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The Sorption of Certain Slash Pine Hemicellulose Fractions by Cellulose Fibers

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THE SORPTION OF CERTAIN SLASH PINE HEMICELLULOSE FRACTIONS BY CELLULOSE FIBERS

A thesis submitted by

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INTRODUCTION

Hemicelluloses are, by definition, the alkali-extractable polysaccharides present in the cell walls of trees and annual plants. The term "hemicellulose" and the chemistry of these materials are discussed by Wise (1). In the present work, only the hemicelluloses from wood will be considered.

Hemicelluloses play an important role in the properties of wood pulps and the papers made from them. For example, bursting strength is improved by their presence whereas color stability is generally reduced.

Two approaches have been used in studies of the effect of hemicelluloses on paper properties. The one treats the hemicelluloses *in situ*. Relationships are described in terms of the quantity of hemicellulose in the fibers and the possible chemical composition of these hemicelluloses. The other approach treats the hemicelluloses as beater adhesives which are extracted from any given wood and then re-added to suspensions of the same, or different, fibers. Although generalizations must be applied cautiously whenever hemicelluloses are reintroduced into pulps in an effort to determine their functions *in situ*., such studies are nevertheless valuable.

Fiber-to-fiber bonding is influenced by the surface properties of the individual fibers. The presence of hemicelluloses on the surface of fibers will, therefore, affect fiber-to-fiber bonding and all sheet properties dependent on it. By using hemicelluloses of different chemical and/or physical composition, the effects of these factors on fiber-to-fiber bonding may be partially isolated.

The mechanism whereby hemicelluloses are sorbed by cellulose fibers has not been investigated. The structural and chemical properties of hemicelluloses which might affect their sorption are not known. The research described in this thesis was undertaken to gain some understanding of the sorption of hemicelluloses by cellulose.

HISTORICAL REVIEW

EFFECT OF HEMICELLULOSES ON PULP STRENGTH PROPERTIES

Hemicelluloses in pulps markedly affect the fiber-water relationships of the fibers. For example, Young and Rowland (2) found an approximate linear relationship between the pentosan content of softwood pulps and their swelling tendency. Houtz and Kurth (3) showed that spruce holocelluloses containing a large proportion of hemicelluloses beat more rapidly and developed greater strength than did alpha pulps prepared from the same holocellulose. March (4) found that when the hemicellulose content of an aspen holocellulose exceeded 20%, a drop in sheet strength properties resulted. He concluded that maximum fiber-to-fiber bonding occurred when the hemicellulose content was 20% because the reciprocal of the opacity and the bursting strength of the sheets were maximal at this point, while the tearing strength was almost at a minimum. Ratliff (5) concluded that the presence of hemicelluloses in fibers permitted the development of a greater specific surface area during beating without much loss in intrinsic fiber strength. An increase in the internal bonded area of the fibers due to the hemicelluloses was also suggested by Ratliff.

Obermanns (6) found that xylan, when added to a rag pulp, increased the rate of beating, the folding endurance, and the tearing strength. He reported that the folding endurance and tearing strength decreased at hemicellulose contents over 6.5% on the fibers. Similar results were obtained when the xylan was added to a purified wood pulp.

Jonas and Rieth (7) reported that two pulps, very similar in chemical properties except for their mannan content, showed large differences in strength properties. The pulp higher in mannan content showed the higher burst and tensile strengths. Thompson, Swanson, and Wise (8) showed that spruce hemicelluloses of about the same degree of polymerization (D.P.) but different mannan content (7.7 and 22.2%) produced different orders of strength improvement when added to an alpha pulp slurry. The hemicellulose with the higher mannan content gave the greater strength improvements. Similar results were reported by Thompson, Swanson, and Wise (8) using four slash pine hemicelluloses ranging in mannan content from 5 to 23%. For a given level of hemicellulose addition and fixed sorption conditions, the bursting strength was found to increase as the mannan content of the fractions increased. Because retentions were not determined, the effectiveness of the four fractions could not be compared on the basis of amounts sorbed. In a subsequent section of this thesis it will be shown that these four slash pine hemicelluloses differ in effectiveness as beater adhesives even when compared at levels of equal retention.

Thompson, Swanson and Wise (8) further reported that hemicelluloses which were hydrolyzed below a certain D.P. lost their effectiveness as adhesives. They concluded that hemicelluloses must have a critical minimum D.P. in order to function as inter-fiber bonding agents. Softwood hemicelluloses containing appreciable quantities of hexose units were apparently more effective adhesives than hardwood hemicellulose, they concluded, because of the higher proportion of hydroxyl groups per unit chain length. The greater mobility possessed by the

primary hydroxyl groups of the hexose units may permit them to enter into bond formation in ways not sterically possible for secondary hydroxyls.

The effect on sorption of the uronic acid carboxyl groups in hemicelluloses is not known. The solubility of the hemicelluloses in water is generally increased when these groups are present in the molecule. Thompson, Swanson, and Wise (8) stated "...carboxyl groups of the uronic anhydride residues would also be expected to influence the adhesive and cohesive properties of the various hemicellulose fractions."

Jayme and Lochmüller-Kerler (12) stated that the presence of an optimum point in curves of a strength index versus hemicellulose content is due to two opposing factors. The factor responsible for the gain in strength is the increase in total bonded area with increasing hemicellulose content. The opposing factor is a decrease in the intrinsic strength of bonds because of the increase in the proportion of molecules of lower D.P. Furthermore, they concluded that, as the amount of hemicelluloses in a pulp increases, the proportion of long chain, strength-imparting cellulose is decreased within a given fiber thus promoting a weakening of the whole fiber structure.

Edge (13) maintains that all beater adhesives give higher strength at lower degrees of beating because the hydrogen bonds required in imparting strength to a sheet of paper can be formed easily with the high polymer additive acting as a "bridge".

Reviews of the role of hemicelluloses in the strength development

of pulps are given by Ross (10), Cottrall (11, 14), Gallay (15), and Wise (1).

THE SORPTION OF HEMICELLULOSES AND OTHER POLYSACCHARIDES BY CELLULOSE

In the work of Obermanns (6) and March (4), hemicelluloses were added to pulp slurries in paste or powder form. The fibers and hemicellulose were then beaten together and the retention was determined by measuring the increase in pentosan content or the increase in alkali-extractable material. Jayme (16) precipitated hemicelluloses in the presence of pulps by acidifying dilute alkaline solutions of hemicelluloses. Little or no information can be obtained from these experiments regarding the sorption of hemicelluloses from aqueous solution because retention may have occurred via the physical entraining of gross hemicellulose aggregates as well as by precipitation within the fiber structure.

In the work of Thompson, Swanson, and Wise (8), hemicelluloses in solution were added to the pulp. No attempt was made to precipitate the hemicelluloses and it may be assumed that retention occurred via a sorption mechanism. In two instances the solutions had to be warmed to dissolve the hemicelluloses and when these solutions were added to the pulp slurry at room temperature some precipitation may have occurred. Only the results obtained using the cold water-soluble hemicelluloses will be discussed. The hemicellulose solutions were added to pulp slurries of 1.5% consistency. The slurry was then stirred for 1/2 hour and handsheets were formed by diluting aliquots of the pulp

slurry to 0.05%. The strength properties of these handsheets continued to increase with increasing amounts of hemicellulose added, despite the subsequent thirtyfold dilution of the pulp suspension. This result is indicative of strong bonding forces holding the hemicelluloses to the fibers. Irreversible sorption may also be indicated. Thompson, Swanson and Wise (8) also reported that strength improvements at pH 4.5 were slightly greater than at pH 9.2. Because the sorption conditions were otherwise the same, this result indicates that pH probably influences the sorption of hemicelluloses.

Yllner and Enström (17) studied the sorption of pentosans removed from birch and spruce wood during the early stages of a kraft cook. The pentosans were sorbed from the cooking liquor on cotton, cotton linters and bleached sulfite fibers. They reported that the amount sorbed increased with time, parallel to the increase in pentosan concentration in the liquor. Sorption stopped only when the pentosan content of the liquor dropped to "negligible levels". The sorption was irreversible with respect to concentration and some 20% of the sorbed pentosans were not removed by a one-hour extraction with 10-20% caustic solutions at 20°C.

Studies of the sorption of amylose, methylcellulose, and locust bean and guar gums will be reviewed to provide a background against which the sorption of the hemicelluloses may be compared.

The sorption of amylose by wood pulps has been studied by Pearl (18). He found that sorption continued slowly over a long period of time until all the amylose was removed from solution. Complete sorption

required times up to 600 hours for initial concentrations of about 0.8 g./l. Sorption was irreversible with respect to concentration. Some desorption could be effected by suspending pulp-sorbed amylose samples in water at temperatures above the original sorption temperature. The sorption rate at pH 10.4 was much lower than at pH 4. Increasing the temperature reduced the rate of sorption. Other factors being equal, the quantity sorbed at any given time was proportional to the initial concentration. Pearl postulated a mechanism of sorption involving the deposition of amylose molecules onto the cellulose surface with a practically simultaneous deposition of amylose on already sorbed amylose. Hydrogen bonding was suggested as the force holding the sorbed molecules to the cellulose and to each other. The process wherein amylose is sorbed by presorbed amylose he termed "retrogradation sorption" because the features of the process were analogous to the retrogradation of starch solutions.

Shriver (19) found that the sorption of methylcellulose required times up to 180 hours to reach equilibrium. The sorption was irreversible with respect to concentration. Increasing the temperature increased the equilibrium sorption values. According to Shriver, this result was due to the increased tendency of methylcellulose solutions to gel when heated. By decreasing the temperature at equilibrium from 38 to 3.3°C. some desorption occurred. However, the new equilibrium value at 3.3°C. was higher than the equilibrium value reached when the same lower temperature was maintained from the beginning of the sorption. The mechanism postulated by Shriver involves an adsorption of the methylcellulose on the fiber surfaces followed by a gelation of the

sorbed molecules. Hydrogen bonding was assumed as the force holding the sorbate to the sorbent.

The anthrone and viscometric concentration measuring techniques used by Shriver in the above study are described in detail by Shriver, Webb, and Swanson (20). These authors found that sorption values computed by the viscometric method were 50 to 100% greater than those obtained by the anthrone method. Although they were unable to give specific reasons for these large differences, they suggested that the deflocculating effect of methylcellulose solutions on pulp resulted in greater quantities of suspended cellulose fines in the solution aliquots. The anthrone technique measures total carbohydrates and, consequently, the cellulose fines are calculated as methycellulose. This results in fictitiously high residual concentrations and low computed sorptions. The viscosity method was found to be less affected by the suspended fines and hence, they concluded, gave concentration values that were more nearly correct.

The use of either of the above methods necessitates careful filtrations and/or centrifugations to obtain aliquots suitable for analysis.

The sorption mechanism of natural gums (e. g., locust bean and guar) has not been studied in great detail. Swanson (21) concluded that gums are adsorbed from solution by cellulose and are present on the fiber surfaces as films of highly swollen material giving the fibers "many of

the same characteristics as mechanical beating". Contrary to the conclusion of Musser and Engel (22), Swanson found that it was not necessary to beat the pulp in the presence of the gums to achieve strength improvements. Swanson added gum solutions to pulp at a consistency of 1.5%, stirred for five minutes, diluted the slurry to 0.5% and then prepared handsheets at 0.05% consistency. Despite these extreme dilutions, sheet strength continued to increase as increasing quantities of gum solution were added to the 1.5% consistency pulp. As in the case of the hemicelluloses, strong bonding forces are probably involved in the retention and irreversible sorption may be indicated.

Unpublished data of Swanson (23) show that the sorption of locust bean gum is a rapid process. At concentrations of 0.5-2.0% on the fibers, retentions of about 96% of the added gum were found at the end of one hour. It is doubtful whether equilibrium was reached in these studies because the sorption appeared to be continuing slowly beyond one hour. This was especially evident at higher levels of gum addition.

In his studies of the reasons for strength improvements when locust bean gum is added to fibers, Leech (24) developed a new method for measuring gum retention. This method is based on an analysis of the galactose content of the sheets after gum addition. He rejected the anthrone and viscometric methods of Shriver (19) for the following reasons: (1) the methods rely on the measurement of small concentration differences and the possible errors become relatively large, (2) the anthrone technique depends on the method of mixing the sample and reagents, (3) the methods are not specific for the gum but are general

carbohydrate techniques, (4) the filterability of the fine cellulosic material is affected by the gum, and (5) the possibility that not all the dispersed gum would pass through the filter, or that a small constant amount of cellulosic material would pass through the filter to be corrected for by a blank determination.

Leech (24) found that washing handsheets made from pulp to which 5% gum had been added did not alter their strength properties relative to the unwashed sheets. This result is strongly indicative of irreversible sorption.

Gruenhut (25) reported that guar gum is sorbed at a slower rate than locust bean. Thus, to compare the effectiveness of the gums on an equal basis would require using a longer sorption time for the guar. Pearl (18) found that although amylopectin (the branched fraction of starch) was sorbed at a lower rate than amylose, it was a better adhesive when the two were compared at the same level of retention.

Swanson (26) has reviewed the literature on the subject of beater adhesives and fiber bonding.

PRESENTATION OF PROBLEM

When hemicelluloses in solution are added to pulps they are sorbed by the fibers and increase the strength properties of sheets made from the pulp. The mechanism of this process has not been studied previously.

The present study was undertaken to elucidate the sorption of four slash pine (*P. caribaea*) hemicelluloses by cellulose fibers. A new, radiochemical method of sorption measurement was to be developed permitting the direct measurement of sorbed hemicelluloses on the fibers. A method of sorption measurement based on the direct analysis of the fibers is needed to eliminate the uncertainties of measurements based on differences in concentration of polysaccharide sorbates in the supernatant solutions of pulp suspensions.

Special attention was to be given to the question of the reversibility or irreversibility of sorption. Valuable information on the type of forces involved in sorption may be derived from such considerations.

GLOSSARY

Hemicellulose Fractions

1 SP - Extract obtained with 1% potassium hydroxide from slash pine holocellulose.

4 SP - Extract obtained by treatment of the holocellulose, previously extracted with 1% potassium hydroxide, with 4% potassium hydroxide.

7 SP - Extract obtained by treatment of the holocellulose, previously extracted with 1 and 4% potassium, with 7% potassium hydroxide.

16 SP - Extract obtained by treatment of the holocellulose, previously extracted with 1, 4, and 7% potassium hydroxide, with 16% potassium hydroxide.

Radioactivity Units

mc. - millicurie, 2.22×10^9 disintegrations/min. for carbon-14.

μc. - microcurie, 2.22×10^6 disintegrations/min. for carbon-14.

mμc. - millimicrocurie, 2.22×10^3 disintegrations/min. for carbon-14.

cpm. - counts per minute, in this work are taken as disintegrations/minute because of the high counting efficiency (98-99%) obtainable with the technique used.

specific activity - the radioactivity per unit weight or volume of material, expressed in any radioactivity units, e.g., mμc./mg., cpm/mg., etc.

Sorption Terms

sorption - the process whereby the hemicelluloses are removed from solution or dispersion by the fibers present. Precommitment to either ad- or absorption is avoided by the use of the term (27).

X/M - weight of hemicellulose sorbed per unit weight of pulp.

C_i - initial concentration, mg./ml. or g./l.

EXPERIMENTAL PROCEDURES

PREPARATION OF HEMICELLULOSES

Four slash pine hemicellulose fractions were extracted from a sample of chlorite holocellulose (28) with successive portions of 1, 4, 7, and 16% potassium hydroxide. The details of the extraction and purification procedure are given in Appendix I.

ANALYSIS OF HEMICELLULOSES

STANDARD CHEMICAL AND PHYSICAL ANALYSES

The hemicelluloses were analyzed for the following: sulfated ash, mannan, D.P., uronic anhydride, total carbon, and pentosans. Details of the analytical procedures are given in Appendix I. A summary of the results is presented in Table I. Table II gives a comparison between the results of these analyses and the published data of Thompson, Swanson, and Wise (8) who worked with similar hemicellulose fractions obtained from a different sample of slash pine chlorite holocellulose.

ELECTROPHORETIC ANALYSIS OF FRACTIONS

Samples of the hemicelluloses were subjected to a glass paper electrophoretic separation by Dr. F. Smith at the Univ. of Minnesota. The author is indebted to Dr. Smith for his kindness. The procedure he used is described in Appendix I. Each of the four hemicelluloses separated into two zones on the glass paper indicating that they were at least heterogeneous with respect to electrical charge. According to

Dr. Smith, such charge differences might arise from differences in the chemical nature of the components of each gross hemicellulose extract. Further conclusions concerning the composition of each gross hemicellulose extract are not possible at present.

TABLE I

ANALYSIS OF SLASH PINE HEMICELLULOSES

	1SP	4SP	7SP	16SP
Yield, %[1]	39	19	15	27
Ash				
Sulfated, %	17.8	11.5	10.6	10.4
Corrected, %	8.1	6.0	5.3	5.0
Mannan, %	5.4	12.6	18.0	25.2
Pentosans, %	45.7	50.0	46.3	28.8
Uronic anhydride, %	28.3	20.4	16.8	12.8
Viscosity data				
Intrinsic viscosity	0.39	0.42	0.51	0.55
Degree of polymerization	90	95	115	125
Total carbon, %	43.3	43.7	43.4	43.2

[1] Based on total, air-dry hemicellulose obtained. All other analyses on an oven-dry, ash-free basis.

TABLE II

COMPARISON OF HEMICELLULOSE ANALYSES

	1SP		4SP		7SP		16SP	
	A	B	A	B	A	B	A	B
Yield, %	42	39	17	19	19	15	22	29
Mannan, %	5.4[1]	5.4	10.2	12.6	15.2	18.0	22.6	25.2
Pentosans, %	49.5	45.7	56.1	50.0	48.9	46.3	27.8	28.8
Intrinsic viscosity	0.44	0.39	0.47	0.42	0.55	0.51	0.59	0.55
Degree of polymerization	100	90	105	95	120	115	130	125

(Column A contains values taken from the literature (8) for four hemicellulose fractions, while column B contains the results obtained in the present research with hemicellulose fractions respectively similar to those given under A.)

[1] Mannan data obtained by precipitation with phenylhydrazine in A, and chromatographically in B.

PREPARATION AND ANALYSIS OF PULP

A Brown Co. alpha pulp was used in all the studies reported in this thesis. This was the same pulp as that used by Thompson, Swanson, and Wise (8) who reported the following analytical data: lignin 0.0%, pentosans 3.1%, alpha-cellulose 90.2%, and organic extractibles 0.3%.

The pulp was beaten to a freeness of 760 ml. S.R. in a laboratory Valley beater, dewatered, and stored in a polyethylene bag out of the light at room temperature. Approximately 0.5% formaldehyde (on the dry fiber basis was added to inhibit bacterial action. The ovendry content of the pulp stored under the above conditions was 32.1%. The carbon

content of the pulp was determined using the wet combustion method to be described subsequently. Duplicate analyses gave a value of 43.3%.

Details of the pulp preparation and storage are given in Appendix I.

METHOD OF SORPTION MEASUREMENT

PRINCIPLE OF METHOD

If a source of radioactivity is introduced into a sorbate molecule, the course taken by such labeled molecules during sorption can be followed. For ease of handling and measurement, the radioactive material is usually diluted with nonradioactive material to a known specific activity. The increase in radioactivity of the sorbent is then directly related to the amount of material sorbed. The introduction of the radioactive atom must not alter the sorption behavior of the labeled material relative to the unlabeled material. The conclusions drawn will hold only for the tagged molecules if their sorption behavior is affected by labeling.

LABELING OF HEMICELLULOSES

The technique of Isbell (29) was employed to introduce radioactivity into the hemicelluloses. This method is an adaptation of the Kiliani cyanohydrin reaction for adding carbon atoms to sugars. The reaction proceeds via the condensation of a cyanide ($-C^{14}N$) radical at the site of the reducing end group on the sugar, followed by the hydrolysis of the cyanide to a carboxyl group. The experimental details of the method as applied to the hemicelluloses are presented in Appendix II.

The results of the labeling reaction are summarized in Table III. Yields were calculated as the percentage of the starting activity (10 μc.) which appeared in the labeled product.

These results indicated that some reducing groups were still present in the hemicelluloses despite the initial chloriting of the wood and the subsequent alkali extractions in the presence of air.

It was estimated that the amount of carboxyl groups introduced into the 1SP fraction by the labeling reaction was 0.085 moles per mole of hemicellulose. This represented an increase of 1 carboxyl group per 2500 already present. The estimate was based on the 28.3% uronic anhydride content of the 1SP hemicellulose (page 15), the 22% yield in the labeling reaction (Table III), and on an assumed molecular weight of 16,000 for the hemicellulose. On the basis of this slight increase in carboxyl content, it was assumed that the sorption properties of the hemicelluloses were not altered by the labeling reaction.

The yield values of 35 and 36% shown in Table III are believed to be spurious results. No differences were found in the sorption data which could be attributed to differences in properties of these apparent high yield fractions relative to the properties of the same fractions with yields in the 22 to 26% range.

DIRECT MEASUREMENT OF SORPTION

To determine the amount of sorbed hemicellulose on the fibers,

TABLE III

YIELDS OF RADIOACTIVE HEMICELLULOSE FRACTIONS

	1SP		4SP		7SP		16SP	
Weight, ovendry of hemicellulose used, mg.	132	50	100	84	73	82	174	94
Specific activity of product, μc./mg.	0.017	0.048	0.023	0.029	0.035	0.043	0.013	0.038
Carbon-14 yield, %	22	24	23	24	26	35	23	36

pulp-sorbed hemicellulose samples were oxidized completely to carbon dioxide and water using the wet combustion method of Van Slyke and Folch (30). The total carbon dioxide generated was made up of the carbon dioxide from the pulp and the hemicellulose. Since the sorbed hemicellulose contained carbon-14, the gas mixture contained a quantity of $C^{14}O_2$ which was directly proportional to the weight of hemicellulose on the sample. The amount of carbon dioxide was determined and converted to the weight of pulp plus hemicellulose oxidized. Next, the radioactivity of the carbon dioxide was determined by proportional counting and was converted to the weight of hemicellulose oxidized. From these data the sorption per unit weight of pulp was calculated. The detailed procedures followed in the preceding analyses are given in Appendix III together with a description and sketch of the apparatus used.

This method is not limited to hemicelluloses alone. For example, Isbell (29) has successfully labeled such polysaccharides as potato and wheat starches, locust bean gum meal, dextrin and inulin. Any sorbent capable of being oxidized to carbon dioxide and water can also be employed.

PREPARATION OF HEMICELLULOSE STOCK SOLUTIONS

To avoid the difficulties inherent in adding dry hemicelluloses to pulp suspensions, stock solutions consisting of mixtures of labeled and unlabeled hemicelluloses were prepared. The concentration and specific activity of the hemicellulose solutions were determined by the wet-combustion and proportional counting methods. The details of solution

preparation and analysis are given in Appendix IV. Duplicate concentration analyses had a precision of ±0.02 mg./ml.

Because of the danger of bacterial attack on the stock solutions, fresh solutions were made up prior to a series of experiments and were stored in a refrigerator. A study was made of the decrease in reduced specific viscosity which occurred upon aging a solution of hemicellulose. The results and details of the method used are given in Appendix IV. It was found that a slow decrease in $n_{sp.}$/conc. occurred with time. After 5-6 days, the rate of change of $n_{sp.}$/conc. decreased and the value became practically constant thereafter. No visible precipitate was formed nor did any turbidity develop in the solution.

PREPARATION OF SORPTION SAMPLES

A charge of wet pulp sufficient to give the desired amount of dry fibers was weighed on an analytical balance. The wet pulp was then dispersed in a measured volume of distilled water to give the desired consistency. The pH of the pulp suspension was adjusted by adding either dilute sulfuric acid or dilute sodium hydroxide. The sample bottles were then closed and placed on a rotating drum in a controlled temperature water bath. After the contents of the bottles had reached the desired temperature, the bottles were uncapped and a measured volume of hemicellulose stock solution was introduced. The sample bottles were again closed and returned to the water bath until the time of sampling.

In the studies of the effect of time on sorption, separate samples

were prepared for each time interval. These samples were identical in all respects. When a measurement was to be made, the contents of one sample bottle were used *in toto* to provide material for analysis. This technique eliminates any disturbing factors which might arise from the repeated sampling of one pulp-hemicellulose mixture.

SAMPLING PROCEDURE

In order to analyze the fibers directly for their sorbed hemicellulose content, it was desirable first to wash them free of residual hemicellulose solution. If desorption were to occur during washing, this technique could not be used. The error which would result if the analysis were done on unwashed samples is discussed below.

Preliminary experiments were designed to determine whether desorption occurred when slurries of pulp containing sorbed hemicelluloses were diluted to very low residual hemicellulose concentrations. The results of these experiments indicated that measurable desorption did not occur within 14 hours after dilution. Later experiments demonstrated that pulp-sorbed hemicellulose samples except those at high specific sorptions could be suspended in distilled water of zero hemicellulose content without causing desorption. These experiments are described in the EXPERIMENTAL RESULTS. As a result of these experiments the following procedure was adopted.

The pulp and residual solution from a given sample were poured into a large, coarse grade sintered glass funnel and diluted to about

500 ml. with distilled water at the same temperature as that of the pulp slurry. Suction was then applied to remove the liquid. The pulp suspension was vigorously stirred during this operation. Two successive portions of 500 ml. each of distilled water were added to the pulp and the procedure repeated. Assuming that 100 ml. of pulp slurry were used and that 2 ml. of solution were left with the fibers after each washing, a total dilution factor of approximately 300,000 resulted. This was sufficient to reduce the residual hemicellulose in the water held by the pulp to negligible levels.

The resulting pad of wet pulp was then removed from the funnel, squeezed free of excess water, picked apart so as to yield small pieces, and dried in a vacuum desiccator over calcium chloride.

An estimate of the error which would result if washing were not employed can be made. The following data represent some typical values encountered for the 1SP fraction. At a sorption level of 6.80 mg./g., a residual concentration of 0.112 mg. hemicellulose/ml. was calculated at the time of sampling. Assuming that 2 ml. of this solution was held by the fibers after filtration, an excess of hemicellulose of 0.448 mg./g. pulp over the amount actually sorbed would be measured. Therefore, without washing, the sorption measured would have been 7.25 mg./g.. This is an error of +6.6%. In order to accurately calculate these errors it would be necessary to measure the solution concentration at the time of sampling and the water content of the wet pulp pad. For lower levels of retention and higher residual concentrations the error would increase, while for higher

levels of retention and lower residual concentrations the error would decrease. By washing the fibers free of residual solution this source of error is eliminated.

In the above method, the loss of fines with high specific surface area could consititute a source of error. A qualitative examination of the filtrate from a typical sample after centrifuging indicated that only a very small quantity of material passed through the pores of the fritted glass filter in the funnel. No attempt was made to recover this material. Leech (24) analyzed the locust bean gum content of handsheets prepared on a wire screen before and after recirculation of the white water through the sheet. He found after recirculation that the gum content based on the dry fiber, had only increased by 0.37%. Hence, he concluded, that despite the high specific surface area of the fines, the actual mass lost was so small that it could be neglected. In the present case the use of a fritted glass filter may be assumed to reduce the fines loss to an even greater extent. By keeping the fibers in suspension during the filtration, the distribution of fines in the resulting pulp pad is kept nearly uniform.

REPRODUCIBILITY OF SORPTION MEASUREMENTS

Duplicate analyses were performed on each pulp-sorbed hemicellulose lot. The precision of measurement was calculated by Equation (1).

$$s = \sqrt{\frac{(X_1 - X_2)^2}{2n}} \qquad (1)$$

where,

s = pooled estimate of standard deviation.

$X_1 - X_2$ = difference between duplicate analyses.

n = number of pairs of measurements.

All analyses where the level of retention was below 10.0 mg./g. were used for calculating a standard deviation and the value was s = ±0.17 mg./g. The corresponding calculations for all values above 10.0 mg./g. yielded a value of s = ±0.8 mg./g. Since s is a pooled estimate, the percentage relative error (defined as s/XM x 100) depends on the magnitude of the sorption value being considered. For example, at a level of retention of 2.00 mg./g., the relative error is about ±8%, whereas at a level of retention of 9.00 mg./g. the relative error becomes about ±2%. The same considerations hold for the retention data above 10.0 mg./g.

SORPTION MEASUREMENT BY CONCENTRATION DIFFERENCE

In principle, the analytical methods described above can be applied to the measurement of sorption by determining the decrease in the concentration of hemicellulose in solution. The major problem in this approach is in obtaining aliquots containing only unsorbed hemicellulose. Since the analysis depends on the measurement of radioactive $C^{14}O_2$, any fiber "fines" containing sorbed hemicellulose, which are present in the aliquots, will introduce an error. Further, any filtration method which removes hemicellulose from solution will cause an error.

In a number of experiments, sorption was measured by concentration difference. Filtration through fritted glass discs and glass filter paper was tried. These experiments and the results therefrom are described in detail in Appendix V. It was concluded that this approach could probably be used most successfully where large changes in solution concentration occurred. Under these conditions, the errors involved would not completely mask the change to be measured. The latter effect was observed in many instances where small differences in concentration were measured.

The combination of measuring techniques used in the present work made it possible to evaluate the nonhemicellulosic carbohydrates present in solution aliquots. If only hemicellulose were present in the filtered aliquots, the total carbon content determined manometrically would agree with the carbon content determined by the carbon-14 analysis. Where the former value was higher than the latter, the presence of dispersed cellulose from the pulp was indicated. In the EXPERIMENTAL RESULTS section, data are presented showing that the amount of this dispersed cellulose present in the supernatant solutions of a series of pulp-hemicellulose slurries varied from 28 to 102 p.p.m.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

INITIAL EVIDENCE OF SORPTION IRREVERSIBILITY

The following experiments were performed to determine if fibers containing sorbed hemicellulose could be washed without inducing desorption. A pulp slurry was prepared by dispersing 1.0 g. of pulp in 200 ml. of distilled water and adding 1SP stock solution to bring the hemicellulose concentration to 0.149 g./l. The total volume of the slurry was 212 ml. The pH was 6.5 and the temperature was maintained at 25 $\pm$ 0.2 °C. Sorption was permitted to proceed for 67.5 hours. During the sorption, aliquots of solution were withdrawn at intervals for analysis, reducing the final volume to 184 ml. The sampling during the initial phase of the sorption was used to determine the feasibility of measuring sorption by concentration difference. The results and discussion of those measurements are presented in Appendix V.

The specific activity of the residual 184 ml. was measured and found to be 661 cpm./ml. After isothermal dilution to 284 ml. it was calculated that the specific activity would be 428 cpm./ml. provided no desorption had occurred. The dilution was performed and the resulting suspension was stirred for one hour. At the end of this time, aliquots were withdrawn and the specific activity of the solution was measured. It was found to be 429 cpm./ml., which agreed with the calculated value. From this experiment it was concluded that no desorption had occurred within one hour.

This experiment was repeated using the same fraction of hemicellulose and the same sorption conditions as above. In this case the slurry was

diluted and permitted to stand for 14 hours before analysis. The predilution solution activity was 657 cpm./ml., and the predicted specific activity after dilution, if no desorption occurred, was 438 cpm./ml. The post-dilution specific activity of the solution after 14 hours was 461 cpm./ml., which agreed with the predicted value within 5.3%. This difference was not considered significant.

These results indicated that probably no significant desorption of hemicellulose had occurred. Hence, it was concluded that fibers containing sorbed hemicelluloses could be washed free of residual solution without desorption. Additional experimental data are presented later showing that desorption did not occur even after 72 hours under more extreme desorption conditions.

EFFECT OF TIME ON SORPTION

The 1SP and 16SP fractions were selected for the orienting time studies on the assumption that the greatest differences would occur between these fractions. Thompson, Swanson, and Wise (8) found that the greatest differences in pulp strength properties occurred when these two fractions were used.

Separate samples were prepared for each interval as described in the EXPERIMENTAL PROCEDURES section. The concentration of hemicellulose was made equal in each sample by adding an equal volume of hemicellulose stock solution to each sample. The pH was lowered to 4.5 and the temperature was maintained at 30 $\pm$ 0.2 °C. Thompson, Swanson, and Wise (8) reported that, at this pH, somewhat greater strength improvements resulted than at alkaline pH.

The pulp consistency before the addition of stock solution was 0.50 g./100 ml. After the addition of the stock solution the actual consistency was reduced by a small amount dependent on the volume of stock solution used. For example, the actual pulp consistency for the 16SP experiments shown in Table IV was 0.46 g./100 ml. at the initial concentration of 0.142 g./l., and 0.41 g./100 ml. at the inital concentration level of 0.266 g./l. In the heading of Table IV and subsequent tables, the phrase "nominal pulp consistency" will be used to indicate the pulp consistency prior to the addition of the hemicellulose stock solution.

The results of the time studies are summarized in Table IV and Figure 1. From these data it is apparent that the over-all rate of sorption of the 16SP fraction is greater than that of the 1SP fraction. During the initial portion of the sorption vs. time curve, the rate for the 16SP fraction (slope of the curve) was considerably higher than that of the 1SP despite the fact that within one hour, the concentration of 16SP has dropped to some 73% of the 1SP concentration. The sorption rates of both fractions decreased markedly after about 10 hours. Beyond ten hours, the sorption continued slowly, at an apparently nearly constant rate, without reaching equilibrium within three days. Increasing the initial concentration of the 16SP fraction resulted in a higher sorption rate throughout the sorption vs. time curve and a higher level of sorption after any given time. The concentration increase of 87% resulted in about a 100% increase in the amount sorbed within a given period. Experiments will be described subsequently, showing the relationship of the amount sorbed at a given time to the initial concentration, for the four hemicellulose fractions.

TABLE IV

EFFECT OF TIME ON SORPTION

pH = 4.5

Temperature = 30 ± 0.2°C.

Nominal Pulp Consistency = 0.50 g./100 ml.

Fraction	Hemicellulose Added, %, based on pulp	Initial Concn., g./l.	Time, hr.	Specific Sorption, mg./g.	Calculated Concn. at Time of Sampling, g./l.	Hemicellulose Sorbed, %, based on amount added
16SP	3.0	0.142	1	10.6	0.094	34.4
			3	13.1	0.082	42.6
			5.5	13.5	0.079	43.8
			12	14.1	0.078	45.7
			24	15.1	0.073	49.1
			30	15.6	0.070	50.7
			72	16.1	0.068	52.3
1SP	3.0	0.143	1	3.46	0.129	11.1
			4	4.36	0.124	14.0
			8	5.29	0.120	17.0
			25	6.41	0.115	20.6
			72	6.80	0.113	21.8
16SP	6.4	0.266	2	22.8	0.172	35.3
			6	23.3	0.170	36.1
			25	28.4	0.149	44.0
			48	29.7	0.144	45.8
			72	32.1	0.134	49.6

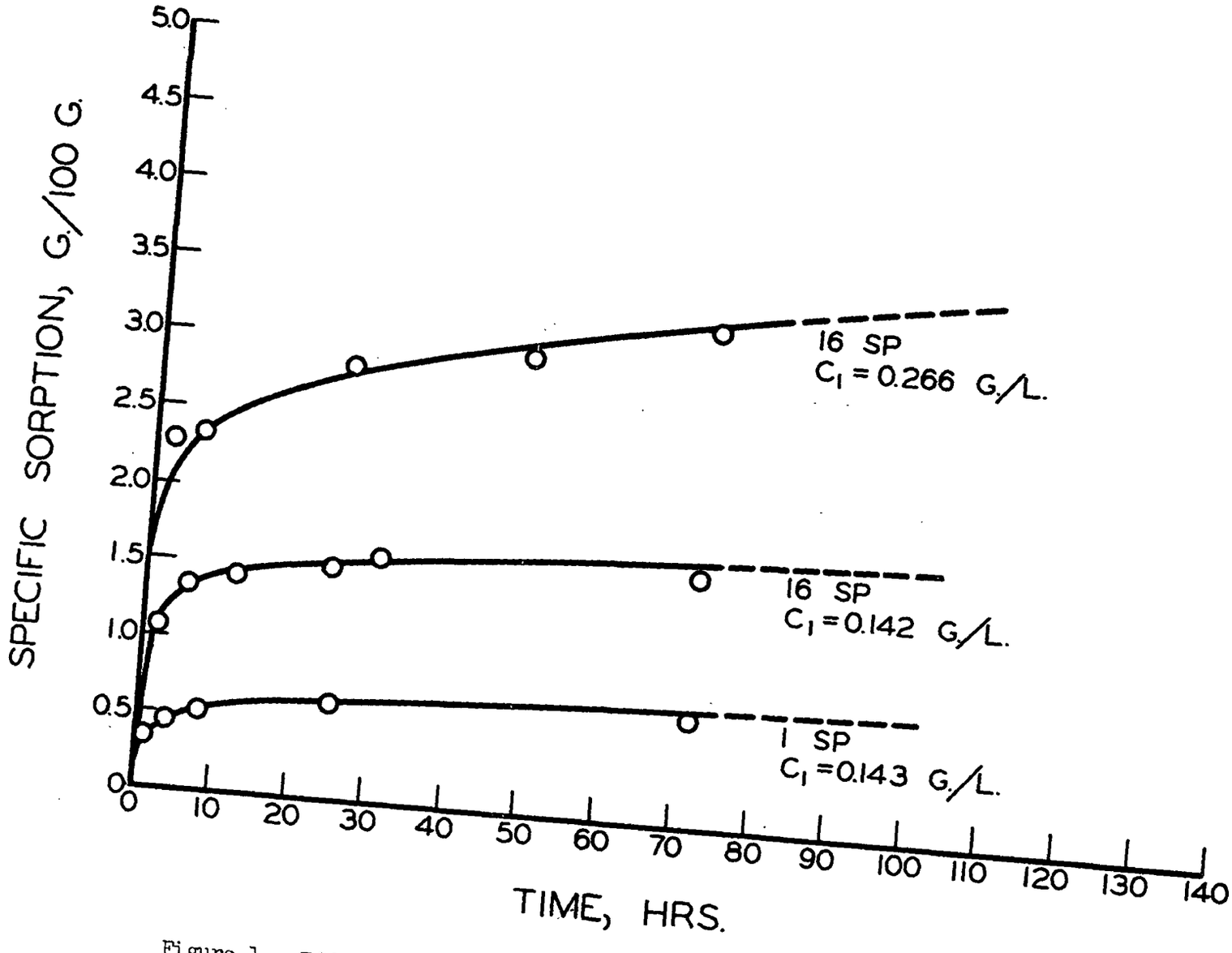

Figure 1. Effect of Time on Specific Sorption of 1SP and 16SP Fractions

T = 30°C; pH = 4.5

Figure 2 is a plot of the sorption as a function of time on a log-log scale. The equation which describes these plots is of the parabolic type, $X/M = at^n$, where X/M is mg. of hemicellulose per g. of pulp, a and n are constants, and t is the time in hours. This is an empirical equation and is generally used to describe the early stages of a sorption process before equilibrium is reached. In the present case the equation fits the data satisfactorily up to 72 hours since no apparent equilibrium was reached.

To determine whether equilibrium occurred within ten days, an additional set of experiments was designed. The 1SP and 16SP fractions were used at two levels of initial concentration. The samples were prepared as before, at pH 4.5, 30°C., and nominal pulp consistency of 0.50 g./100 ml. For each fraction at each concentration level, two separate samples were prepared thus providing material for analysis at five and ten-day intervals. For the ten-day trials, additional samples of the 1SP and 16SP fractions were prepared at the higher concentration level and five drops of formaldehyde solution were added to inhibit bacterial attack. These samples served as checks on the possible effects of bacterial attack on the samples prepared without formaldehyde.

Sorption was measured by direct fiber analysis and also by the change in concentration of the solution. Prior to washing the fibers, a portion of the supernatant solution was filtered through a plug of glass wool and then through glass filter paper. Aliquots of these filtered solutions were analyzed for total carbohydrate content and hemicellulose content. Thus, in addition to comparing the sorption

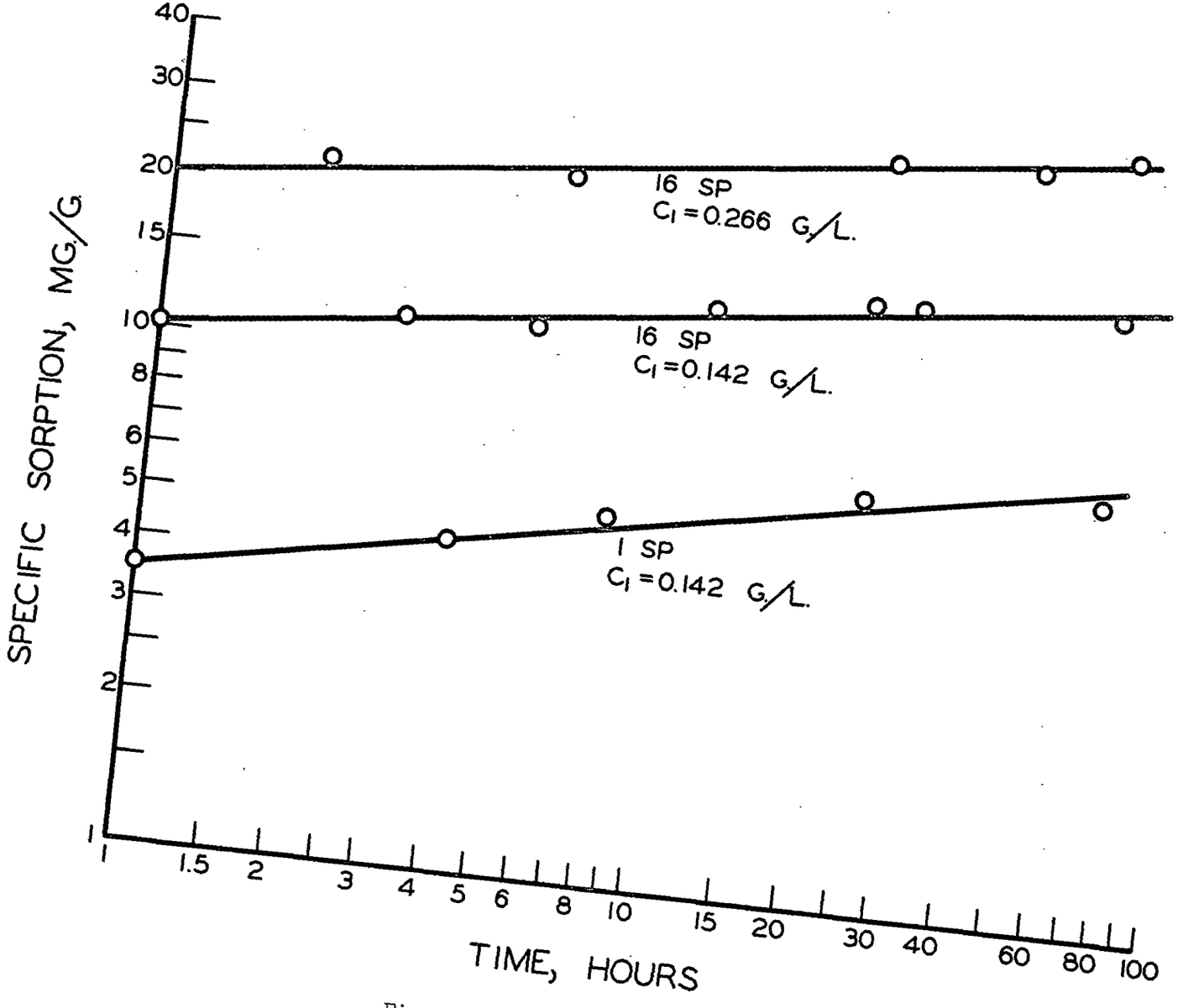

Figure 2. Log X/M vs. Log Time

$(X/M = at^n)$

pH = 4.5; Temp. = 30°C.

values obtained by both sampling methods, the amount of "soluble" or "dispersed" cellulose passed by the filter could be measured. The latter results will be discussed subsequently in a separate section of the EXPERIMENTAL RESULTS.

Table V summarizes the sorption measurements made in this experiment. These data show that equilibrium was not reached within ten days. The rate of sorption of both fractions was quite slow, as indicated by the small increase in the amounts sorbed between five and ten days. The results based on the solution concentration measurements do not agree well with the results obtained by the direct fiber analyses. However, the general conclusion that sorption continues up to ten days is supported by both sets of data.

The sorption values obtained in the presence of formaldehyde agree with the results obtained from the unprotected samples. This indicated that bacterial attack was not a problem during the time intervals employed. Because the wet pulp was originally stored with formaldehyde, every sorption sample prepared retained a small quantity of preservative.

From the results of these experiments and the preliminary evidence of sorption irreversibility on pages 27 to 28, it was concluded that the ultimate equilibrium must lie well over in the direction of higher sorption. At equilibrium, the extent of the reverse, or desorption, reaction is probably quite limited.

TABLE V

EFFECT OF TIME ON SORPTION

Temp. = 30°C.
pH = 4.5
Nominal Pulp Consistency = 0.50 g./100 ml.

Fraction	Initial Concn., g./l.	Total Vol., ml.	Time, hr.	Residual Concn., g./l.	Specific Sorption: By Concn., Difference, mg./g.	Specific Sorption: By Direct Analysis, mg./g.
1SP	0.171	106	120	0.147	5.08	9.43
			240	0.137	7.20	10.0
1SP	0.326	111	120	0.277	11.1	12.9
			240	0.241	18.9	14.6 (15.0)[1]
16SP	0.165	106	120	0.073	19.5	21.0
			240	0.065	21.2	22.3
16SP	0.315	111	120	0.162	34.0	34.4
			240	0.124	42.3	36.0 (35.7)[1]

[1] Values obtained with added formaldehyde in system.

"DISPERSED CELLULOSE" IN SUPERNATANT SOLUTION ALIQUOTS

As indicated in the preceding experiment, the data in Table V were used to evaluate the quantity of "dispersed cellulose" present in each solution aliquot. Table VI summarizes these data in the form used to determine the quantity of "dispersed cellulose" passed by the glass filter paper. The results of the duplicate total carbon and hemicellulose analyses on each sample are given. By subtracting the hemicellulose content from the total carbohydrate content of each sample, the quantity of "dispersed cellulose" in each sample was obtained.

The range of "dispersed cellulose", or nonhemicellulosic carbohydrates in the aliquots, was 28 to 102 p.p.m. Each sample, although ostensibly prepared and handled in the same fashion as the others, contained a different amount of dispersed material. Since the method of sampling was constant, the variations in quantity must arise from real differences in the extent to which each fiber sample has been peptized. The most probable source of this variation is in the original dispersal of the fibers in the water. Each pulp-water mixture was shaken until the pulp pieces were all dispersed. However, neither a constant time nor a constant shaking force was used. These differences in the degree of physical treatment of the pulp slurries could give rise to the variations in quantity of the "dispersed cellulose" found.

A more subtle factor may be involved if these hemicelluloses have flocculating or deflocculating properties. Differences in the quantity

TABLE VI

NONHEMICELLULOSES CARBOHYDRATES PASSED BY GLASS FILTER PAPER

Fraction	Initial Concn., g./l.	Time, hr.	Total Carbohydrate Concn., g./l.	Hemicellulose Concn., g./l.	Nonhemi. Carbohydrate Concn., g./l.	Av. Nonhemi. Carbohydrate Content, p.p.m.
1SP	0.171	120	0.235	0.146	0.089	
			0.212	0.148	0.064	76
		240	0.201	-----	-----	
			0.194	0.137	0.057	57
1SP	0.326	120	0.381	0.276	0.105	
			0.377	0.278	0.099	102
		240	0.315	0.242	0.073	
			0.315	0.241	0.074	74
16Sp	0.165	120	0.101	0.069	0.032	
			0.101	0.077	0.024	28
		240	0.152	0.064	0.088	
			-----	0.067	-----	88
16SP	0.315	120	0.238	0.155	0.083	
			0.254	0.170	0.084	84
		240	0.174	0.118	0.056	
			0.175	0.130	0.045	50

and nature of each fraction present in solution would then affect the amount of "dispersed cellulose". In the absence of any definite evidence, this possibility remains purely speculative.

Strachan (31) reported that even after repeated water extractions at 15 to 18°C., some 13 to 21 p.p.m. of cellulose continued to be "dissolved". It is the presence of this cellulosic material in solution which necessitates a correction factor when a general carbohydrate measuring technique is employed to measure the sorption of polysaccharides by pulps. The correction due to the dissolved cellulose is subtracted from the apparent concentration of polysaccharide in solution.

For example, it was found (32) that the anthrone technique gave a value corresponding to 0.00224 g. of locust bean gum in the white water (3760 ml.) from a handsheet prepared without the addition of any gum. When gum was actually added to the pulp suspension, the indicated total residual gum content in the same volume of white water ranged from 0.00258 g. to 0.00940 g. These data show that the correction amounted to 24 to 87% of the total carbohydrate content as indicated by the anthrone measurement. If the correction factor were not constant, as the present data indicate it might not have been, then serious errors in the calculated sorption would occur.

The poor precision of measurement reported by Shriver (19), in the case of methylcellulose sorption determinations by the anthrone technique, may also have been due to changes in the value of the correction, from sample to sample, due to the "dissolved" cellulose.

In summary, the data of Table VI showed that significant variations occurred in the amount of "dissolved" cellulose present in the supernatant solutions of pulp samples believed to have been prepared and sampled reproducibly.

EFFECT OF INITIAL CONCENTRATION ON SORPTION

In the time studies described previously, it was found that the initial concentration had a large effect on the amount of hemicellulose sorbed in a given time. To compare the sorption affinity of each fraction for the cellulose, experiments were designed in which the sorption of each fraction after 72 hours was measured as a function of the initial concentration.

After 72 hours, the rates of sorption of the fractions had diminished considerably. Therefore, by measuring the sorption at the end of 72 hours, the differences in the amount of sorption among the four fractions could be demonstrated in each case by a single measurement. For a given initial concentration, these differences in over-all sorption rates may reflect the differences in the tendency to become sorbed (sorption affinity) of the several fractions.

For each fraction, a series of samples was prepared in which only the concentration of hemicellulose was varied; the pH of 4.5, temperature of 30°C., and nominal pulp consistency of 0.50 g./100 ml. were retained as heretofore. At the end of 72 hours of sorption, the fibers were collected and analyzed for their hemicellulose content. The data in Table VII and the curves in Figure 3 summarize the results.

TABLE VII

EFFECT OF INITIAL CONCENTRATION ON SORPTION

Temp. = 30°C.
pH = 4.5
Nominal Pulp Consistency = 0.50 g./100 ml.
Sorption Time = 72 hrs.

Fraction	Hemicellulose Added, % based on pulp	Initial Concn., g./l.	Specific Sorption, mg./g.	Specific Activity of Hemicellulose, cpm./mg.
1SP	1.0	0.050	2.37	9,473
	3.1	0.144	6.80	9,473
	6.2	0.269	12.6	9,473
	10.4	0.412	13.7	9,473
4SP	1.0	0.050	4.48	4,565
	2.0	0.096	8.59	4,565
	3.4[a]	0.156	13.6	8,247
	4.1	0.182	15.1	4,565
	6.9	0.284	27.1	4,565
	6.9[a]	0.286	26.0	8,247
	8.6	0.341	32.1	4,565
	8.6[a]	0.343	29.4	8,247
7SP	1.2	0.064	7.53	11,918
	2.7	0.124	14.8	11,918
	2.9[a]	0.133	15.8	15,135
	3.8[a]	0.172	22.7	15,135
	4.8[a]	0.210	23.8	15,135
	5.7[a]	0.246	27.9	15,135
	8.8	0.363	39.4	11,918
	9.2[a]	0.365	42.2	15,135
	11.0	0.437	49.2	11,918
16SP	1.0	0.049	6.47	6,928
	2.0[a]	0.095	12.9	6,928
	3.1[a]	0.142	15.6	7,011
	4.0[a]	0.182	21.3	6,928
	6.0	0.262	30.5	6,928
	10.0	0.406	42.9	6,928
	12.2[a]	0.503	45.6	13,214
	15.2[a]	0.603	53.4	13,214

[a] Data obtained at later time and with stock solutions of different specific activity.

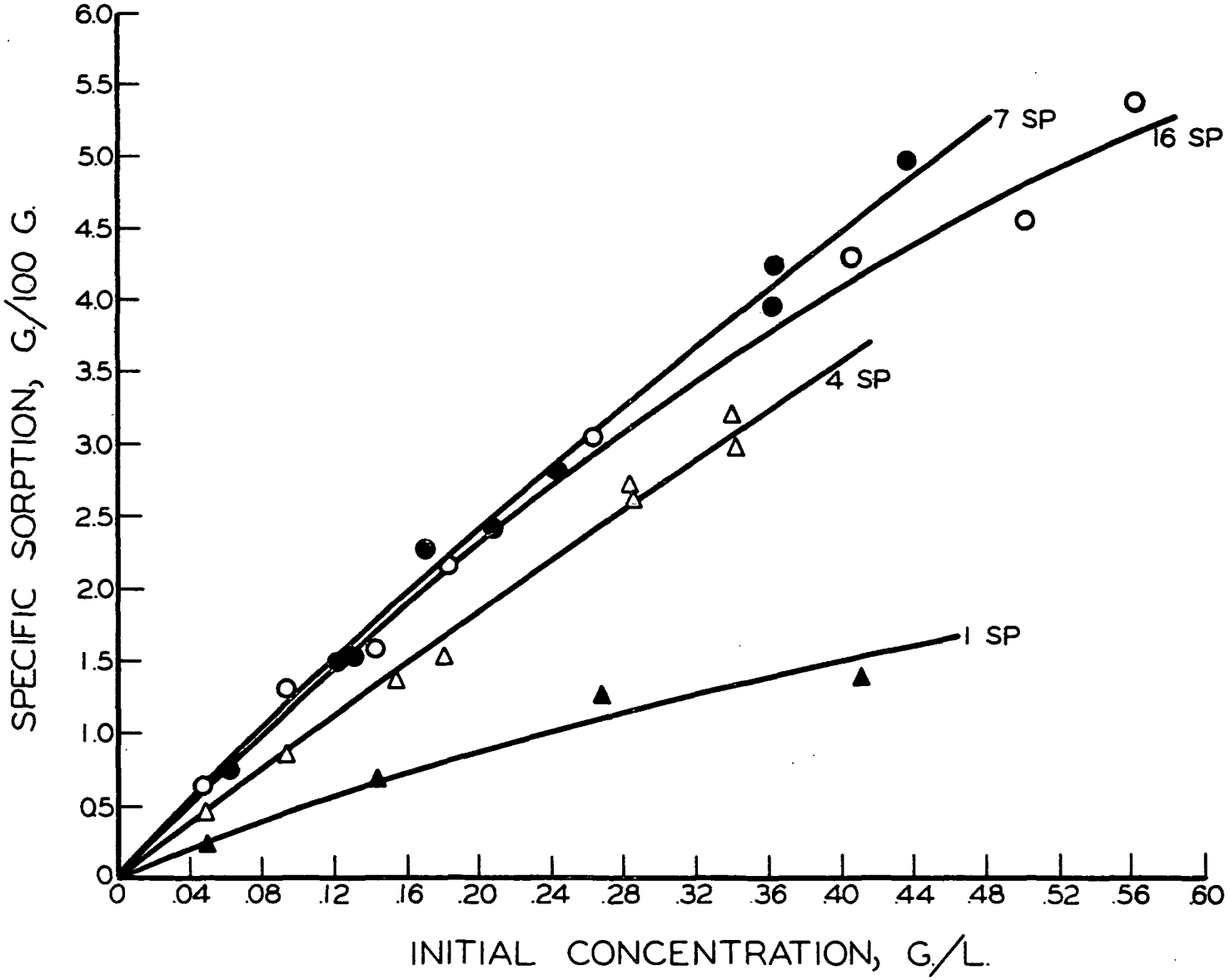

Figure 3. Effect of Initial Concentration on Specific Sorption of Four Fractions

pH = 4.5; Temp. = 30°C.; Time = 72 hr.

The assumption was made previously that the sorption properties of the hemicellulose molecules were unaffected by labeling. The data on the specific activities of the several stock solutions given in Table VII, support the validity of this assumption. For example, assume that the labeled molecules were sorbed more rapidly than the unlabeled. Therefore, measurements made with a hemicellulose mixture of high specific activity i.e., high ratio of labeled to unlabeled hemicellulose, would result in X/M values higher than those which occur if a mixture of lower specific activity were used. Figure 3 shows that the data fall along smooth curves without any marked deviations which might be attributed to differences in the specific activities of the several stock solutions used.

Under the given experimental conditions, the order of sorption of the fractions was 1SP $<$ 4SP $<$ 7SP $\lessapprox$ 16SP. The shapes of the curves of Figure 3 indicate that the fibers will sorb additional hemicellulose with only a slow approach to saturation. The 1SP fraction showed the lowest affinity for the cellulose and the greatest tendency to reach a sorption saturation at some higher initial concentration than those employed. The curves for the 4 and 7SP fractions are almost linear over the concentration range measured. The 7SP and 16SP curves showed very nearly equal sorption values up to about a retention level of 3% on the fibers. Beyond this level, however, the 16SP curve showed a more pronounced concavity towards the concentration axis and, consequently, a somewhat lower sorption than the 7SP for equal concentrations.

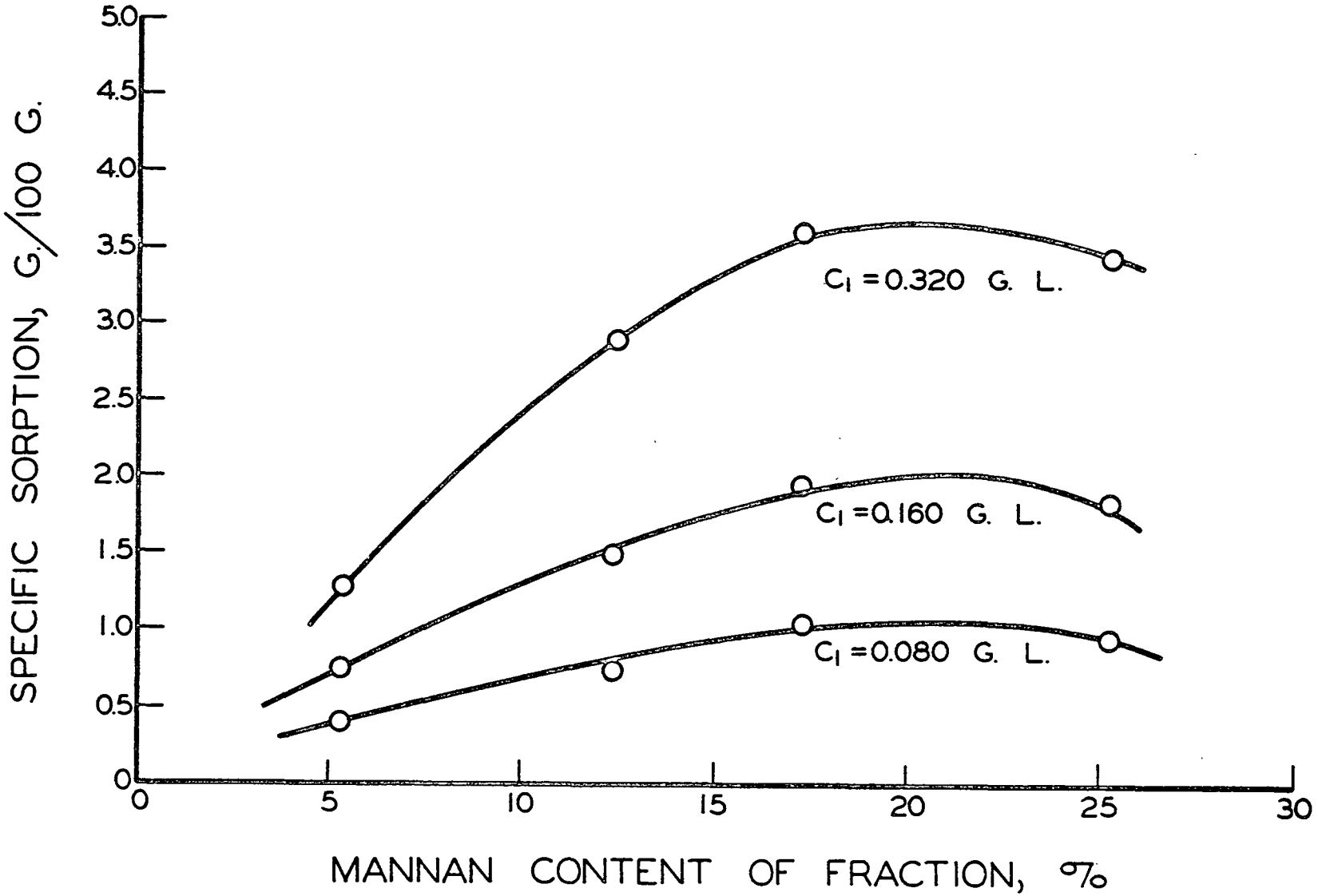

Figure 4. Specific Sorption vs. Mannan Content

pH = 4.5; Temp. = 30°C.; Time = 72 hr.

Data from Figure 3 were plotted to show the amount sorbed as a function of the mannan content of the fractions at three levels of initial concentration. Figure 4 shows these curves. These curves are merely graphical representations of the order of sorption shown in Figure 3 for the four slash pine hemicelluloses, and should not be interpreted as implying a general functional relationship between mannan content and sorption.

The effect of the uronic anhydride content of the fractions on their sorption properties must be considered. The amount of uronic anhydride decreases as the mannan content increases. In the case of polyelectrolytes such as the hemicelluloses, higher carboxyl contents tend to increase water solubility. If increased solubility decreases the sorption tendency of molecules, the order in which the uronic anhydride content of the fractions decreases is in harmony with the sorption order of the fractions. That is, the LSP fraction which has the highest carboxyl content shows the lowest sorption affinity, and is the most soluble. Because the effects of the carboxyl content and the mannan content cannot be separated for these hemicelluloses, the conclusion may be drawn that the fractions having the highest mannan content and lowest uronic anhydride content are sorbed to the greatest extent.

The role of the mannan content of beater adhesives has been discussed in the HISTORICAL REVIEW section. The above conclusion is in general agreement with the conclusions of other workers on the beneficial effects of mannan in beater adhesives.

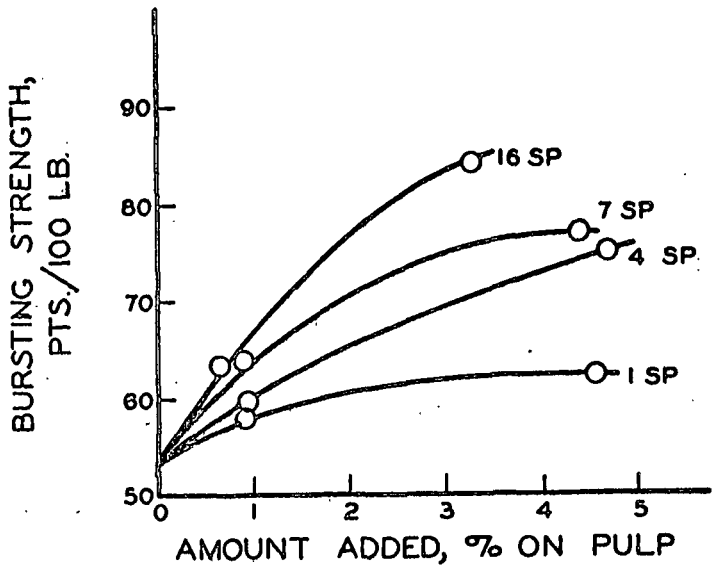

Figure 5. Bursting Strength Increases of Alpha Pulp to Which Slash Pine Hemicelluloses were Added [From data of Thompson, Swanson, and Wise (8)]

By combining the present results with those of Thompson, Swanson, and Wise (8), an attempt was made to compare the adhesive efficiencies of the fractions at equal levels of sorption. The curves of Thompson, et al., relating bursting strength to the amount of hemicellulose added, are reproduced in Figure 5. All the sorption conditions in the present experiments and those of Thompson, et al., were not identical. They added the hemicelluloses in solution to alpha pulp at a consistency of 1.5%, stirred for 1/2 hour at a pH of 4.5 (temperature not given but probably around 20-25°C.), and then diluted the pulp to

0.05% in the sheet mold and formed handsheets. It is assumed for the following discussion that the relative behavior of the four fractions towards the same pulp is the same for any set of constant sorption conditions.

The shape of the 1SP curve in Figure 5 indicates that the adhesive efficiency of this fraction is quite limited. A fivefold increase in the amount added to the fibers resulted in an increase in bursting strength of only 4 pt./100 lb., or 7%. The 1SP curve in Figure 3 shows that the sorption was increased 400% in 72 hours by this five-fold concentration increase. The curves of X/M vs. time shown in Figure 1 indicate that such concentration changes would also result in greatly increased sorption even during the very early stages of the process. Because of the pronounced tendency of the 1SP curve in Figure 5 to rapidly level off, it is apparent that increased retention of this fraction beyond a relatively low value is unaccompanied by significant strength improvements.

The curves of Figure 3 show that in order to obtain the same retention of the 1SP as the 4SP fraction in the same time (e.g., 1.0 g./100 g.), the addition of about 2.5 times as much 1SP as 4SP is required. From the curves of Figure 5, however, it is evident that even an addition ratio of 4:1 (1SP to 4SP) would not result in nearly the same strength increase. Thus, it appears that the 4SP fraction is a better adhesive than the 1SP fraction.

Applying similar reasoning to the 7SP and 4SP fractions leads to the following conclusions. Approximately 1.4-1.5 times as much 4SP as

7SP is required to reach a level of retention of 1.0 g./100 g. Figure 5, however, indicates that about 1.8 times as much 4SP as 7SP must be added to obtain the same bursting strength. On the basis of these estimates it appears that the 7SP fraction is a somewhat better adhesive than the 4SP fraction.

The curves of Figure 3 show that the 7SP and 16SP fractions are sorbed in almost equal amounts when equal concentrations are added to the fibers. However, the curves of Figure 5 show that the 16SP fraction produced greater strength improvements than the 7SP for any level of addition. Therefore, it may be concluded that the 16SP fraction is a better adhesive than the 7SP fraction.

To summarize, the tentative conclusion has been drawn that the strength improving efficiencies of the fractions, when compared on an equal retention basis, are in the same order as the mannan contents of the fractions i.e., 16SP $>$ 7SP $>$ 4SP $>$ 1SP. These findings substantiate the hypotheses of others on the effect of mannan on the strength improving properties of hemicelluloses. The HISTORICAL REVIEW contains a discussion of these hypotheses.

A hypothesis might be offered in which a single "active" polysaccharide is considered to be common to the four fractions. For solubility reasons, or because of the nature of the distribution of this polysaccharide in fibers, the quantity of it may increase in the fractions extracted with higher concentrations of alkali. If this polysaccharide were the agent chiefly responsible for improving sheet

strength, then the hypothesized differences in quantity of this "active" polysaccharide could explain the strength improvements obtained as one proceeds from the 1SP fraction to the 16SP fraction.

REVERSIBILITY STUDIES

EFFECT OF pH, DRYING, AND LEVEL OF RETENTION

Previous data led to the conclusion that sorption equilibrium had not been reached within ten days. Furthermore, the preliminary experiments described on pages 27 to 28 indicated that desorption did not occur in 1 to 14 hours at 25°C. at pH 6.5 when the residual hemicellulose concentration in contact with a pulp-sorbed hemicellulose sample was considerably reduced. These results are indicative of a process wherein equilibrium is reached only after protracted periods of time. The reverse, or desorption reaction in such cases generally proceeds to a very slight, often immeasurable, extent. The experiments in the present section were undertaken to explore the indicated sorption irreversibility of the hemicelluloses under a variety of conditions.

Samples of pulp, containing sorbed hemicelluloses of each fraction, were resuspended in water for 72 hours at the same temperature and pH as that prevailing during the original sorption. The samples for the desorption experiments at pH 10 were obtained from experiments to be described in the next section. The other samples were obtained from the previous concentration studies. In some cases, the pulp-sorbed hemicellulose samples had been air-dried prior to desorption while in other cases the samples were undried. This approach made it

TABLE VIII

EFFECT OF pH, AIR DRYING, AND LEVEL OF RETENTION ON DESORPTION

Fraction	pH	Desorption Time, hours	X/M Before Desorption, mg./g.	X/M After Desorption, mg./g.	Moisture Condition of Sample
1SP	4.5	72	2.37	2.41	A.D. (Air-dry)
1SP	4.5	72	12.6	12.4	Wet
4SP	4.5	72	8.59	8.59	A.D.
4SP	4.5	72	27.1	27.7	Wet
7SP	4.5	72	7.53	7.54	A.D.
7SP	4.5	72	22.0	21.7	Wet
16SP	4.5	3	15.6	15.3	A.D.
16SP	4.5	3	12.5	12.6	A.D.
16SP	4.5	72	44.6	42.0	Wet
16SP	4.5	72	62.0	57.7	Wet
1SP	10	72	4.61	3.69	Wet
1SP	10	72	9.08	7.49	Wet
1SP	10	72	3.42	2.76	A.D.
1SP	10	72	6.41	5.21	A.D.
16SP	10	72	11.6	11.1	Wet
16SP	10	72	27.2	26.4	Wet

possible to determine whether air-drying of the pulp-hemicellulose samples affected the desorption tendencies of the hemicelluloses. Samples at different retention levels were used to determine whether the concentration of sorbed hemicellulose on the fibers was an important factor. The results are summarized in Table VIII.

To determine if desorption had occurred to any significant extent, it was necessary to compare the mean values of the duplicate fiber analyses before and after desorption. The statistical method known as the "Student t" test was employed. A value of t is computed from Equation (1), and this value

$$t = \frac{\bar{X}_B - \bar{X}_A}{\sigma}$$

$\bar{X}_B$ = mean hemicellulose content before desorption

$\bar{X}_A$ = mean hemicellulose content after desorption

σ = standard deviation of measurements

is compared to a table of calculated values of t, at the appropriate number of degrees of freedom, for a test of significance at any chosen confidence level. The value of σ was computed as described in pages 24 and 25.

At pH 4.5, significant desorption was indicated by only the 16SP fraction at the highest levels of retention. When the 1SP fraction was studied at pH 10, significant desorption was apparent at all retention levels. No significant differences in desorption were

found between air-dried and wet pulp-hemicellulose samples. Since the bonding forces were apparently effective in preventing desorption from undried fiber-hemicellulose samples, any increase in these forces upon drying could not have been detected by the above experimental approach. If, on the other hand, air-drying decreased these forces sufficiently enough to permit desorption, then this effect would have been detected. Consequently, it may be concluded that air-drying of pulp-sorbed-hemicellulose samples does not decrease the attractive forces between the hemicellulose and the cellulose.

The desorption of the 16SP fraction, which occurred at the high levels of retention, was interpreted as indicating that the total bonding force holding the last sorbed molecules was probably lower than that holding the molecules sorbed earlier in the process. Implicit in this interpretation is the assumption that the desorbed molecules were those which had been deposited last in the sorption process.

EFFECT OF TEMPERATURE ON SORPTION REVERSIBILITY

For this series of experiments, pulp-hemicellulose samples from sorption runs at 30°C. and pH 4.5 were resuspended in water at pH 4.5 and 45°C. for 72 hours. The hemicellulose content of the fibers was measured at the end of this time and compared with the value before desorption. The "Student *t*" test described in the preceding section was employed to determine whether significant desorption had occurred. Table IX summarizes the results.

TABLE IX

SPECIFIC SORPTION BEFORE AND AFTER
DESORPTION TESTS AT 45°C.

pH = 4.5
Time = 72 hours

Fraction	X/M Before Desorption, mg./g.	X/M After Desorption, mg./g.
1SP	12.6	11.0
1SP	2.77	2.82
4SP	13.6	13.4
4SP	32.1	31.4
7SP	14.8	14.1
7SP	39.4	38.0
16SP	6.47	6.85
16SP	45.6	43.5

These data indicate that only the 16SP fraction at the 45.6 mg./g. level of retention showed significant desorption. Significant desorption of the 16SP fraction at 30°C. was also found in the preceding desorption experiments for samples at, or greater than, this level of retention. In view of this observation, and the fact that significant desorption of the other fractions did not occur at 45°C., it may be concluded that the 15°C. temperature increase was insufficient to desorb the hemicelluloses.

For systems displaying a dynamic equilibrium between sorbed and unsorbed material, resuspension of the sorbent-sorbate in pure solvent, should result in the removal of a significant portion of the sorbate with the establishment of a new equilibrium. That this type of behavior

does not occur, is evident in favor of a "chemical" type of sorption wherein moderately high energy bonds are formed. A mechanism will be proposed in a later section to account for the observed results.

EFFECT OF pH ON SORPTION

To determine the effect of pH on sorption, experiments were run in which the sorption after 72 hours was determined as a function of the initial concentration at a pH of 10. The extreme 1SP and 16SP fractions were selected for study. The results of these experiments are summarized in Table X and are compared in Figure 6 with the results of the same experiments made at pH 4.5, from Table VII.

The sorption after 72 hours at pH 10 was lower than that at pH 4.5 for both fractions. Consequently, the over-all rate of sorption must be lowered at pH 10. This effect may explain why Thompson, Swanson and Wise (8) obtained slightly lower strength improvements at a high pH than at pH 4.5.

The reduced retention under alkaline conditions may be related to the greater solubility of the hemicelluloses in alkaline solutions. Also, the molecular configuration of polyelectrolytes containing ionizable carboxyl groups is affected by pH. Since the sorption of polymers is affected by their molecular configuration in solution, pH may be expected to play an important role. This factor will be discussed more fully in the section on MECHANISM OF SORPTION.

Pearl (18) obtained a similar pH effect in the case of amylose

sorption. He explained the effect as being due to a minimizing of the "retrogradation sorption" of amylose onto already sorbed amylose. However, he reported that the sorption of amylose on cellulose was also reduced by pH in the alkaline range.

TABLE X

SORPTION AT pH 10 AS A FUNCTION OF INITIAL CONCENTRATION

Temp. = 30°C.
Nominal Pulp Consistency = 0.50 g./100 ml.
Sorption Time = 72 hours

Fraction	Hemicellulose Added, % based on pulp	Initial Concn., g./l.	Specific Sorption, mg./g.	Hemicellulose Specific Activity, cpm./mg.
1SP	2.0	0.094	3.42	8511
	4.0	0.181	4.61	8511
	6.0	0.260	6.41	8511
	8.0	0.333	9.10	8511
	10.0	0.400	10.5	8511
16SP	1.0	0.049	5.12	9237
	3.3	0.152	11.6	9237
	4.0	0.181	17.3	9237
	5.0	0.221	19.4	9237
	7.0	0.296	27.2	9237

EFFECT OF TEMPERATURE ON SORPTION

Experiments were designed to evaluate the effect of temperature on the sorption of the 1SP and 16SP fractions. The procedure and sorp-

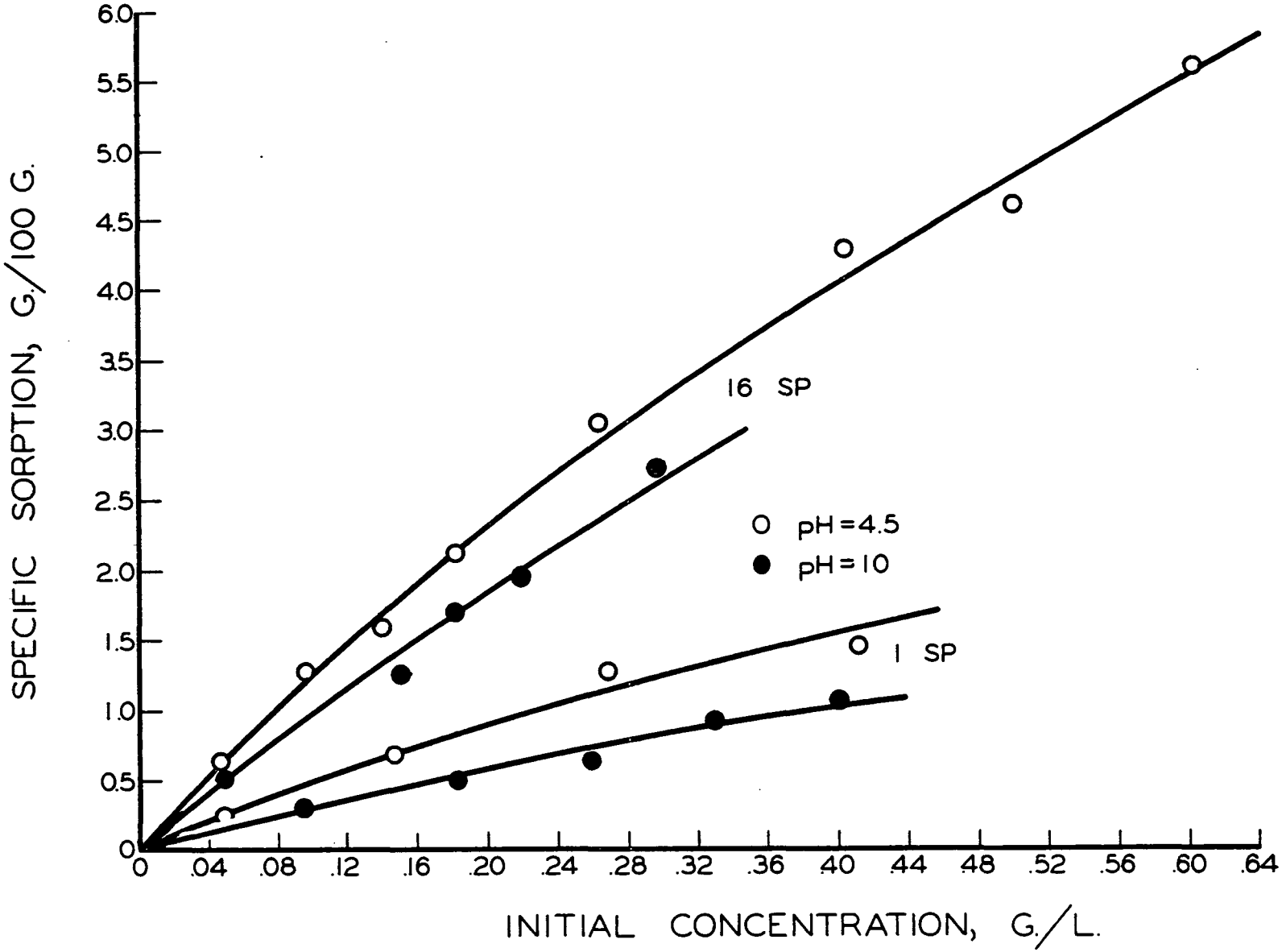

Figure 6. Effect of pH on Specific Sorption

T = 30°C; Consistency = 0.50 g./100 ml.

tion conditions used were the same as those given in the preceding time experiments except that a temperature of 45°C. was employed. The data of Table XI and the curves of Figure 7 summarize the results of these experiments. For purposes of comparison, the curves at 30°C. for the same fractions and initial concentrations are given in Figure 7.

The sorption rates (slope of curves in Figure 7) of both fractions during the early rapid phase of sorption were not significantly affected by the increased temperature. In the case of the 1SP fraction, the retention level at which the slow rate period began was slightly lower than at 30°C. The retention at the end of 72 hours was lowered for the 1SP and slightly increased for the 16SP fraction. These results indicated that differences in the direction of response to temperature changes existed among the fractions.

To study this point further, experiments were conducted in which the sorption after 72 hours was studied as a function of the initial concentration at 45°C. The data from these experiments were compared with the results of the same experiments at 30°C. Table XII shows the data for sorption as a function of initial concentration at 45°C. The curves based on these data are shown in Figure 8. Figures 9 and 10 compare the curves for the four fractions at both temperatures.

At 30°C. (see Figure 3) it was found that at equal initial concentrations the 7 and 16SP fractions were sorbed in nearly equal amounts over a broad range of C_i values. The curves of Figure 8, however, show that at 45°C. the 7SP fraction was sorbed to a greater extent than the 16SP over the entire concentration range. The sorption

TABLE XI

SORPTION AS A FUNCTION OF TIME AT 45°C.

pH = 4.5
Nominal Pulp Consistency = 0.50 g./100 ml.

Fraction	Initial Concn., g./l.	Time, hr.	Specific Sorption, mg./g.	Hemicellulose Sp. Activity, cpm./mg.
1SP	0.141	2	3.98	2236
		6	4.70	2236
		24	4.78	2236
		48	5.44	2236
		72	5.51	2236
16SP	0.142	2	12.1	3046
		6	13.8	3046
		24	15.9	3046
		48	16.3	3046
		70[a]	17.4	1960
		72	17.7	3046
		96[a]	18.4	1960
		125[a]	20.4	1960

[a] Data obtained at a different time with a stock solution of different specific activity.

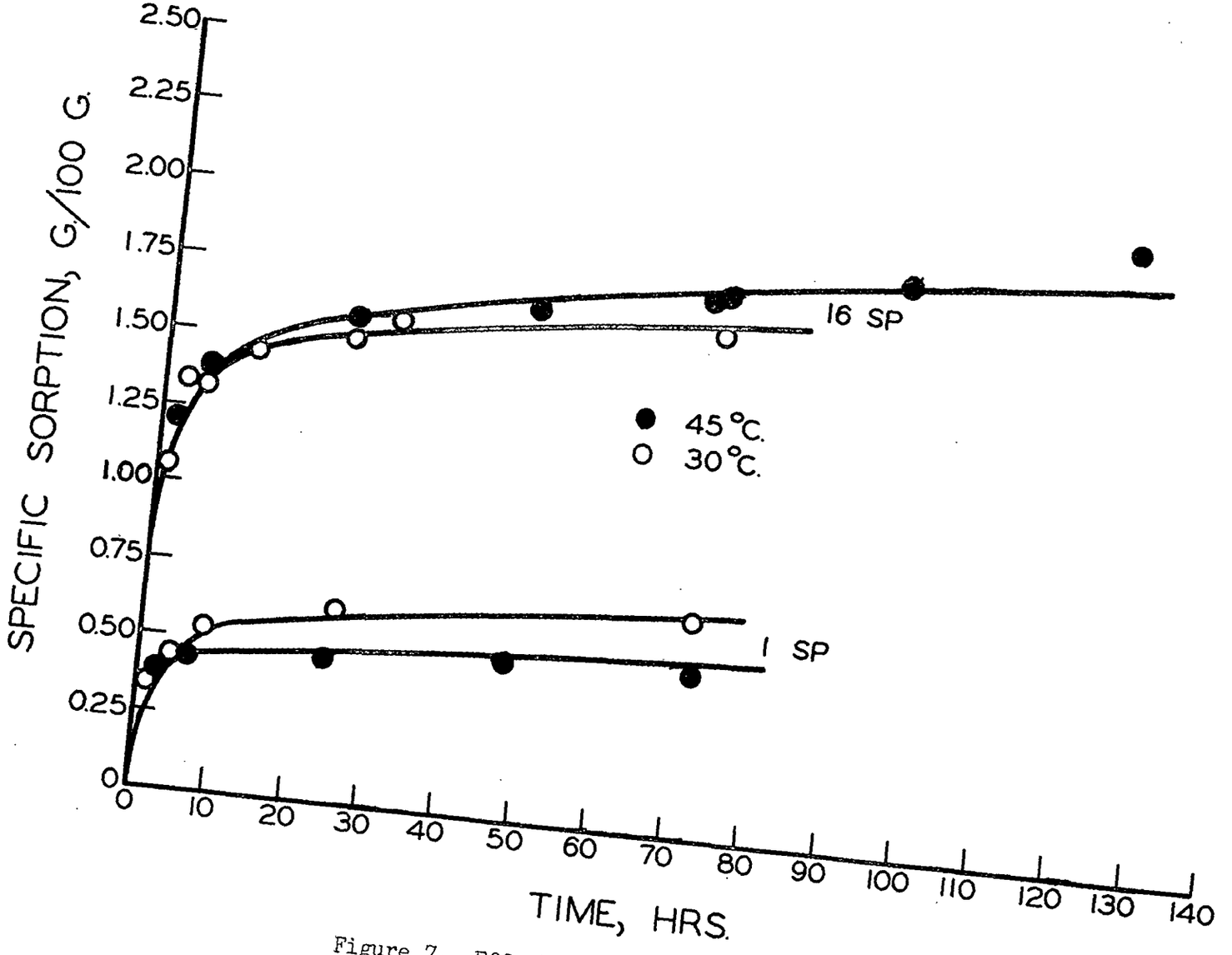

Figure 7. Effect of Temperature on Sorption Rate

C_i = 0.142 g./l.; pH = 4.5

TABLE XII

EFFECT OF INITIAL CONCENTRATION ON SORPTION AT 45°C.

pH = 4.5
Nominal Pulp Consistency = 0.50 g./100 ml.
Sorption Time = 72 hrs.

Fraction	Specific Activity of Hemicellulose cpm./mg.	Hemicellulose Added, % based on pulp	Initial Concn., g./l.	Specific Sorption, mg./g.
1SP	2236	1.5	0.070	3.56
		2.9	0.138	5.61
		5.9	0.262	8.61
		9.9	0.408	11.9
		12.3	0.490	14.9
4SP	4224	1.4	0.070	7.52
		2.9	0.137	12.0
		4.3	0.202	17.5
		7.2	0.324	28.1
		10.8	0.466	38.1
7SP	8500	1.5	0.073	9.46
		3.0	0.141	18.9
		4.5	0.206	26.9
		6.0	0.267	35.1
		10.1	0.417	55.0
16SP	3046	1.8	0.087	10.0
		3.0	0.142	17.2
		6.0	0.270	27.8
		9.0	0.388	37.9
		15.0	0.595	57.5

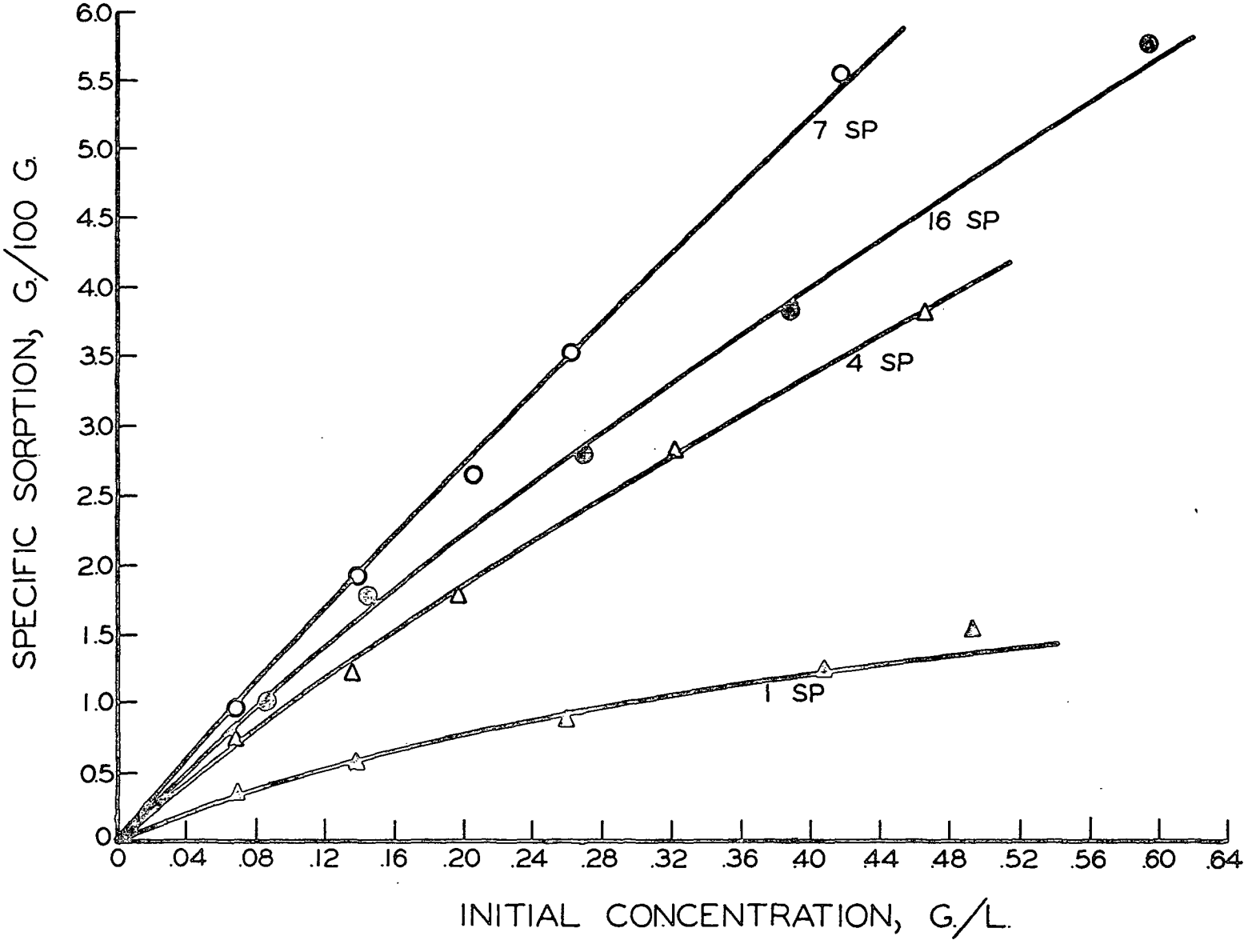

Figure 8. X/M vs. C_i at 45°C.

pH = 4.5; Time = 72 hrs.; Consistency = 0.50 g./100 ml.

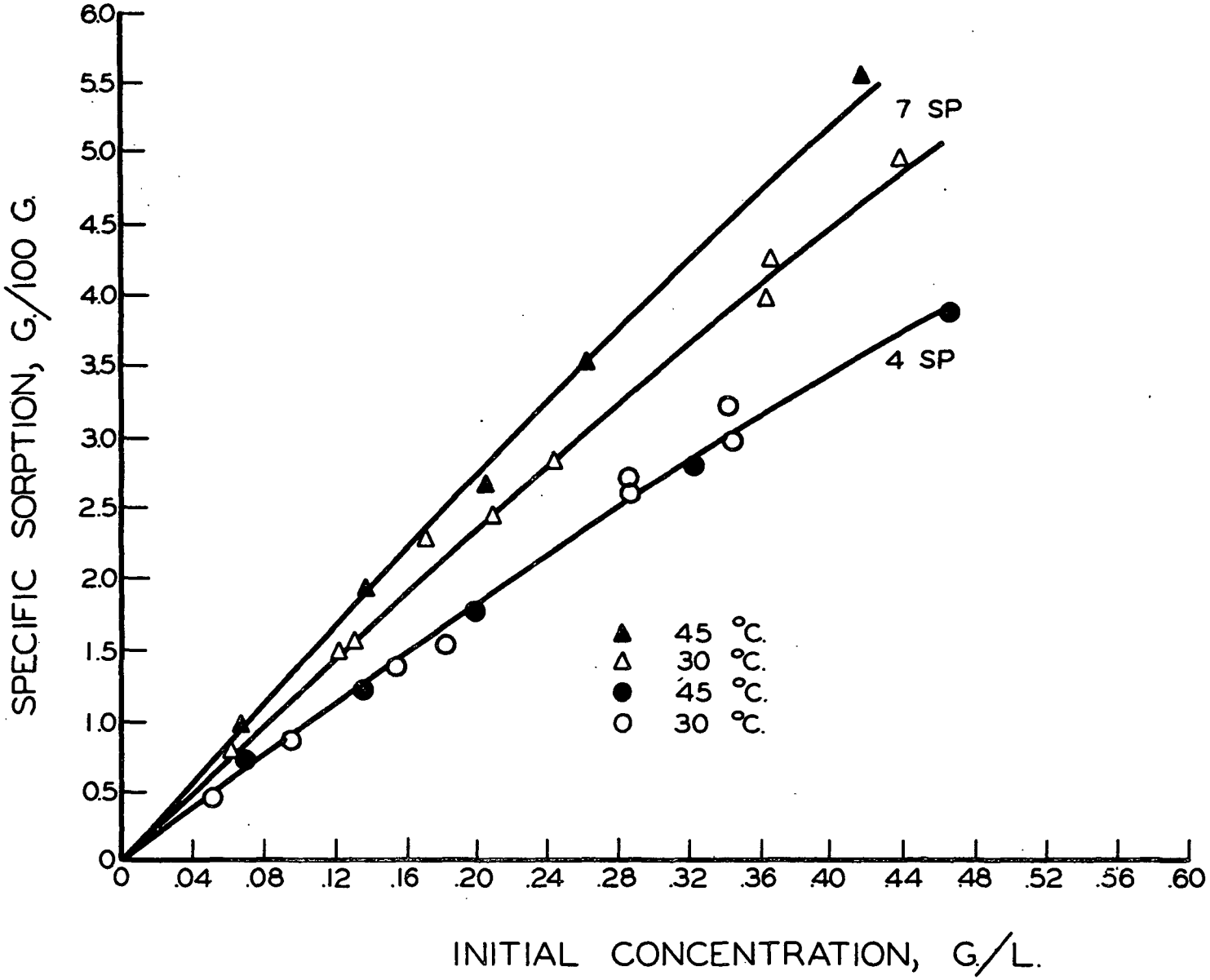

Figure 9. Effect of Temperature on Specific Sorption of 4SP and 7SP Fractions

pH = 4.5; Time = 72 hr.

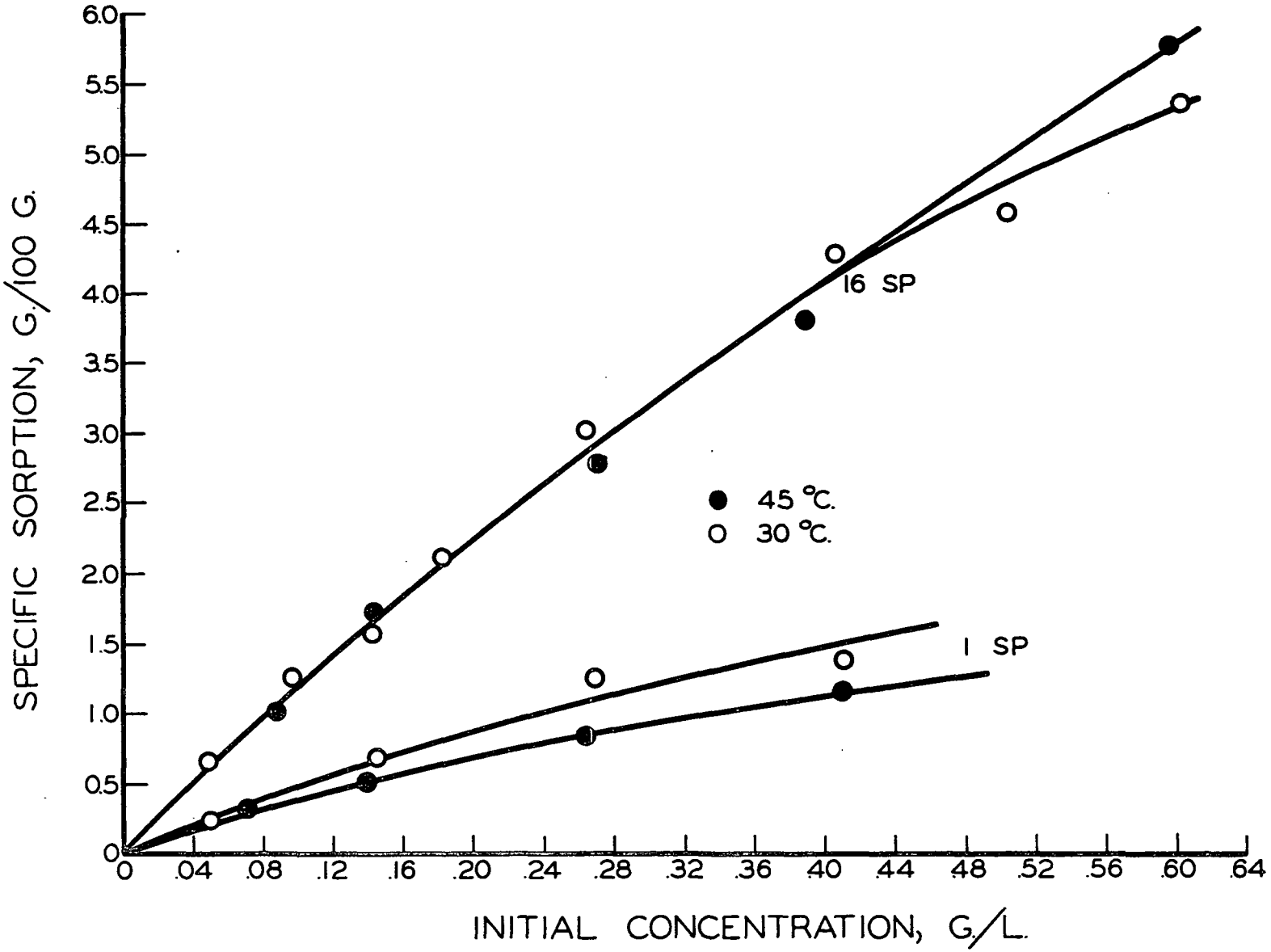

Figure 10. Effect of Temperature on Sorption of 1SP and 16SP Fractions

pH = 4.5; Time = 72 hrs.

of the 16SP fraction was apparently unaffected by the increased temperature (see Figure 10) whereas the sorption of the 7SP fraction was increased (see Figure 9). The 4SP sorption, like the 16SP, was unaffected by the higher temperature. The sorption of the 1SP fraction was reduced at 45°C.

Temperature changes affect both the rate of a reaction and the equilibrium distribution of the components of the reaction. In the present experiments, the effect of temperature on the rate of sorption was considered. In light of the three different effects observed among the four hemicelluloses, no generalizations can be made. The differences among the four hemicelluloses in response to temperature changes is apparently related to the chemical and/or physical differences between them.

EFFECT OF CONSISTENCY ON SORPTION

Pulp slurries were prepared at a consistency of 0.20 g./100 ml. Aliquots of a 7SP stock solution were added to 100-ml. samples of the slurries to adjust the hemicellulose concentration to the desired levels, at 45°C. and a pH of 4.5. Sorption was measured at the end of 72 hours. The results of this experiment were compared with the results of a similar experiment in which the consistency was 0.50 g./100 ml. Table XIII contains the results of the experiments at both consistency levels. Figure 11 is a plot of the sorption as a function of the initial concentration at both consistencies.

The results show that for equal initial concentrations, the samples at the 0.2% consistency had sorbed 100 $\pm$ 20% more hemicellulose

than those at 0.5% consistency. A portion of the observed increase in specific sorption may be attributed to the higher solution concentration maintained during sorption at the low consistency. However, Table XIII shows that the final concentrations in the 0.2% consistency runs were only some 15 to 30% greater than the corresponding final concentrations in the 0.5% consistency runs at the end of the sorption period. Assuming that this margin of difference was maintained throughout the sorption, it would then be necessary to attribute the approximately doubled sorption to these 15 to 30% concentration differences. However, at constant consistency (either 0.5 or 0.20 g./100 ml.), the data show that the solution concentration must be approximately doubled to double the sorption.

A similar consistency effect has been reported in the sorption of other materials by cellulose. Pearl (18) found that when he reduced the consistency of his pulp slurries twelvefold, amylose retentions increased by a factor of 3 to 4. The total suspension volumes and initial concentrations of amylose were held constant and the weight of pulp was reduced. He attributed the pronounced increase in retention solely to the effect of the higher concentrations of amylose in solution during the sorption at the reduced consistency. Shriver (19) reported qualitatively that increased consistency decreased the sorption. He suggested that the greater "frictional effects" between the fibers at higher consistencies may prevent "loosely held methylcellulose from being retained". Thode (32) found that in the case of dye adsorption by cellulose fibers, a consistency decrease of 33% resulted in about a 20% increase in specific sorption at the same final concentration.

TABLE XIII

EFFECT OF CONSISTENCY ON SPECIFIC SORPTION

Temperature = 45°C.
pH = 4.5
Volume of Pulp Slurry = 100 ml.
Time = 72 hrs.

Fraction	Nominal Pulp Consistency, g./100 ml.	Initial Concn., g./l.	Specific Sorption, mg./g.	Final Concn., g./l.[2]	Final Concn., % of initial
7SP	0.50[1]	0.073	9.5	0.028	38.3
		0.141	18.9	0.053	37.6
		0.206	26.9	0.084	40.7
		0.267	35.1	0.112	41.8
		0.417	55.0	0.189	45.3
7SP	0.20	0.073	20.8	0.033	45.2
		0.141	43.1	0.061	43.3
		0.206	60.9	0.095	46.1
		0.267	69.6	0.144	54.0
		0.417	105	0.243	58.3

[1] Data for this consistency taken from Table XII.

[2] Calculated values.

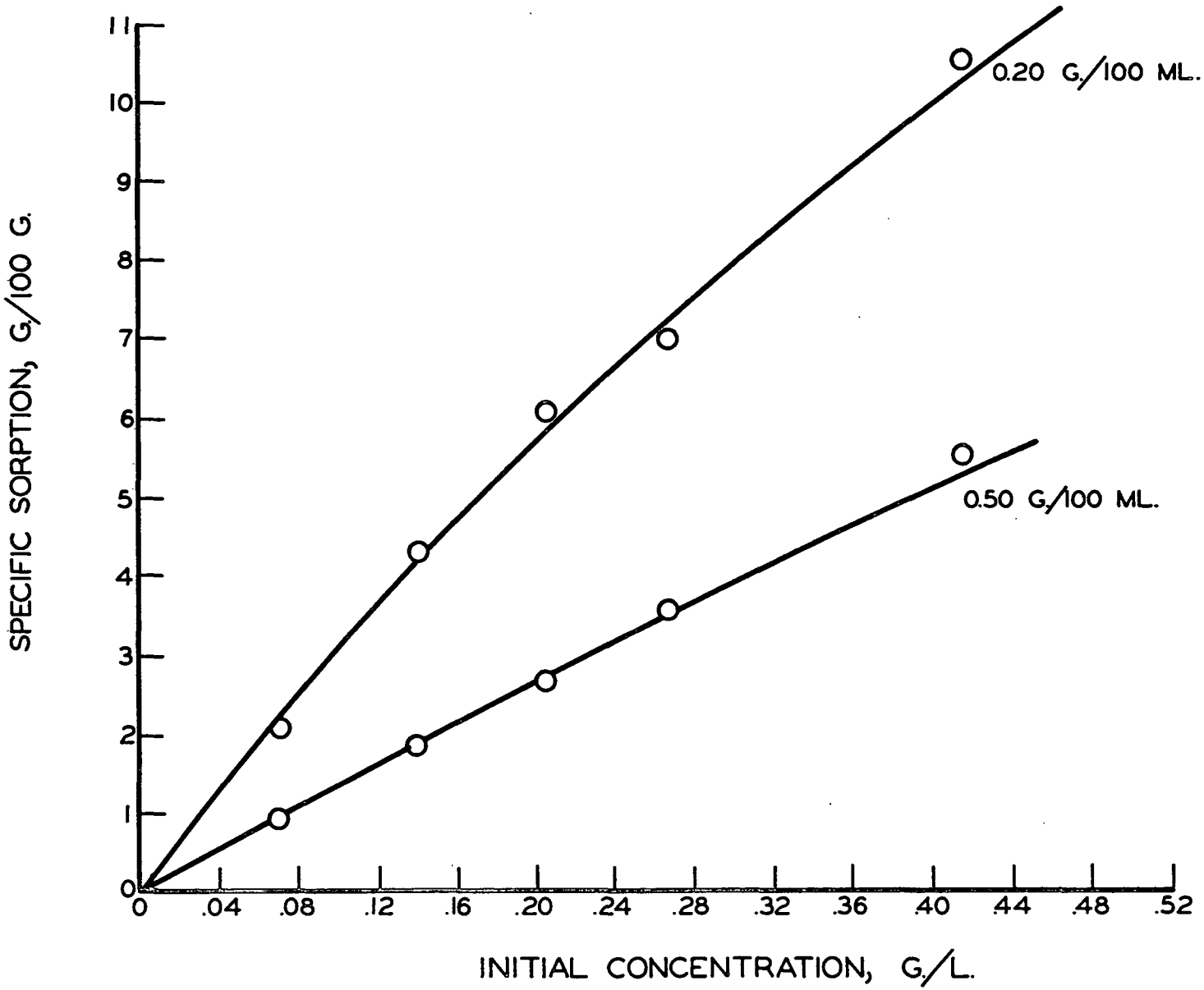

Figure 11. Effect of Consistency on Sorption

Fraction = 7SP; pH = 4.5; Temp. = 45°C; Time = 72 hrs.

The difference between the curvatures of the graphs in Figure 11 is significant. At the 0.50% consistency, the data showed an almost linear relationship. At 0.20%, however, much higher levels of retention were reached for the same concentrations and the curve showed definite concavity downward. These data and similar data obtained previously (see page 42) indicate that, except for the 1SP fraction, levels of retention of 4-6% on the fibers must be reached before the curves of specific sorptions vs. concentrations begin to indicate a tendency to level off at some higher specific sorption level.

APPROACH TO INFINITE BATH CONDITIONS

Additional experiments were designed to determine the amount of hemicellulose which would be sorbed under more nearly constant concentration conditions than those which prevailed in the preceding experiments. Pulp slurries were prepared at a consistency of 0.048 g./100 ml. and the sorption of the 16SP fraction, at two levels of initial concentration, was measured after 72 hours. The results were then compared with the 16SP sorption at 0.50% consistency at the same conditions of initial concentration, temperature, time, and pH. The results are shown in Table XIV.

At the higher 16SP initial concentration, 0.122 g./l., a 4.8% decrease in concentration occurred as a result of sorption at the low consistency. This relatively slight change in concentration indicates that infinite bath conditions were nearly achieved. For the initial

TABLE XIV

EFFECT OF CONSISTENCY ON SORPTION

Temperature = 30°C.
pH = 4.5
Fraction = 16SP
Time = 72 hours

Initial Concn., g./l.	Pulp Consistency, g./100 ml.	Total Vol., ml.	Specific Sorption, mg./g.	Final[1] Concn., g./l.	Final Concn., % of initial
0.080	0.048	416	44.6	0.058	72.5
0.080[2]	0.500	104	10.5	0.030	37.5
0.122	0.048	425	62.1	0.116	95.2
0.122[2]	0.500	106	15.0	0.052	41.1

[1] Concentration after sorption was calculated on the basis of the measured sorption.

[2] Data for these levels taken from 16SP curve of Figure 3.

concentration of 0.122 g./l., the ratio of the final concentration at 0.048% consistency to the final concentration at 0.5% consistency was 2.2:1. The ratio of the specific sorptions, however, was 4.1:1.

At the lower initial concentration, 0.080 g./l., the concentration reduction after sorption at the low consistency was 27.5%. This result showed that infinite bath conditions were not achieved as adequately as when a higher initial concentration was used. The same 2:1 ratio between the final concentrations at the two consistency levels was found in this case, as in the higher initial concentration case. Also, the ratio of the specific sorptions was about 4:1.

The results of these experiments confirmed the previous results for the 7SP fraction. In those experiments a 2.5-fold consistency reduction increased the specific sorption by a factor of about 2. In the present experiments, a 10-fold consistency reduction increased the specific sorption by a factor of about 4. On the basis of these results, it appears that the much greater sorption rates at the low consistencies are probably partly due to factors other than the higher concentration of hemicellulose prevailing during the sorption at low consistencies.

EFFECT OF PRESORBED HEMICELLULOSES ON SORPTION OF OTHER FRACTIONS

These experiments were designed to determine whether the nature of the hemicellulose molecules sorbed initially by fibers would influence the sorption of hemicelluloses from a different fraction onto the same fibers.

A series of pulp slurries was made up as before (pH 4.5, consistency 0.50 g./100 ml., temperature 30°C.) and brought to a hemicellulose concentration of 0.171 g./l. by the addition of 1SP stock solution. The sorption was then determined as a function of time by the usual method. Three identical samples were run for 72 hours and the amount sorbed was measured on one of these samples. After dewatering the pulp samples and washing off the residual 1SP solution, the two pulp-hemicellulose samples were redispersed in solutions of 16SP hemicellulose at the concentration which had existed in the 1SP samples at the end of 72 hours. The two samples were then re-

placed in the constant temperature bath and the sorption of the 16SP fraction by the fibers already containing the 1SP fraction was determined after 24 and 48 hours.

Obviously, there was a marked increase in the sorption rate and amount sorbed when the system was changed from the 1SP fraction to the 16SP fraction, at the same concentration, despite the fact that the fibers used had already sorbed 0.8% (based on the dry fiber) of 1SP hemicellulose. As shown previously, the sorption of the 16SP fraction continued increasing with time.

TABLE XV

THE EFFECT OF PRESORBED 1SP HEMICELLULOSE ON FURTHER SORPTION OF 16SP HEMICELLULOSE

Temperature = 30°C.
pH = 4.5
Nominal Pulp Consistency = 0.50 g./100 ml.

Fraction	Initial Concn., g./l.	Time, hr.	Total Sorption, mg./g.
1SP	0.171	9	5.51
		24	6.66
		48	7.23
		72	8.05
16SP Added to 72 hr. 1SP samples	0.133	24	19.6
		28	24.6 (total sorption time of 120 hrs.)

In the absence of presorbed 1SP hemicellulose, Figure 3 shows that the 16SP sorption would be 16 mg./g. in 72 hours from a solution

of C_i = 0.133 g./l. The results in Table XV show that 16.6 mg./g. of 16SP were sorbed in 48 hours by the fibers containing 1SP hemicellulose. From the time studies shown in Figure 1, it is apparent that at low initial concentrations, e.g. 0.142 g./l., the sorption after 72 hours is only slightly greater than after 48 hours. Thus, it appears that the presence of the 1SP fraction on the fibers did not significantly affect the further sorption of 16SP hemicellulose.

In order to estimate the extent of coverage of the fiber surface at the retention level of 8 mg./g. of 1SP hemicellulose, certain assumptions were made. The hemicellulose was considered as a straight chain molecule of D.P. 100 and molecular weight 16,000. The cross-sectional area of the monomer units was taken as 40 square Ångstroms, the value for glucose. Assuming a flat, parallel arrangement of the sorbed molecules, 8 mg./g. covers an area of 110,000 $cm.^2$. Since the pulp probably had a specific surface area in the range 10 - 50,000 $cm.^2/g.$, it follows that sufficient hemicellulose was sorbed not only to cover this area but also to build up layers approximately 2-10 chains deep. Obviously, these are idealized hypotheses since the sorption arrangement is probably much more random than that assumed. Also, the extent of branching of the hemicellulose and the influence of such branching on sorption are not known. However, the calculations may serve to show the orders of magnitude involved.

It appears, therefore, that despite the extensive surface

coverage by the 1SP fraction, sufficient sorption sites were still available for the 16SP sorption to be unaffected. These sites probably include portions of the sorbed 1SP molecules as well as residual cellulose sites still accessible for sorption.

MECHANISM OF SORPTION

The experimental results will be reviewed briefly before the postulated mechanism is described. The results discussed will be limited initially to those obtained at pH 4.5, 30°C., and 0.50% consistency. The effects of changes in these variables will be discussed separately.

No sorption equilibrium was reached within ten days. Except at levels of retention greater than about 4% on the fibers, resuspending pulp-hemicellulose samples in water at pH 4.5 and 30°C. for three days, did not result in any significant desorption. The reversibility found at these high levels of retention and the irreversibility under the same conditions at the lower levels of retention suggested that a change in the mechanism of sorption probably occurred as greater amounts of hemicellulose were deposited on the fibers.

The sorption rate, as indicated qualitatively by the slopes of the sorption vs. time curves of Figure 1, was initially high but decreased quite rapidly. To study the rate of sorption as a function of concentration, the data in Table IV were recalculated. The mean sorption rate over a given time interval and the mean concentration which existed during the same time interval were calculated. Table XVI summarizes these calculated values. Figure 12 is a plot of the sorption rate vs. the mean concentration for both the 1SP and 16SP fractions at the same initial concentration. The curves of Figure 12 are not meant to represent a general relationship between rate and concentration. They represent, rather, the relationship which prevailed for one particular set of values of such important factors as initial concentration, level of fiber surface coverage, etc.

TABLE XVI

SORPTION RATE AS A FUNCTION OF HEMICELLULOSE CONCENTRATION
(Based on Data from Table IV)

pH = 4.5
Temp. = 30°C.
C_i = 0.142 g./l.

Time Interval, hr.	Length of Time Interval, hr.	Total Sorption, X/M, at end of interval, mg./g.	Increase in X/M in Time Interval, mg./g.	Sorption Rate During Interval, mg./g./hr.	Av. Concn. During Time Interval, g./l.
			1SP FRACTION		
0 - 1	1	3.46	3.46	3.46	0.136
1 - 4	3	4.36	0.90	0.30	0.126
4 - 8	4	5.29	0.93	0.23	0.122
8 - 25	17	6.41	1.12	0.066	0.117
25 - 72	47	6.80	0.39	0.008	0.114
			16SP FRACTION		
0 - 1	1	10.6	10.6	10.6	0.118
1 - 3	2	13.1	2.5	1.25	0.088
3 - 5.5	2.5	13.5	0.4	0.160	0.080
5.5 - 12	6.5	14.1	0.6	0.092	0.078
12 - 24	12	15.1	1.0	0.083	0.075
24 - 30	6	15.6	0.5	0.083	0.071
30 - 72	42	16.1	0.5	0.012	0.069

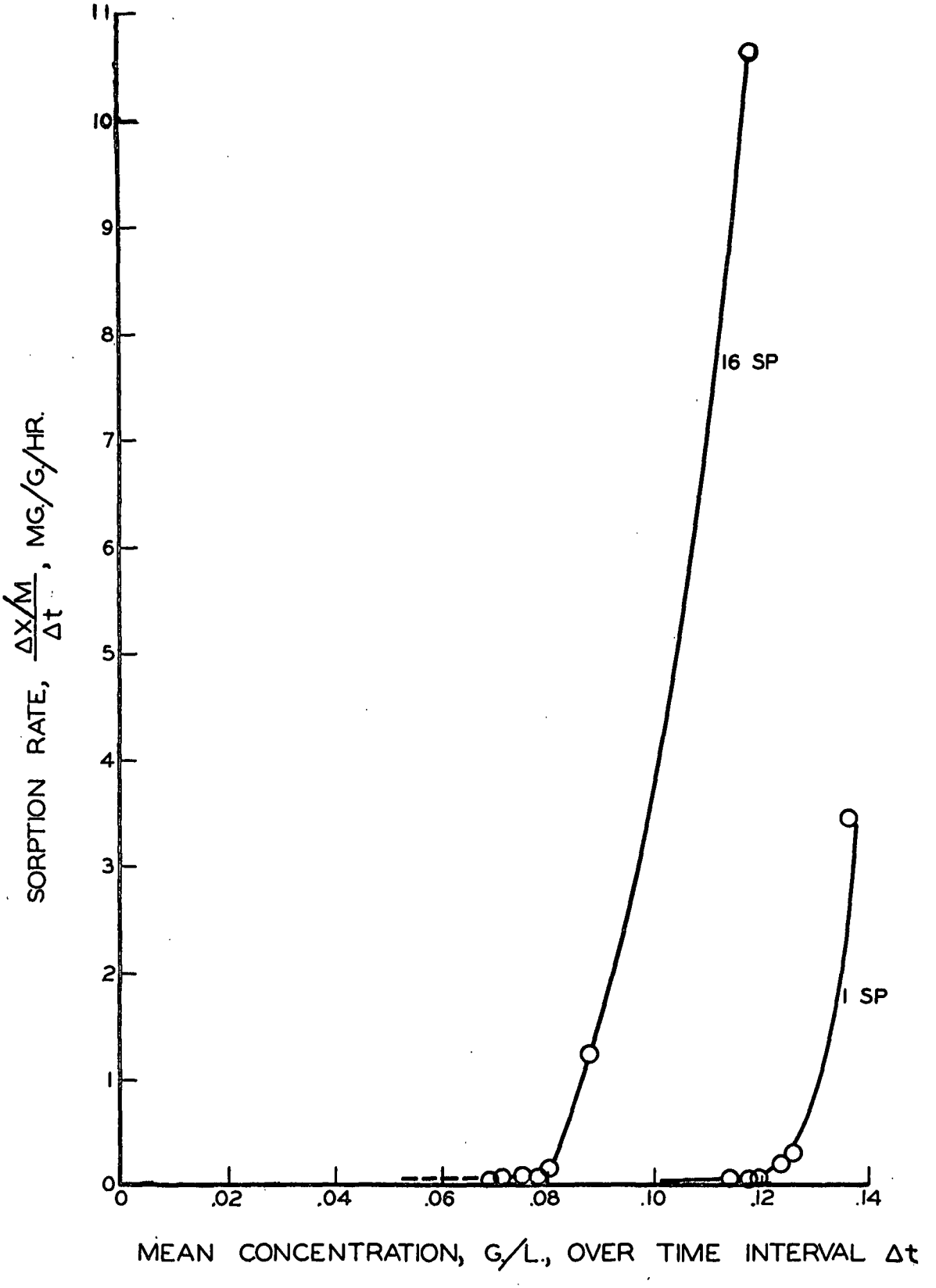

Figure 12. Sorption Rates vs. Solution Concentration. Empirical Relationship for Course of Given Experiment. pH = 4.5; Temp. = 30°C.; C_i = 0.142 g./l.; Consistency = 0.50 g./100 ml.

The curves of Figure 12 show the rapid decrease in sorption rate with decreasing concentration. The sudden, almost abrupt, change to very slow rates at a certain concentration is of considerable interest. If the driving force for sorption were solely a function of concentration, such an abrupt change in rate would not occur. In physical adsorption systems, the rate of sorption is decreased in proportion to the increase in the rate of the reverse, or desorption, reaction. In the present hemicellulose-pulp systems, no desorption reaction could be detected for retention levels below about 40 mg./g. Thus, it appears that after the initial rapid sorption of hemicellulose on the surface of the cellulose has occurred, the resulting new cellulose-hemicellulose surface tends to continue sorbing additional molecules at a slower rate. The nature of the bonding forces responsible for sorbate retention are important and their consideration follows.

The hemicelluloses are rich in strongly electronegative groups i.e., carboxyl and primary and secondary hydroxyls. According to Pauling (34), these groups can form hydrogen bonds relatively easily with similar groups. In the case of polymers containing these electronegative groups distributed all along their length, multiple hydrogen bond formation is possible. Such multiple bond formation between a polymeric sorbate and a sorbent also having electronegative groups distributed along its surface, could result in a high degree of sorption irreversibility. In the present case of cellulose-hemicellulose sorption systems, such irreversibility was encountered. Only at high levels of retention did some reversibility occur. Hence,

it has been concluded that multiple hydrogen bond formation between the hemicelluloses and the exposed cellulose surface occurred. Furthermore, it appears that the hemicelluloses hydrogen bond to already sorbed hemicellulose to form the equivalent of many "layers" of firmly bound hemicellulose molecules on the fiber surface. The steric factors involved in this phase of the over-all sorption process will be discussed subsequently.

At the particular time and concentration (ca. 0.08 g./l.) where the 16SP curve of rate vs. concentration (Figure 12) broke sharply, it was estimated that the retention level of 13-14 mg./g. which had been reached was sufficient not only to cover the available cellulose surface, but also to form multilayers of sorbed hemicellulose many molecules thick. At the corresponding time and concentration, the retention level of the 1SP fraction was 3-4 mg./g., a quantity estimated to be adequate to cover the cellulose surface. However, these estimates were based on calculations which assumed that the polymer molecules were sorbed in a flat, parallel type of arrangement on the fiber surface. In this type of arrangement, each polymer molecule would occupy an area equal to the sum of the areas occupied by each of the monomeric units.

The above assumption is not fully in harmony with the recent polymer adsorption theory proposed in papers by Frisch, Simha and Eirich (35), Simha, Frisch, and Eirich (36), and Frisch and Simha (37). According to their statistical mechanical interpretation,

flexible macromolecules are adsorbed on substrates via segments, or short sequences of chains. The adsorbed segments are linked to each other via unadsorbed "bridges" or "loops" which extend into the solution. Segments at the ends of the molecules may also be unadsorbed and extend into the solution. Therefore, according to this theory, the calculations made previously of the surface area covered by a given mass of sorbed hemicellulose gave values which were too high. A cellulose surface which was considered covered by sorbed hemicellulose was actually available for further sorption. However, these areas would be rendered less accessible to hemicellulose molecules in solution by the partial blocking effect of the adjacent sorbed molecules, segments of which could extend into the solution immediately above and around the otherwise available area. Sorption at these sites would then proceed slowly, and probably only to a limited extent, because the blocking effect around individual sites would increase as the over-all amount sorbed increased.

Increased sorption, however, continued to result as the hemicellulose solution concentration was increased (see for example, Table VII). The major portion of the sorption which occurs after the initial cellulose surface coverage must occur via bonding between already sorbed hemicelluloses and the hemicelluloses in solution. As greater amounts of hemicellulose become sorbed, the extent of multiple bond formation probably decreases. The appearance of some sorption reversibility at high levels of retention supports this conclusion. A molecule is desorbed when all the bonds

holding it to the sorbent are broken simultaneously. Therefore, the probability of desorption would increase as the number of bonds involved in the retention of each polymer molecule become smaller. The decrease in the number of bonds formed between the sorbate and sorbent at the high levels of retention is attributed to the increased randomness of arrangement of the sorbed molecules. This increased randomness makes it more difficult for the necessary presorption orientation to occur between sorbate and sorbent. Consequently, the probability is increased that fewer bonds will be formed.

The sorption mechanism may be represented illustratively as follows:

(1) Cellulose surface + hemicellulose $\xrightarrow{\text{rapid}}$ cellulose-hemicellulose

(2) Cellulose-hemicellulose + hemicellulose $\underset{\text{very slow}}{\overset{\text{slow}}{\rightleftharpoons}}$ cellulose-hemicellulose-hemicellulose

Reaction (1) occurs as soon as the fibers and hemicellulose solution are brought into contact. When this rapid reaction has proceeded until the cellulose surface is essentially covered, Reaction (2) begins to occur at a slower rate. Reaction (2) can occur as soon as the first molecule of hemicellulose is sorbed by the cellulose. However, as long as cellulose surface is available, Reaction (1) will be favored. When Reaction (2) has proceeded to a sufficient extent, desorption can occur to a limited degree and at a very slow rate. The rate of desorption in Reaction (2) will increase as the

amount of sorbed hemicellulose increases until the desorption rate equals the sorption rate and an equilibrium is established. This equilibrium probably occurs at much higher levels of retention than any reached in the present experiments.

The above mechanism is applicable to each of the four hemicelluloses studied. The quantitative differences which were found, are attributable to differences in the chemical and/or physical composition of the fractions. It was found that the sorption of the four fractions increased with increasing mannan content up to about 18% mannan after which the sorption decreased slightly.

Diffusion of the hemicellulose polymers into the pores of the cellulose is possible. If diffusion occurred to a significant extent and at a rapid rate during the initial phase of the sorption, its effect could not be separated from the surface adsorption that has been assumed. If, however, diffusion proceeded at a slow rate, as is most likely, its effect on the mechanism as postulated would be slight. The initial rapid surface coverage would reduce the possibility of further intracellulose diffusion by partially blocking the crevices and pores with segments of adsorbed chains in the immediate vicinity of the pore openings. Heuser (38) states that these pores, or "canals" in the fibers, range in width from 1000 to 50 Å, and even down to 10 Å. Thus, a linear polymer molecule would have to migrate through the solution with its long axis parallel to the walls of the pore to avoid becoming adsorbed very near the beginning of the pore. With flexible polymer

molecules, such orientation is highly unlikely. Pearl (18) concluded that the total volume of these pores was small enough to consume "very little amylose" filling them. In light of the considerations discussed, diffusion of the hemicelluloses into the fibers is ruled out as an important factor in the sorption of hemicelluloses from solution.

RETROGRADATION AS RELATED TO SORPTION

Pearl (18) found that the sorption of amylose by cellulose continued slowly until the amylose was completely removed from solution. Up to 600 hours were required depending on the initial concentration of amylose. He concluded that the continuing deposition of amylose on amylose already sorbed was analogous to the retrogradation of starch solutions. In order to cause his otherwise stable stock solutions of amylose to retrograde, he had to seed the solutions with some previously retrograded amylose. Pearl reasoned that cellulose containing sorbed amylose could act as a seeding agent to induce retrogradation sorption.

The continuing sorption of the hemicelluloses with time is analogous to the continuing increase of amylose sorption with time. However, no direct evidence is available on the stability or instability of aqueous hemicellulose solutions. Some indirect evidence may be cited. In the present work, it was found that hemicellulose solutions underwent a slow decrease in specific viscosity with time. No measurable decrease in concentration was found. It is possible that some type of molecular aggregation, short of precipitation, occurred

in the solution. Yundt (9) found that under certain conditions, xylan could be crystallized from aqueous solutions. Crystallization is basically a retrogradation phenomenon in which the molecules become associated in highly ordered aggregates. These results suggest that the hemicelluloses in solution may retrograde. Consequently, the observed continuing slow sorption of the hemicelluloses with time may be partly due to a retrogradation effect.

ROLE OF pH IN HEMICELLULOSE SORPTION

At pH 10, the amount of 1SP fraction sorbed was reduced 40% relative to the amount sorbed at pH 4.5, while the sorption of the 16SP fraction was reduced about 20-25% at pH 10. These data were obtained from Figure 6 which shows the sorption after 72 hours as a function of the initial concentration at pH 4.5 and 10.

The solubility of hemicelluloses and their molecular configuration in solution are affect by pH. It is interesting to note that the sorption of the fraction extracted with the lowest concentration of KOH i.e., the 1SP, was affected the most by the increase in pH. The greater solubility of this material at high pH may be partly responsible for its reduced sorption.

Cellulose is negatively charged in aqueous suspensions. The hemicelluloses used contain relatively large proportions of negatively charged carboxyl groups. Therefore, a net electrostatic repulsive force must exist between the suspended cellulose and the hemicellulose in solution. Since sorption did occur at both pH

4.5 and 10, the magnitude of this charge barrier was apparently insufficient to prevent the molecules from approaching closely enough to become sorbed. However, changes in the magnitude of this repulsive force could produce changes in the over-all rate of sorption of the molecule.

At low pH, the ionization of the carboxyl groups is reduced and the net repulsive force between the cellulose and hemicellulose is consequently reduced. This would result in an increased tendency for sorption. According to Michaels (39), however, an opposing effect is also introduced, which is due to the increased tendency of the macromolecules to become more coiled at low pH. Such coiling increases the degree of intramolecular association and reduces the number of available bonding groups along the chain.

At high pH, the ionization of the carboxyl groups increases as, consequently, does the repulsive force between sorbate and sorbent. This would tend to decrease the sorption. However, as in the low pH case, an opposing effect also occurs. The extent of intramolecular association is decreased, resulting in a more elongated, or less coiled configuration. This configuration tends to favor adsorption. Since it was found that sorption diminished at high pH, the increased repulsive force must be of greater importance than the decrease in intramolecular association. Conversely, at pH 4.5, the coiling of the molecules is probably not great enough to offset the effect of the decreased repulsive force. Michaels and Morelos (40) reported that certain polyelectrolytes e.g., partially

hydrolyzed polyacrylamide, can exist in relatively uncoiled forms in the pH range of 3.0-6.0.

EFFECT OF TEMPERATURE

When the temperature of sorption was raised from 30 to 45°C., three different effects were observed. The 1SP sorption was reduced, the 7SP sorption was increased, and the 4SP and 16SP sorptions were unaffected. These results are shown in Figures 8-10.

Where an activation energy requirement is significant, higher temperatures tend to increase the speed of reaction. Considering the present results as a whole, therefore, it appears that the activation energies involved in the adsorption of the hemicelluloses by cellulose are low. The extent of a reaction at equilibrium, however, depends on whether it is exothermic or endothermic. Since equilibrium was not reached in any case, the extent of hemicellulose adsorption was compared after an arbitrary, but constant, time interval (72 hours). As a result of this experimental approach, therefore, the results described above refer to differences in the over-all rates of sorption of the four fractions caused by the 15°C., increase in temperature.

The reversibility studies described on pages 51 to 52 showed that none of the hemicelluloses were desorbed when pulp-hemicellulose samples from 30°C. sorption runs were redispersed in water at 45°C. Thus, it may be concluded that when once formed, the hydrogen bonds between the hemicellulose and the cellulose are

strong enough to resist the rupturing tendency introduced by the increase in thermal agitation at 45°C.

Simha, Frisch, and Eirich (36) discussed the various factors which influence the temperature coefficient of sorption of polymeric materials from solution. These factors were listed by them as follows: (a) the dissociation from the surface of isolated polymer segments and the loosening of lateral interactions, (b) the improvement of the solvent with temperature, (c) the contribution of translational and vibrational degrees of freedom and of solvent density, and (d) the flexibility parameter of the dissolved polymer molecules. Of these several effects, only the possible repulsion between segments in (a), the density and vibrational changes in (c), and the change in flexibility parameter, (d), with increased temperature, tend to make for a positive temperature coefficient of sorption. They concluded that although the change in flexibility parameter with temperature is small, it can overbalance the other factors listed in (a) through (c) and produce increased sorption with increased temperature. Obviously, for a given solvent, the physical and/or chemical composition of the polymer will determine whether a positive or negative coefficient of sorption will obtain.

In the present case, the multiplicity of observed temperature effects on the sorption of the hemicelluloses may be attributed to differences in the relative magnitudes of the above factors among the several fractions.

Both positive and negative temperature coefficients have been reported for many other polymers. For example, Pearl (18) found a negative coefficient in the case of amylose-on-cellulose sorption. Shriver (19) found a positive coefficient for methylcellulose-on-cellulose. Koral, Ullman, and Eirich (41) reported that the sorption of partially hydrolyzed polyvinyl acetate on solid surfaces was affected in only a "minor way" by temperature changes. Trout (42) found a negative coefficient for the sorption of polyethylenimine on cellulose.

EFFECT OF CONSISTENCY

The experimental results described on pages 63 to 69 showed that the specific sorption of the hemicelluloses was increased as the pulp consistency was decreased, other conditions being equal. For equal initial concentrations of hemicellulose, the concentration in the low consistency solutions at any time after the start of sorption was higher than that in the corresponding high consistency runs. However, it was concluded that the magnitude of these concentration differences was insufficient to account satisfactorily and entirely for the large increase in the specific sorption.

When a beaten, unfractionated pulp sample is dispersed in water, a system containing an extremely broad spectrum of particles in various degrees of aggregation is created. These particles range in size from colloidal, and perhaps even molecular, dimensions, to the large, and more obvious, discrete fibers. The specific surface

area of each group of particles of given dimensional limits also varies widely. For example, Ingmanson (43) obtained the following specific surface data, from filtration resistance measurements, for a bleached sulfite pulp beaten to 765 ml. S.R. freeness; whole pulp, 24,000 $cm.^2/g.$, discrete fibers, 10,000 $cm.^2/g.$, and material passing through the 150-mesh screen of a Bauer-McNett classifier, 120,000 $cm.^2/g.$ The latter value is actually conservative because some relatively large fiber fragments had passed through the screen and were included in the measurement. The material which passed through the 150-mesh screen represented 10% of the total weight of the pulp.

Where one is dealing with a phenomenon strongly dependent on surface, such as adsorption, the availability or accessibility of the tremendous surfaces represented by the smaller particles is particularly important. Grace (44) found that the effective specific surface area for a given mass of particles in the flocculated state was less than when the same quantity of particles was in a dispersed state. He measured the filtration resistance of cakes composed of particles such as calcium carbonate, polystyrene latex, Super Cel, titanium dioxide, etc., deposited on a septum from dispersions in various degrees of flocculation. The more irregular the particle shapes, the more readily did they tend to flocculate.

For flocculation effects to alter the sorption of the hemicelluloses, it would be necessary for the fibers in the flocs to be bound together very tightly so that the surface areas of the fibers

in contact would be unavailable to macromolecules in solution. Also, the total weight of fibers and/or "fines" involved in such flocculation would have to be great enough to represent more than a very small fraction of the total weight of pulp in the suspension. Furthermore, it would be necessary for these flocs to disperse, or to form more slowly, when the consistency was reduced from 0.5 to 0.2%. In flocculation terms, such a consistency change is not normally considered great enough to materially alter the gross flocculation behavior of pulp suspensions.

The hemicelluloses conceivably could affect the flocculation of the fibers. For example, it has been observed (45) that at very low concentrations methylcellulose acts as a flocculating agent and decreases the value of the "cellulose blank" in the supernatant solution of pulp slurries. At high concentrations, however, it acts as a deflocculent and the value of the "cellulose blank" is increased. A similar effect might be involved in hemicellulose-pulp suspensions but in the absence of any evidence the existence of this effect must remain purely speculative.

From mass action considerations alone, the specific sorption at low consistencies should be greater than at high consistencies. In solutions of equal initial hemicellulose concentration, the instantaneous concentration after the start of sorption will be higher at all times for the pulp samples at low consistency than at high consistency. A smaller quantity of hemicellulose is removed from solution by the lower weight of pulp and, therefore, the con-

centration of hemicellulose remains higher. If the concentration of hemicellulose were the only factor affecting the rate of sorption, a closer correspondence between the final concentrations and the specific sorptions than that found would be expected.

It was shown previously (see pages 73 to 80) that, for a given initial concentration, the sorption rate decreases much more rapidly than would be expected from the drop in concentration alone. This was attributed to the onset of the slower process of hemicellulose-on-hemicellulose sorption after the fiber surface had become essentially covered with adsorbed hemicellulose. Therefore, it is not possible to quantitatively relate specific sorption values with final concentrations after an arbitrary time interval. A detailed study of the sorption rate as a function of the extent of fiber surface coverage, for several values of initial concentration, would be required to develop this relationship.

Consistencies were reduced by two methods. In one set of experiments a constant volume of about 100 ml. of hemicellulose solution was used and sorption samples of equal initial concentration were prepared at two consistencies. These samples differed only in the total weight of pulp present in each, e.g. 0.5 g. of pulp in 100 ml. of solution compared with 0.2 g. of pulp in 100 ml. of equal initial hemicellulose concentration. As discussed above, the 0.2 g. of pulp removed less hemicellulose from the 100 ml. of solution than the 0.5 g. of pulp thus maintaining a higher hemicellulose concentration during the entire sorption. This higher concentration

tended to increase the specific sorption in a given time. In the other set of experiments, 0.2 g. of pulp were dispersed in about 400 ml. of hemicellulose solution producing a consistency of about 0.05%. The specific sorption at this consistency was about double the specific sorption at 0.2% (0.2 g. pulp in 100 ml. total volume) despite the fact that equal weights of pulp were dispersed in solutions of equal initial concentration.

Since the specific sorption was greater at the lower consistency (for the same total quantity of pulp), it appears that more sorption sites, or a greater available area per unit weight of pulp, became available at the lower consistency. Additional experimentation is required to show whether still greater consistency reductions, using a constant weight of pulp and a constant initial concentration, would produce still greater specific sorption.

It has been tentatively hypothesized that the total fiber surface area available for the adsorption of hemicelluloses or other macromolecules increases with decreasing consistency. However, this increase in total available surface probably does not become significant until very low consistencies are reached.

GENERAL SUMMARY

A new method for studying the sorption of polysaccharides by cellulose was developed. The method was applied to a study of the sorption, on alpha pulp fibers, of four hemicellulose fractions isolated from slash pine. The essential points of the method are as follows:

(1) The polysaccharide is labeled with carbon-14 by a Kiliani cyanohydrin reaction, using $KC^{14}N$, followed by hydrolysis to the corresponding $-C^{14}O_2H$.

(2) The labeled product is diluted with unlabeled material and the specific activity of the mixture is determined.

(3) The pulp sample containing the sorbed hemicellulose mixture is oxidized completely to carbon dioxide and water.

(4) The amount of carbon dioxide is measured manometrically and is directly proportional to the weight of the pulp-polysaccharide sample oxidized.

(5) The radioactivity of the total carbon dioxide is measured by gas phase proportional counting. This quantity is directly proportional to the weight of sorbed hemicellulose in the sample.

Although the method has been used to measure sorption by direct analysis of the sorbent, it is also applicable to sorption measurements based on concentration differences before and after sorption. In the case of pulp-polysaccharide systems, the effective separation of the additive solution from the pulp suspension is complicated by

the presence of finely divided cellulose in the supernatant solution of the suspension.

Any method of introducing carbon-14 into the sorbate molecules is acceptable, provided the sorption properties of the molecules are not affected by the labeling reaction. Any organic sorbent capable of being oxidized to carbon dioxide by wet combustion can be used. Inorganic sorbents having carbon-containing groups, e.g., calcium carbonate, may also be used.

The following conclusions have been drawn concerning the sorption of slash pine hemicelluloses by cellulose fibers:

1. The hemicelluloses are retained by the cellulose by adsorption on the accessible surfaces of the fibers.
2. Hemicelluloses are also sorbed by previously adsorbed hemicelluloses to form randomly oriented multilayers. This process occurs at a slower rate than does the hemicellulose-on-cellulose adsorption.
3. Sorption at pH 4.5 is irreversible with respect to concentration except at high levels of retention. The rate of desorption, however, is very slow.
4. Multiple hydrogen bond formation occurs between the hemicellulose molecules and the cellulose substrate as well as between hemicellulose and hemicellulose.
5. Higher mannan contents increase the sorption tendencies of the hemicelluloses. The beater adhesive efficiencies of the four hemicelluloses are in the order 1SP < 4SP <

7SP < 16SP < which is also the order of mannan content.

6. Sorption is decreased at pH 10, relative to pH 4.5, because of the increased electrostatic repulsive force between the carboxyl-containing hemicelluloses and the cellulose.

7. A series of pulp suspensions, ostensibly prepared and handled in a uniform manner, will not necessarily have a constant concentration of "dissolved cellulose" in the supernatant liquor. Small differences in the preparation of the suspensions cause varying quantities of "dispersed cellulose" to be present in the supernatant solution.

8. The effect of temperature on the sorption of a hemicellulose depends upon the chemical and/or physical composition of the hemicellulose. The over-all sorption rates of the 4SP and 16SP fractions were unaffected by a 15°C. temperature increase, whereas the sorption rate of the 7SP was increased and that of the 1SP was decreased.

9. Low consistencies tend to increase specific sorption for two reasons. First, a lower weight of pulp in a constant volume of given initial concentration removes less total sorbate and, hence, the driving force for sorption remains higher throughout the sorption period. Second, when the total amount of pulp is kept constant for a given initial concentration but is dispersed in a greater volume, an increase in the fiber surface available for adsorption occurs. This latter effect has been hypothesized and requires additional study for corroboration.

SUGGESTIONS FOR FUTURE RESEARCH

The following recommendations for additional research are suggested to further elucidate the mechanism of sorption of the hemicelluloses by cellulose.

1. Sorption over a broad pH range should be investigated. The acid value just short of precipitating the hemicelluloses could be the starting point. If possible, correlations of pH with polymer configuration in solution should be obtained. Hemicelluloses essentially free of ionizable groups should be included in the study to determine if the response to pH is wholly dependent on the ionizable groups along the chain.
2. Sorption over a wider temperature range should be investigated. The sorption of the 4 and 16SP fractions, in particular, should be studied at higher temperatures, since a 15°C. increase was inadequate to produce any changes in their over-all rates of sorption.
3. With the technique developed, it is now possible to study sorption under truly infinite bath conditions. Such studies permit measurement of sorption rates at constant concentration and make it possible to follow the rate of sorption as a function of the amount of sorbed material. From these studies, a more quantitative description of the entire sorption process could be developed.
4. The effect of consistency on sorption should be studied in an experiment as follows: prepare dispersions of 1.0 g. of

pulp in volumes of water such that a consistency range of 1 to 0.001% is covered. Adjust the initial concentration of hemicellulose in each slurry to an equal value and then measure the amounts sorbed at any time thereafter. According to the hypothesis presented in this thesis, the specific sorption at the lower consistencies should increase.

5. The strength improving properties of the hemicelluloses should be determined as functions of the amount of each actually present in a handsheet. With the present technique, such measurements are relatively simple. These results would then permit direct comparison to be made between the adhesive properties of the various hemicelluloses.

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APPENDIX I

PREPARATION AND ANALYSIS OF RAW MATERIALS

PREPARATION OF HEMICELLULOSES

The raw material from which the hemicelluloses were prepared was an air-dry slash pine holocellulose prepared by the chloriting technique of Wise, Murphy, and D'Addieco (28). The author is indebted to Dr. L. E. Wise, of The Institute of Paper Chemistry, for supplying him with this material.

Each 150-g. portion of the holocellulose was extracted with 2 liters of 1% potassium hydroxide for two hours in a stoppered flask at room temperature. The mixture was agitated frequently during the extraction. the residual holocellulose was collected on a Buchner funnel and washed with successive 500-ml. portions of 1% potassium hydroxide and distilled water. The washings were combined with the filtrate. The extracted material was then transferred to another flask and the procedure was repeated with 4, 7 and 16 % potassium hydroxide.

The alkali extraction liquors were neutralized with glacial acetic acid. Vigorous stirring was employed to prevent excessive heat generation in localized areas. Upon reaching a pH of 6, the addition of acetic acid was halted and the solution was poured into 8 liters of 95% ethanol, again with vigorous stirring. The flocculent hemicellulose thus obtained was allowed to settle overnight, and the supernatant liquor was then decanted. The hemicellulose was collected

on a medium porosity sintered glass funnel and washed thoroughly, without being allowed to dry out during the process. Several washings were performed with the following solvents in portions of about 300 ml. each: 95% ethanol, absolute ethanol, and ether. During each washing the material was stirred vigorously with a rubber policeman and rubbed against the sides and bottom of the funnel to break up agglomerates. This procedure resulted in a fine, fluffy powder, readily dispersible in water.

ANALYSIS OF HEMICELLULOSES

Hemicelluloses prepared in the preceding manner generally contain occluded potassium acetate. This material gives rise to high values of sulfated ash. To remove as much of this material as possible, the hemicelluloses were resuspended in hot, 95% ethanol on a steam bath, and stirred continuously for 3-4 hours. Approximately 60 ml./g. of ethanol was used in these extractions. The extracted hemicellulose was then collected on a medium porosity sintered glass funnel and washed with several portions each of 95% ethanol, absolute ethanol, and ether. After the anhydrous ether washes, a current of air was drawn through the filter to remove residual ether. The hemicellulose was allowed to equilibrate with the moisture in the air of the laboratory. It was then placed in a tightly covered jar and its moisture content determined. Moisture was determined by placing weighed samples in a vacuum oven at 55°C. until the weight became constant.

SULFATED ASH

Approximately 100-mg. samples (in duplicate) were weighed into micro porcelain crucibles and carefully charred over a micro burner. Two or three drops of concentrated sulfuric acid were added to each charred residue, and the crucibles were then placed on a hot plate until the evolution of sulfur trioxide ceased. The crucibles were then ignited in a muffle furnace at 600°C. to constant weight. If any carbon particles were visible at the end of the reaction two more drops of acid were added and the procedure repeated. The insoluble portion of this ash was measured by dissolving the sulfated residue in distilled water and filtering through an ash-free filter paper. The filter paper was then carefully ignited and the residue weighed as insoluble ash. Duplicate analyses of the sulfated ash content agreed within ±1%.

MANNAN CONTENT

Approximately 200-mg. samples of each hemicellulose were hydrolyzed by dissolving in 2 ml. of 72% sulfuric acid at 20°C.. A nearly constant temperature was maintained for twenty minutes after which the samples were diluted to 116 ml. with distilled water and refluxed for three hours on a hot plate. The cool solutions were then filtered through a pad of asbestos in a gooch crucible to remove the small quantity of acid-insoluble material suspended in the solutions.

The hydrolyzates were then neutralized with barium hydroxide solution to a pH of 4.5 and centrifuged. The clear supernatant

solution was decanted off and passed successively through ion exchange columns of Amberlite IR-120 and IR-4B in the hydrogen and acetate forms respectively. These clear solutions were then concentrated under vacuum to a total volume of 2-5 ml.

Mannose contents were then determined by spotting the sugar solution on paper with micropipets, developing, spraying, and comparing the optical density of the spots thus obtained with the optical densities of spots of mannose prepared from standard solutions. The mannose values were recalculated to equivalent mannan.

This technique is still in the experimental stage and has not been published. However, since exact values of the mannan content of the hemicelluloses were not necessary, it was felt that the relative rapidity and ease of the method justified the somewhat poor precision (± 10-20%) obtained for duplicate analyses. Further, the results obtained using this method were in fairly good agreement with the results of Thompson, Swanson, and Wise (8). They used the phenylhydrazine technique to determine the mannan contents of similar slash pine hemicelluloses prepared according to the method described above. Table II (page 16) shows the results obtained by both methods.

DEGREE OF POLYMERIZATION

The method described by Thompson and Wise (46) was used to estimate the D.P. of the four hemicelluloses. The reduced specific viscosity in 10% potassium hydroxide was determined at three concentrations and curves of η sp./conc. vs. concentration were drawn. Extrapolation

to zero concentration gave a value for the intrinsic viscosity. The equation $K = [\eta]/D.P.$ was used to calculate the D.P. The constant, K, obtained by Thompson and Wise (46) from osmotic pressure measurements of aspen hemicellulose solutions was substituted in the equation. Ostwald-Fenske viscometers were employed.

It was found that in order to obtain complete solution of the hemicelluloses in the 10% potassium hydroxide they first had to be dissolved in water. These aqueous solutions were then brought to 10% potassium hydroxide concentration by the addition of a predetermined quantity of more concentrated potassium hydroxide solution. This approach produced clear solutions with no undissolved material present. The solutions were filtered through glass wool before they were introduced into the viscometer. Duplicate determinations were made and a single straight line was drawn through the combined points.

URONIC ANHYDRIDE DETERMINATION

The method used to determine the uronic anhydride content of the hemicelluloses was not the commonly employed decarboxylation reaction. This method gave poor precision when employed on a micro scale on the four slash pine hemicellulose fractions. Instead, a method being developed at The Institute of Paper Chemistry was employed based on the reaction of the uronic acid residues with calcium ions. The author is indebted to the Analytical Department of The Institute of Paper Chemistry for performing these analyses.

About 15-mg. samples of the hemicelluloses were suspended in 30 ml.

of 1 N hydrochloric acid in ethanol. The mixture was shaken for a few minutes to allow the exchange reaction to occur between the carboxylic potassium ions and the hydrogen ions of the solution. The suspended hemicellulose was collected on glass wool placed in the constriction of a tube which had been drawn down to provide a sealable tip. The material was washed with 30 ml. of 95% ethanol and the tip of the tube was then sealed. Calcium acetate, 2.5 ml. of 0.04 N solution in 60% ethanol, was then added to the tube. The tube was stoppered, shaken well, and allowed to stand for 24 hours. At the end of this reaction period the stopper was removed and the seal on the tip broken. The excess calcium ions were then titrated with 0.00429 N Versene after washing the residue with 60% ethanol to remove the residual calcium solution. The results are calculated as uronic anhydride but more nearly represent the total carboxyl content of the hemicelluloses.

The results obtained with the above method have been compared with the results obtained by the usual decarboxylation method for some hemicelluloses of black gum wood. The titration method gave results about 1% higher in actual magnitude than the decarboxylation method and somewhat better precision. The standard deviation of the duplicate analyses for the four fractions was s = ±0.3%. A very similar method has recently been published for pulp analyses (48).

PENTOSANS

Pentosans were determined on a micro scale by the analytical

department of The Institute of Paper Chemistry. The method involved measuring the U.V. absorption of the distillate from the reaction of the hemicelluloses with 12% HCl. The method was standardized using samples of pure xylose and arabinose and the results were found to be in good agreement with the usual bromide-bromate method (Institute Method 424). The standard deviation of duplicate analyses was found to be s = ±1.2%.

ELECTROPHORETIC ANALYSIS

The procedure used by Dr. F. Smith, of the U. of Minn., to investigate the heterogeneity of the hemicelluloses was as follows: The materials were first dissolved in 0.1 N sodium hydroxide solution buffered with 0.1 M sodium tetraborate. These solutions were then spotted on glass paper and subjected to a potential gradient of 500 volts for 1-1/4 hours. The paper was then sprayed with 1% potassium permanganate for development. The results of this analysis indicated that each fraction could be separated into at least two zones on the paper. It was concluded, therefore, that the fractions were at least heterogeneous with respect to electrical charge. Such charge differences might arise, for example, from an unequal distribution of uronic acid residues or other constituent groups among the hemicellulose components. For example, Wethern (47) found that spruce hemicelluloses could be fractionated into products ranging in pentosan content from 30 to 57% and ranging in D.P. from 50 to 300.

PULP PREPARATION

The dry lap alpha pulp, which had been in dark storage for 2-3

years, was soaked in water overnight before being beaten. Institute method 403-3 was followed in furnishing the Valley laboratory beater and in sampling the pulp for freeness determinations. A bed plate loading of 5500 g. was used. When the pulp reached a freeness of 760 ml., the beater was stopped and the entire pulp charge was removed. The pulp was dewatered on a muslin-covered wash box and then centrifuged in a basket-type centrifuge until the flow of water from the centrifuge stopped (about 10-15 min.). The pulp pad thus obtained was manually separated into small pieces. The pulp was stored, at room temperature, in a polyethylene bag with 0.5% formaldehyde (on the dry fiber basis).

The moisture content was determined in triplicate by drying weighed samples to constant weight in an oven at 100-105°C. Under the storage conditions employed, the moisture content remained constant. No visible or olfactory evidence of degradation could be observed after six months of storage.

The carbon content of the pulp was determined by the wet combustion method. The results obtained, on the ovendry basis, were as follows:

Weight of Sample, mg.	Weight of Carbon, mg.	Carbon Content, %
8.28	3.58	43.2
5.49	2.38	43.4
		Av. 43.3

APPENDIX II

REACTION OF HEMICELLULOSES WITH $KC^{14}N$

Weighed hemicellulose samples in the range of approximately 100-200 mg. (air-dry) were dissolved in 5 ml. of solution containing 10 μc. of activity ($KC^{14}N$), and about 0.0014 mmol. of potassium hydroxide. The amount of $KC^{14}N$ was about 0.003 mmol. The flasks containing the samples were then tightly stoppered and set aside for ten days at room temperature. At the end of this period the flasks were opened and heated in a bath at 65°C. for four hours. The solutions were then concentrated almost to a syrup by further heating at 65°C. with the aid of a stream of dry air blowing into the flasks. This evaporation was repeated three times. The hemicelluloses were redissolved in about 5 ml. of distilled water after each evaporation. A fourth concentration was carried out with the addition of one drop of acetic acid to the solution.

The hemicelluloses were recovered by first redissolving them in a minimum of water and then precipitating then in 95% ethanol. The hemicellulose was collected on a medium porosity glass filter and thoroughly washed with several portions each of 95% ethanol, absolute ethanol, and ether. As in the preparation of the hemicelluloses, it is essential to keep the material wet with solvent until all the water has been removed. If this precaution is not taken, the hemicelluloses will hornify making them difficult to redissolve. The labeled products were dried <u>in vacuo</u> at 55°C. for four hours and stored in a desiccator over calcium chloride.

APPENDIX III

WET COMBUSTION AND PROPORTIONAL COUNTING TECHNIQUES

CARBON DETERMINATION BY WET COMBUSTION

Figure 13 is a sketch of the wet combustion apparatus, and the accessories used in conjuction with it for gas phase proportional counting. Reference will be made to this labeled sketch throughout the description of the method.

Into the combustion tube containing the sample to be analyzed is added approximately 0.3 g. of dry combustion reagent (10 parts potassium iodate:1 part potassium dichromate), and a clean boiling chip. The combustion tube is connected to the calibrated gas buret by means of a snug fitting rubber coupling. After the air is removed from the combustion apparatus, 2 ml. of a sodium hydroxide-hydrazine solution are added to the buret to absorb the carbon dioxide generated during the combustion. The normality and hydrazine concentration are preadjusted according to the amount of carbon dioxide anticipated.

The mercury level in the buret is then set to provide a gas space of about 1 ml. volume above the absorbing solution and the buret is opened to the evacuated combustion tube. The liquid combustion reagent is then added to the combustion tube through the cup above the tube. This reagent is composed of equal volumes of concentrated sulfuric and syrupy phosphoric acids saturated with potassium iodate.

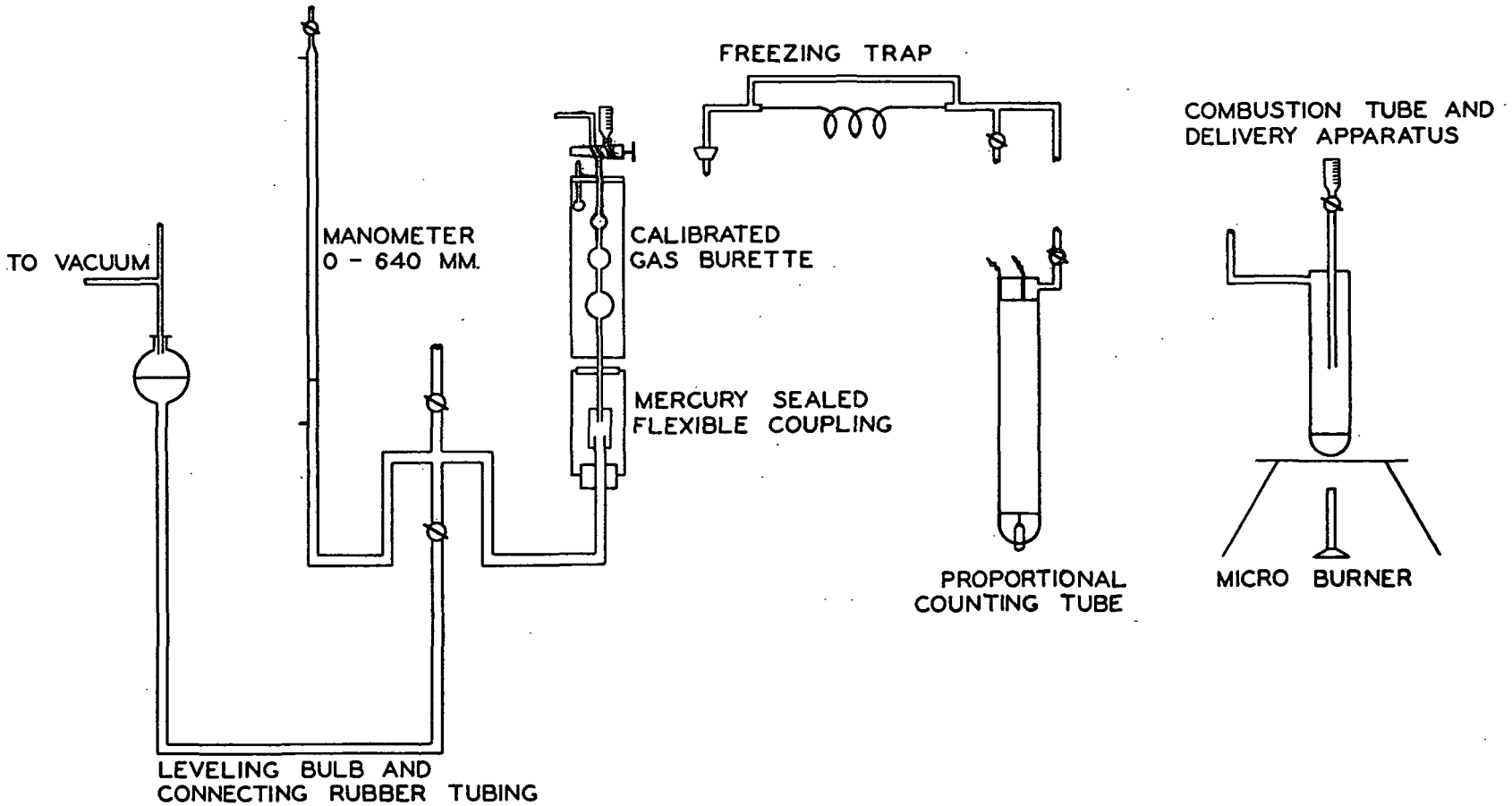

Figure 13. Combustion and Gas Transfer Apparatus

A small flame is brought under the tube and the contents are gradually heated to boiling. The combustion reaction is continued for 2.5 - 3.5 minutes, depending on the amount of sample. During the combustion, the carbon dioxide and other gases formed or already present pass into the buret and are absorbe. by the alkaline solution. The slightly soluble inert gases remain in the vapor phase above the solution. The hydrazine reduces any free halogens which may be formed in the reaction.

Upon completion of the combustion, the gases are swept back and forth between the buret and the combustion tube. This is accomplished by alternately raising and lowering the level of the mercury in the buret. Van Slyke and Folch (30) present data showing that 20 of these excursions (requiring about 2 min.) produce 100% absorption of the liberated carbon dioxide in the presence of the inert gases.

After the carbon dioxide has been absorbed, the combustion apparatus is disconnected from the buret and set aside to cool. The inert gases present above the solution in the buret are carefully ejected through the cup above the stopcock. The solution is then extracted under vacuum for two minutes by pulling the mercury level down to the 50-ml. mark of the buret. The buret assembly is shaken, during this time, by a motor-driven assembly attached to the water jacket around the buret. The inert gases removed from the solution during this extraction are also ejected through the cup above the buret.

A measured volume (2 ml.) of 2 N lactic acid is then added to the absorbing solution to liberate the carbon dioxide. Lactic acid is

strong enough to liberate carbon dioxide from carbonates, but not strong enough to liberate sulfur dioxide from sulfites. If any sulfur dioxide were generated at this point, the analysis would be useless. Sulfur dioxide could be formed during the combustion. The reaction of the acid with the carbonate solution is allowed to proceed under vacuum for two minutes while the buret is shaken. At this stage of the procedure, the gas mixture is solely carbon dioxide and water vapor. The volume of the gases is then carefully set at either of the calibration points on the buret (50, 10, or 2 ml.) and the pressure is read from the attached manometer and recorded as p_1. The temperature of the water bath and the volume of the gas are also noted.

For measurements not involving a determination of the radioactivity of the gas, the carbon dioxide is then expelled from the buret. The gas space above the absorbing solution is set at the same volume as before and the corresponding pressure is noted and recorded as p_2. Therefore, $p_1 - p_2$ is the total carbon dicxide pressure corresponding to the temperature and volume of the measurement. The carbon dioxide due to the reagents alone is obtained by running a blank analysis. This value is subtracted from the measured total carbon dioxide pressure. The final corrected value of carbon dioxide pressure is then multiplied by the appropriate factor, as listed by Van Slyke and Folch (30), giving the weight of carbon in the original sample.

To check the over-all accuracy and precision of the apparatus and method, samples of pure dry glucose were oxidized and their carbon

contents determined. Table XVI summarizes the results of these determinations.

TABLE XVI

CARBON CONTENT OF GLUCOSE BY WET COMBUSTION

Wt. of Glucose, mg.	Calc'd Wt. of Carbon, mg.	Wt. of Carbon Found, mg.	Carbon, %
6.836	2.734	2.716	39.73
5.291	2.116	2.122	39.99
8.418	3.367	3.365	39.97
		Av. =	39.89
		Theoretical =	40.0

Because of the excellent agreement between the theoretical carbon content and the measured value, the conversion factors of Van Slyke and Folch (30) were used uncorrected.

The carbon contents of three of the four hemicelluloses were determined by wet combustion. Table XVII summarizes these results. It was found that the three fractions had carbon contents, on the ash-free, ovendry basis, within ± 0.3 of the mean value of 43.4%. The carbon content of the 7SP fraction was determined by the standard dry combustion method. This analysis gave a value of 43.4%. On the basis of these results, it was concluded that the carbon contents of the four fractions were equal. Hence, an average of the four values was computed and used in all subsequent calculations. The standard deviation was $s = \pm 0.2$.

TABLE XVII

CARBON CONTENT OF SLASH PINE HEMICELLULOSES

Fraction	Sample Wt., mg.	Carbon mg.	Carbon,[1] %	Ash, %	Average Carbon,[2] %
1SP	6.182	2.457	39.74		
	8.610	3.441	39.96	8.12	43.3
4SP	5.689	2.341	41.14		
	5.366	2.205	41.09	6.00	43.7
16SP	5.974	2.463	41.22		
	4.146	1.694	40.85	4.99	43.2

[1] On an ovendry basis

[2] On an ovendry, ash-free basis

In the present work, the carbon dioxide generated by the oxidation contains both carbon-12 and carbon-14 dioxide. To transfer this carbon dioxide mixture to a proportional counting tube, the water trap (shown in Figure 13) is connected to the cup above the buret while the counting tube is connected to the other end of the trap. A vacuum pump is connected to a stopcock fitting on the water trap and the whole space thus enclosed is evacuated to a pressure of 0.3 mm. or less (checked by a tilting McLeod gauge in the line). The pump is then removed from the system by closing the cock on the water trap and

the buret is opened to the system. The pressure of gases in the buret causes a mixture of water vapor and carbon dioxide to distill over towards the counting tube, the bottom end of which is immersed in liquid nitrogen. The water is removed from the gas stream in the coils of the freezing trap which are immersed in a dry ice-alcohol bath. The carbon dioxide passes into the counting tube and is condensed at the bottom. When all the gas has been transferred, the buret and counting tube are closed. The tube is removed from the liquid nitrogen and allowed to warm to room temperature. The pressure above the absorbing solution, now stripped of carbon dioxide, is measured as described above and the same correction is applied for the carbon dioxide content of the reagents.

When the carbon dioxide in the counting tube has come to room temperature, it is simultaneously diluted with methane and brought to atmospheric pressure by means of the leveling bottle shown in Figure 14. The detailed procedure for this operation is described by Van Slyke, Steele, and Plazin (49).

The sample thus prepared is ready for counting. In the present work, a Nuclear Instrument and Chemical Corp. scaler, model 182X, was used. This instrument meets the specifications outlined by Bernstein and Ballentine (50) for proportional counting of low energy beta-ray emitters.

The counting tube is then placed in a special shielded holder and attached to the scaler. The voltage is set at the proper value for the particular tube being used and the counting rate of the gas is measured. The equation relating sample counting rate, background

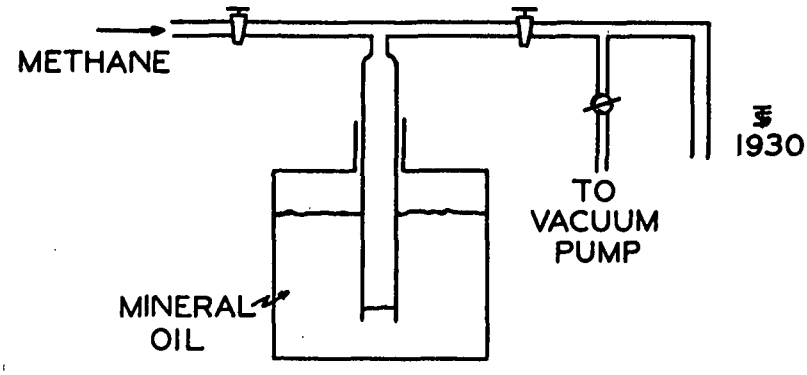

Figure 14. Methane Leveling Bottle

counting rate, standard deviation, and time spent counting, will be described below. The observed counting rate, corrected for background activity, is directly proportional to the weight of hemicellulose oxidized. Therefore, by dividing the weight of hemicellulose found by the weight of the pulp oxidized, the amount sorbed per unit weight of pulp is obtained.

CALIBRATION OF COUNTING APPARATUS

It has been demonstrated by Bernstein and Ballentine (50), and by Van Slyke, Steele, and Plazin (49), that the counting rate of

mixtures of carbon-14 dioxide and carbon-12 dioxide in methane depends, to a certain extent, on the partial pressure of the total carbon dioxide (at constant carbon-14 dioxide content). Therefore, it was necessary to establish a curve showing the counting rate, at constant carbon-14 content, as a function of the total carbon content of each proportional counting tube (excluding the carbon of the methane).

Four proportional counting tubes of the type described by Bernstein and Ballentine (50) were obtained from Nuclear Instrument and Chemical Corp. of Chicago, Illinois. Preliminary experiments showed that the counting plateaus of these tubes were not the same. The counting plateau is that portion of the curve of counting rate vs. applied voltage which shows the minimum slope over a certain range of voltages.

A series of six solutions of sodium carbonate was made up, each solution containing the same quantity of labeled carbonate but ranging in total carbon dioxide carbon content from 1 to 7.5 mg./m. Aliquots (2 ml.) of each solution were introduced into the gas buret of the manometric apparatus and extracted with 1 ml. of 5 N lactic acid. The gas was then transferred to a proportional counting tube and the counting rate was determined as a function of the applied voltage for each of the four tubes and at each level of total carbon content. The data from this experiment are summarized in Table XVIII.

Smooth curves of counting rate vs. voltage were then constructed for each tube at each loading level. From these curves, the operating

TABLE XVIII

COUNTING RATE AS A FUNCTION OF VOLTAGE, TUBE, AND TOTAL CARBON CONTENT

$C^{14}O_2$ content $\sim$ 1 mμc. = 2,200 d/m

Total carbon content	2.08 mg./tube		6.97		9.00		11.0		13.0		14.9	
Tube counted	A	B	A	B	A	B	A	B	A	B	A	B
3900	2119	2169	2119	2065	2257	2277	2152	2177	2097	2136	2081	1999
4000	2280	2282	2297	2301	2292	2333	2231	2287	2252	2314	2212	2179
4100	2376	2348	2374	2367	2376	2409	2365	2363	2310	2368	2265	2294
4200	2417	2457	2393	2435	2383	2400	2402	2416	2369	2420	2350	2321
4300	2434	2444	2390	2444	2427	2478	2404	2438	2446	2458	2406	2407
4400	----	----	2458	2487	2483	2472	2462	2465	2454	2523	2441	2457
4500	2486	2469	----	----	----	----	----	----	----	----	----	----
	C	D	C	D	C	D	C	D	C	D	C	D
3200	2194	2293	2339	----	2297	2314	2394	2366	2119	2303	2298	----
3300	----	----	2449	2302	2429	2354	2405	2398	2347	2363	2329	2259
3400	2325	2394	----	2380	2414	2375	2406	2448	2437	2381	2431	2260
3500	2384	2438	2462	2401	2474	2429	2455	2438	2554	2432	2521	2300
3600	----	----	----	----	2444	2470	2512	2469	2734	2449	2609	2372
3700	2394	2423	2467	2448	2505	2446	2571	2467	----	2471	2713	2370
3800	2427	2444	2510	2471	2569	2481	2646	2484	----	2481	----	----

voltages for the tubes were selected. The voltages were chosen so that, as nearly as possible, the same counting rate was given by each tube at the selected plateau voltage. For tubes A and B, 4200 volts was chosen and for tubes C and D, 3400 volts. The type of curves obtained are shown in Figures 15 and 16 at two carbon loading levels. At the higher loading level shown in Figure 16, the plateaus became considerably shortened.

The data taken from all the curves of the type of Figures 15 and 16 are summarized in Table XIX, which gives the average of the counting rates for all four tubes at each level of carbon content. Figure 17 is a plot of the average counting rate of all four tubes as a function of the carbon dioxide content (expressed in terms of carbon). The radioactive carbon dioxide content was constant at all loading levels.

From the curve of Figure 17 it is apparent that above a partial pressure of carbon dioxide corresponding to a carbon content of about 9 mg./tube, there is a decrease in the efficiency of counting. To avoid the necessity of making corrections in counting rate data, as a result of this effect, the sample size used for combustion and analysis was kept below 9 mg. of total carbon.

Based on Equation (1) below, as given by Van Slyke, Steele, and Plazin (49), an estimate was made of the standard error which could be expected in the measured counting rate under the conditions which prevailed for these experiments.

$$(1) \qquad N_s = \frac{1 + \sqrt{4N_bTs^2 + 1}}{Ts2}$$

where,

N_s = sample counting rate (2400 cpm.)

N_b = background counting rate (200 cpm.)

s = standard error (?)

T = minutes spent counting sample (3 min.)

The calculation showed that s = ±2.0% could be expected. Analysis of the data of Table XIX showed that the standard errors fell within the predicted limits.

TABLE XIX

CALIBRATION DATA FOR COUNTING TUBES, COUNTS/MIN. VS. CARBON CONTENT

Carbon Content, mg./tube	A	B	C	D	Av.	Standard[1] Error, s
2.08	2410	2420	2360	2390	2395	± 1.08%
6.97	2390	2420	2450	2370	2407	1.45
9.00	2380	2410	2430	2400	2405	0.87
11.0	2390	2400	2410	2400	2400	0.30
13.0	2360	2400	2410	2380	2387	0.92
14.9	2350	2360	2410	2300	2355	1.92

[1] The standard error is defined as (standard deviation from mean)/(mean).

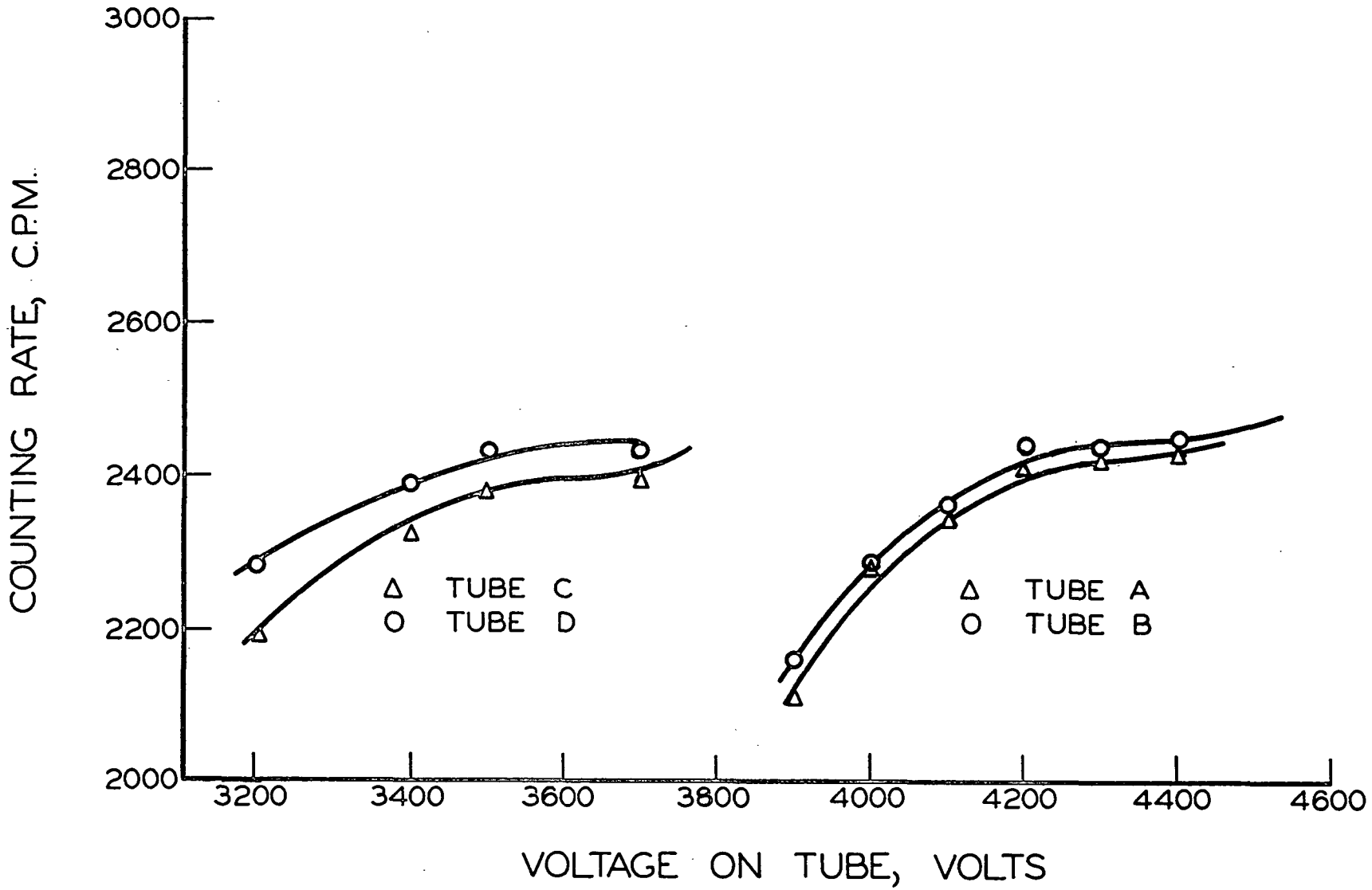

Figure 15. Counting Rate vs. Applied Voltage on Tubes

Total Carbon Content = 2.08 mg./tube
Carbon-14 Content = 1 μc.

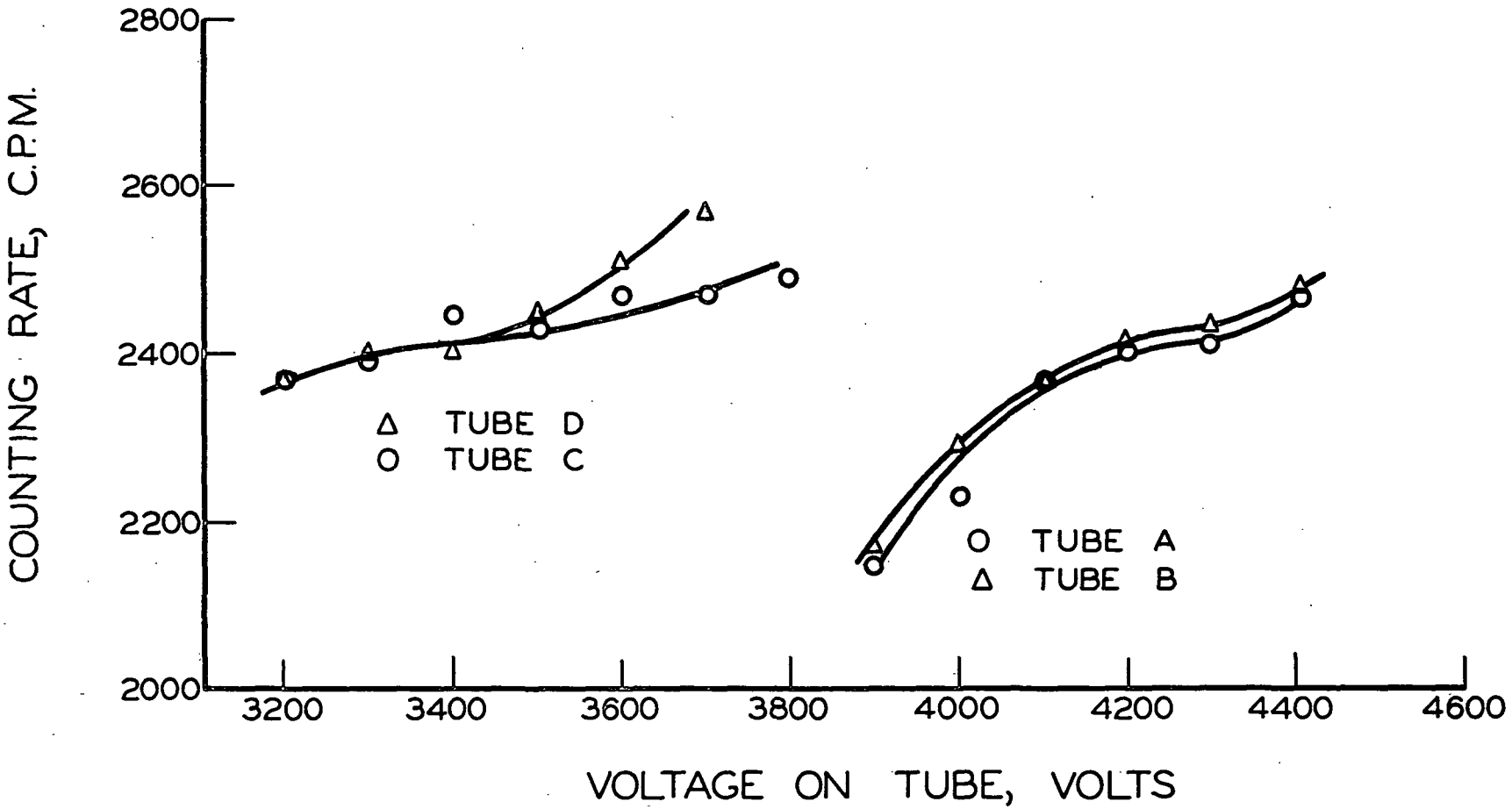

Figure 16. Counting Rate vs. Voltage

Total Carbon = 11.0 mg./tube
Carbon-14 ≅ 1 μc.

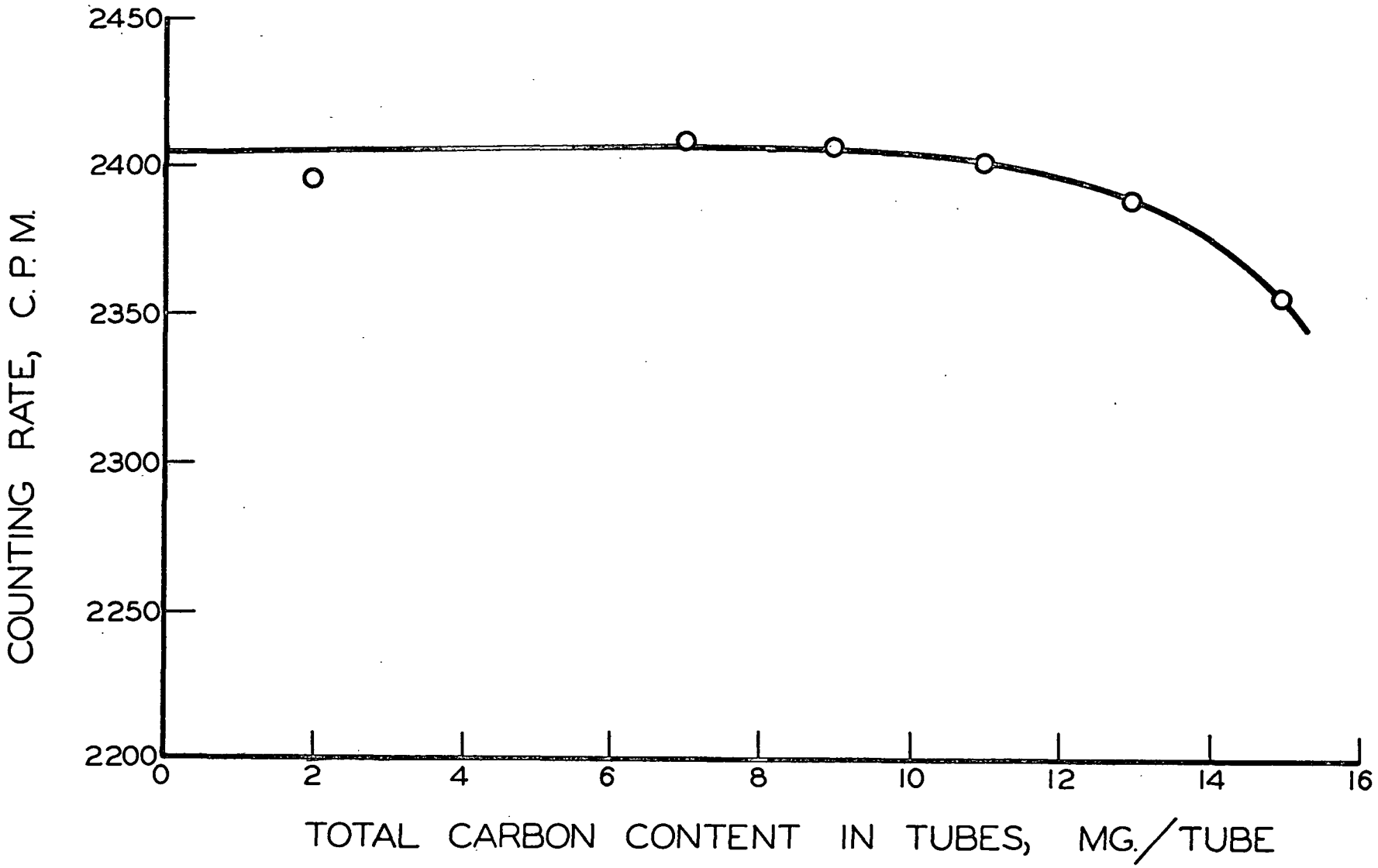

Figure 17. Counting Rate vs. Carbon Content in Proportional Counting Tubes for Constant $C^{14}O_2$ Content

APPENDIX IV

PREPARATION AND ANALYSIS OF STOCK SOLUTIONS

To prepare a stock solution of hemicellulose, a sample (10-40 mg.) of the labeled material was weighed on an analytical balance and this material was then diluted with about 10-25 times its weight of unlabeled hemicellulose. The dry materials were mixed together in a covered weighing bottle. Solution was effected by slowly sprinkling the mixture into about 50-75 ml. of distilled water at room temperature while stirring vigorously. After dissolving the hemicellulose, the solution was diluted to about 100 ml. with distilled water and filtered through a plug of glass wool into a glass-stoppered bottle for storage.

To analyze these stock solutions, aliquots (1-2 ml.) were pipetted into combustion tubes, evaporated slowly to dryness, and subjected to the wet combustion-proportional counting measurements described above. Duplicate analyses were performed on each stock solution. For determinations of the radioactivity, a proportional tube from each of the two pairs was used to provide additional data on the similarity of counting rates of the tubes.

Table XX summarizes the results obtained from the analyses of the several stock solutions.

Statistical analysis showed that the standard deviation of an individual concentration determination by the wet combustion technique was $\sigma = \pm 0.02$ mg./ml. The same analysis applied to the specific

TABLE XX

REPRODUCIBILITY OF STOCK SOLUTION ANALYSES

Fraction	Concn., mg./ml.	Solution Sp. Act., cpm./ml.	Hemicellulose Sp. Act., cpm./mg.	Prop. Tube Used
1SP	3.13	16,000	5,112	A
	3.13	16,013	5,116	D
	3.07	16,262	5,297	A
	3.06	15,950	5,212	D
	3.07	16,045	5,226	B
	3.06	16,012	5,233	C
	2.06	19,513	9,472	A
	2.09	19,803	9,475	D
	2.11	17,746	8,410	D
	2.07	17,830	8,613	B
	2.46	5,556	2,258	D
	2.49	5,514	2,214	A
	3.62	8,227	2,273	A
	3.62	8,314	2,297	C
4SP	1.72	7,875	4,578	A
	1.72	7,829	4,552	C
	1.72	14,308	8,318	C
	1.75	14,166	8,095	A
	3.60	15,304	4,251	C
	3.59	15,068	4,197	B
7SP	2.21	26,106	11,813	A
	2.16	25,971	12,023	C
	1.83	27,925	15,259	C
	1.85	27,771	15,011	A
	2.52	21,180	8,405	D
	2.52	21,660	8,595	A

TABLE XX (cont.)

REPRODUCIBILITY OF STOCK SOLUTION ANALYSES

Fraction	Concn., mg./ml.	Solution Sp. Act., cpm./ml.	Hemicellulose Sp. Act., cpm./mg.	Prop. Tube Used
16SP	2.07	14,303	6,909	B
	2.06	14,650	7,112	C
	2.31	15,800	6,840	B
	2.30	16,140	7,017	C
	3.04	40,116	13,196	D
	3.05	40,359	13,232	B
	2.08	19,270	9,264	D
	2.08	19,159	9,211	A
	1.61	7,260	4,509	C
	1.61	7,329	4,552	A
	3.01	9,180	3,050	D
	2.99	9,097	3,042	A
	2.68	5,235	1,953	C
	2.68	5,271	1,967	A
	3.52	7,270	2,065	B
	3.48	7,100	2,040	D

σ = $\pm$0.02 mg./ml. σ = $\pm$71 cpm./mg.

activity data gave a value of σ = ±71 cpm./mg. At the counting rates involved, the ±71 cpm./mg. represents a standard error range of ±0.5 - 3.5%, depending on the level of activity of the sample. The 3.5% figure applies only to the two samples having counting rates of approximately 2000 cpm.

EFFECT OF STORAGE ON STOCK SOLUTIONS

In order to determine how long an aqueous solution of a mixture of radioactive and nonradioactive hemicellulose could be held in storage without serious viscosity loss or bacterial degradation, a solution of 1SP hemicellulose was made up containing 7% labeled, and 93% unlabeled material. The solution was filtered through a plug of glass wool to remove visible suspended particles and a portion of this clear solution was placed in an Ostwald-Fenske viscometer. The initial flow time of the freshly prepared solution was then determined. Both the viscometer containing the sample and the bulk of the stock solution were placed in the refrigerator to age. A daily check was made of the viscosity in a water bath at 30.0 ± 0.1°C. Table XXI summarizes the results of these daily viscosity measurements.

The data of Table XXI indicate a maximum drop in value of reduced specific viscosity of 3.4% over the 12-day period, with an apparent leveling off and subsequent slow decrease after the first five days.

TABLE XXI

EFFECT OF STORAGE ON VISCOSITY OF STOCK HEMICELLULOSE SOLUTIONS

Time, days	n_{sp}/Conc.
0	0.667
1	0.662
2	0.659
3	0.650
4	0.649
5	0.647
6	0.646
7	0.646
8	0.645
9	0.647
10	0.645
11	0.644
12	0.644

During this prolonged storage period no visible precipitate formed in the bulk of the same stock solution which was present in the viscometer. Had any agglomerates formed in the viscometer, the narrow capillary would probably have become blocked producing a marked increase in the flow time of the solution.

APPENDIX V

SORPTION MEASURMENT BY CONCENTRATION DIFFERENCE

The following experiments were performed to determine the feasibility of measuring sorption by the change in concentration of the sorbate solution.

A pulp slurry of 1.0 g. of pulp in 200 ml. of distilled water was prepared. The pH of the suspension was 6.5. To the suspension was added 10 ml. of a 1SP stock solution containing 3.13 mg./ml. of hemicellulose at a specific activity of 5,120 cpm./mg. The sample bottle was placed in a water bath at 25°C. and the fibers were kept in suspension by stirring gently. At selected time intervals, samples of the solution were withdrawn through a Corning coarse-grade glass filter. The filter was washed with hot water between samples. Duplicate aliquots of the filtered solution were evaporated to dryness in combustion tubes and the total carbohydrate content and radioactivity of the samples were measured.

If the filtration produced solutions containing only dissolved hemicellulose, then the total carbohydrate content of each sample, as determined manometrically, would equal the hemicellulose content, determined by the radioactivity measurement. The data are shown in Table XXII with the calculated sorption values based on the carbon-14 content of the filtered aliquots.

These data showed that the total carbohydrate content of the

TABLE XXII

EFFECT OF TIME ON SORPTION OF 1SP FRACTION AS MEASURED BY CONCENTRATION DIFFERENCE

C_i = 0.149 g./l.
Temp. = 25°C.
Nominal Consistency = 0.50 g./100 ml.
pH = 6.5

Time, hrs.	Total Carbo. Concn., g./l.	Residual Hemicellulose Concn., g./l.	Solution Volume, ml.	Calculated Sorption, mg./g.
0.13	0.236	0.134		
	0.202	0.137	212	2.3
0.25	0.275	0.142		
	0.206	0.140	208	2.4
0.50	0.191	0.130		
	0.179	0.137	204	3.1
1.0	0.180	0.140		
	0.208	0.136	200	2.1
2.0	0.177	0.120		
	0.184	0.130	196	4.6
13.0	0.170	0.123		
	0.173	0.127	192	4.6
48.0	-----	0.131		
		0.136	188	3.1
67.5	-----	0.129		
		0.128	184	3.9

aliquots was greater than the hemicellulose content at all times. Furthermore, the differences between the results of duplicate analyses of the total carbohydrate content ranged from 2-30%. The variation in duplicate hemicellulose analyses, however, was under 5% with but one exception of 8%. Finely divided cellulose particles had apparently passed through the filter. The excessive variability of the toal carbohydrate analyses was attributed to real differences between the amounts of carbohydrate in each pair of "duplicate" aliquots.

The radioactivity measurements showed a general trend of increased sorption with time. However, individual points showed considerable deviation from the over-all trend. If the filtration actually removed hemicellulose from solution, either by adsorption or ultrafiltration, the measured sorption would be high. If, on the other hand, the finely divided pulp contained sorbed hemicellulose, the measured sorption would be low.

To ascertain if part of the error were due to the removal of hemicellulose from solution by the fritted glass filter, the following experiment was carried out. The concentration of a 1SP stock solution was measured, in duplicate, before and after filtration through the same filter used above. Before filtration, the concentration was 3.29 mg./ml., whereas after filtration the concentration was 3.21 mg./ml. This difference was statistically significant at the 99% confidence level. It was concluded, therefore, that some hemicellulose was removed from solution by the

fritted glass filter tending to produce a high calculated sorption. The opposing error caused by sorbed hemicellulose on the pulp fragments which passed through the filter, however, was indeterminate.

Before dropping an experimental approach dependent on filtration, glass filter paper was tried. The concentration of a stock solution of 1SP hemicellulose was measured before and after filtration and in this case the concentration was found to be unaffected by the filtration i.e., concentration before filtration = 3.07 mg./ml., concentration after filtration = 3.07 mg./ml.

On the basis of these filtration results another experiment was designed to measure the effect of time on the sorption of the 1SP fraction. In this case, the aliquots were pipetted from solution through a glass filter paper before being transferred to the combustion tubes for analysis. The data in Table XXIII summarizes these results.

These data show that the glass paper filtration resulted in duplicate aliquots having nearly equal total carbohydrate concentrations. However, the calculated sorption values still showed considerable scattering. Apparently, the cumulative errors involved in this type of sampling were sufficient to mask the small concentration changes which occurred as a result of sorption.

In light of the above results, and those of Shriver (19), Shriver, Webb, and Swanson (20), and Pearl (18) who investigated several filtration techniques for separating solutions of polysaccharide additives

from pulp suspensions, it was concluded that a single filtration through such filters was inadequate to provide samples at a sorbate concentration equal to that in the suspension prior to sampling. Shriver (19) and Shriver, et al., (20) reported that finer porosity filters had a more pronounced effect on the removal of polysaccharides from solution and required excessive filtration periods.

TABLE XXIII

EFFECT OF TIME ON THE SORPTION OF 1SP HEMICELLULOSE BY CONCENTRATION DIFFERENCE (GLASS PAPER FILTRATION)

C_i = 0.145 g./l.
Temp. = 25°C.
Nominal Consistency = 0.50 g./100 ml.

Time, hr.	Total Carbohydrate Concn., g./l.	Hemi.[1] Concn., g./l.	Solution Volume, ml.	Calc'd Specific Sorption, mg./g.
0.5	0.196 0.226	0.135	212	2.1
1.5	0.187 0.185	0.138	208	1.6
4.5	0.190 0.187	0.137	204	1.7
11.0	0.184 0.181	0.125	200	4.1

[1] Average of two determinations agreeing within ±4%.