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J. Becher
E. B. Dickey
J. W. Swanson

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Joseph Becher

PRELIMINARY EXPERIMENTS ON THE RETENTION OF LOCUST BEAN GUM ON CELLULOSE AS MEASURED BY RADIOACTIVE TAGGING

SUMMARY

Employing a modified Gaver (1) technique it was found possible to methylate locust bean gum in two steps resulting in a product containing approximately 5% methoxyl. The methoxyl grouping is believed to be held mainly at the No. 2 carbon position and the yield represents approximately 1/3 of theoretical. After the method proved to be fairly reproducible by repetition, radioactive locust bean gum was prepared by employing methyl iodide containing C^{14} as the methylating agent. The active product was blended with inactive purified gum and a dispersion of it was added to Weyerhaeuser bleached sulfite at 0.0, 0.1, 0.5, 1.0, and 2.0% based on fiber weight. Handsheets were prepared on the Rapid K8then sheet mold and an attempt was made to gain a balance in radioactivity by "counting" the activity in the handsheets, in the fines contained in the white water, and in the white water itself with a thin-window Geiger-Mueller counter.

The amounts of gum retained by the handsheets and by the fines and the white water followed predictable trends. Gum retention by the handsheets ranged from 38.5% at the 2.0% addition level to 73% at the 0.1% addition level. The summation of radioactivity indicates an apparent loss of gum at the higher addition levels and, consequently, the radio-

chemical method as employed in these experiments is accurate enough for only approximations in the measurement of the total amount of gum used.

The carbohydrate content in the white water was also determined by the anthrone technique and the results were compared with the radioactive counting technique. The determinations of white water gum content by both methods were in generally good agreement. The results indicate that the anthrone method may be valid in such measurements when corrected for carbohydrates which arise from the pulp.

INTRODUCTION

The use of beater adhesives in the paper industry has been and is still the object of considerable attention. One of the major problems still to be solved in this field is that of measuring the retention by cellulose fibers of various carbohydrate-type additives. This report covers the initial work carried out on retention measurements of a mannogalactan (locust bean gum) on a bleached sulfite pulp by a radioactive counting procedure.

EXPERIMENTAL PROCEDURES AND DISCUSSION

Preparation of Methylated Locust Bean Gum

A partially methylated locust bean gum labelled with Carbon-14 in the methoxyl groups was prepared by a modification of the procedure employed by Gaver (1) for the synthesis of 2-methyl starchate. The procedure involved the formation of the corresponding sodium alcoholate of

the gum followed by the reaction of the alcoholate with methyl iodide. A total of three trials were run to test the reproducibility of the technique prior to the preparation of the radioactive gum.

Trial I

Alcoholic sodium hydroxide was prepared by dissolving 80 g. of NaOH in one liter of absolute ethanol. The solution was filtered three times through glass wool to remove insoluble carbonates. Sixty ml. of the NaOH solution and 5 grams of purified locust bean gum were refluxed four hours at approximately 83°C. in a water bath. After refluxing, the sodium salt of locust bean gum was washed three times with 95% ethanol by centrifuging. Thirty ml. of 95% ethanol and 5 g. of methyl iodide were added to the moist gum and this mixture was refluxed 8 hours at 80-83°C. with ice water circulating through the condenser. After refluxing, the methylated locust bean gum was washed five times by centrifuging with 50 ml. portions of acetone. The product was then dried under vacuo at 33°C. A portion of the gum was analyzed for sulfated ash, moisture, methoxyl, and iodine. This product was given the code No. 1467-M-LBG-1.

One-half gram of the above product was dissolved in 25 ml. of distilled water by stirring at room temperature. The pH of the dispersion was found to be 9.5. The alkalinity was neutralized with 5% acetic acid. The gum was then precipitated by addition of 50 ml. of 95% ethanol. The supernatant was decanted and the gum was washed with another 50 ml. of ethanol. The product was collected on a Büchner funnel, washed with acetone

and dried under vacuo at 50°C. This sample was coded 1467-M-LBG-1A and was analyzed for sulfated ash, moisture, and methoxyl.

Trials II and III

Two additional methylations were carried out starting with 1.0 g. of the purified locust bean gum. Accordingly, the quantities of all other materials involved were 1/5 of those described in Trial I. The product obtained in Trial II was not purified by dissolving, neutralizing, and reprecipitating as in Trial I. This sample is identified by code No. 1467-M-LBG-2. The sample was analysed for moisture, sulfated ash, iodine and methoxyl contents.

The purification procedure was carried out in Trial III, however and this product was analysed for all except iodine. The sample was coded 1467-M-LBG-3.

Preparation of Radioactive Locust Bean Gum

Two grams of purified locust bean gum (prepared by Howard J. Leech) and 24 ml. of alcoholic NaOH (40 g. NaOH dissolved in 500 cc. of absolute ethanol and filtered three times through glass wool) were refluxed 4 hours at 83°C. After refluxing, the sodium salt of locust bean gum was washed three times with ethanol. The product was then divided into two approximately 1-gram samples for successive methylations.

A special device was prepared for the radioactive methylation. The apparatus consisted of two condensers and two 50-ml. round bottom

flasks. The condensers were connected by a glass tube and adaptor so that residual methyl iodide and ethanol could be distilled over from the first reaction to a second flask for a second methylation. This procedure was designed to avoid unnecessary loss of C^{14} methyl iodide.

The ampoule of C^{14} methyl iodide (146 mg., 1.0 millicurie) as received from Tracerlab, Inc., was cooled in dry ice and acetone until the contents had solidified in the bottom of the tube. The tube was broken open and the methyl iodide was dissolved in a small portion (0.5 ml.) of a solution composed of 0.35 ml. (0.8 g.) of inactive methyl-iodide as a carrier and 2.0 ml. of 95% ethanol. The mixture was transferred quantitatively to the first reaction flask by the use of successive portions of the inactive solution.

This mixture was refluxed 8 hours at 80-83°C. with well water (5°C.) circulating through the condenser. After the 8 hour period, the reaction was stopped, the condenser was drained, and the unused methyl iodide and ethanol were distilled over into the second flask. A few cc. of ethanol were added and also distilled over to the second flask. The second reaction mixture was then refluxed 8 hours as in the first case. Both of the methylation products were washed five times with acetone (25 cc. portions) dried under vacuo, and dissolved in water.

The solution of the first product in 80 cc. of distilled water resulted in a pH of 8.0. One drop of 5% acetic acid was needed to bring the solution to neutrality. The gum was then precipitated by addition

of 120 cc. of ethanol. Collection of the gum on a Büchner funnel proved to be unsuccessful when the filter paper plugged badly. Consequently, the majority of the product was collected by centrifuging. After washing once with absolute ethanol and three times with acetone the gum was finally dried under vacuo over P_2O_5 .

The second methylation product was dissolved in 50 cc. of distilled water with slight heating on the steam bath. The pH of this solution measured 10.5. Addition of 5% acetic acid brought the pH to 7.0. The gum was precipitated by addition of 100 cc. of 95% ethanol. The product was collected by centrifuging, washed once with absolute ethanol and three times with acetone. The product was again dried over P_2O_5 under vacuo.

After the two products proved to be reasonably "active" by spot checks they were blended in a mortar (combined yield 1.64 g.) and a portion of the blend was analyzed for ash, moisture, and methoxyl contents. This product is identified by code No. 1467-M-LBG-4. The results of the foregoing analyses together with the analyses from Trials I, II, and III are presented in Table I.

PREPARATION OF HANDSHEETS CONTAINING RADIOACTIVE LOCUST BEAN GUM

Beater Run

Three hundred and ninety grams (air-dried basis) of Weyerhaeuser bleached sulfite pulp were soaked 4 hours in 6 liters of distilled water. The soaked pulp was beaten 30 minutes in distilled water in the Valley

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Beater to a Schopper-Riegler freeness of 715 cc. with the balance weight plus 5500 gram weight on the bedplate. Standard conditions of 25°C. and pH 7.0 were maintained in the beater. The beater consistency was 1.44%. This pulp was used for all subsequent handsheet preparations.

TABLE I

PERTINENT DATA ON LABORATORY-PREPARED METHYLATED LOCUST BEAN GUM SAMPLES

Code No.	Methoxyl Content, %	Moisture Content, %	Sulfated Ash, % (Considered Na_2SO_4)	Total Sodium Content, % (as calcu- lated from Na_2SO_4)	NaI Content, % (as calcu- lated from iodine con- tent)	Sodium in the form of NaI, %	Corrected Ash, %	Corrected Methoxyl, %
1467-M-LBG-1	5.44	5.84	14.96	4.85	17.48	3.15	1.70	6.85
1467-M-LBG-1A	7.09	8.69	2.13	0.69	--	--	0.69	7.09
1467-M-LBG-2	5.20	6.80	8.08	2.62	8.76	1.58	1.04	5.80
1467-M-LBG-3	4.34	9.90	1.00	0.324	--	--	0.324	4.34
1467-M-LBG-4 (Cl ¹⁴ -methyl LBG)	4.23	5.10	0.92	0.298	--	--	0.298	4.23

Basis of Report: Oven-dry; except moisture, which is as received.

Preparation of Radioactive Locust Bean Gum Dispersion

A 0.25% locust bean gum dispersion was prepared as follows:
0.3333 g. of the radioactive blend was mixed with 0.6667 g. of the purified inactive gum and the mixture was sprinkled into 400 ml. of distilled water contained in a 1-liter Erlenmeyer flask. The gum slurry was agitated thoroughly while being heated on the steam bath. After cooking 15 minutes at 95°C. the dispersion was allowed to cool to room temperature. This stock dispersion was used in handsheet preparations and for calibration purposes with respect to radioactive counting.

Handsheet Preparation

Forty-five pound sheets (1.88 g. for 25 x 40/500 ream size) were prepared on the Rapid K8then sheet mold in order that the white water might be readily saved. Locust bean gum was added to the beaten pulp at 0.0, 0.1, 0.5, 1.0, and 2.0% oven-dry gum based on the fiber weight. The gum was allowed to stir in contact with the pulp for 30 minutes prior to dilution to 0.5% consistency. The pulp consistency was controlled in the sheet mold at 0.05% requiring a total volume of 3760 ml. Distilled water was used throughout. Handsheets were removed from the wire without couching; they were pressed 5 minutes at 50 lb. pressure and were dried seven minutes sheetside up on the steam drier at 3.5 lb. of steam. The sheets were identified by the following code No.

Amount of Gum Added, % (Based on fiber weight)	Code No.
0.0 (control)	1467-H-LBG-0
0.1	1467-H-LBG-0.1
0.5	1467-H-LBG-0.5
1.0	1467-H-LBG-1.0
2.0	1467-H-LBG-2.0

Two-liter samples of white water were collected from each set (3 samples from the control set and 2 from each of the remaining sets). The two-liter aliquots were filtered on a Büchner funnel and the amount of fines was determined by weighing on a filter paper. The results of these determinations are presented in Table II. The activity in the handsheets and on the fines was determined by "counting."

One-liter portions of the white water filtrates were condensed to 5 ml. and the carbohydrate content was determined by two methods; by radioactive count and by the anthrone technique employed by Shriver, Webb and Swanson (2). The anthrone technique involves measuring changes in transmission which result from color reactions between the anthrone and carbohydrate and is dependent upon concentration. The procedure employed in the present study was as follows: anthrone reagent was prepared by dissolving 2 g. of anthrone in 1 liter of concentrated sulfuric acid. Ten ml. of this reagent were added to 5 ml. of unknown solution contained in a 1 by 8-inch test tube. The test tubes were held at an angle of approximately 45° during the addition of anthrone in order to form a double layer. The mixture was shaken vigorously for 15 seconds and then allowed to cool to room temperature. The sample was then transferred to a 1-cm. absorption cell and the transmission was measured on the Coleman spectrophotometer at a wavelength of 625 mμ. The reference liquid was distilled water and reagent. A calibration curve (Figure 1) was obtained by measuring the transmission resulting from 0.0, 0.002, 0.005, 0.008, and 0.01% locust

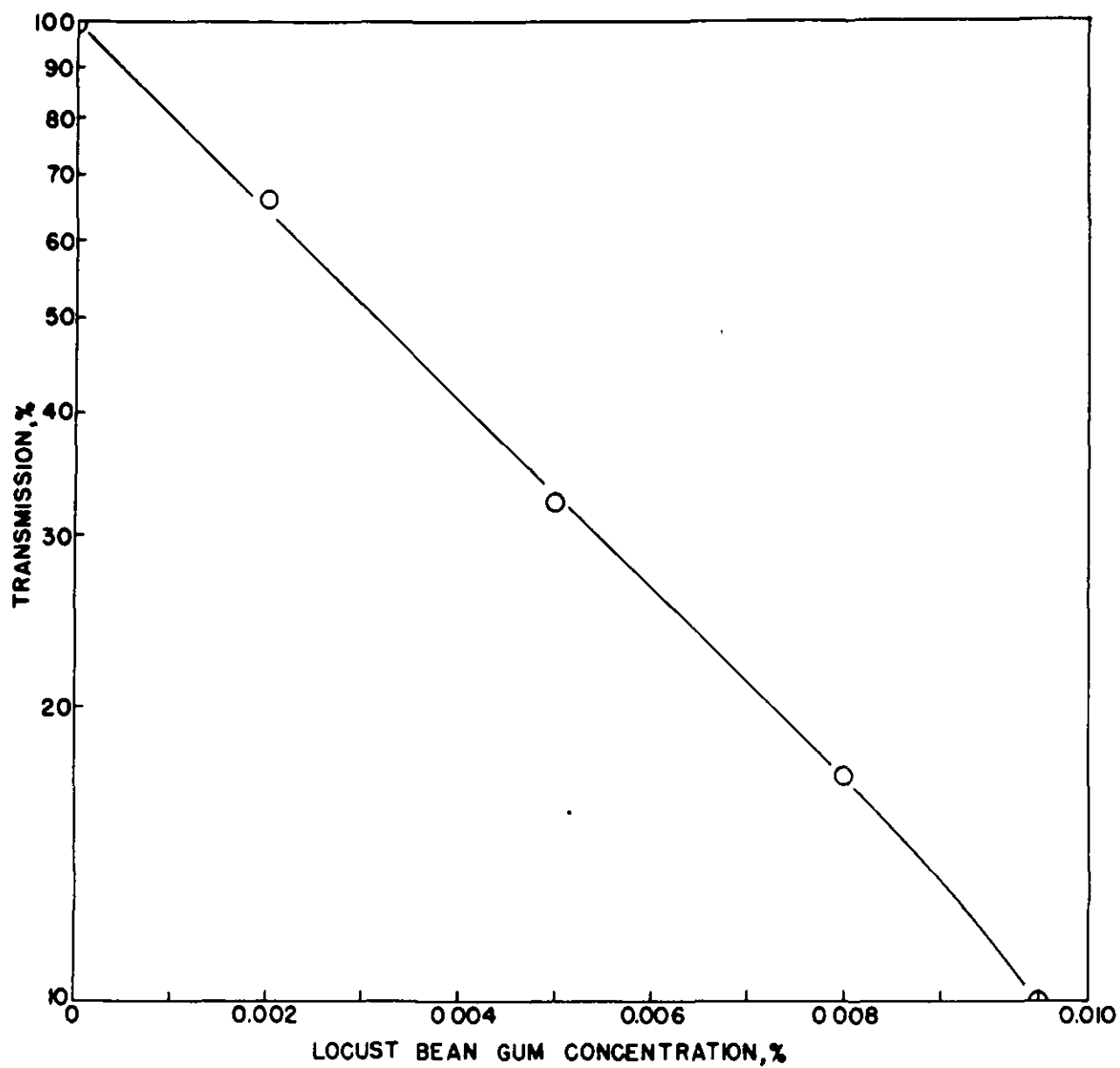


Figure 1.
Anthrone Analysis Calibration Curve

bean gum solutions. The following transmissions were obtained:

Gum Concentration, %	Transmission, %		Average
	Run No. 1	Run No. 2	
0.0	100	100	100
0.002	66.2	66.1	66.15
0.005	32.3	32.3	32.3
0.008	16.9	16.9	16.9
0.010	9.5	10.5	10.0

TABLE II

THE WEIGHT OF FINES COLLECTED ON SS NO. 589 FILTER
PAPER BY SUCTION FILTRATION

Set No.	Sheet No.	Weight of Fines/ 2 liters of white water, g.	Weight of Fines/ 3760 ml. of white water, g.	Average, g.
1467-H-LBG-0	1	0.028	0.0526	0.0602
	5	0.032	0.0602	
	9	0.036	0.0677	
1467-H-LBG-0.1	3	0.050	0.0940	0.0884
	5	0.044	0.0827	
1467-H-LBG-0.5	1	0.058	0.1091	0.1034
	5	0.052	0.0977	
1467-H-LBG-1.0	1	0.056	0.1053	0.0940
	5	0.044	0.0827	
1467-H-LBG-2.0	1	0.056	0.1053	0.0949
	5	0.045	0.0846	

Portions of the condensate obtained from the white water samples were diluted in the proper ratio with distilled water to yield transmissions in an operable range. The results of these measurements together with gum content calculations are presented in Table III.

(A) CALIBRATION OF THE RADIOCHEMICAL MEASUREMENTS

Locust Bean Gum

A stock dispersion, 0.25% in water, was prepared of the C^{14} -labelled gum. The calibration of the radiochemical method of measuring the gum retained on handsheets was then accomplished by the application of the dispersion, in appropriate portions of 0.1-0.2 ml. with intermittent drying, to each of four 5.0 cm. circular areas which were marked on each handsheet. The dry sheets were counted with a thin-window Geiger-Mueller counter centered over the treated area. Each handsheet weighed 1.88 g. (oven-dry basis) and was 20 cm. in diameter. Thus, each 5.0 cm. circle was equivalent to 0.1175 g. of paper. The results are listed in Table IV and the calibration curves based on these data are shown in Figure 1.

(B) DETERMINATION OF RADIOACTIVE GUM RETAINED BY THE HANDSHEETS

The eight handsheets obtained for each level of locust bean gum were counted in the same manner with the thin-window Geiger-Mueller counter as employed in the calibration samples. The data are summarized in Table V.

TABLE III

THE CARBOHYDRATE CONTENT OF THE WHITE WATER AS DETERMINED
BY THE ANTHROME TECHNIQUE

Gum Addition Level, % on pulp	Dilution of Condensate	Transmission, % In Duplicate	*Grams of Carbohydrate/ Handsheet	Corrected For Control, g.	Amount of Gum by Radiochemical Method, g.
0.0	1 ml. diluted to 5 ml.	58.8 59.8	0.00224	—	
0.1	0.5 ml. diluted to 5 ml.	74.2 73.8	0.00258	0.00034	0.00021
0.5	0.5 ml. diluted to 5 ml.	70.6 70.3	0.00299	0.00075	0.00094
1.0	0.25 ml. diluted to 5 ml.	74.7 74.7	0.00498	0.00274	0.00291
2.0**	0.1 ml. diluted to 5 ml.	80.9 80.2 81.4 79.7	0.00940	0.00716	0.01175

* These values are obtained by multiplying the concentration by a dilution factor.

** The transmission values were rechecked.

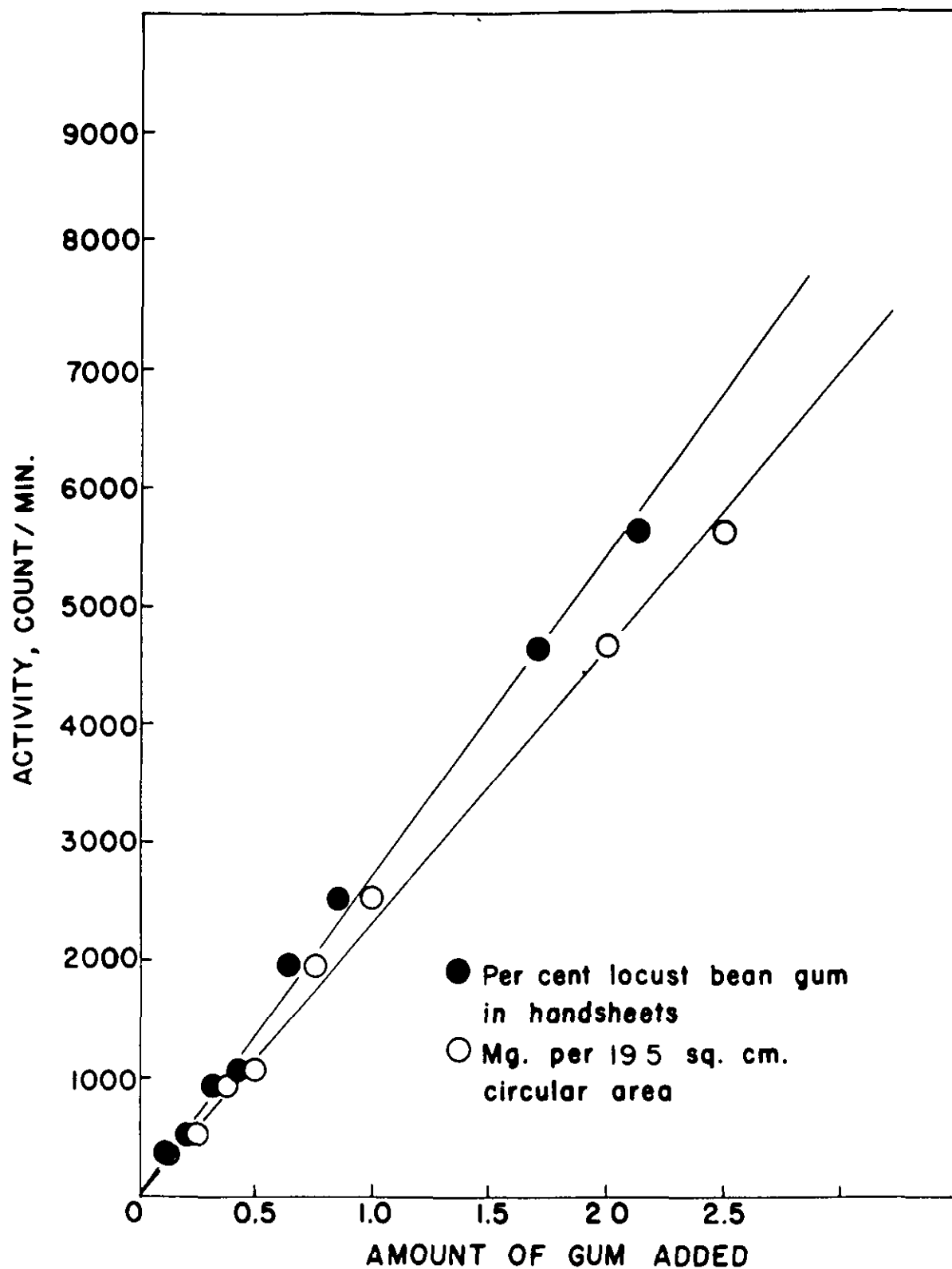


Figure 2.

Calibration of Handsheets with C^{14} Labelled Locust Bean Gum

TABLE IV
CALIBRATION DATA FOR C¹⁴ - LABELLED LBG IN HANDSHEETS

Sheet No.	Gum Added to 5.0 cm. Circle mg. %		Activity, Corrected for Background, counts/min. (c/m) (Average of 6)
1	0.125	0.106	355
2	0.250	0.213	516
4	0.375	0.319	939
5	0.500	0.425	1091
7	0.75	0.64	1966
9	1.00	0.85	2510
10	2.00	1.70	4660
11	2.50	2.13	5610

TABLE V
 C^{14} LABELLED GUM RETAINED ON HANDSHEETS

Gum Added, %	Gum Found				Average of 16 Counts on 8 Handsheets		mg. Handsheet	Per Cent of Gum Added
	c/m	High Content, %	c/m	Low Content, %	c/m	Content, %		
0.1	235	0.084	182	0.065	205	0.073	1.37	73
0.5	937	0.34	753	0.27	836	0.80	5.64	60
1.0	1441	0.52	1294	0.46	1348	0.48	9.03	48
2.0	2250	0.80	2040	0.73	2152	0.77	14.48	38.5

(C) RADIOACTIVE GUM RECOVERED IN FINES, WHITE WATER, AND ON BLOTTERS

The gum recovered on the fines was determined in the same manner as employed with the handsheets. The white water, 1.0 liter, was concentrated to a volume of 5.0 ml. and 0.2 ml. was applied in duplicate to a 5.0 cm. circle on a handsheet and counted. These data are presented in Table VI. Table VII is a summation of radioactive gum found in handsheets, fines, and white water.

In order to account for apparent loss of gum at the higher levels the blotters and felt were counted. The felt was inactive but the blotters contained a very small amount of activity. However, the radiochemical method was not calibrated for the measurement of gum in the blotter and the amounts were therefore not estimated.

Hydrolysis of Methylated Gum

An amount of 20-30 mg. of each, the C^{14} labelled and inactive methylated gum, was hydrolyzed by boiling in 0.5 N hydrochloric acid for three hours. The solutions were chromatographed on paper, using developers of ethyl acetate, acetic acid, water (9:2:2) and *n*-butanol-pyridine-water (10:3:3), and aniline hydrogen phthalate as a spray reagent. Inspection of the paper with a thin-window Geiger-Mueller counter located the main lot of radioactive material with approximately the same R_f as rhamnose. Two smaller amounts of activity were located. The position of one spot corresponded to that of xylose and the other moved at a much faster rate than rhamnose. These results indicate that, in addition to unmethylated sugars, the partially methylated sugars were separated on the chromatograms.

TABLE VI

¹⁴C - LABELLED GUM FOUND IN FINES AND IN WHITE WATER

Fines collected on 11.0 cm. filter paper from 2.0 l. of 3.76 l. total white water from one handsheet.			White water, 1.0 l. of filtrate after removal of fines, concentrated to 5.0 ml., and 0.2 ml. of concentrate applied to 5.0 cm. circular area for counting.		
Gum Added, %	Gum found in 5.0 cm. circular area of collected fines, c/m	Gum retained in fines from one handsheet, mg.	Gum found in 5.0 cm. circular area of white water concentrate, c/m	Gum retained in white water from one handsheet, mg.	
0.1	120	0.05	5	0.0022	0.21
0.5	384	0.16	23	0.010	0.94
1.0	549	0.23	71	0.031	2.91
2.0	846	0.36	287	0.125	11.75

TABLE VII
SUMMARY OF C¹⁴-LABELLED GUM FOUND IN HANDSHEETS, FINES, AND WHITE WATER

Gum added to furnish %		Gum Found Handsheet mg.		Fines mg.		White Water mg.		Total mg./sheet		%
0.1	1.88	1.37	73	0.45	24.0	0.21	11	2.03	108	
0.5	9.40	5.64	60	1.43	15.0	0.94	10	8.01	85.0	
1.0	18.80	9.03	48	2.06	11.0	2.91	15.5	14.00	74.5	
2.0	37.60	14.48	38.5	3.22	8.6	11.75	31.2	29.45	78.3	

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J. W. Swanson
D. R. Sears

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D. R. Sears

THE RETENTION OF LOCUST BEAN GUM IN EXPERIMENTAL HANDSHEETS—AN EXPLORATORY STUDY OF LOCUST BEAN GUM VAT-DYED WITH CERTAIN DU PONT "PONSOL" ORGANIC PIGMENTS

ABSTRACT

A method has been developed for vat dyeing crude locust bean gum with a number of Du Pont "Ponsol" organic pigments. Handsheets were prepared using dyed gum as a beater adhesive. These handsheets were subjected to several physical tests and spectral reflectance measurements. In particular, Du Pont "Ponsol" Jade Green Supra Double Paste was studied, and the dispersibility, viscosity, and spectral transmittance of gum vat-dyed with this pigment were observed.

These studies indicated the method is not suitable for retention measurements in as much as the properties of the gum are adversely affected by vat treatment in the absence of dye, and a significant portion of the gum is rendered nondispersible by sorption of the dye.

INTRODUCTION

In recent years there has been an increasing interest in the use of hydrophilic gums and mucilages as beater or headbox additives to improve hydration and fiber bonding and reduce beating times.

It is naturally desirable to obtain a quantitative measure of the effectiveness of retention of these additives, both from an economic and a technical point of view.

For this reason, considerable work has been devoted lately to the development of analytical techniques for the measurement of gum concentrations in formed handsheets. Shriver (8) and Laurell (5) have studied retention of cellulose derivatives, while Webb (9) studied sorption of locust bean gum on bleached sulfite pulps.

These studies suffered from the lack of an appropriately precise analytical tool; in each case retention in the handsheet was determined by analysis of backwater concentration and comparison with furnish concentration. The presence of cellulose "fines" interfered with carbohydrate analyses in the backwater. Webb's technique involved predyeing locust bean gum before beater addition, and measurement of the optical transmission of the backwater containing unsorbed dyed gum. There was, however, no suitable correction for the contribution to the apparent optical absorption due to the turbidity of the "fines."

Progress in these retention studies therefore awaited development of an improved technique for measurement of sorbed gum on the handsheet, rather than in the backwater.

This was accomplished by Leech (6, 7) and Dickey (2). Their method involved acid hydrolysis of the gum on the handsheet, followed by quantitative chromatographic separation of the sugars of the hydrolysate, and periodate oxidation of the galactose which represents roughly 16% of purified locust bean gum poly-mannogalactan.

Leech's method was entirely too time consuming for routine use, and involved correction for somewhat erratic blanks.

Dahn (1) therefore investigated a possibility suggested earlier by Webb, loc. cit., namely, measurement of the reflectance of handsheets containing gum dyed previous to beater addition. He selected a direct dye produced by Du Pont; "Pontamine" Fast Blue 4G-L, the same dye used previously by Webb.

Although his results were encouraging, there was some indication that the dye might "bleed" from the gum to the cellulose fibers, yielding spurious reflectance data.

Ambiguity as to proper wavelengths for reflectance measurements resulted from a shift of the optical absorption maximum of the dye upon sorption on the gum, and sorption of the dyed gum on the cellulose fibers.

There was the further possibility that the sorption characteristics of the gum might be adversely affected by the dyeing. This was indicated in Webb's studies by somewhat inferior bursting strengths of handsheets made from a dyed gum furnish.

In spite of these difficulties, Dahn's technique seemed promising enough to encourage further study, specifically with dyes less likely to exhibit "bleeding" to the backwater and cellulose fibers.

Laughlin (4) suggested a number of vat-type organic pigments of Du Pont's "Ponsol" series. These show no substantivity to cellulose (3), and are insoluble in their pigment (oxidized) form. The soluble, or leuco, form is obtained in a caustic, reducing vat; under vat conditions these

pigments become substantive to cellulose and protein fibers. Oxidation to the insoluble pigment form is achieved by air oxidation or treatment with acidified hydrogen peroxide or sodium perborate.

It was felt that it should be possible to vat dye other, non-cellulosic, polysaccharides, such as the locust bean gum mannogalactan, and after appropriate oxidation procedures have a gum in which a truly insoluble pigment was bound; this should eliminate the possibility of "bleeding."

The present investigation was therefore undertaken in an effort to produce such a dyed, or pigmented, locust bean gum suitable for retention studies.

EXPERIMENTAL

Initial work was designed to yield a qualitative picture of the conditions necessary for formation of leuco vats, and the dyeing in such vats of crude locust bean gum.

The following dyes were studied. Letter symbols preceding their names shall be used in the body of this report:

JG Jade Green supra double paste

YG Yellow G double paste

BBF Blue BF double paste

DBBR Dark Blue BR paste

FGC Flavone GC double paste

These dyes are provided in a thixotropic paste form, the solids content of which may be subject to some variation from one lot to the next. However, tinctorial powers are reportedly (4) standardized. Since the

pigments showed a tendency to settle on prolonged standing, it became evident that, in order to maintain constant tinctorial power, it is necessary to shake or stir the pastes very thoroughly before withdrawing a sample.

A solids assay was made on each paste by withdrawing a small sample, weighing, and oven drying to constant weight at 106°C. Assays are reported in Table I.

TABLE I
SOLIDS CONTENT OF "PONSOL" DYES.*

<u>Dye</u>	<u>Assay, % by weight</u>
JG	24.4
YG	25.6
BBF	22.1
DEBR	24.6
FGC	20.4

* Du Pont lot designation: CG-6324, 2/24/54

These solids contents are not to be construed as representing dye concentration, since the pastes contain, in addition, dispersing agents and sugars or similar filler.

Since the presence of sugars might interfere with future analyses of dyed gums, a chromatographic analysis of the dye pastes was conducted, using as elution liquid 6:4:3 butanol:pyridine:water, running for 24 hours at room temperature in a chromatographic tank containing the vapors of these

solvents at equilibrium concentration.

The chromatograms were air dried after removal, and sprayed with a standard formulation of aniline acid phthalate in water-saturated butanol. Development was at 108°C. for five minutes. Only DBBR and FGC yielded developable spots, and these were of such low intensity as to create no interference in either qualitative or quantitative analytical techniques.

Spectral transmittance measurements were made on a number of aqueous suspensions of these dyes. A Coleman Model 14 "Universal" Spectrophotometer having an approximately 20 to 25 mμ slit was used. The instrument was calibrated against the General Electric Recording Spectrophotometer using a didymium filter studied by Wink (10), et al., with the latter instrument in 1950. The principal absorption maximum of this filter was found at 584 mμ using the Coleman instrument, and at 582.6 mμ with the GERS. Bureau of Standards studies (11) on a similar filter report an absorption maximum at 583 mμ. The resolution obtainable with the Coleman instrument, though much inferior to the resolution obtainable with the GERS, is nevertheless adequate for this study.

Tracings of the original spectral transmittance curves for the aqueous dye suspensions appear in Figures 1 to 4 at the end of this report. The significance of the double curves will be discussed in a later section. The dyes were found to obey Beer's law over a wide concentration range.

Introductory Experiments with Vats

A 0.75% dispersion of crude locust bean gum was prepared in the following manner. Two grams of crude gum were stirred into 200 ml. cold distilled water and beaten in a Waring Blendor for fifteen minutes. The dispersion was then heated to approximately 70°C. over an open flame, and returned to the blender for an additional ten minutes. An additional 62 ml. of distilled water were added slowly to the Waring Blendor, maintaining the temperature of the dispersion at approximately $60 \pm 10^\circ\text{C}$. by occasional heating.

Since this gum must be flocculated for recovery from the dye vats, and since the addition of H_2SO_4 and similar ionic materials must be avoided, some crude experiments with flocculation by methyl and isopropyl alcohol were conducted.

Aliquots of gum dispersion were diluted to concentrations from 0.15 to 0.5%, and these, as well as straight stock were titrated with methyl and isopropyl alcohols. Addition of the alcohols was regulated to approximately 0.1 ml./sec. and the dispersions were stirred during titrations. Advent of flocculation, first clotting, massive clotting, and exhaustion of the gum were noted. Occasional straining through 60-100 mesh brass screens was necessary in order to observe the point of exhaustion of gum.

The results of these experiments are summarised in Table II and Figure 9.

TABLE II
ALCOHOLIC FLOCCULATION OF CRUDE LOCUST
BEAN GUM FROM AQUEOUS DISPERSIONS

Flocculant:	Methanol (tech.)					Isopropanol (ACS)	
Gum Conc.*, % (wt./vol.)	0.15	0.25	0.37	0.50	0.75	0.25	0.50
Alcohol Conc.**, %							
1st flocculation	--	31	--	19	--	12-19	10-18
1st clotting	30	37	34	34	29	30	28
	--	38	--	--	--	--	--
Massive clotting	--	43	--	47	--	30	31
Exhaustion of gum (total flocculation)	--	45	--	53	--	31	36

* Gum concentrations calculated as grams gum per 100 ml. water.

** Alcohol concentrations based on volume % alcohol assuming additivity of volumes.

From these alcoholic flocculation data it is evident that isopropanol is superior to methanol as a gum flocculant, provided vat stability can be maintained equally well in both cases. This is indeed the case (4).

Nevertheless, some experiments were now conducted using methanol flocculation from vats. These experiments were purely qualitative, and no attempt was made to formulate accurately the vats used.

Jade Green

Twenty ml. water, 1.5 ml. 10% NaOH, and roughly 75 mg. sodium hydrosulfite were mixed in a small beaker. A stirring rod was dipped into the Jade Green (JG) supra double paste, and into the vat, which was warmed gently. A deep bluish color developed characteristics of the leuco form of the pigment.

Air oxidation occurred readily at the surface of the vat. When a drop of this blue (leuco) vat was touched to a filter paper, it was immediately air-oxidized to its jade green form.

About 0.5 ml. 10% caustic added to 10 ml. 0.75% locust bean gum, 50 mg. "hydro" were stirred into the dispersion to which 3-5 ml. vat were added. The mixture was stirred briskly and heated to 60-80°C., and the gum was flocculated with 15 ml. methanol containing 10 mg. NaOH and saturated with "hydro." The resulting clot was removed with a stirring rod, transferred to an alcoholic rinse having the same composition as the flocculant. The clot was then transferred to roughly 30 ml. tap water, where its color changed immediately from leuco blue to jade green.

The methanol rinse supernatant and tap water both remained colorless. Upon heating, the pigmented clot was easily dispersed in tap water. These experiments were repeated a number of times.

In each case results were substantially the same. Jade green vats seem to have satisfactory tolerance for 50% methanol only if considerable caustic and hydrosulfite are present. Considerable difficulty arises from the tendency of the vat to air oxidize on its surface, and on the liquid-glass interface.

Yellow G, Blue BF, Flavone GC, and Dark Blue BR.

These dyes were made up in vats under substantially the same conditions. Leuco colors were:

YG brilliant blue
BBF grayish green-blue
FGC violet
DBBR magenta

Yellow G (YG) seemed to have an inferior tinctorial power, though subsequent experiments (described later) proved this to be incorrect. Methanol tolerance was barely acceptable.

BBF was difficult to convert to the leuco form, which also is harder to detect since little color change is evident. An attempt was made to oxidize BBF pigmented gum using acidified sodium perborate. Although the oxidation rate was indeed improved, the flocculated gum was rendered completely nondispersible.

FGC showed excellent tolerance to methanol (up to 50-75% by volume). FGC leuco color is obtained only after several minutes of gentle heating. The vat can be completely exhausted with respect to substantivity to Watman No. 50 filter paper by the addition of only moderate quantities of locust bean gum. However, gum which is dyed until vat exhaustion is rendered completely nondispersible.

Normal Dyeing Conditions

As a result of these qualitative studies and further conversation with Dr. E. Laughlin, conditions for a "normal" vat and standard dyeing conditions were formulated as follows:

Vat:
6 grams single or double paste
30 ml. 10% caustic

70 ml. water

Heat to 50-70°C. and add 1.5 grams "hydro." Stir and let stand three minutes.

Gum:

Disperse and filter or centrifuge to yield an 0.5% totally dispersed gum. Mix as follows:

80 ml. gum dispersion as above.

20 ml. 10% caustic.

Dyeing:

Mix 100 ml. vat with 100 ml. alkaline gum dispersion, let stand ten minutes at 50-60°C., with occasional agitation.

Flocculation:

Add alcohol until desired degree of flocculation is attained.

For complete flocculation this will be 50% methanol or 35% isopropanol (cf. Figure 9)

Rinse:

Rinse in 50% methanol or isopropanol. Remove clots quickly, and repeat rinsing until clear, nearly colorless, and neutral supernatants are obtained.

N.B.:

If a Jade Green vat becomes red at any time following addition of the flocculant, there is insufficient alkali and more must be added.

Yellow G may be used at temperatures as high as 71°C; Blue BF

cannot be used above 60°C.

Preparation of Dyed Gums under Standard Conditions and Preparation of
Handsheets from Dyed Gum Furnishers:

Approximately 4.3 grams crude locust bean gum (3.8 g. O.D. basis) were dusted through a 40-mesh and 60-mesh screen and stirred into 750 ml. cold distilled water. The mixture was beaten in a Waring Blender for five minutes and heated on a steam bath with gentle stirring for one hour. It was then replaced on a Waring Blender for one hour maintaining the temperature at 50-60°C. by occasional heating.

A sterile flask was prepared meanwhile by boiling for 1/2 hour. A cotton plug was placed in the neck of the flask and steamed during this period. The gum dispersion was then diluted again to 750 ml., boiled a few minutes, and poured into the sterile flask, which was plugged immediately.

Further alcoholic flocculation data were obtained with this dispersion, and are included in the data of Table II and Figure 9. Identical techniques were used.

Before dyeing this dispersion, an attempt was made to remove non-dispersible matter (cellulosic and proteinaceous material) by filtration. Five hundred milliliters of the 0.5% dispersion were filtered through a large "coarse" Buchner type sinter, and an effort was made to force the filtrate through a "medium" sinter. However, the filter became plugged and the filtration was discontinued, the few ml. "medium" filtrate being combined with the remainder of the "coarse" filtrate.

Jade Green:

Using the standard dyeing conditions formulated in the previous section, 100 ml. of this "coarse" filtered 0.5% dispersion were dyed with Jade Green. Note that this represents a 25% increase in gum over the concentration recommended for a 100 ml. vat. Flocculation was achieved with 35% isopropanol.

The clot was removed from the vat using a 100 mesh brass screen. The dyed gum was rinsed three times in 50 ml. 50% isopropanol, by which time the pigment had been air-oxidized to its Jade Green nonleuco form.

A standard oxidizing reagent was formulated as follows:

"Superoxol" 100 ml.

Glacial acetic acid 50 ml.

Water to make 500 ml.

Forty ml. of this reagent were added to 40 ml. isopropanol, and the entire mixture was added to a fourth 50% isopropanol rinse containing the JG dyed gum. This was stored overnight at 9.5°C.

After removal from storage, the dyed gum was rinsed briefly in a minimum of water to remove mechanically held alcohol, and dispersed in 250 ml. cold water using a Waring Blender. The mixture was then removed from the blender, heated to boiling, filtered through "coarse" and "medium" sinters, reboiled to insure sterility, and set aside for five days at 9.5-10.5°C.

Yellow G:

Using standard vat conditions at 60°C., 80 ml. of 0.5% crude locust bean gum were dyed with Yellow G. The only deviation from standard conditions was a set-up, whereby the vat and first alcoholic rinses could be flushed with prepurified nitrogen to sweep out dissolved oxygen and prevent surface oxidation of the vat. Isopropanol was used for flocculation. Although the dyed gum clot was separated from the vat and first two rinses by straining through a 100-mesh brass screen, subsequent separations from the rinse solutions were achieved by centrifugation at 2900 r.p.m. in the International Size II Centrifuge. This corresponds to 2000 gravities at the bottom of the centrifuge tubes.

The dyed gum was redispersed in water using steam heat and the Waring Blender, after first adding 10 ml. of the standard oxidizing reagent.

Blue BF:

Using essentially the same conditions, 80 ml. of "coarse" filtered 0.5% gum dispersion were dyed with Blue BF. Nitrogen flushing was used again.

The clot was removed from the vat by 100-mesh straining and rinsed twice. The major portion of the clot in the second rinse possessed a very definite gray-blue color, while the portions of flocculated gum in the first rinse which passed through the screen exhibited the typical brilliant BBF color. Attempts to oxidize the twice-rinsed clot were unsuccessful, and it remained gray even after final dispersion in water. This final "dispersion" was in reality a mechanical suspension, since the gum had apparently been rendered nondispersible.

Dark Blue BR:

Standard conditions were used. When the gum was poured into the vat, it was flocculated immediately, apparently by sorption of large quantities of dye. The vat was very unstable, and very vigorous nitrogen flushing was required to prevent air-oxidation.

Centrifugation was again used for clarification of first and second rinse supernatants, and for separation of entire clot from third alcoholic rinse. The dyed gum was redispersed in water using steam heat and the Waring Blendor.

Blank:

Using standard conditions with nitrogen flushing and isopropanol flocculation, a blank was prepared in which no dye was used in the vat.

However, contamination from the flushing apparatus caused a trace of Dark Blue BR to dye the gum. The "blank" gum was very lightly hued, and probably contained only minute quantities of the DBBR dye, which has an extremely high tinctorial power.

Since it was felt that this trace of DBBR would not alter the physical properties of the "blank" run gum, the flocculation, rinsing, and redispersion were continued in the usual fashion. Dispersion proceeded without difficulty.

Final Isolation of Dyed Gums:

After several days storage in water dispersion at 9.5°C., the JG, YG, BBF, and "blank" dyed gum dispersions were poured into equal volumes

isopropanol and the clots were allowed to stand overnight at room temperature. They were then centrifuged at 2900 r.p.m. for 15 to 30 minutes, and the solids were transferred to weighing bottles and oven dried in vacuo at 100-110°C. for 12 hours, and over magnesium perchlorate to constant weight.

Yields are reported in Table III, in the next section, together with storage times of undyed and dyed gum before handsheet preparation, described in the following section.

The control gum listed in this table is merely an 0.25% dispersion untreated in any way other than removal of 13% cellulosic and proteinaceous nondispersibles by centrifugation. Moisture assay revealed 12% water removable by oven drying in vacuo. The effective gum concentration is therefore 0.187%, and this concentration was used in handsheet preparation.

Preparation of Run Two Handsheets from Dyed Gum Furnishes.

The Jade Green, Yellow G, Blue BF, and "blank" gums were dispersed in water by overnight heating on a steam bath preceded and followed by beating in the Waring Blender. Final concentration was 0.25%.

Meanwhile 1385 grams of 25% Weyerhaeuser bleached sulfite prebeaten to a freeness of 720°S.R. were stirred into 23 liters of deionized water. After several hours of stirring with a small "Lightning" mixer, the freeness was reduced to 618°S.R. and the consistency was 1.57%.

The pulp slurry was diluted in four-liter batches to a consistency of 0.785%, and to these batches 63 ml. of the 0.25% dyed gum and "blank" dispersions, and 84 ml. of the 0.187% control dispersion were added, to give

a furnish containing 0.5% gum based on O.D. fiber.

A system of air bubblers was set up so that each four-liter batch of pulp slurry could be agitated very gently overnight, thereby assuring uniform exposure of the pulp to the gums.

After pulp-gum exposure times varying from 17 to 28 hours, handsheets were prepared, diluting the slurries to a consistency of 0.5% before addition of 300 to 325 ml. aliquots to 3500 ml. of water in a 6 in. by 6 in. Valley sheet mold. At least one basis weight sheet was made for each set of handsheets of each furnish. Furnish volume was adjusted to give a 1.5 gram handsheet.

Seven handsheets of each furnish were prepared, including a set of seven handsheets from waterleaf furnish. Pulp-gum exposure times varied from 17.25 to 22.75 hours. A second set of seven sheets of each furnish was then made after pulp-gum exposure times of 23 to 28.25 hours.

Furnish data, exposure (sorption) times, basis weights, and handsheet code designations are presented in Table III together with data concerning yields of dyed gum and storage times of undyed and dyed gums.

Four handsheets of set C-0-C-2 and five handsheets of each of the other eleven sets were submitted for physical testing as follows: basis weight, caliper, Mullen bursting strength, M.I.T. fold, and Schopper tensile strength.

TABLE III

ISOLATION DATA OF RUN TWO DYED GUMS AND HANDSHEET
PREPARATION DATA FOR RUN TWO HANDSHEETS

Handsheet Code Designation	Description of Furnish (All gum added at 0.5% of O.D. fiber)	Furnish Volume ml.	Basis Weight, g.	Pulp-Gum Exposure (Sorpton) Time, hrs.	Yield of Dyed Gum from STD. Vat, %	Gum Storage Time, days Before Dyeing	After Dyeing
C-0-0-2.	Waterleaf--no gum	310	1.497	--	--	--	--
C-0-0-2.1	Waterleaf--no gum	--	--	--	--	--	--
C-0.5-0-2	Control, untreated gum	315	1.494	18.25	--	6	--
C-0.5-0-2.1	Control, untreated gum	--	--	23.00	--	6	--
B-0.5-DBER-2	"Blank" contaminated	315	1.500	21.00	75	10	5
B-0.5-DBER-2.1	with DBER	--	--	24.00	75	10	5
D-0.5-JG-2	Gum furnish--JG	320	1.492	21.50	46	6	5
D-0.5-JG-2.1	Gum furnish--JG	--	--	27.75	46	6	5
D-0.5-YG-2	Gum furnish--YG	317	1.502	19.00	66	7	5
D-0.5-YG-2.1	Gum furnish--YG	--	--	23.50	66	7	5
D-0.5-BBF-2	Gum furnish--BBF	323	1.492	22.75	41	9	5
D-0.5-BBF-2.1	Gum furnish--BBF	--	--	28.00	41	9	5

Two handsheets of each set were submitted for GERS reflectance measurements as follows: on blank and dyed gum series ("B" and "D") a spectral reflectance curve throughout the visible range (400 to 700 m μ) was determined for the second sets ("2.1" sets). For both "2" and "2.1" sets of the "B" and "D" series, reflectance measurements were made at wavelengths corresponding to suitable absorption maxima or plateaus as discovered from spectral reflectance curves.

On the "C" series, i.e., C-0-0-2 and C-0-0-2.1, reflectance measurements were made at all wavelengths at which absorption maxima or plateaus were discovered in "B" and "D" handsheets.

Results of physical testing are reported in Table IV, spectral reflectance curves are presented in Figures 5-8, and reflectance measurements are given in Table V.

Spectral transmittance curves were determined for the dyed gums, with the exception of BBF. The transmittance data may be in error by as much as 2% due to the residual turbidity of these gum dispersions. Only Jade Green dyed gum produced a water clear dispersion. Curves for JG, YG, and DBBR will be found in Figures 1-3, together with transmittance curves for the free dye in aqueous suspension.

These data are presented primarily for comparison of the positions of the absorption maxima and minima, since the turbidity correction is indeterminate, although it should increase as the fourth power of λ .

TABLE IV
PHYSICAL TESTING DATA FOR RUN TWO
HANDSHEETS

Code No.	Basic Weight, lb. 25 x 40/500	Caliper, in.	Bursting Strength, (Mullen) points	pt. per 100 lb.	M.I.T. Fold	Schopper Tensile lb./inch
Max.						
Min.						
Av.						
	44.0	0.0043 0.0041 0.0042	30.0 26.0 27.8	63	101 50 76	17.4 13.4 15.3
Av. dev. from mean		0.00004	0.95		18.3	1.27
Max.						
Min.						
Av.						
	43.2	0.0042 0.0041 0.0042	29.0 25.0 27.0	62	112 51 78	16.3 13.9 15.2
Av. dev. from mean		0.00002	1.25		17.1	0.66
Max.						
Min.						
Av.						
	43.7	0.0043 0.0041 0.0042	38.5 32.0 35.0	80	326 84 235	19.5 15.2 17.2
Av. dev. from mean		0.00006	1.45		62.5	1.32
Max.						
Min.						
Av.						
	42.9	0.0043 0.0041 0.0042	35.0 30.0 33.5	78	386 172 273	18.1 16.3 17.2
Av. dev. from mean		0.00008	1.20		57.3	0.58

TABLE IV (Continued)

Code No.	Basis Weight, lb. 25 x 40/500	Caliper, in.	Bursting Strength, (Mullen) points	pt. per 100 lb.	M.I.T. Fold	Schopper Tensile lb./inch
D-0.5-YG-2	Max.	0.0048	39.0		232	19.6
	Min.	0.0041	31.0		72	14.7
	Av.	0.0043	33.2	73	126	16.6
	Av. dev. from mean	0.00018	1.73		40.8	0.89
D-0.5-YG-2.1	Max.	0.0043	33.0		124	17.8
	Min.	0.0042	29.0		58	14.4
	Av.	0.0043	30.5	70	97	15.9
	Av. dev. from mean	0.00004	1.10		17.3	0.82
B-0.5-DBBR-2	Max.	0.0044	35.0		237	18.5
	Min.	0.0041	31.5		97	15.9
	Av.	0.0042	33.2	76	173	16.9
	Av. dev. from mean	0.00008	0.78		37.1	0.58
B-0.5-DBBR-2.1	Max.	0.0043	33.0		197	17.3
	Min.	0.0042	28.0		151	14.4
	Av.	0.0042	31.2	72	170	15.6
	Av. dev. from mean	0.00002	1.55		14.8	0.66
D-0.5-JG-2	Max.	0.0045	36.0		183	18.8
	Min.	0.0043	28.0		114	16.3
	Av.	0.0044	33.2	75	160	17.2
	Av. dev. from mean	0.00006	2.27		19.7	0.69

TABLE IV (Continued)

Code No.	Basis Weight lb. 25 x 40/500	Caliper, in.	Bursting Strength (Mullen)		M.I.T. Fold	Schopper Tensile lb./inch
			points	pt. per 100 lb.		
D-0.5-JG-2.1	Max	0.0044	35.5		223	17.8
	Min	0.0042	30.0		96	15.9
	Av.	0.0043	32.7	74	168	16.9
	Av. dev. from mean	0.00006	1.46		32.4	0.47
D-0.5-BBF-2	Max.	0.0045	35.5		250	18.5
	Min.	0.0043	29.5		89	16.3
	Av.	0.0044	33.8	75	174	17.5
	Av. dev. from mean	0.00004	1.29		44.5	0.68
D-0.5-BBF-2.1	Max.	0.0043	33.0		210	18.1
	Min.	0.0042	30.0		86	15.9
	Av.	0.0043	31.8	72	145	16.8
	Av. dev. from mean	0.00004	0.99		28.1	0.58

Note: The samples were conditioned and tested at 50% R. H., 73°F.

TABLE V
REFLECTANCE DATA FOR RUN TWO HANDSHEETS

Code No.		Reflectance, %, on G.E.R.S. ^a		
		Wavelength, mμ		
		590	620	670
C-C-C-2	Max.	87.4	87.7	87.0
	Min.	87.1	87.3	86.4
	Av.	87.3	87.5	86.8
C-O-O-2.1	Max.	88.7	89.0	88.6
	Min.	88.5	88.4	88.2
	Av.	88.6	88.8	88.4
C-O.5-O-2	Max.	86.5	86.8	86.2
	Min.	86.0	86.4	85.5
	Av.	86.4	86.6	86.0
C-O.5-O-2.1	Max.	87.5	87.8	87.3
	Min.	87.3	87.5	87.2
	Av.	87.4	87.7	87.2
D-O.5-YG-2	Max.			86.5
	Min.			86.2
	Av.			86.3
D-O.5-YG-2.1	Max.			87.7
	Min.			87.1
	Av.			87.4
B-O.5-DBBR-2	Max.			86.7
	Min.			86.6
	Av.			86.7
B-O.5-DBBR-2.1	Max.			87.5
	Min.			87.2
	Av.			87.4
D-O.5-JG-2	Max.		80.1	
	Min.		80.0	
	Av.		80.1	
D-O.5-JG-2.1	Max.		80.4	
	Min.		79.6	
	Av.		80.1	

^a G. E. recording spectrophotometer

TABLE V (Continued)

Code No.		Reflectance, %, on G.E.R.S. ^a		
		Wavelength, μ		
		590	620	670
D-0.5-BBF-2	Max.	75.8		
	Min.	75.1		
	Av.	75.5		
D-0.5-BBF-2.1	Max.	75.6		
	Min.	75.0		
	Av.	75.3		

G. E. recording spectrophotometer curves were obtained for four of the above samples. These samples are as follows:

D-0.5-YG-2.1
B-0.5-DBBR-2.1
D-0.5-JG-2.1
D-0.5-BBF-2.1

The original curves were water damaged in the fire. These curves have therefore been traced as accurately as possible under the circumstances, and are presented in Figures 5-8 at the end of this report.

Beer's law plots were made for several of the free dye suspensions, and very approximate data for the concentration of dye in the Jade Green dyed gum of this and subsequent dyeing will be presented in a later section.

Preparation of Jade Green Dyed Gums of Varying Dye Concentration

Approximately 6.7 grams of air-dried 60-mesh crude locust bean gum were mixed with a little water to make a thick paste. By grinding the paste in a glass mortar and pestle and slowly adding additional water, a thin homogeneous paste was obtained.

This thin paste was now transferred to a 2-liter beaker, heated over an open flame to 85-90°C., and maintained at this temperature by slow addition of water to a total volume of 800 ml. The dispersion was now beaten in a Waring Blendor for ten minutes, diluted to one liter, beaten in a blendor another five minutes and placed on a steam bath with gentle stirring for two hours. It was then stored at 9.5 to 10°C. for two days. At the end of this time some settling out of undispersed material was noted. The mixture was heated to 80-95°C. on the steam bath for ninety minutes with vigorous stirring and centrifuged hot at 2000 gravities for one-half hour.

The residue from this centrifugation was stirred into 200 ml. water and recentrifuged in the same fashion. The two supernatants were combined and diluted to one liter.

Gum concentration was determined by pipetting three 10-ml. samples of this clear dispersion into weighing bottles and evaporating to dryness and constant weight overnight. The concentration thus determined was $0.58 \pm 0.01\%$ (O.D. gum/vol.).

Standard vat conditions were now used for dyeing this gum except that dye concentrations were varied: 0, 4, 6, 8% dye. Two 80-ml. lots of 0.58% gum dispersion were dyed at each dye concentration. The vat and first rinses were flushed continuously with water-pumped nitrogen from which appreciable quantities of oxygen were removed by bubbling through two 500-ml. gas-washing towers containing 7% pyrogallol in 1% aqueous NaOH.

Flocculation was achieved with 45% isopropanol or mixtures of isopropyl and methyl alcohol and rinsings were done in either 50% isopropyl or methyl alcohol.

Yield, rinsing, and storage data are assembled in Table VI. Entries in the column entitled "Gum storage time, days, after dyeing" refer to the time between dyeing and handsheet preparation. As before, storage was at 9.5-10°C., and only storage as dispersion, in distinction to dried gum, is tabulated. Great difficulty was experienced in redispersing the 0, 6, and 8 JG gums. They had been ground in a ball mill, water was added to the mill, and rotation was continued for half-hour intervals. Sample 4 JG went into dispersion easily by shaking with water and beating in a Waring Blendor.

The appearance of 0.25% dispersions of these gums showed remarkable variation. It will be recalled that the Jade Green dyed gum of run 2, corresponding to handsheets D-0.5-JG-2 and D-0.5-JG-2.1, formed a water-clear, deeply hued 0.25% dispersion. In contrast, 0.25% dispersions of 4 JG and 6 JG were somewhat turbid, and more deeply colored. Sample 0 JG formed a deep amber dispersion, while 8 JG formed a very pale yellow dispersion with only a hint of jade green "overtone"

TABLE VI
DATA FOR RUN THREE JG DYEINGS

Designation of gum	Vat Strength, % Dye	Floculant MeOH, IsopropOH, %	Rinse Data		Supernatants		Yield, %	Gum Storage Time, days
			Composition, %	First pH Color	Second pH Color	Third pH Color		
0 JG	0.0	0	50 isopropOH	—	None	8 None	45	4
4 JG	4.0	0	50 MeOH	10 pale JG	7.5 None	7.0 None	69	4
6 JG	6.0	0	50 MeOH	10 pale JG	7.7 very pale JG	7.0 None	79	4
8 JG	8.0	21.0	50 MeOH	10 blue	7.5 pale blue	7.0 None	73	4

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Spectral transmittance measurements were made, and very approximate estimates for the concentration of dye in gum were made. These measurements appear in Table VII. In addition, viscosities were measured at 25°C., using a Brookfield "Synchro-Lectric" viscometer. These data appear in Table VIII.

TABLE VII
DYE CONCENTRATIONS IN RUN TWO AND THREE JADE
GREEN GUMS

Dispersion Designation	Concentration %	λ $m\mu$	T_{λ}^{+} %	Dye Concentration %	% Dye in Gum
Run 2:					
JG	0.25	520	71.6	0.0190	7.6
		620	26.9	0.0184	7.4
Run 3:					
4 JG	0.24	520	57.3	0.0316	13.2
		620	3.3	0.0495	20.6
6 JG	0.25	520	45.2	0.0456	18.3
		620	1.1	0.069	27.6
8 JG	0.26	520	95.7	0.00056	0.23
		620	95.8	0.00060	0.23

* No corrections made for residual turbidity of the dispersions.

* Measured with the Coleman Model 14 "Universal" Spectrophotometer.

TABLE VIII
BROOKFIELD VISCOSITIES OF RUN THREE
JADE GREEN DYED GUMS

Dispersion Designation	Concentration %	Viscosity, cp.
Control	0.39	48.8
	0.25	14.3
0 JG	0.24	4.0*
4 JG	0.24	3.2
6 JG	0.25	3.3
8 JG	0.26	3.0

* This viscosity was determined in a cylinder of inside diameter 2-3/16 in., with the instrument baffle in place. Spindle No. 2 was used, immersed halfway between the bob and the fiducial notch on the shaft.

Preparation of Run Three Handsheets

Approximately 1385 grams of prebeaten Weyerhaeuser bleached sulfite dried to a consistency of 25% were stirred into 23 liters of deionized water. After one-half hour stirring the consistency was 1.44%, and the freeness was 619°S.R. (average of two measurements).

The 1.44% pulp slurry was divided into ten batches of 1040 ml. each, appropriate quantities of gum dispersion were added to yield 0.5% and 1.0% gum on the basis of O.D. fiber (cf. Table IX), and the mixtures were stirred for 15 minutes. Following this the mixtures were allowed to stand undisturbed for five minutes, and were then diluted with 2570 ml. deionized water to a consistency of 0.5% and basis weight sheets were made.

Handsheet preparation data are given in Table IX. The "control" gum dispersion was an untreated material stored for two days before furnish addition. Dyed gums were stored 4 days before dyeing, 2 days after dyeing.

One handsheet of each designation (set) was submitted for GERS reflectance measurement at 620 $m\mu$. A complete spectral reflectance curve in the visible range was requested for handsheet D-1.0-6 JG-3.

The remaining four or five handsheets of each set were submitted for physical testing as follows: basis weight, caliper, Mullen burst, M.I.T. fold, and Schopper tensile.

Results of optical and physical measurements of these handsheets are not yet available. The general appearance of these sheets indicated good formation. Sheets made from 4 JG and 6 JG furnishes were very much more deeply colored than the jade green sheets of run 2 (D-0.5-JG-2 and D-0.5-JG-2.1).

TABLE IX

RUN THREE HANDSHEET PREPARATION DATA

Handsheets Designation	Description of Furnish	Gum Added to 1040 ml. 1.44% Pulp Conc., % Vol., ml.	Furnish Volume ml.	Basis Weight, g.	Pulp-Gum Exposure (Sorption) Time, hrs.	No. of Sheets Made	Freeness
C-0.0-0-3	Waterleaf no gum	---	380	---	---	5	619
C-0.5-0-3	0.5% untreated gum--control	0.25	390	---	0.833	6	not measured
B-0.5-0-3	0.5% undyed, vat treated gum (0 JG)-- blank	0.24	405	1.505	0.833	5	not measured
B-1.0-0-3	1.0% undyed, vat treated gum (0 JG)-- blank	0.24	405	1.505	0.835	6	not measured
D-0.5-4 JG-3	0.5% dyed (4 JG) gum	0.24	400	1.512	0.833	6	not measured
D-1.0-4 JG-3	1.0% dyed (4 JG) gum	0.24	395	---	0.833	6	not measured
D-0.5-6 JG-3	0.5% dyed (6 JG) gum	0.25	390	---	0.767	6	not measured
D-1.0-6 JG-3	1.0% dyed (6 JG) gum	0.25	400	---	0.917	5	not measured
D-0.5-8 JG-3	0.5% dyed (8 JG) gum	0.26	400	1.512	0.917	6	not measured
D-1.0-8 JG-3	1.0% dyed (8 JG) gum	0.26	400	1.512	c.833	6	not measured

CONCLUSIONS

Qualitative observations of the vat-treated locust bean gum indicate considerable lack of reproducibility, both in tinctorial power, and in dispersibility of the products.

An attempt was made to measure quantitatively the relative fractions of run 3 vat-treated gums rendered nondispersible. However, the results of these measurements were not suitable for analysis since nondispersible contaminants were added by ball mill treatment.

In the case of the 4 JG gum, which was not milled, centrifugation of the easily dispersible gum and subsequent solids assay of the residue indicated the presence of 3.18% nondispersible material. All gums of run 2 and 3 were clarified before dyeing by "coarse" filtration (run 2) or centrifugation (run 3), and rinse solution analyses indicated the absence of unsorted dye; it can be presumed therefore that this figure represents the actual fraction of gum rendered nondispersible under these particular vat conditions.

Data of Table VI represent percentage of dye paste, and in accordance with the earlier data on solids assay of the pastes and information received from Dr. E. Laughlin (4), these figures must be reduced by an indeterminate amount in excess of 75% to yield actual dye concentrations.

The behavior of the 8 JG vat preparation in respect to the color of its product is anomalous. No explanation of the almost total lack of jade green color of the 8 JG dyed gum is apparent.

Viscosity measurements (Table VIII) on vat-treated gums indicate that even in the absence of dye the alkaline, reducing "atmosphere" of the vat creates an inferior gum. For this reason and because the gum is apparently rendered partially nondispersible by the dye, "Ponsol" dyed gums are not suitable for retention measurements.

Two further observations are of some interest. First, a study of Table IV reveals that the state of dispersion of well-mixed gums has only small effect on the physical properties of the resulting handsheet. Jade Green dyed gums of run 2 were completely dispersed, forming water-clear solutions. On the other hand, BBF and YG dispersions were turbid, and the YG dispersion was in reality a mechanical suspension of nondispersible gum.

Secondly, analysis of reflectance data of run 2 indicates that even after some 20-hour pulp-gum exposure (sorption) time, further sorption can occur. This is made more apparent if we consider ΔR , defined as $[\text{Reflectance (C-0-0-2)}] - [\text{Reflectance (D-0.5-X-2)}]$, and $[\text{Reflectance (C-0-0-2.1)}] - [\text{Reflectance (D-0.5-X-2.1)}]$. Such data are presented in Table X.

TABLE X
INCREMENTS OF REFLECTANCE AS FUNCTIONS OF GUM SORPTION TIME

Handsheet Designation	Sorption Time, hrs.	ΔR , %	Reflectance measured at:
C-0.5-0-2	18.25	---	---
C-0.5-0-2.1	23.00	---	---
B-0.5-DBBR-2	21.00	0.08	plateau (670 m μ)
B-0.5-DBBR-2.1	24.00	1.07	plateau (670 m μ)
D-0.5-JG-2	21.50	7.44	abs. max. (620 m μ)
D-0.5-JG-2.1	27.75	8.20	abs. max. (620 m μ)
D-0.5-YG-2	19.00	0.45	plateau (670 m μ)
D-0.5-YG-2.1	23.50	0.99	plateau (670 m μ)
D-0.5-BBF-2	22.75	11.39	plateau (590 m μ)
D-0.5-BBF-2.1	28.00	13.30	plateau (590 m μ)

The physical properties of the control handsheets of run 2 are not subject to comparison with the test data on dyed-gum furnish handsheets; differences in storage time may well have created differences in the degree of bacterial degradation of the gum. Run 3 was designed to yield more adequate control data, although loss of material necessitated again significant differences in storage time.

We should, of course, expect some sort of chemical interaction between the sorbed dye and locust bean gum. Evidence of this is found in Table XI in which the positions of characteristic absorption minima,

maxima, and plateaus are compared for dye, dyed gum, and handsheets made from dyed gum furnishes. These data would seem also to indicate an alteration of the dye-gum complex, or formation of a dye-cellulose complex, in the formed handsheet. If the latter is the case, then we have bleeding from the gum to the cellulose.

In any event, shifts in the absorption maxima upon dye and gum sorption lead to ambiguities in the interpretation of Kubelka-Munk, and Preston and Tsien relations.

TABLE XI

COMPARISON OF SPECTRAL TRANSMITTANCES OF "PONSOL" DYES AND DYED GUMS AND REFLECTANCES OF HANDSHEETS MADE FROM DYED GUM FURNISHES

Dye	Characteristics of Spectra	Dye	λ , m μ Dyed Gum	Handsheet
Jade Green	Abs. max.	636	624	620
	Abs. min.	516	502	555
Yellow G	Abs. max.	435	420	402, 670
	Abs. plateau	none	none	600-650
Dark Blue BR	Abs. max.	565	none	403, 670
	Abs. min.	475	none	none
	Abs. plateau	none	480-495	610-625
Blue BF	Abs. max.	616	—	590
	Abs. min.	465	—	555

RECOMMENDATIONS

1. Efforts to use gums dyed with vat-type pigments of the "Ponsol" series in retention studied should be discontinued.
2. The behavior of locust bean gum under vat conditions presents an interesting problem, and some studies should be directed toward determining the nature of the degradation occurring under these conditions.
3. The sorption kinetics of locust bean gum on bleached sulfite pulps over long-term exposure intervals should be studied.
4. Efforts to measure retention kinetics under laboratory conditions should be directed toward the preparation of radio-carbon tagged gum. The possibility of using direct dyes of high tinctorial power should be investigated.

However, the qualities required of such a dye create formidable restrictions; a "brief" list follows:

- a. Optimum or permissible

pH = 7.0

- b. Little change with pH
- c. Little change with alum or size.
- d. No affinity for cellulose, hemis, or lignin.
- e. Low two sidedness.
- f. Complexing with gum.
- g. No bleeding to back water.
- h. High tinctorial power.
- i. Fair or good water solubility (must be true solution, not a suspension)

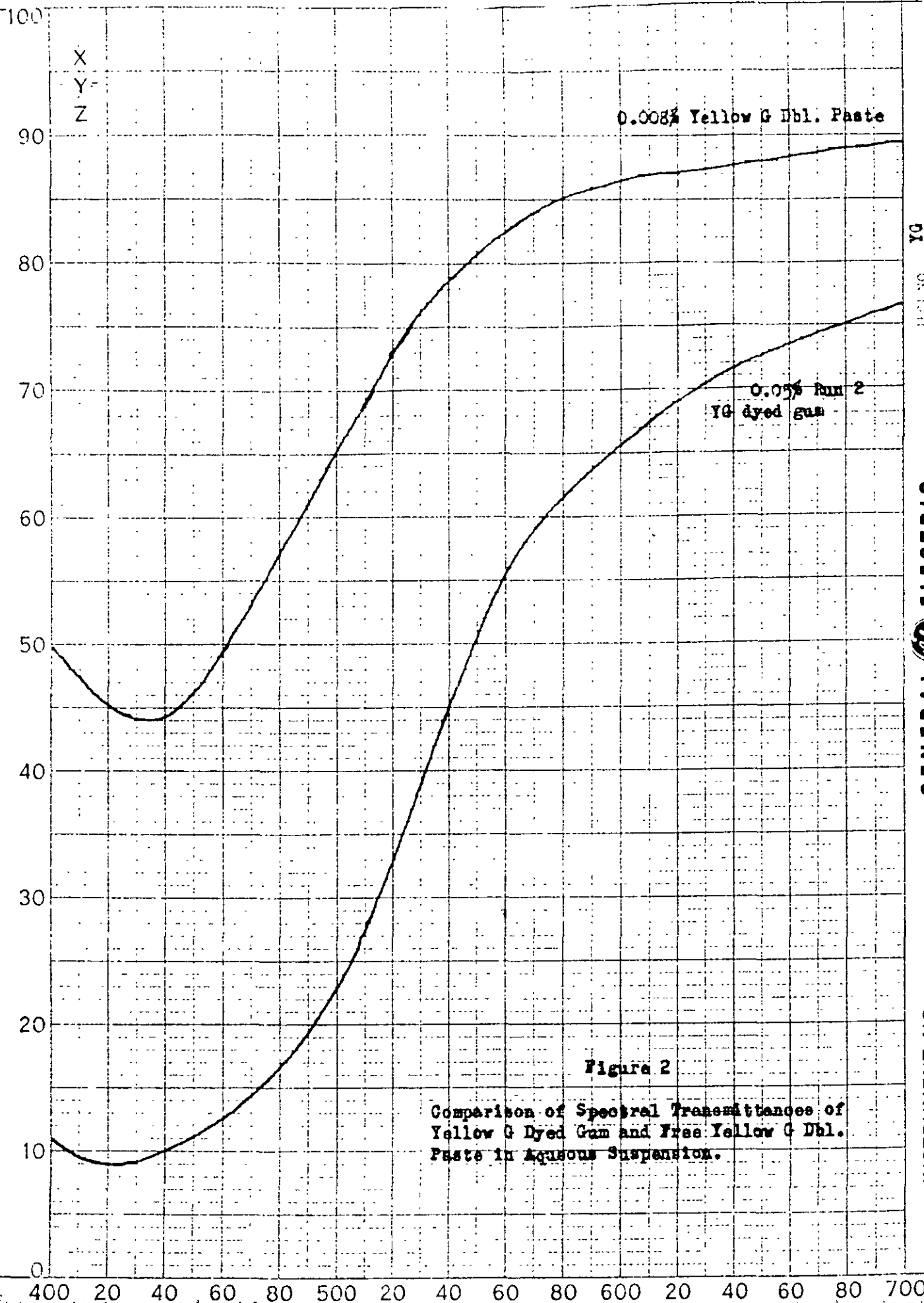
- j. Fair light-fastness over a period of several weeks.
- k. There should be no shift in the position of the absorption maxima and/or absorption plateaus when the dye is sorbed on the gum.

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RELATIVE TO Project 1467

PERCENT TRANSMITTANCE REFLECTANCE



X
Y-
Z

YG
D.R.S.

TEST NO
DATE

GENERAL ELECTRIC
RESEARCH AND DEVELOPMENT DEPARTMENT

INSTRUMENT NO.
Coleman "Universal"

TRANSMITTANCE (PERCENT)

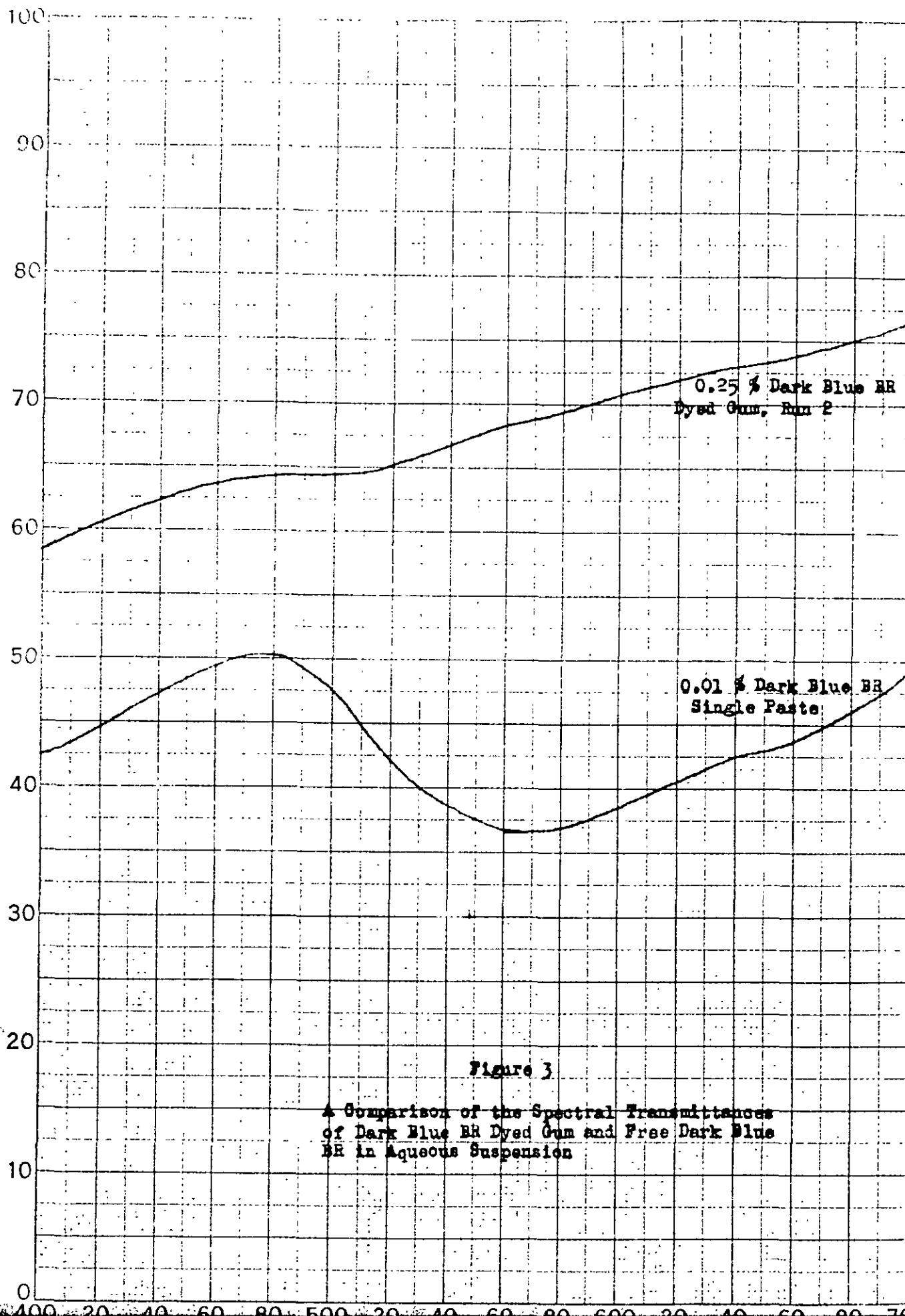


Figure 3

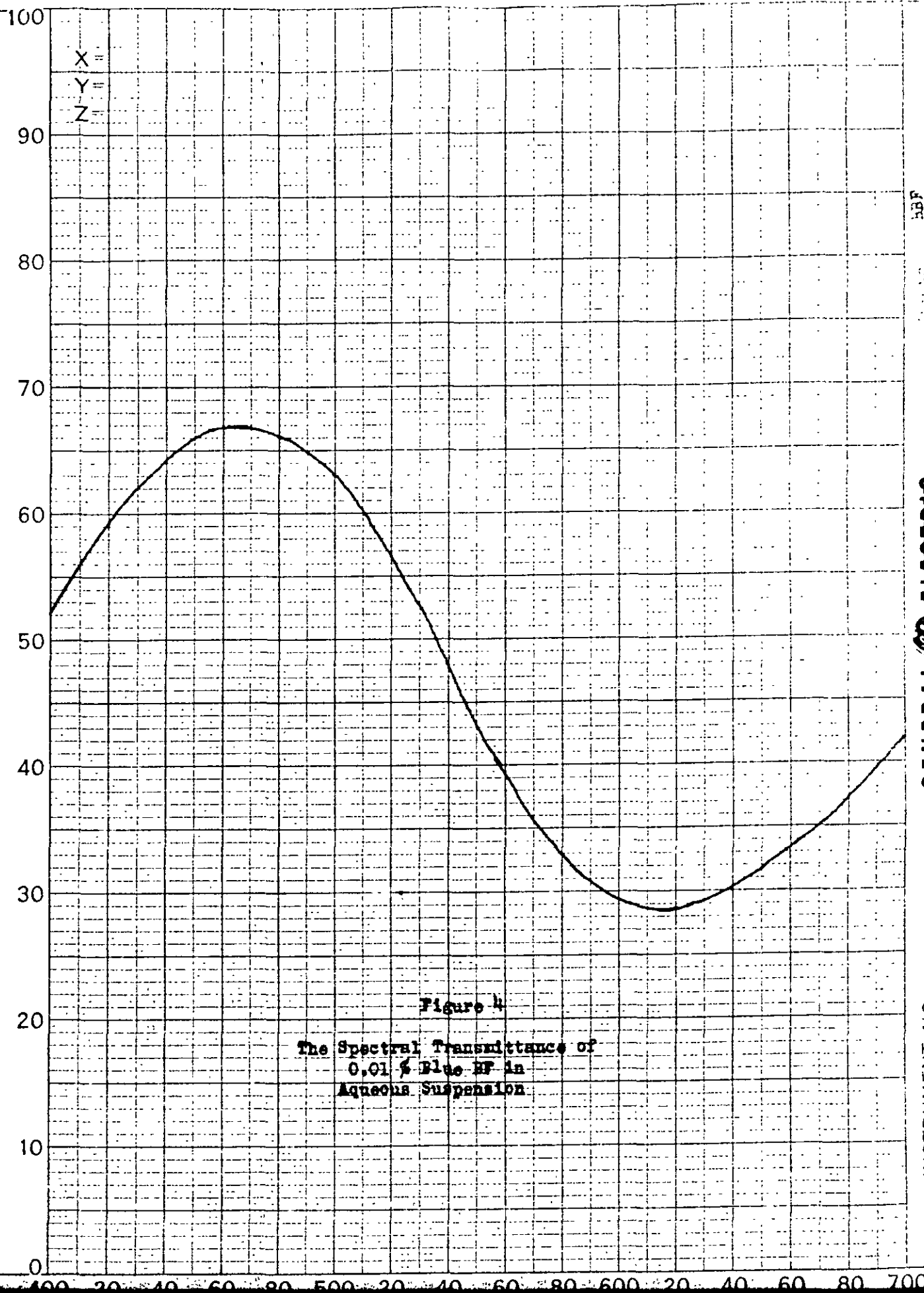
A Comparison of the Spectral Transmittances
of Dark Blue BR Dyed Gum and Free Dark Blue
BR in Aqueous Suspension

TEST NO. DBB BY D.F.S.

DATE

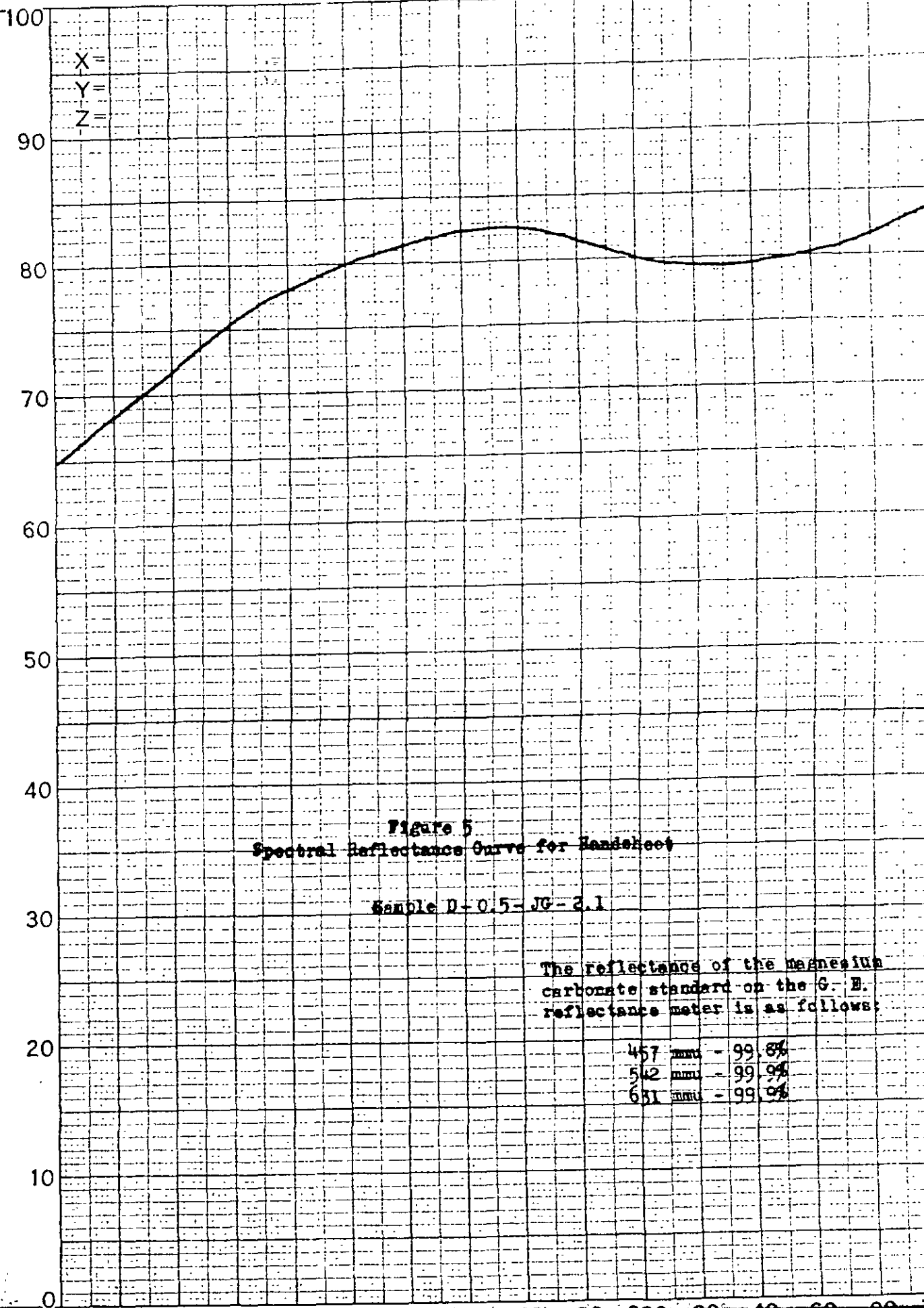
GENERAL ELECTRIC
RECORDING SPECTROPHOTOMETER

INSTRUMENT NO.
Coleman "Universal"



GENERAL ELECTRIC
RECORDING ELECTROPHOTOGRAPH

INSTRUMENT NO.
Colerian "Universal"



The reflectance of the magnesium carbonate standard on the G. E. reflectance meter is as follows:

457 mμ	-	99.8%
542 mμ	-	99.9%
631 mμ	-	99.9%

150497
W.S.

DATE

GENERAL ELECTRIC
RECORDING SPECTROPHOTOMETER

INSTRUMENT NO.

PERCENT TRANSMITTANCE REFLECTANCE

RELATIVE TO Project 1467

100

X
Y
Z

90

80

70

60

50

40

30

20

10

0

400 20 40 60 80 500 20 40 60 80 600 20 40 60 80 700

Figure 6

Spectral Reflectance of Handsheet

Sample D - 0.5 - TC - 2.1

The reflectance of the magnesium carbonate standard on the C. E. reflectance meter is as follows:

457 mμ	-	99.8%
542 mμ	-	99.9%
631 mμ	-	99.9%

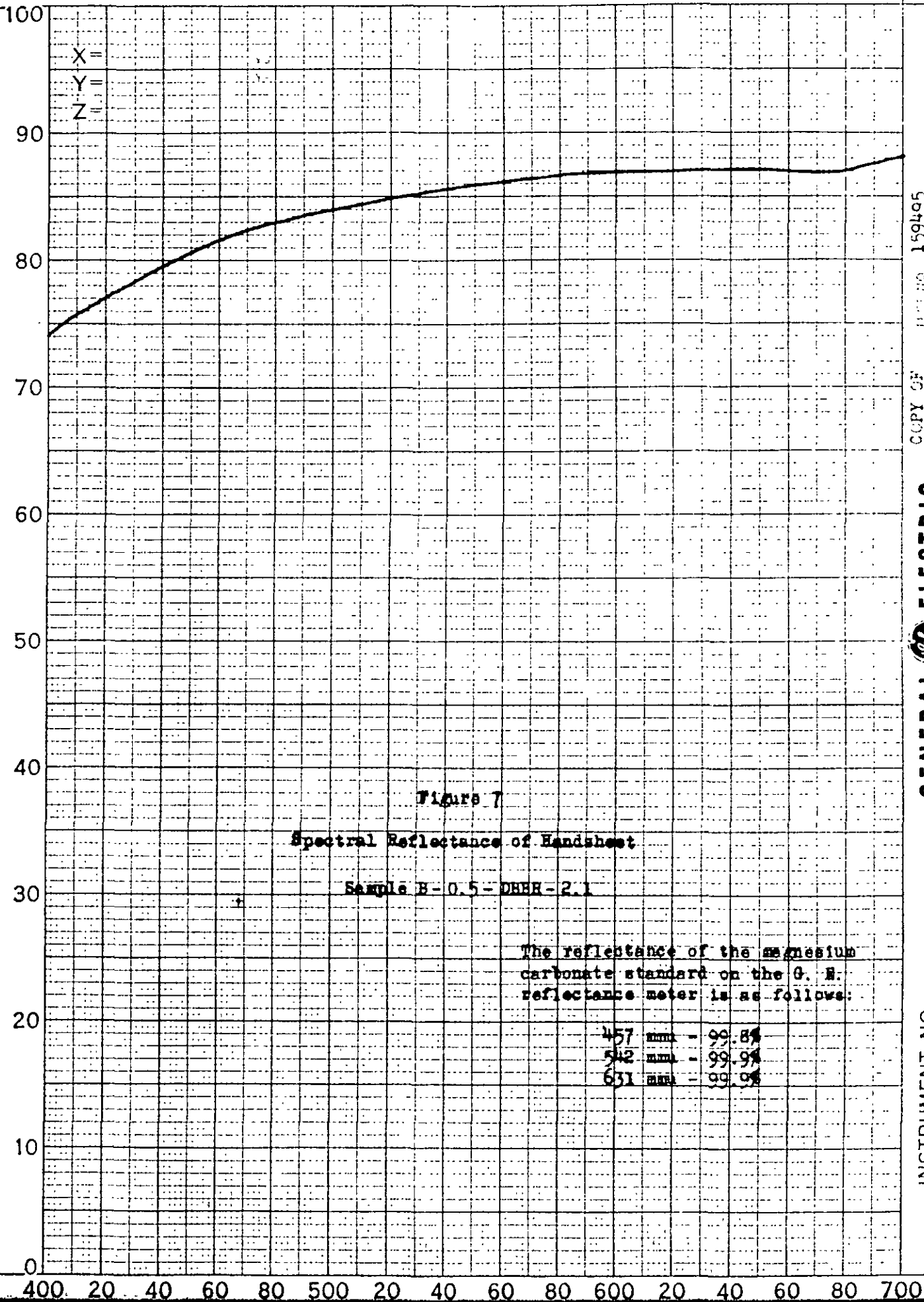
TEST NO. 159493
BY W.S.

COPY OF

GENERAL ELECTRIC



INSTRUMENT NO.



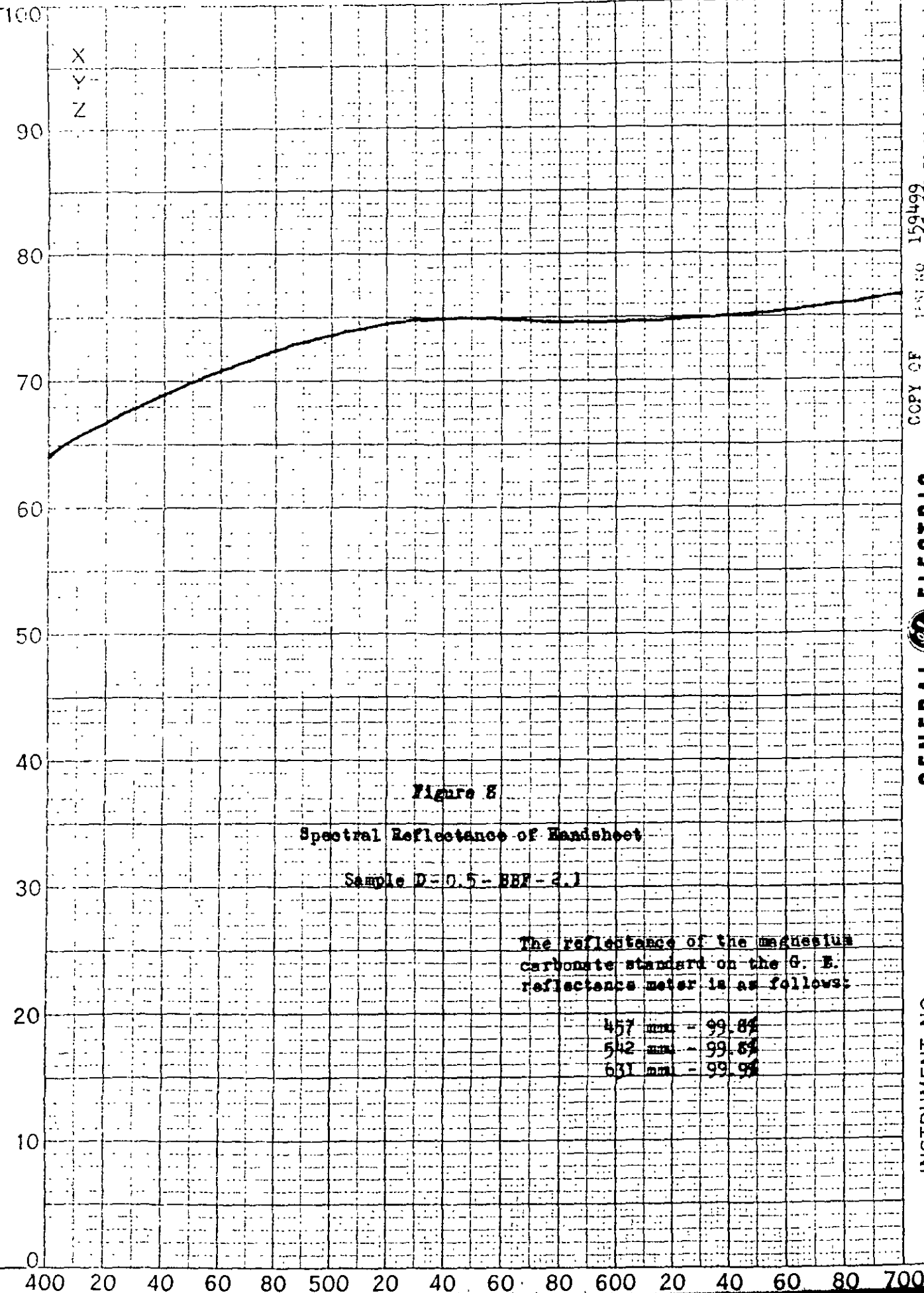
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DATE
159495
W.S.

INSTRUMENT NO.

GENERAL ELECTRIC

RECORDING SPECTROPHOTOMETER

PERCENT REFLECTANCE RELATIVE TO Project 1467



The reflectance of the magnesium carbonate standard on the G. E. reflectance meter is as follows:

457 nm	- 99.84
542 nm	- 99.84
631 nm	- 99.98

COPY OF INSTRUMENT NO. 159499

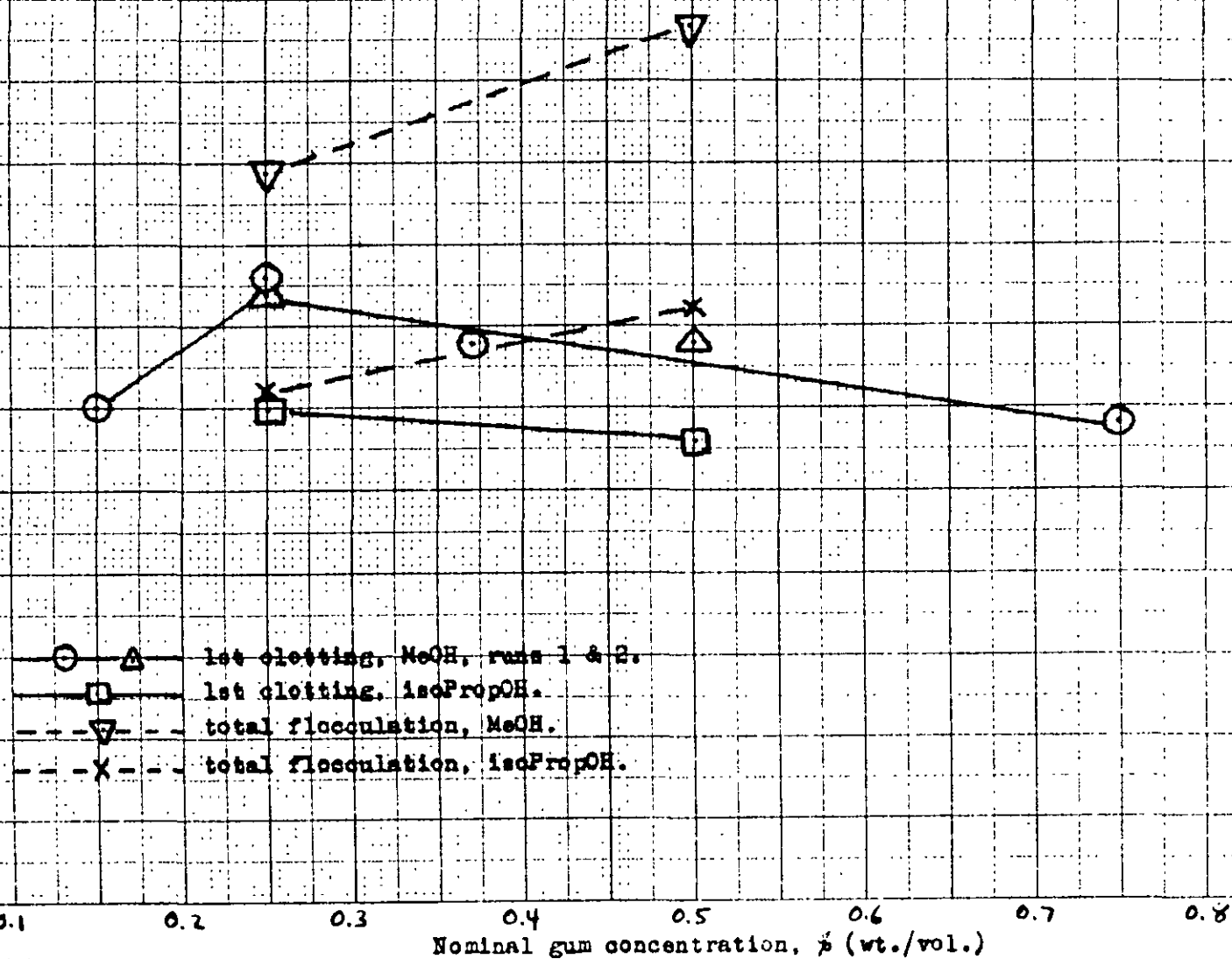
GENERAL ELECTRIC

RECORDING SPECTROPHOTOMETER

INSTRUMENT NO.

Figure 9

Alcoholic Flocculation of Crude Locust Bean Gum from
Aqueous Dispersions



PROJECT REPORT FORM

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G. R. Sears
J. W. Swanson
P. Dahm

PROJECT NO. 1467 ✓
COOPERATOR Institute
REPORT NO. 7
DATE April 27, 1953
NOTE BOOK 1155
PAGE 42 TO 60
SIGNED _____

P. Dahm

SUMMARY

It has been shown that,

1. Dyeing of Locust Bean gum does not alter its sorption on pulp.
2. Gum and dye is sorped independently from what is believed to be a gum-dye complex.
3. The sorption of gum and dye individually follow Freundlich adsorption isotherms.
4. The amount of dye sorped can be determined accurately from G.E.R.S. reflectance data by use of either Kubelka and Munk's reflectance formula or a modified form of Spellings formula.
5. Leech's method can be applied with satisfactory precision in analysis of retention of Locust Bean gum.

INTRODUCTION

The use in the paper industry of hydrophilic polymers as additives in the beater or in the headbox of a paper machine, in order to improve "hydration" and strength and reduce beating expenses, has shown steady increase through recent years. As might be expected, a parallel development is noticed in the emphasis put on studies of retention of additives in paper and sorption on the cellulose fiber in general. From the economic point of view it is important to get information about the relation between the amount of material originally added to the furnish, and the amount of material actually retained in the paper produced under varying conditions. From the theoretic point of view the study of sorption on cellulose offers an opportunity to broaden the knowledge of a field that is still little explored when compared with the large amount of research done on related fields of cellulose chemistry. A

large number of variables have been shown to influence retention. Prominent among these are variables introduced by the kind and previous treatment of the pulp and additives. To reduce the number of variables in a study of retention it will be necessary to use the same pulp and gum and standardize the procedure as far as possible throughout the work. Then the variables, the influence of which could be studied, would include concentration of pulp and gum, temperature and pH in the furnish and time between addition of the gum to the furnish and the formation of the paper.

Paper properties are often influenced by as small gum additions as 1/2%. To get significant retention data in this concentration range high precision of analytical data is necessary. This has to be kept in mind when reviewing the work done previously in this field.

Two studies of retention of beater additives on cellulose have been made in recent years. Shriver (5) investigated the sorption of water soluble cellulose ethers by cellulose, in particular the sorption of methyl cellulose. Laurell (6) determined the retention of carboxymethylcellulose in wood pulp under varying conditions. In these studies and in the earlier work on the present project (7) the additive retained on a handsheet was determined by analyzing the backwater for additive and subtracting the value found from the amount of additive originally added to the furnish. Because the presence of cellulose "fines" in the filtrate interfere with the determination of gum in an unaccountable way, a method of determining the gum content of paper directly would be more desirable. Leech (4) has worked out such a method in his Doctor's Dissertation. This method is based on hydrolysis of the paper that has been treated with Locust Bean gum. Galactose content of the hydrolysate is determined by quantitative paper partition chromatography. The

galactose content of Locust Bean gum is known to be 15.8%, and when the galactose content of the pulp itself is negligible, the amount of gum retained on the handsheet can be found.

This method is not easily adapted for routine retention measurements as it takes about five days to complete an analysis. Another disadvantage is that the precision of this method, even if fairly high compared to that of previously used methods, still is lower than what might be desired. For galactose content in Locust Bean gum, Leech found values scattered between 10.5% and 20.0% with an average of 15 analyses of 15.8%. Analyses of gum on paper gave much better results, a series of five analyses gave a scattering of gum content values between 1.11% and 1.32% with an average of 1.18% and a series of six analyses of another paper gave values between 1.42% and 1.79% with an average of 1.55%.

In the present work an attempt is made to get the necessary information about retention of gum by dyeing the gum and measuring the reflectance of the paper treated with this dyed gum at the wavelength where the dye has its absorption maximum.

In a previous project report (1) Webb added gum dyed with Pontamine 3B Fast Blue 4G-1 to handsheets and determined the retention of the gum by spectrophotometric measurements on the backwater. As mentioned earlier the principal disadvantage by such a method is that the backwater contains varying amounts of "fines" which interfere considerably with the measurements. Although this trouble can be overcome by, for example, making up the standard dye-gum solution in whitewater, or by elaborate filtering procedures, or by introducing corrections for turbidity, none of these devices appear to be entirely satisfactory. In a study of the retention of dyestuff on paper North (8) reached

this conclusion, and introduced a method in which the dye is extracted from the paper by 25% aqueous pyridine and estimated spectrophotometrically.

A still more convenient method would be to obtain the retention data directly by reflectance measurements on the handsheets. However, this method can be used only if certain conditions can be shown to hold. These conditions are:

1. The dye used should be completely adsorbed by the gum.
2. The dye should not affect the sorption of the gum.
3. The dye should remain with the gum and not be transferred from the gum to the pulp.
4. A constant relationship between concentration of dyed gum and reflectance of the handsheet should exist.

1 has been shown to hold by Webb (1), 2 can be shown to hold by preparing parallel series of handsheets containing dyed and undyed gum and analyzing the handsheets with Leech's method. By analyzing the dyed sheets by Leech's method and simultaneous extraction of the dye with aqueous pyridine and determination of dye in the extract by spectrophotometric methods, 3 can be shown to hold. If reflectance data are obtained on the handsheets, 4 can be shown to hold by comparing with the extraction data. The main purpose of the work described in the present project report was to prove or disprove the validity of the four conditions mentioned.

OUTLINE OF PRESENT WORK

The work followed this course. First some introductory experiments with Leech's method and with the spectrophotometric method of dye determination, were made. Then two series of handsheets were prepared. The first series (A) consisted of 40 handsheets, 20 with dyed gum and 20 with undyed gum added at

ten different concentration levels ranging from 0.5% to 13% gum based on the weight of oven-dry pulp. The second series (B) consisted of 12 handsheets, six with dyed gum and six with undyed gum at six different concentration levels ranging from 1/2% to 12%. The only difference between series A and B was that in series B the gum was left in contact with the pulp for 20 hours before the sheets were prepared, while in the case of series A the sheets were prepared immediately after the addition of gum. The difference in sorption time influences retention very markedly. The handsheets of series A and B were analyzed by Leech's method, by extraction of the dyed sheets followed by spectrophotometric determination of the dye and by measurement of reflectance with the General Electric recording spectrophotometer.

A third series (C) of handsheets was then prepared. Three per cent gum was added to a large batch of pulp slurry and handsheets formed at times ranging from 1 minute to 72 hours since the addition was made. These sheets were analyzed by Leech's method and by extraction of dye.

EXPERIMENTAL

Galactose content in Locust Bean gum was determined by the quantitative chromatographic method described by Leech. The results were widely scattered. One of the difficulties in this method lies in determining the blank value given by the filter paper in the periodate oxidation. Leech (4) has not described this part of the method in details in his thesis. It was found to be necessary to establish a method of getting reproducible blank values before the main part of the work was started.

The Blank Value

After describing the separation of the monosaccharides contained in the hydrolysate by paper partition chromatography and the way of locating and

cutting out the parts of the chromatogram containing the galactose, Leech continues (4):

"The sugars are recovered from the paper portions by the process of elution. One end of the small paper sample is held between two microscope slides at their ends. The slides in turn dip into a Petri dish filled with water, so that by capillary action, water is fed to the top of the paper sample. Water slowly flows down the paper flushing the sugars along with it. It has been established that the sugars follow the water interface very closely. When the water reaches the bottom of the strip a small portion containing the sugar is cut off with scissors and allowed to fall into another Petri dish. This strip is then carefully transferred with forceps to a ground glass stoppered added to the tube so that quantitative transfer of the sugar is effected.

One ml. of 0.25 molar sodium periodate is added to the reaction tube and the tube is stoppered. The mixture is heated on the steam bath for ten minutes. The stopper is then pulled open and the tube is cooled under a cold water tap. Three drops of methyl red indicator and 0.5 ml. of ethylene glycol are added and the tube is allowed to stand a few minutes for reaction of the ethylene glycol with the excess sodium periodate. The formic acid which is produced by periodate oxidation of the sugar is then titrated with very dilute alkali (0.001 to 0.005 normal). The blank or control strip, the galactose strip and the rhamnose strip are all titrated in this manner. The relative amounts of galactose and rhamnose are found by subtracting the blank titration from each."

When the galactose content of the sugar mixture is low, the titration value of the blank strip may be a large fraction of the titration value of the galactose strip. Then it will be very important to eliminate random variations in the determination as far as possible.

The blank value obviously arises from the action of periodate on the paper strip itself. This could be avoided by complete elution of the sugar from the paper. The method described by Leech is however very convenient and sufficient reproducibility of the blank value is obtained by standardizing the conditions to the least detail.

By setting the oxidation time to ten minutes, Leech shows that he is aware of the necessity of standardized oxidation conditions.

In the present work it was found that it was also necessary to cut off a constant area of paper, use a constant volume of liquid in the reaction tube and heat the tube in exactly the same way each time to get constant blank values. A 17 cm. wide chromatogram minus four 2 cm. guide strips left a 9 cm. wide chromatogram for the oxidation. The 9 cm. strip was cut into 3 x 3 cm. strips and a piece 1 cm. high was cut off the bottom of the strip after completed elution. Thus a total of 9 cm.² paper was oxidized. The 1 x 3 cm. strips were held with forceps while cut off and put directly into the reaction tube. When all three strips had been transferred to the reaction tube, the forceps were rinsed off into the tube with 10 ml. distilled water and 1 ml. 0.25N NaIO_4 added. The reaction tube was a Kjeldahl flask where the ground glass stopper was replaced by a ground glass "cold finger." By using a "cold finger" loss of formic acid was avoided and the danger of getting the ground glass stopper stuck in the opening was eliminated. The reaction tube was now heated for ten minutes by immersion in boiling water. The tube was immersed to the same level each time. After completion of the reaction, the procedure of Leech was followed as outlined by him.

By using this method it was found that a very reproducible blank value of 0.63 ml. 0.005N NaOH could be kept and the maximum variation was about ± 0.02 ml. This blank value was therefore used throughout the work and care was taken to keep strictly to the procedure described.

Transmission Measurements

It has been shown by several workers (2), (3), that the light absorption maximum of dye sorped on fibers is displaced, as compared to aqueous solutions, toward the long wavelength, varying from 7-8 m μ to 30 m μ .

Some experiments were carried out to see if a displacement of this kind would take place also by adsorption of dye on gum in aqueous solution. A solution of Pontamine Fast Blue 4G-1 in water has a quite sharp maximum in its absorption curve at 600 m μ and a somewhat broader minimum at 440 m μ . The same location of maximum and minimum absorption is found for solutions of the dye-gum complex. Both the dye-solution and the dye-gum solution follow Lambert-Beer's Law.

Preparation of a Gum Dispersion

The gum dispersions were prepared from a sample of purified Locust bean gum with a moisture content of 11.47%.

To prepare 1000 ml. 0.5% gum dispersion, an amount of this sample corresponding to 5 g. oven-dry material was weighed out. This gum was dusted through a 16-mesh screen into about 800 g. of distilled water in a 1-liter beaker. The water should be agitated, but not too vigorously at this stage, because the still dry gum may be blown to the side walls of the beater and stick there as a gelatinous layer which will be hard to dissolve completely. After the gum has been added the maximum effect of the stirrer is applied and the dispersion is heated on a steam bath until no gel particles can be seen. Occasionally it may be difficult to discover highly swollen particles. Many of these will however show up because of the air bubbles trapped in them. The dispersion will not become completely clear. After cooling down to room temperature, the dispersion is transferred to a 1000 ml. volumetric flask, the gum remaining in the beater is rinsed out with several portions distilled water with which the level in the flask is raised to the mark.

Preparation of a Dye Solution

A stock solution of dye is prepared by dissolving 2.5 g. 38 Pontamine Fast Blue 4G-1 in 500 ml. water. Twenty-five ml. of this solution contains 0.125 g. dye and will, when added to 475 ml. gum dispersion containing 2.5 g. gum, give a solution holding five parts dye to 100 parts gum.

Preparation of Pulp Suspension

For handsheets of series A Weyerhaeuser bleached sulfite pulp beaten to a freeness of 806° S.-R. at a consistency of 1.47-g/100 ml. was used. For handsheets of series B and C the same pulp beaten to a freeness of 725° S.-R. at a consistency of 1.82-g/100 ml. was used.

Preparation of Handsheets

One and five-tenths gram handsheets are prepared from a 0.3% pulp slurry which is diluted in the sheet mold to 0.07%. In series A distilled water was used, in series B and C ordinary tap water. The easiest way of adding small amounts of gum dispersion is by using pipettes that are rinsed out with water after addition of the gum, larger additions are made by weighing out the necessary amount of gum dispersion.

Before addition of the gum a test is made to see if the adsorption of dye on gum is complete. The dyed gum is precipitated from solution by Na_2SO_4 . If the supernatant liquid is colorless it has according to Webb (1), been proved that the adsorption is complete.

Extraction of Dye From Handsheets

The dye is extracted from the handsheets with a solvent holding one

part of water to three parts of nujol. The paper is cut into small pieces

and covered completely with solvent in 50 ml. Erlenmeyer flasks. After 20 hours the solvent is filtered through sintered glass filters into 25, 50 or 100 ml. volumetric flasks. The paper is disintegrated and washed with the solvent until completely colorless, and the solutions in the volumetric flasks are made up to the marks.

The transmittance of the extracts at 600 $m\mu$ is measured in a Coleman spectrophotometer with the pure solvent as blank, and the dye concentration is found by comparing the transmittances formed with those of solutions of known concentration.

A better procedure would have been to use extracts of undyed handsheets as blanks. It was found however, that the colored material extracted from the pulp itself had a negligible absorption as compared with the absorption of the extracted dye, and the easier procedure of using pure solvent as blank might be adopted without introducing serious errors.

RESULTS AND DISCUSSION

The results of the analyses of the handsheets in series A and B are shown in Table I.

TABLE I

Nr.	Leech's Method			Extraction	Reflectance	
	Dyed	Undyed	Average	Dyed	Dyed	Undyed
A1/2	0.20	0.47	0.33	0.11*	77.3	92.1
A 1	0.13	0.93	0.53	0.14*	73.9	92.1
A 2	0.31	0.37	0.34	0.30*	66.8	92.1
A 3	0.39	0.43	0.41	0.39*	61.9	92.1
A 4	0.40	0.45	0.42	0.45*	59.8	92.1
A 5	0.42	0.50	0.46	0.60*	55.6	92.1
A 7	0.35	0.43	0.39	0.69*	54.2	92.1

TABLE I (Continued)

Nr.	Leech's Method			Extraction		Reflectance	
	Dyed	Undyed	Average	Dyed	Dyed	Undyed	
A 9	0.61	0.53	0.57	0.86*	49.8	92.1	
A 11	0.51	0.51	0.51	1.00*	46.8	92.1	
A 13	0.68	0.44	0.56	1.19*	44.2	92.1	
B1/2	0.63	0.61	0.62	0.33	62.2	89.2	
B 1	0.91	0.71	0.81	0.77	50.0	89.3	
B 2	1.62	1.37	1.50	1.47	39.3	88.9	
B 4	1.22	1.70	1.46	2.37	31.8	88.9	
B 8	2.31*	2.15*	2.23	6.14	18.6	88.8	
B 12	2.73*	2.76*	2.75	9.15	14.7	88.5	

*Averages of two analytical results.

The handsheets are numbered with a capital letter, showing what series they belong to, and a figure indicating percentage gum added to the furnish. Handsheet A7 is thus a handsheet prepared in the A series with seven per cent gum originally added to the furnish.

The extraction results are given as the corresponding amounts of dyed gum, or 20 x the actual amount of dye throughout this report. The sheets have their minimum reflectance at 630 m μ . This is a displacement of 30 m μ towards longer wavelengths as compared to the absorption maximum of the dye in aqueous solutions. The reflectance data for the undyed sheets of series A differ very little, and the average value is therefore given. The correlation between gum content in handsheets containing dyed gum and handsheets containing undyed gum is shown in Figure 1. The correlation is fairly good when a few points which are far off are disregarded. With a complicated analytical method as quantitative chromatography some "wild" results might be expected in the course of a series of analysis. These results therefore conclusively show that the sorption of gum on pulp is independent of the presence of dye.

Figure 2 shows the correlation between gum content found by chromatography (average of content of dyed and undyed sheet) and gum content corresponding to the amount of dye found by extraction of the handsheets with pyridine-water 3:1.

The regression lines of series A and B have about the same slope. This slope is however different from the slope expected if gum and dye was sorped to the same extent. At low degrees of sorption the gum is sorped to a larger extent than dye, at high degrees of sorption the dye is sorped more strongly. It should be kept in mind here that dye content is given as the corresponding amount of dyed gum. The reason why regression line B lies higher than regression line A is the time allowed for the gum to be sorped on pulp before the handsheets were formed. As will be recalled series B was prepared 20 hours after mixing gum and pulp while series A was prepared immediately after mixing (approximately 20 seconds). The data from series C (Table II) are plotted in Figure 2 as triangles and show how the regression lines are raised with increasing sorption time. The handsheets of series C were prepared from a pulp slurry containing 3% dyed gum at varying lengths of time expired since the addition of the gum.

TABLE II

Nr		% gum found by chromatography of handsheet hydrolysate	% gum found by extraction of dye from handsheet
C	1	0.81	1.37
C	5	1.24	1.64
C	15	1.65	1.75
C	70	1.99	1.83
C	240 (4h)	2.36	1.92
C	480 (8h)	2.48*	1.96
C	1440 (24h)	2.73	1.96
C	4320 (72h)	2.91	2.05

*Average of 2.46 and 2.51.

Originally added amount of dyed gum = 3%.

If the sorption after 72 hours is taken as 100%, the data show that after one minute the dye is sorped 67% while the dye is sorped only 28%.

Thus it appears that gum and dye is sorped independently on pulp even when precipitation experiments have shown that they form a complex before addition. The reason may be either that the gum-dye complex is dissociated

under the influence of selective sorption forces, or that the precipitation reaction is wrongly interpreted. There is another thing that should be pointed out in connection with Figure 2. The 24 hour point of series C, with co-ordinates (1.96, 2.73), should have been close to regression line B, since series B is prepared after 20 hours under otherwise identical conditions. While the value of the abscissa, 1.96, falls between the values of 2% and 4% added dye-gum in series B, as expected, the ordinate has a far too large value, 2.73, instead of about 1.50. Series B and series C were prepared with the same batch of dyed gum. After preparation of this batch, it was allowed to come to equilibrium for one day. After contact with the pulp for the next 20 hours, series B was prepared. Two days later series C was started, and the particular handsheet mentioned above, was prepared one day later. Thus the gum used in this handsheet was five days old, while the gum used in series B was only two days old. At room temperature the bacterial deterioration of Locust bean gum solutions is rapid when no preservative has been added, and precipitation of the gum may be expected after about one week. Therefore it is not surprising to find higher retention of gum from an old batch than from one relatively freshly prepared.

Figure 3 shows the relation between dye added to the furnish and sorped dye. The relation is perfectly linear in case of data from series B. The point at C = 4% is disregarded as, for unknown reasons, it was impossible to extract the dye completely from the disintegrated pulp of this sample. The relation for data of series A is linear at higher concentrations, but shows a slight curvature at concentrations below 2%. These data are therefore plotted logarithmically in Figure 4. The relation is now linear as would be expected if Freundlich's adsorption isotherm was followed. The best straight line is statistically found to be $\log x = 0.71 \log c - 0.75$. In Figure 5 the sorption of gum is shown

as function of added gum. This relation has a relatively strong curvature, but straightens out in a log-log plot. The best straight line is found to be $\log x = 0.49 \log c - 0.075$. Thus it is seen that even if dye and gum is sorped independently, the sorption of both follows Freundlich's adsorption isotherm.

The Relation Between Dye Concentration and Reflectance of the Handsheets

The relation between reflectance at 630 m μ of the handsheets of series A and B and the percentage of dyed gum originally added to the fiber is shown in Figure 6. In Figure 7 the reflectance data are plotted against concentration of dye gum found by extraction. The reflectance data have also been plotted according to Kubelka and Munk's formula (9), Preston and Tsien's formula (10) and Spelling's formula (11). Preston and Tsien's formula fails at higher concentrations while both Kubelka and Munk's and Spelling's formula give linear plots for data of series A. The points from series B, represented by squares, were marked after the best straight lines through the points of A had been determined. In Figure 8 the complete number of data from series A and B are plotted according to the two formulae. It is seen that the data from series B are closer to the straight line through the data of series A when Kubelka and Munk's formula is used than when Spelling's formula is used. Spelling's formula can however easily be modified to straighten out the curvature that is evident already in Figure 7. When the formula $[R - 1.07] 1.26 = \text{const. by } c$ is used a very good plot is obtained.

In Figure 8 only three of the points obtained by use of the modified formula are shown (marked S,2). Table IV shows that the agreement between the data and the straight line $y = 0.84 x + 0.005$, that was originally determined as the best straight line through data from series A, is better over the whole concentration range.

TABLE III

Nr.	% Dyed gum (by extraction)	Reflectance data treated according to,			
		K&M	P&T	S.1	S.2
A 1/2	0.11	0.033	0.038	0.07	0.07
A 1	0.14	0.047	0.034	0.12	0.12
A 2	0.30	0.083	0.029	0.25	0.23
B 1/2	0.33	0.115		0.295	0.276
A 3	0.39	0.117	0.024	0.35	0.34
A 4	0.45	0.135	0.023	0.41	0.39
A 5	0.60	0.177	0.017	0.52	0.51
A 7	0.69	0.193	0.015	0.57	0.56
B 1	0.77	0.25		0.654	0.648
A 9	0.86	0.253	0.009	0.73	0.73
A 11	1.00	0.302	0.005	0.86	0.87
A 13	1.19	0.354	0.000	0.98	1.00
B 2	1.47	0.469		1.18	1.25
B 4	2.37	0.732		1.78	1.98
B 8	6.14	1.78		4.17	5.21
B 12	9.15	2.47		5.77	7.51

K&M = Kubelka and Munk's equation. $[k/s]_A = (1-R_A)^2 / 2R_A = \text{const. } c.$

R_A = monochromatic reflection, intensity of light reflected from dyed fiber.

k_A = absorption coefficient

s_A = scattering coefficient

P&T = Preston and Tsiens equation. $\log \left[\frac{R(1 - \frac{2}{A}) + A - 4}{A - R} \right] = \text{const. } c.$

S.1 = Spellings equation $[R - 1.1]^{1.1} = \text{const. } c.$

S.2 = Spellings equation modified $[R - 1.07]^{1.26} = \text{const. } c.$

$R = \frac{\text{Intensity of light reflected from undyed fiber.}}{\text{Intensity of light reflected from dyed fiber.}}$

C = Concentration of dye.

$A = \frac{1}{\text{coefficient of reflection}}$

Coefficient of reflection = 0.045 for cellulose when angle of incidence $< 30^\circ$.

TABLE IV

Nr.	Value of formula		$y=0.84x+0.005$	Absolute deviation		Percent deviation	
	S.1	S.2		S.1	S.2	S.1	S.2
A 1/2	0.07	0.07	0.10	0.03	0.03	30	30
A 1	0.12	0.12	0.12	0.00	0.00	0	0
A 2	0.25	0.23	0.26	0.01	0.03	4	10
B 1/2	0.295	0.276	0.282	0.013	0.006	5	2
A 3	0.35	0.34	0.33	0.02	0.01	6	3
A 4	0.41	0.39	0.38	0.03	0.01	8	3
A 5	0.52	0.51	0.51	0.01	0.00	2	0
A 7	0.57	0.56	0.58	0.01	0.02	2	3
B 1	0.654	0.648	0.651	0.003	0.003	0	0
A 9	0.73	0.73	0.73	0.00	0.00	0	0
A 11	0.86	0.87	0.85	0.01	0.02	1	2
A 13	0.98	1.00	1.00	0.02	0.00	2	0
B 2	1.18	1.25	1.23	0.05	0.02	4	2
B 4	1.78	1.98	1.99	0.21	0.01	10	1
B 8	4.17	5.21	5.15	0.98	0.06	19	1
B 12	5.77	7.51	7.68	1.91	0.17	25	2

Precision of Leech's Method

After some introductory difficulties, Leech's method has worked satisfactorily throughout the series of experiments reported here. Some "wild" results occur, but are easily recognized, because most results will show definite trends. Five analyses were run in duplicate. The results are shown in Table V.

TABLE V

Nr.	B 8	B 8d	B 12	B 12d	C 480
Result 1	1.98	2.26	2.71	2.72	2.46
Result 2	2.32	2.37	2.82	2.73	2.51

d = dyed

In this concentration range the precision seems to be high, and if time was available for running a number of analyses sufficient to eliminate "wild" results, Leech's method would be very satisfactory. One of the most

interesting parts of the gum concentration scale is however the part below 1/2% added gum. At these concentrations the method works less satisfactorily, and very high precision is desired.

FUTURE WORK

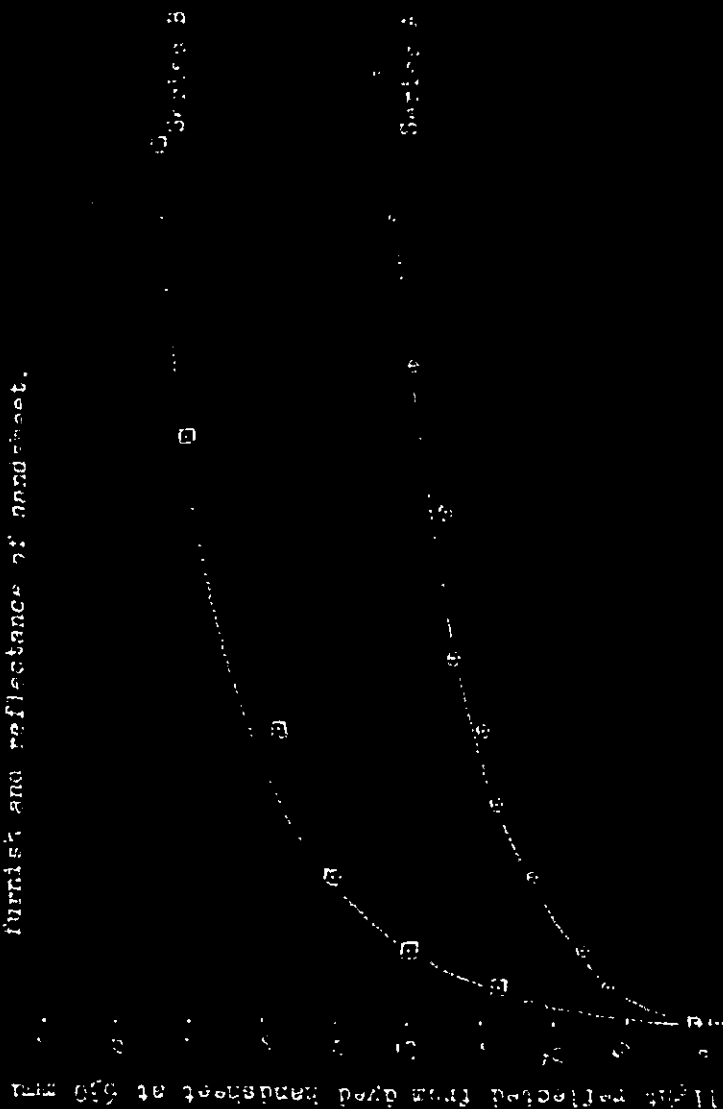
Future work should be concentrated on working out other methods of determining gum sorped on paper. A method quicker than Leech's is desired. The chromatographic separation of the sugars is too time consuming to allow the analyses of a large number of samples. The method should be independent of a blank value and give high precision even at low concentrations. A method that might fill these requirements is the use of gum "labeled" with radio-active carbon.

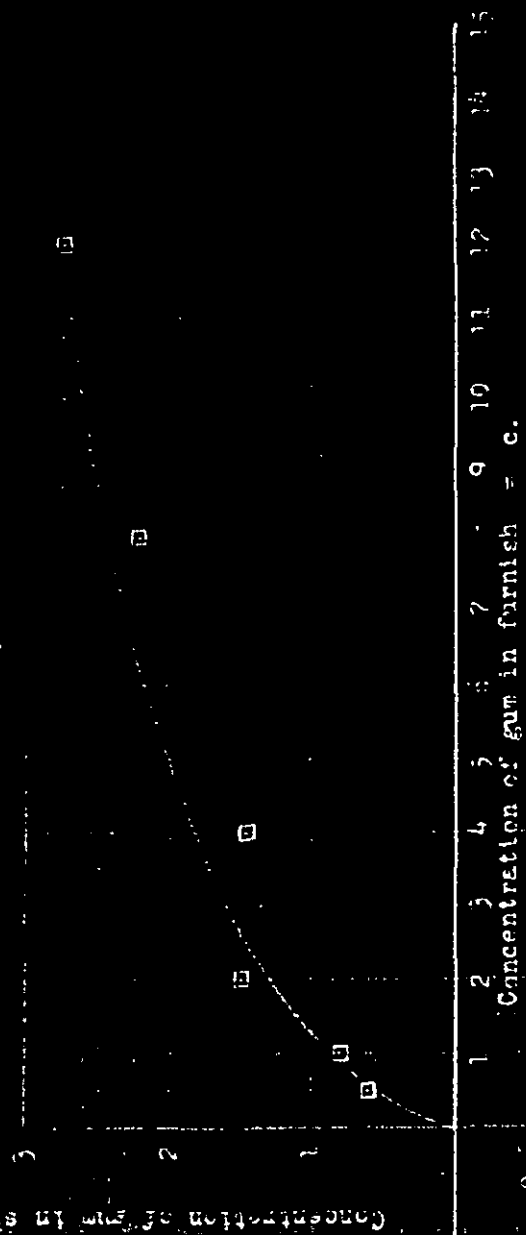
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Figure 6

The relation between dyed run added to
furnish and reflectance of handloom.





5. Salinity

Freundlich adsorption isotherm
Log x for gum series B.

□ $\log x = 0.40 \log c - 0.075$

12

$$y = 0.04x + 0.005$$

Soelling 1

Rebellen and Vink

Figure 7

Relation between eye content and

reflectance.

Preston and Eslen

Kay, Soelling.

Reflectance

Reflectance of
Preston and Eslen

CONCENTRATION OF LIVER AND BLOOD IN RELATION TO THE EYE.

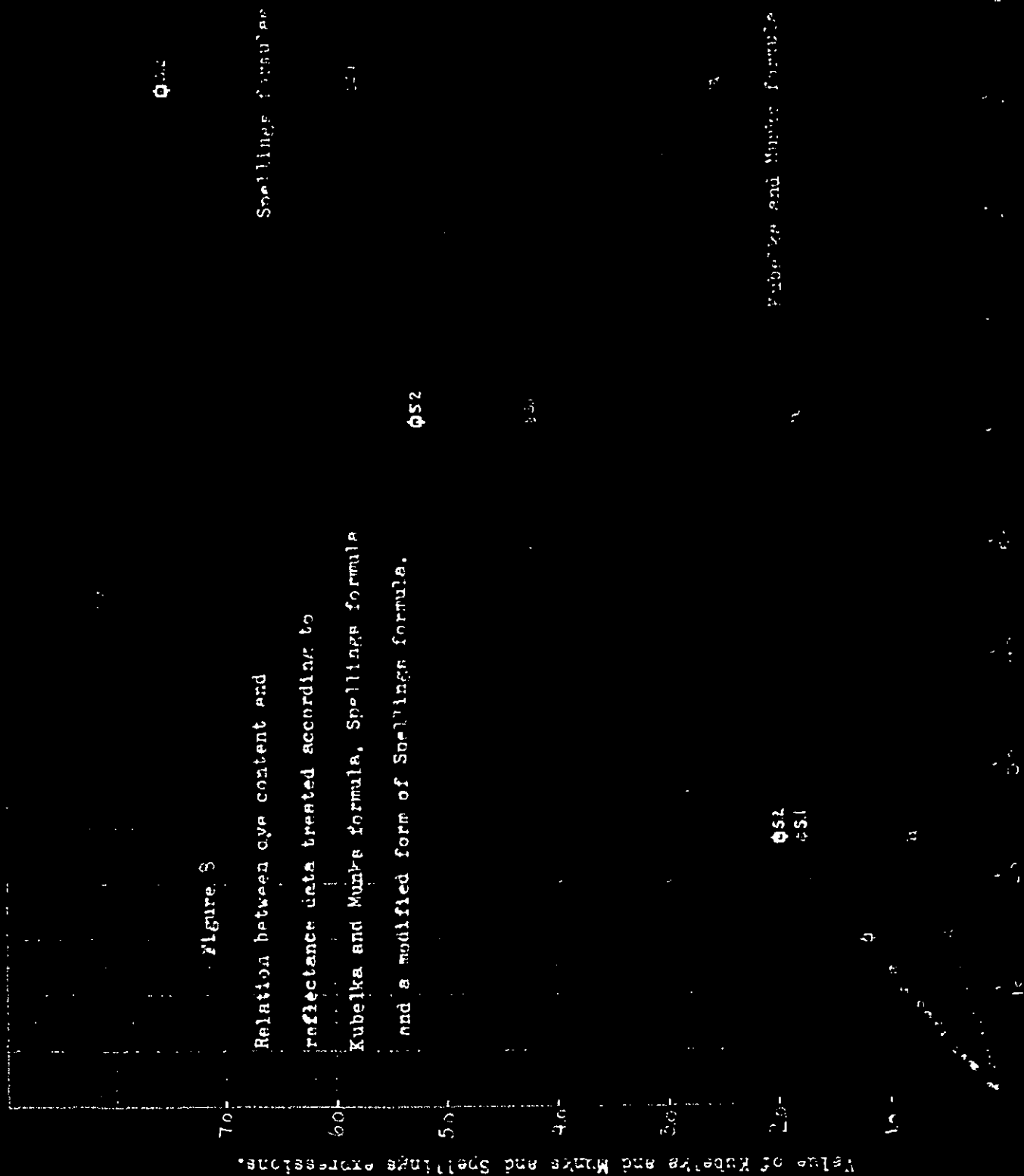
Figure 5

Relation between eye content and

reflectance data treated according to

Kubelka and Munk formula, Spelling's formula

and a modified form of Spelling's formula.



9

8

100

9

Figure 4.

Practical absorption isotherms

for eye. Series A.

0.5

0.2

0.0

for x

0.2-1

0.2-1

0.2-1

0.2-1

0.2-1

Figure 1

Correlation diagram
w data from series A
E data from series B

Q
[data correlation]

Q

Q

Q

White,

Correlation diagram

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▲ data from series C

Ideal correlation

gatti uclasiologi in

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PROJECT REPORT FORM

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COOPERATOR Institute
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AN EXPLORATORY INVESTIGATION OF THE POSSIBILITY OF USING DYED LOCUST BEAN GUM IN DETERMINING ITS ADSORPTION ON CELLULOSE

SUMMARY

It is possible to prepare a dyed gum by adding a direct dye solution to a gum dispersion. Up to 48 parts dye per thousand parts gum the dye is completely exhausted from the solution. The concentration of dyed gum can be determined colorimetrically. Sorption of dyed gum on pulp can be determined by measuring the concentration remaining in the white water and subtracting from the initial concentration added. This technique is more convenient than the anthrone analysis and is not subject to errors due to the cellulose blank and filtration. The sensitivity of the analysis is dependent upon the depth of color of the dyed gum. The sorption isotherms measured by this means are comparable to those made with other methods. The method is particularly well suited for measuring the rate of sorption.

The method still indicates variability between different series of sorption experiments. It is therefore supposed that these differences are not due to the analytical method.

The strength properties of sheets made with dyed gum and undyed gum are comparable. This can be taken as an indication that the dye does not appreciably affect the sorption of the gum. It remains to be demonstrated that the dye remains with the gum and is not transferred from the gum to the pulp.

There is a good possibility that the sorption can be determined directly by optical measurements on the sheet of paper.

INTRODUCTION

Several analytical methods have been used in the study of locust bean gum sorption by cellulose. Two of these, the anthrone technique and the viscometric technique determine the sorption by measuring the difference in concentration of the gum in the white water after sorption has occurred and then calculating the sorption indirectly. This in itself limits the accuracy of the determination. The anthrone technique is hindered by the apparently soluble cellulose blank. To date it has not been possible to eliminate or correct for this blank with certainty. The viscometric method is not as accurate as would be desired and is limited by the effect of fiber fines with the well-beaten pulps. A gravimetric method which measures the increase in weight of the pulp on sorption is being used. It is limited in the study of rate of sorption and is in general more tedious than would be desired. None of the methods are capable of reproducing sorption values from one day to the next with satisfactory precision.

In view of the desirability to measure sorption more easily and perhaps measure the quantity of gum on the sheet, several experiments have been performed investigating the possibility of studying sorption using a heavily dyed gum. In such a method it would be necessary to demonstrate that the quantity of gum could accurately be determined with colorimetric measurements and that the presence of the dye did not affect the sorption. It would also be necessary to demonstrate that the direct dye was held by the gum throughout the sorption and not transferred to the pulp.

This is the general approach of the experiments covered in this report.

EXPERIMENTAL

Preparation of dyed gum.

Throughout the work Pontamine 3B Fast Blue 4G-1 was used.

Spot experiments indicated that when gum was precipitated from a dispersion to which dye had been added, the precipitated gum was dyed. When alcohol was used for the precipitation the gum was dyed a light blue and the supernatant was also blue. This is because the alcohol removed some of the dye from the gum. When the gum was salted out with sodium sulfate, the gum was a dark blue and the supernatant was colorless if small enough quantities of dye were used. Test tube experiments indicate that although the dye does not dissolve in saturated sodium sulfate solution, dissolved dye will not precipitate in the saturated solution.

To avoid the use of salt in the preparation of a dyed gum, it was advisable to introduce only that amount of dye that would be completely exhausted by the gum. In order to determine this quantity, small samples of 0.5% gum dispersions were treated with various quantities of concentrated dye solutions. Samples containing 8, 16, 24, 32, 40, 48, 56, and 64 parts dye/1000 parts gum were made and held at 50° C. for two hours. These samples were then precipitated with excess sodium sulfate solution and allowed to stand. The supernatant liquids in these samples containing 48 parts per thousand and below were clear after filtration of the fine suspended flocc. It was decided to use 48 parts dye/1000 parts gum for further experiments. A two liter batch of freshly dispersed 0.5% dispersion was

dyed with 0.43 gr. dye dissolved in 100 ml. distilled water. The dye addition was made when the gum dispersion was still warm and the mechanical stirring was continued for two hours after the addition. This gum was used throughout the experiments discussed below. A small sample of the dyed dispersion was salted out with sodium sulfate and it gave a clear supernatant liquid.

Preparation of Pulp.

Weyerhaeuser bleached sulfite beaten in distilled water in the Valley beater for 19 minutes to a freeness of 790 cc. with a bedplate load of 5500 gr. gave a consistency of 1.32%. This pulp was used throughout the experiments.

Calibration Curve.

In order to determine white water concentrations of dyed gum a calibration curve was made. The 0.5% dyed gum dispersion prepared above was diluted. These known concentrations were compared with distilled water in a photometer using a Wratten #23 and a Jena BG 13 filter. The plot of the concentration vs. the log of the percent transmission gave a straight line. Two different curves were made several days apart and these agreed within the experimental error. This calibration curve was used throughout the work.

TABLE I

CALIBRATION CURVE FOR COLORIMETRIC DETERMINATION OF DYED LOCUST BEAN GUM

Concentration of Locust Bean Gum in Percent	Percent Transmission	
	First Curve	Second Curve
.05%	46.5%	45.0%
.005%	92.0%	--
.01%	85.0%	--
.025%	--	67.5%

The plot of these data is included in Figure 1.

Experiments on Locust Bean Gum Sorption by Pulp.

Six 2.5 gr. samples of the pulp prepared above were diluted to 0.5% consistency (allowing for the volume of gum to be added). To these samples various amounts of both undyed and dyed gum were added, these containing undyed gum serving as a correction for the turbidity of the white water. The gum was added with mechanical stirring which was continued for two hours at which time it was assumed the system had reached equilibrium. The white water was then filtered through coarse fritted glass crucibles by suction, and the transmission of the filtrate was compared with distilled water in the photometer.

TABLE II

TRANSMISSION DATA FOR SORPTION OF LOCUST BEAN GUM
ON BLEACHED SULFITE

Sample Percent gum based on pulp and color	Percent Transmission	Percent Transmission Blue Percent Transmission White
1.0% white	96.5	—
3.0% white	98.0	—
5.0% white	97.5	—
1.0% blue	96.0	99.5
3.0% blue	89.0	91.0
5.0% blue	78.0	80.5

TABLE III

SORPTION DATA FOR DYED LOCUST BEAN GUM
ON BLEACHED SULFITE PULP

Percent gum added on wgt. of fiber	Concentra- tion added	Concentration remaining after sorption	Concentration adsorbed	Percent of gum available adsorbed	Percent gum adsorbed, based on wgt. fiber
5.0%	0.025	0.014	0.011	44.0	2.2
3.0%	0.015	0.0051	0.0099	66.0	2.0
1.0%	0.005	0.0004	0.0046	92.0	0.92

PER CENT CALCIUM SULFIDE AND SULFUR

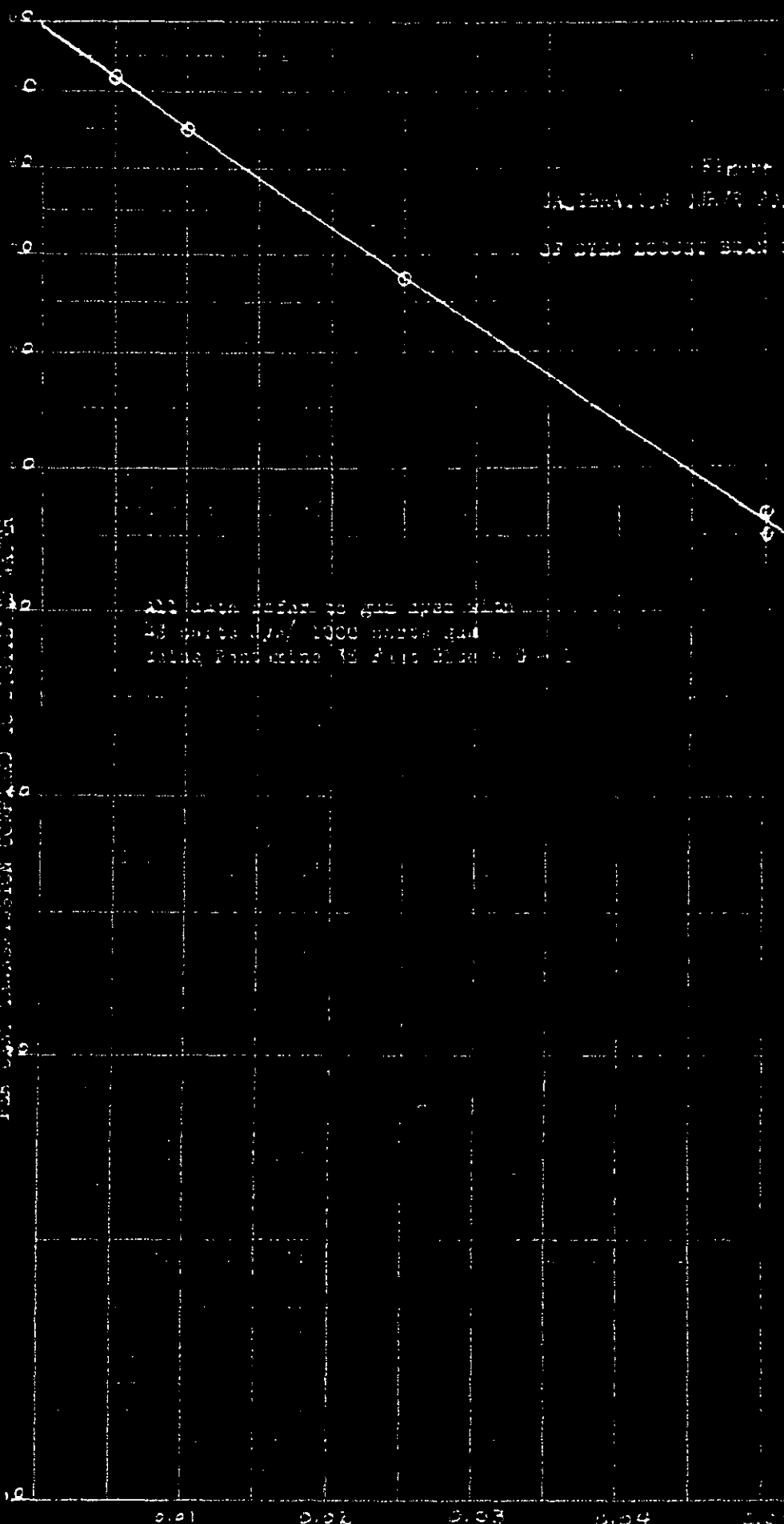


Figure 1
CALCULATION METHOD FOR DETERMINATION
OF DYED LOCUST BEAN GUM

All data refer to gum open with
10 parts 1/2% 1000 water gum
being produced 15 Part Ethanol 1-1

RESEARCH & DEVELOPMENT DIVISION
U.S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D.C.

0.01 0.02 0.03 0.04 0.05
CONCENTRATION OF DYED LOCUST BEAN GUM IN PER CENT

A second adsorption experiment was run this time using ten gram samples of pulp and including a sample with ten percent gum of the weight of the fiber. After the transmission data had been taken and the white water returned to the pulp 1.5 g. handsheets were made. These handsheets were submitted for Mullen burst and MIT fold tests. The comparison of the strength properties of the sheets with dyed and undyed gum should indicate whether the dye was affecting the adsorption and the action of the gums on the sheet.

TABLE IV

TRANSMISSION DATA FOR SORPTION OF DYED LOCUST BEAN GUM

Sample, percent gum based on wgt. pulp and color	Percent Transmission	<u>Percent Transmission Blue</u> <u>Percent Transmission White</u>
1.0% white	93.5	--
3.0% white	93.0	--
5.0% white	93.0	--
10.0% white	92.0	--
1.0% blue	92.0	98.4
3.0% blue	82.5	88.7
5.0% blue	77.0	82.8
10.0% blue	62.5	67.9

TABLE V

SOEPTION DATA FOR DYED LOCUST BEAN GUM ON BLEACHED SULFITE

Percent added on wgt. fiber	Concentration added	Concentration re- maining after sorption	Concentra- tion sorbed	Percent of available gum sorbed	Percent gum on wgt fiber sorbe
1.0%	0.005	0.0008	0.0042	84.0	0.84
3.0%	0.015	0.0070	0.008	53.2	1.6
5.0%	0.025	0.012	0.013	52.0	2.6
10.0%	0.050	0.025	0.025	50.0	5.0

TABLE VI

STRENGTH PROPERTIES FOR SHEETS CONTAINING DYED AND UNDYED GUM

Percent gum based on wgt. fiber	Color	Mullen Burst points/100 lbs.	MIT Fold
0.0	--	51	23
1.0	white	71	119
1.0	blue	73	114
3.0	white	80	145
3.0	blue	77	127
5.0	white	80	207
5.0	blue	77	163
10.0	white	88	184
10.0	blue	86	232

DISCUSSION OF RESULTS

The sorption isotherms obtained by the dyeing technique are similar in shape and order of magnitude to some obtained by the other methods. The variability between duplicate experiments is not improved. Since the same variability is found regardless of the analytical technique, and since all of the methods have experimental errors less than this variability, the differences in sorption seem real; that is, due to some variable not controlled during the actual sorption. This variability can be either in the pulp, gum, or experimental conditions during the time of contact between pulp and gum. Throughout this and previous work there is no recognizable trend in sorption with the age of the gum. Some experiments done earlier with anthrone indicate that the mode of addition and length of time since final dilution of the gum are not critical. Other earlier experiments indicate that the sorption of locust bean gum is not greatly affected by the temperature or degree of agitation. For locust bean gum there have been indications that equilibrium is reached in periods of time shorter than the two hours allowed during these experiments. The variability

is also present when experiments are run on successive days with pulp from the same beater run. No trend is recognized with the age of such a batch of pulp. Some other factors, not understood to date, are probably responsible for this variation, but it does not appear that the difficulty lies in the analytical technique.

The sensitivity of the technique depends entirely on the depth of color of the gum. In the present experiment, using 48 parts dye per thousand parts gum, concentrations can be determined to the nearest 0.001% from the calibration curve. The range of the present curve is from about 0.001% to 0.05%. This range could be contracted and the sensitivity increased by using heavier dyeing.

The comparison of the strength properties of the sheets containing dyed and undyed gum, as shown in Figure III, indicates that the dye does not change the effect of the gum appreciably. There is some question whether the differences indicated in Figure III are within the experimental error of the sheet making and paper testing methods.

FUTURE WORK

One of the great advantages of the use of dyed gum would be the determination of the sorption by measuring the optical properties of a sheet formed after sorption. This would eliminate entirely the problem of filtration and would give the sorption directly instead of as a difference between two concentrations. Such a determination is made possible by the Kebelka-Munk equations. The procedures for the determinations are found in work by Ward D. Harrison, Paper Trade Journal, September 23, 1937 and Philip Nolan, Paper Trade Journal, September 30, 1950.

FIGURE II
THE ABSORPTION OF LACUST BEAN GUM ON BLEACHED
SULFITE PULP DETERMINED USING DYED GUM

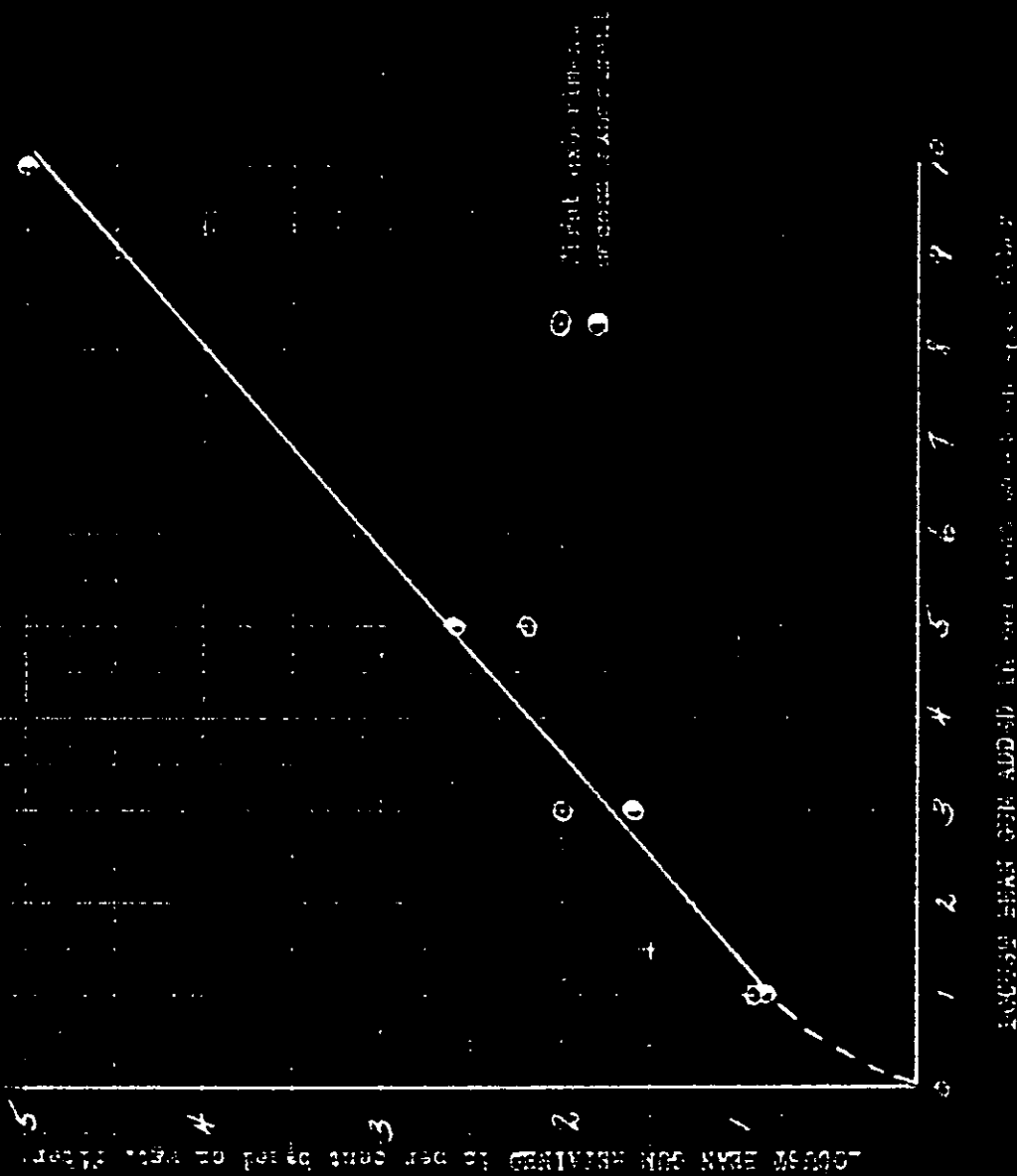
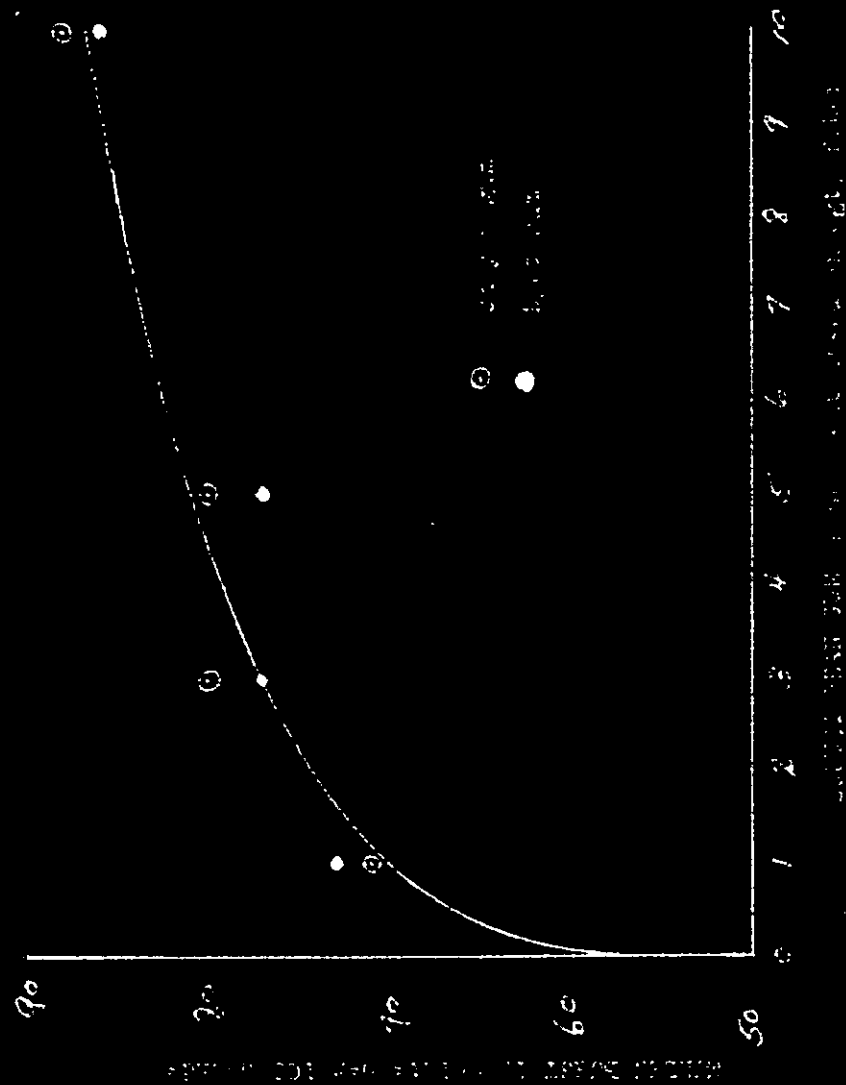


Figure 111
A COMPARISON OF THE HEATING STABILITY OF HARDENERS
CONTAINING DYED AND UNDYED POLYMERIZABLE EPOXY



If determinations of white water concentrations are used for the determination of sorption, it should first be demonstrated that the dye actually remains with the gum and is not transferred to the pulp or removed in any manner during sorption. Also it seems necessary to demonstrate more conclusively that the presence of the dye does not affect the sorption of the gum.

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