilages
I Locust Bean Gum

Introduction:

One of the simplest and cheapest methods of converting or reducing the potential viscosity of polysaccharides is heat dextrinization in the presence of an acid catalyst. It seemed desirable to apply this procedure to mannogalactan mucilages for making tubsizing and coating adhesives. The preliminary experiments of this report were made with locust bean gum. Experiments with guar mucilage are in progress and will be reported upon soon.

Experimental:

Dextrinizing Equipment.

A Cenco De Khotinsky constant temperature oven was laid on its side and a mechanism installed in the interior for rotating a 2-liter pyrex bottle. A piece of spring steel was placed between two of the shelf supports and a sheet metal flanged holder for the bottle attached by means of a small bolt. A 1/2 inch hollow shaft was passed through a bearing placed in the thermometer hole in the side of the oven and attached to the bottle by means of a rubber stopper. Small bolted collars maintained rigidity and prevented sliding of the shaft. A six inch pulley was attached to the outside end of the shaft and rotated by a belt arrangement from a 1-1/2 inch pulley and variable speed Cenco

stirring motor. The speed of rotation of the bottle could thereby be changed by adjusting the motor.

Addition of Hydrochloric Acid Gas.

The HCl gas was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid. Two hundred ml. of sulfuric acid were placed in a one liter suction flask fitted with a rubber stopper containing a 5.ml burette and a glass tube reaching below the surface of the acid. The glass tube was connected to an air pressure line and a flow meter and the air flow adjusted to approximately 600 ml per minute. The side arm of the flask was connected to a trap and then to a long glass tube inserted through the rotating shaft into the bottle.

Fifty to 150g of locust bean gum (14.% moisture) were placed in the bottle which was attached to the rotating mechanism. Twenty-three porcelain balls were also placed in the bottle to prevent lumping of the mucilage. While rotating the mechanism fairly rapidly, at room temperature, gaseous HCl and air were passed into the bottle by dropping various quantities of concentrated acid into the aerated sulfuric acid. Air was bubbled through the $H_2SO_4$ for two minutes after all the HCl had been added. A sample of the mucilage was then removed for determination of acid content.

Procedure.

A one gram sample of the mucilage was weighed accurately and suspended in 350 ml of distilled water in a 500 ml Erlenmeyer flask. The mixture was heated just to the boiling point and titrated with

0.1N NaOH to a phenolphthalein end point. According to this method the untreated locust bean gum contained an average of 0.331% of acid calculated as HCl.

After the acid had been absorbed, the mucilage was allowed to condition or temper at room temperature for at least 16-24 hours before dextrinizing in order to distribute the acid as uniformly as possible.

Tubsizing.

Fifteen grams of the dextrinized mucilage having a workable viscosity were mixed with 250 ml of distilled water and heated with direct steam to 87°C. The temperature was held at 85-87°C. for 10 minutes and then stirred for 10 minutes more while cooling. The mixture was diluted to 4% concentration and also used as a tubsize at 55-60°C. The relative viscosities of the various products were determined at one per cent concentration and 30°C. using modified Ostwald Viscometers.

Results and Discussion:

The conversion data are given in Table I and the tubsize data of the suitably converted products are in Table II.

It appears from the tubsize data that this method of conversion yields products possessing outstanding properties as tubsize adhesives. Product C 151-654 dextrinized for 8 hrs. at 150°C. and an acid concentration of 0.47% gave a 50% increase in bursting strength and 242.% and 194% increase in the machine and cross directions respectively in folding endurance. Further dextrinization progressively lowered these strength increases but the lower

TABLE I

Conversion Data on Dextrinization of Locust Bean Gum at Various Temperatures and Acid Contents

| Code No. | Conc. HCl Used ml | Amount of Gum in grams | Time of Adding HCl to $H_2SO_4$ in Seconds | HCl % in Gum | Dextrinization Temp °C. | Dextrinization Time Hours | Relative Viscosity 1% and 30°C. |
|---|---|---|---|---|---|---|---|
| G140-654 | — | 50 | — | 8.3* | 80° | — | — |
| G142-654 | 1 | 50 | 112. | 0.697* | 100° | 0 | 319.6 |
| | | | | | | 1 | 66.2 |
| | | | | | 100 | 2 | 15.6 |
| | | | | | 100 | 3-1/4 | 5.73 |
| | | | | | 100 | 4-1/4 | 3.96 |
| | | | | | 100 | 5-1/4 | 3.32 |
| G142-1-654 | 2 | 50 | 202 | 1.24* | 80° | | |
| G142-2-654 | 0.5 | 50 | 43 | 0.464* | 80° | | |
| G143-654 | 0.5 | 50 | 96 | 0.407* | 25° | 0 | 1432. |
| | | | | 0.525 | 150° | 1 | — |
| | | | | | | 2.5 | 4.81 |
| | | | | | | 5.5 | 2.27 |
| G143-1-654 | 0.2 | 50 | 48 | 0.272* | 25° | | |
| G143-2-654 | 0.1 | 50 | 23 | 0.204* | 25° | | |
| G143-3-654 | 0.025 | 50 | 23 | 0.193* | 25° | | |
| G144-654 | 0.2 | 50 | 82 | 0.213* | 25° | | |
| G144-1-654 | 0.2 | 50 | 45 | 0.213* | 25° | 0 | to high to measure |
| | | | | | 80 | 1 | |
| | | | | | 80 | 2 | |
| | | | | | 80 | 5 | to high to measure |
| G151-654 | 1.5 | 150 | 288 | 0.474 | 25° | — | — |
| | | | | | 150 | 3 | 29.5 |
| | | | | | 150 | 5 | 10.5 |
| | | | | | 150 | 8 | 3.59 |
| | | | | | 150 | 10 | 2.73 |
| | | | | | 150 | 12 | 2.18 |
| | | | | | 150 | 14 | 1.84 |
| | | | | | 150 | 19 | 1.36 |

* not boiled for determination of acidity

TABLE II

Tubsize Characteristics of Dextrinized Locust Bean Gums

100% rag stock

| Code | Hours Dextrinized | Concentration % | Temp. °C. | Basis Weight 17/22/500 | Caliper inch | Bursting Strength Points | Bursting Strength Pts. per 100 lbs. | Per Cent Increase in Burst | MIT Fold In | MIT Fold Across | Gurley Porosity sec/100 cc | Elmendorf Tear g/sheet In | Elmendorf Tear g/sheet Across | Institute File No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Blank | — | — | -- | 19.6 | 0.0034 | 30.2 | 154 | -- | 221 | 65 | 232 | 94 | 108 | 121514 |
| G143-654 | 5.5 | 4.0 | 55 | 20.1 | 0.0039 | 44.5 | 221 | 42.9 | 471 | 117 | 286 | 99 | 102 | 121510 |
| | 5.5 | 2.0 | 58 | 20.0 | 0.0039 | 40.4 | 202 | 31.2 | 292 | 78 | 210 | 96 | 110 | 121511 |
| G151-654 | 8.0 | 4.0 | 61 | 20.0 | 0.0039 | 46.1 | 231 | 50.0 | 760 | 191 | 386 | 92 | 105 | 121521 |
| | 8.0 | 2.0 | 61 | 19.7 | 0.0039 | 40.4 | 205 | 33.1 | 403 | 95 | 216 | 105 | 117 | 121522 |
| | 10.0 | 4.0 | 59 | 19.9 | 0.0039 | 45.0 | 226 | 46.7 | 631 | 145 | 314 | 99 | 103 | 121523 |
| | 10.0 | 2.0 | 59 | 20.0 | 0.0039 | 39.5 | 198 | 28.6 | 346 | 80 | 218 | 104 | 116 | 121524 |
| | 12.0 | 4.0 | 61 | 20.0 | 0.0040 | 44.1 | 221 | 42.9 | 557 | 121 | 304 | 91 | 100 | 121538 |
| | 12.0 | 2.0 | 60 | 20.0 | 0.0040 | 40.8 | 204 | 32.5 | 310 | 88 | 204 | 95 | 106 | 121539 |
| | 14.0 | 4.0 | 58 | 19.9 | 0.0039 | 42.7 | 215 | 39.6 | 413 | 109 | 229 | 94 | 102 | 121540 |
| | 14.0 | 2.0 | 60 | 19.7 | 0.0039 | 39.0 | 198 | 28.6 | 296 | 88 | 176 | 95 | 101 | 121541 |
| | 19.0 | 4.0 | 61 | 19.9 | 0.0039 | 41.0 | 206 | 33.8 | 343 | 105 | 199 | 95 | 105 | 121542 |
| | 19.0 | 2.0 | 61 | 19.7 | 0.0039 | 37.7 | 191 | 24.0 | 253 | 84 | 171 | 100 | 108 | 121543 |

viscosity products of high adhesive strength were much better than starch tubsize adhesives.

One detrimental property of the dextrinized mucilage is the dark brown color. It is believed that this may be alleviated to a considerable extent by using a bleaching type of acidic catalyst such as chlorine.

Future Work:

Work on dextrinization of guar mucilage will be pushed as rapidly as possible. Other acidic catalysts will be investigated.

# PROJECT REPORT FORM

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PROJECT NO. 849
COOPERATOR Institute
REPORT NO. 17
DATE January 24, 1946
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111-130
PAGE 669, TB. 15-16
SIGNED John W. Swanson
John W. Swanson

## STUDIES ON MANNOGALACTAN CONVERTING ENZYMES
## I. The Relative Rate of Sugar Production Under Various Conditions

### INTRODUCTION

Enzymes capable of converting mannogalactan mucilages suitable for tubsizing were prepared and described in Report No. 16 of this project. The strength features of the converted mucilages prepared with these enzymes were not as great as expected or desired. The reasons are unknown at present but several were suggested in the discussion of Report No. 16. One of these reasons--rapid sugar production--has been investigated to some extent. It was conceivable that the rates of both sugar production and reduction of viscosity might differ materially at various temperatures and pH values because of the effects of these conditions on various components of the enzyme mixture. The present report is concerned with several experiments of this nature.

### EXPERIMENTAL

It was decided that the best technique would be one in which both viscosity and sugar could be measured on the same sample at any specific degree of hydrolysis. After several series of orienting experiments the following method was decided upon:

One hundred grams of 0.5% borax cooked G4-H mucilage was weighed into a 250 ml. Erlenmeyer flask and the appropriate quantities of buffer and water added, leaving room for the enzyme. The flask was placed in a water bath at the desired temperature, and after 15 minutes,

0.0025 ml. of the enzyme was added with shaking (0.5 ml. of a solution made by dissolving 0.5 ml. of the concentrated enzyme in water to make 100 ml.). At 10, 30, 60, and 120 minute intervals, 25 ml. aliquots of the hydrolyzed mixture were removed and added to large test tubes containing 2 drops of 5N sodium hydroxide. The tube was immediately cooled under the tap (if necessary) and 10 ml. added to an Ostwald Viscometer at 30° C. The viscosity was determined and calculated as the percentage of the original viscosity of a blank.

The remainder of the sample was used immediately for determination of the apparent percentage of sugar by a modified Somogyi micromethod.

The copper reagent had the following composition:

| | |
|---|---|
| $CuSO \cdot 5H_2O$ | 7.5 g./liter |
| $KNaC_4H_4O_6 \cdot 4H_2O$ | 25.0 g. |
| $Na_2CO_3$ | 25.0 g. |
| $NaHCO_3$ | 20.0 g. |
| KI | 5.0 g. |
| $KIO_3$ | 0.535 g. accurate |

The chemicals were dissolved in the order given in 850 ml. of distilled water. The $KIO_3$ was dissolved separately and added to the solution quantitatively. Two liters of solution were made up at one time and the bottle fitted with a siphon and soda-lime tube.

A Somogyi reagent containing potassium oxalate was also tried but found to be unsuitable.

A standard sugar curve was made with a mixture of mannose and galactose. Vacuum dried d-mannose, 0.3744 g. and d-galactose, 0.2656 g. were dissolved in water, three drops of toluene added and the mixture diluted to 100 ml. Then 5 ml. of this solution was diluted to 100 ml., various volumes placed in large test tubes (5, 4, 3, 2, 1, 0 ml; two each) and sufficient water added to make 5 ml. in each tube. Five ml. of the copper reagent was added to each tube and the tubes heated in a boiling water bath 30 minutes, acidified with 5 ml. of N $H_2SO_4$ and titrated with 0.005 N sodium thiosulfate in the usual manner. Blanks were also run and the differences in ml. of 0.005 N thiosulfate between the blank and the sugar sample were plotted against the amount of sugar present. This curve was used in subsequent experiments to determine the apparent amount of sugar present in the enzyme hydrolyzed sample

TABLE I

THIOSULFATE EQUIVALENTS FOR A MIXTURE OF MANNOSE AND GALACTOSE
(58.5% d-mannose, 41.5% d-galactose)

| Amount of Sugar mg. | Thiosulfate Equivalent in ml. of 0.005 N |
|---|---|
| 0.00 | 0.00 |
| 0.32 | 1.89 |
| 0.64 | 3.92 |
| 0.96 | 6.13 |
| 1.28 | 8.11 |
| 1.60 | 10.03 |

## Determination of Apparent Sugar Present in the Enzyme Hydrolyzed Mucilage

It was necessary to first determine the effect of the length of heating the sample in the presence of the copper reagent. A sample of G4-H was hydrolyzed with 0.5% of enzyme No. 97 at a consistency of 0.45%, 30°C. and pH of 5.2 for various lengths of time. Samples were removed at 10 minute, 60 minute and 22 hr. intervals and the apparent sugar determined at various intervals of heating in the boiling water bath. The data are presented in Table II where it may be noted that a 10 minute hydrolyzed product reached a constant apparent sugar value at 35 minutes and remained fairly constant up to 60 minutes.

TABLE II

EFFECT OF TIME OF HEATING ON APPARENT SUGAR CONTENT OF GUAR G4H HYDROLYZED WITH ENZYME NO. 97 FOR VARICUS INTERVALS.*

| Hydrolysis Time, minutes | Time Heated in Boiling Water Bath | Thiosulfate Requirement 0.005 N | Apparent Percentage of sugar |
|---|---|---|---|
| 10 | 0 | 0.0 | 0.000 |
| | 15 | 0.60 | 0.422 |
| | 35 | 0.75 | 0.511 |
| | 45 | 0.75 | 0.511 |
| | 60 | 0.78 | 0.533 |
| | 70 | 0.65 | 0.444 |
| 60 | 35 | 1.10 | 0.778 |
| | 45 | 1.22 | 0.867 |
| | 60 | 1.20 | 0.845 |
| | 70 | 1.05 | 0.733 |
| | 80 | 0.80 | 0.555 |
| 22 hr. | 15 | 4.55 | 3.22 |
| | 35 | 6.77 | 4.78 |
| | 45 | 7.05 | 4.98 |
| | 60 | 7.15 | 5.04 |
| | 70 | 7.25 | 5.11 |

*0.45% G4-H as substrate
0.0025 ml. No. 97 enzyme
pH = 5.2

A 60 minute enzyme hydrolyzed product required about 45 minutes heating and a 22 hr. hydrolysis required better than 70 minutes heating although the increase beyond 50 minutes is perhaps negligible. On the basis of these findings it was believed that a 50 minute heating period would be adequate for the determination of apparent sugar in the enzyme hydrolyzed mucilages.

Procedure for Determining Apparent Sugar

Five ml. of the same alkaline sample used for viscosity measurements was placed in each of two 8 x 1 inch test tubes containing 5 ml. of the Somogyi copper reagent and loosely stoppered. The tubes were placed in a wire rack and immersed in a vigorously boiling water bath for exactly 50 minutes. They were cooled immediately to 20-25° C. in tap water with the stoppers pressed on tight and then allowed to stand at room temperature until titrated. Five ml. of 1 N $H_2SO_4$ was added to the tube to be titrated and after shaking and standing for 2 minutes the liberated iodine was titrated with 0.005 N thiosulfate using starch indicator for the end point. A blank on the reagents was also determined in the same way.

The data for conversion of G4-H mucilage with enzyme No. 97 at 30° and 65° C. and various pH values are given in Table III, and are plotted in Figures 1 and 2. Conversion data for enzyme No. 97-2 at 65° C. For sources of these enzymes and methods of preparation Report No. 16 should be consulted.

TABLE III

VISCOSITY--SUGAR DATA FOR CONVERSION OF GUAR G4-H WITH ENZYME NO. 97 AT VARIOUS pH AND TEMPERATURES

| Time of Hydrolysis, minutes | Temp. °C. | pH | Percent Original Viscosity | Percent Sugar in Sample |
|---|---|---|---|---|
| 0 | 30 | 3.1 | 100 | 0.41* |
| 10 | 30 | 3.1 | 13.8 | 0.49 |
| 20 | | | 8.47 | - |
| 30 | 30 | 3.1 | 6.25 | 0.62 |
| 60 | 30 | 3.1 | 3.77 | 0.69 |
| 120 | 30 | 3.1 | 2.38 | 1.04 |
| 20 hr. | 30 | 3.1 | 1.06 | 3.96 |
| 10 | 30 | 5.2 | 10.2 | 0.53 |
| 20 | 30 | 5.2 | 6.1 | - |
| 30 | 30 | 5.2 | 4.51 | 0.60 |
| 60 | 30 | 5.2 | 2.84 | 0.89 |
| 120 | 30 | 5.2 | 1.94 | 1.16 |
| 10 | 30 | 8.75 | 48.0 | 0.42 |
| 20 | 30 | 8.75 | 34.6 | - |
| 30 | 30 | 8.75 | 25.3 | 0.49 |
| 60 | 30 | 8.75 | 14.7 | 0.41 |
| 120 | 30 | 8.75 | 8.4 | 0.46 |
| 20 hr. | 30 | 8.75 | 1.08 | 3.20 |
| 10 | 65 | 3.1 | 3.91 | 0.84 |
| 30 | 65 | 3.1 | 2.04 | 1.29 |
| 60 | 65 | 3.1 | 1.49 | 1.73 |
| 120 | 65 | 3.1 | 1.19 | 2.18 |
| 10 | 65 | 8.7 | 74.3 | 0.47 |
| 30 | 65 | 8.7 | 72.9 | 0.49 |
| 60 | 65 | 8.7 | 64.3 | 0.47 |
| 120 | 65 | 8.7 | 52.2 | 0.42 |
| 10 | 65 | 6.9 | 4.37 | 0.67 |
| 30 | 65 | 6.9 | 2.15 | 1.18 |
| 60 | 65 | 6.9 | 1.58 | 1.46 |
| 120 | 65 | 6.9 | 1.25 | 1.75 |

* Average of several determinations

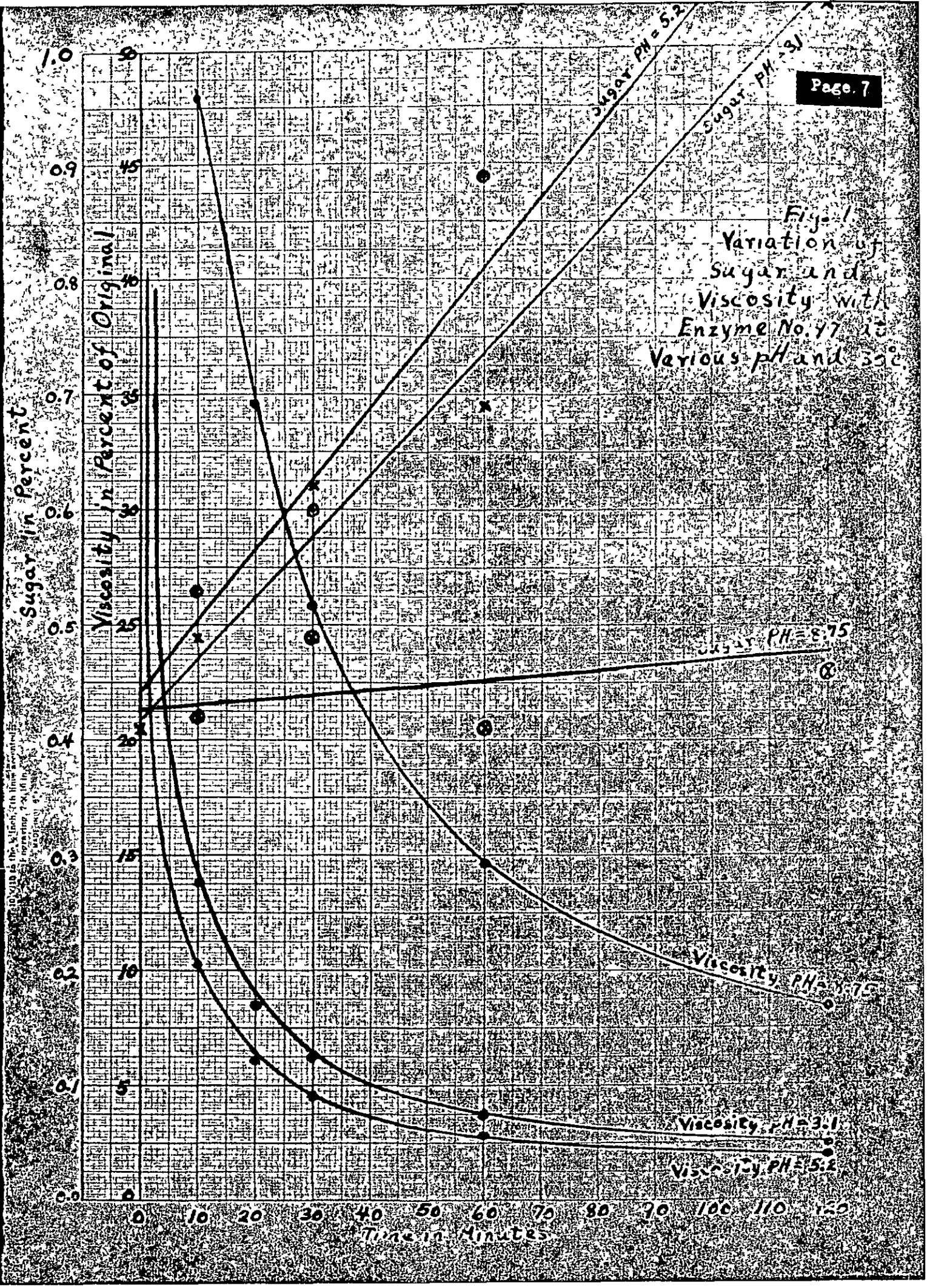


Fig. 1.
Variation of Sugar and Viscosity with Enzyme No. 47 at Various pH and 35°C.

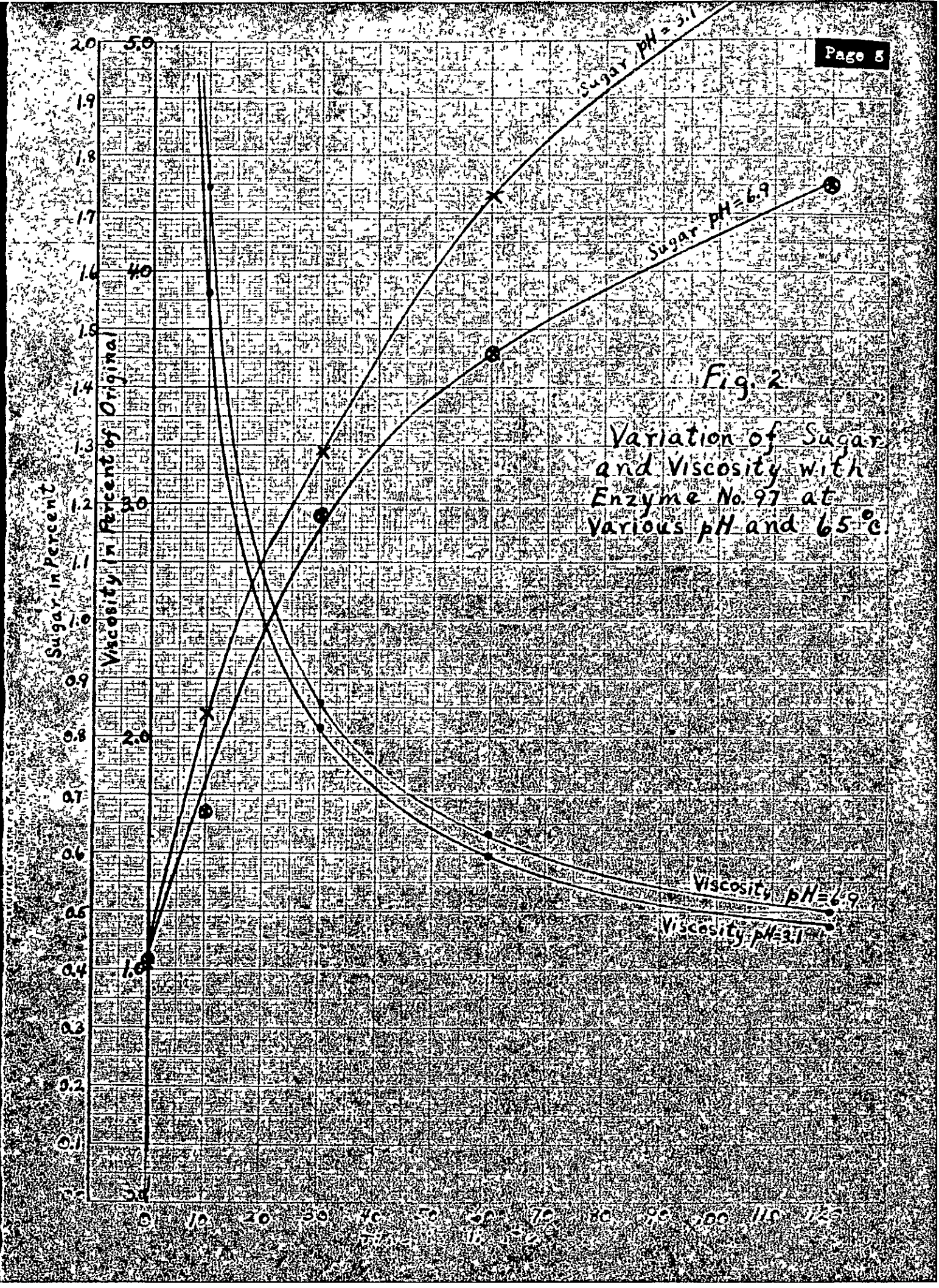


Fig. 2.

Variation of Sugar and Viscosity with Enzyme No. 97 at Various pH and 65°C.

TABLE IV

VISCOSITY--SUGAR DATA FOR CONVERSION OF GUAR G4-H ENZYME NO. 97-2 AT VARIOUS pH AND 65° C.

| Time of Hydrolysis, minutes | pH | Percent Original Viscosity | Percent Sugar in Sample |
|---|---|---|---|
| 0 | 3.13 | 100. | 0.53 |
| 10 | 3.13 | 3.22 | 1.04 |
| 30 | 3.13 | 1.32 | 1.62 |
| 60 | 3.13 | 1.32 | 1.86 |
| 120 | 3.13 | 1.07 | 2.76 |
| 240 | 3.13 | 0.96 | 3.47 |
| 10 | 7.9 | 5.7 | 0.58 |
| 30 | 7.9 | 3.16 | 0.75 |
| 60 | 7.9 | 2.65 | 0.845 |
| 120 | 7.9 | 2.56 | 1.04 |
| 10 | 8.15 | 7.9 | 0.80 |
| 30 | 8.15 | 5.4 | 0.733 |
| 60 | 8.15 | 5.0 | 0.69 |
| 120 | 8.15 | 4.82 | 0.82 |
| 240 | 8.15 | 4.37 | 0.87 |
| 10 | 7.15 | 4.41 | 0.69 |
| 30 | 7.15 | 2.25 | 0.89 |
| 60 | 7.15 | 1.74 | 1.12 |
| 120 | 7.15 | 1.41 | 1.56 |

Fig 3

Variation of Sugar and Viscosity with Enzyme No 97-2 at Various pH and 65°C

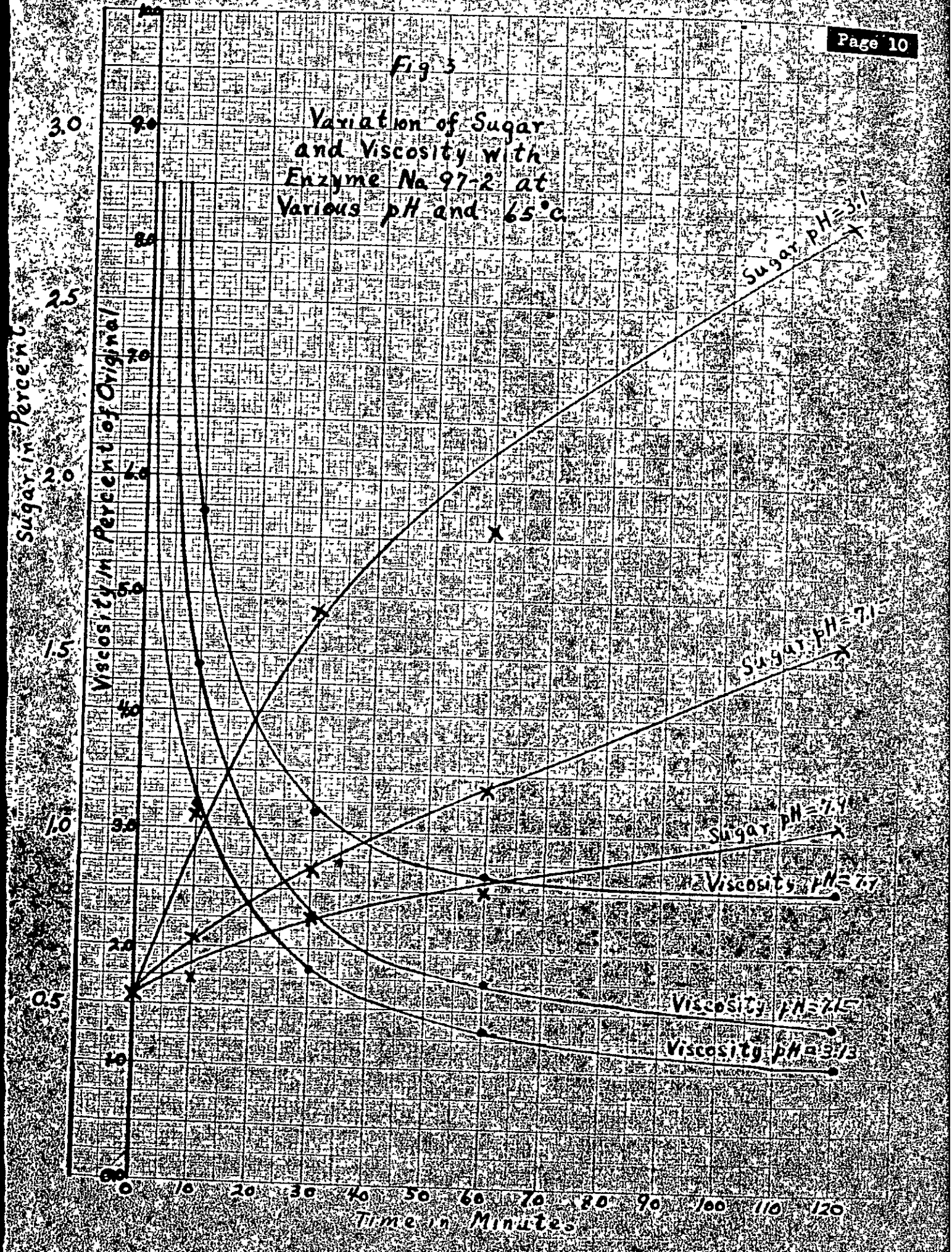

TABLE V

VISCOSITY--SUGAR DATA FOR CONVERSION OF LOCUST BEAN GUM WITH ENZYMES NO. 26 AND 97-2
Hydrolysis at 65° C.

| Enzyme | Time of Hydrolysis, minutes | pH | Percent Original Viscosity | Percent Sugar in Sample |
|---|---|---|---|---|
| 26 | 0 | 6.49 | 100. | 0.00 |
| | 10 | 6.49 | 17.6 | 0.133 |
| | 30 | 6.49 | 7.41 | 0.20 |
| | 60 | 6.49 | 4.73 | 0.38 |
| | 120 | 6.49 | 3.38 | 0.31 |
| 97-2 | 10 | 5.77 | 4.77 | 0.29 |
| | 30 | 5.77 | 2.86 | 0.69 |
| | 60 | 5.77 | 2.25 | 1.02 |
| | 120 | 5.77 | 2.00 | 2.40 |

DISCUSSION OF RESULTS

From an inspection of the data plotted in Figures 1 to 3, it appears that the amount of sugar produced is not excessive. Two hours hydrolysis at 65° C. produced an apparent sugar content of 2.18%. There were only small differences in the rate of apparent sugar production at different pH values although the differences at 65° C. were relatively greater than at 30° C. because of inactivation rates. This is apparent from the non-linear sugar curves at various pH values at 65° C. (Fig. 2). Autoclaving the mucilage solution at 120° C. for 30 minutes did not increase the apparent sugar content of the blank.

On the basis of the fact that somewhat less sugar is produced at pH values of 7.0 a tubsize conversion was made at this pH value. It required several times the usual quantity of enzyme 97-2 to reduce the viscosity to a workable value and the tubsize characteristics were not outstanding (see T131-654).