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A Study of Certain Phenomena of the Liquid Exchange of Water-Swollen Cellulose Fibers and Their Subsequent Drying from Hydrocarbons

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A STUDY OF CERTAIN PHENOMENA OF THE LIQUID EXCHANGE OF WATER-SWOLLEN CELLULOSE FIBERS AND THEIR SUBSEQUENT DRYING FROM HYDROCARBONS

A thesis submitted by

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INTRODUCTION

Cellulose as an industrial raw material has many varied and important uses, many of which depend on its fibrous structural property of surface area. In most industrial processing, cellulose is transported and treated in an aqueous medium. In the preparation and use of wood pulps, the behavior towards water is one of the most important physical properties of cellulose, and this behavior is intimately related to the cellulosic surface area.

The total surface area of cellulose fibers varies considerably, depending on the history of the fibers. For example, fibers dried from water have a total area of 0.5 to 1.0 sq. m. per gram determined microscopically (1) or by gas adsorption (2). Whereas, these same fibers if again brought into contact with water vapor develop a total area of at least 200 sq. m. per gram (3).

The large differences between these areas may be attributed to the collapse of the internal fiber structure during drying from water (4). When water is adsorbed on the dry cellulose structure, the extensive capillary voids are opened and imbibe a considerable quantity of water to a point of equilibrium saturation. These capillaries will not reopen to the same extent in liquids other than water. In general, liquids of less polarity than water will be less effective in entering the capillary structure. Liquids of no polarity will not enter the structure at all; consequently, such liquids swell cellulose very little (5, 6). The extent to which the capillary system is swollen or opened determines the amount of cellulosic surfaces accessible to any medium.

Important physical and chemical properties of cellulose are often interrelated by the fibers' accessible surface area. For example, the rates of hydrolysis of cellulose may be different for fibers of different structures although the chemical concentrations and reaction conditions are the same (7). The accessibility of cellulose to the hydrolyzing agent is controlled by the capillary structure which, in part, influences the reaction rate. Other chemical reactions, such as acetylation, will proceed at different rates and to different limits depending on the accessibility of cellulose in the reaction medium (8, 9). As cellulose fibers become more swollen, their accessible capillary structure becomes more extensive and their chemical reactivity increases (8). Therefore, it is of fundamental importance to be able to evaluate and probe the capillary structure and surfaces of these fibers in their swollen states.

It has been noted that the capillary structure almost disappears when fibers are dried from the polar liquid water. To overcome this effect several investigators (9, 10, 11) have proposed that water held in saturated fibers be replaced with a nonpolar liquid by simple liquid exchange methods. By this method, water is replaced with a water-miscible organic liquid such as methanol and the latter is replaced with a methanol-soluble, nonpolar liquid such as benzene. This thesis is concerned with such liquid exchanges. Normally, the course of exchange will be from water (W) to an alcohol (A) to a nonpolar (N) liquid hydrocarbon. For the sake of simplicity this process will hereafter be referred to as WAN-exchange. The process of evaporating the final hydrocarbon will be termed drying and the entire process of exchanging and drying will be referred to as WAN-drying. It is known that when fibers are WAN-dried, an expanded cellulose structure is obtained (9, 11). It is also known (12) that this structure retains a measurable quantity of the final organic liquid often referred to herein as "residual".

Since handsheets formed in water and WAN-dried have very little strength, these fibers are commonly thought to have few, if any, interfiber bonds. Thus, liquid-exchanged handsheets have been used in studies on the bonded area of paper (13, 14), and on the reactivity and morphological character of cellulose (8, 11).

The literature survey which is to follow will show that considerable gaps exist in the knowledge of WAN-exchanging and WAN-drying. For example, it is not known with any certainty why or how residual hydrocarbons are so tenaciously held in WAN-dried fibers. The contribution of the fiber structure to the retention of hydrocarbons has never been described. Also, the properties of the hydrocarbons have never been clearly related to the WAN-exchange process or to the effects of WAN-drying.

Since WAN-dried fibers are known to have large total surface areas and since the hydrocarbons retained in such fibers occupy area and volume within the fiber structure, information on total fiber area and pore volumes should provide a new perspective of these fibers. Gas adsorption techniques will give this information. Such information should lead to a better understanding of the phenomena related to the development of WAN-dried fibers.

HISTORICAL INTEREST IN FIBERS DRIED FROM ORGANIC LIQUIDS

The earliest interest in fibers dried from organic liquids resulted from the observation that extraction thimbles made of cotton, wool, silk, and rayon retained an appreciable amount of alcohol even when dried to constant weight at temperatures above the boiling point of the alcohol (15). Wiertelak and Garbaczowna (12) investigated the extent to which various cellulose samples held alcohols, pyridine and benzene-alcohol mixtures after drying from these liquids. They noted that the retained liquids could not be removed by prolonged heating at 105°C. but that they could be removed by washing the samples with ether or water. They also stated that benzene, gasoline, and ether were not retained in the cellulose fibers they investigated. Russell, Maass and Campbell (16) showed that completely dried fibers when exposed to alcohol vapors at a relative vapor pressure above 50% retained as much as 2% of alcohol even when subjected to a high vacuum for a week.

The work cited thus far was performed on fiber samples which were air-dried or completely dried prior to immersion in the organic liquids; no liquid exchanging was involved. Assaf, Haas, and Purves (11, 17) studied the reactivity of water-swollen cotton fibers WAN-dried from benzene. These investigators attained a highly accessible sample by their WAN-drying method. They observed a loss in chemical reactivity when moisture was readsorbed on the WAN-dried sample prior to a thallous ethylation reaction in polar and nonpolar organic liquids. For the polar liquids, the degree of chemical substitution varied with the molecular volume of the polar molecule, whereas for the nonpolar liquids the degree of substitution was independent of molecular volume.

INVESTIGATIONS RELATED TO PHENOMENA OF EXCHANGING AND DRYING OF FIBERS FROM ORGANIC LIQUIDS

Several investigations have provided information for a better understanding of certain phenomena of the liquid exchange and subsequent drying processes.

Kistler (10) appears to have been the first investigator to liquid exchange and dry cellulose from an organic liquid. He extracted swollen cellophane with ether, replaced the ether with propane, and removed the propane above its critical temperature. He thereby created an expanded aerogel which, it was assumed, had not been subjected to any liquid surface tension forces. This work indicated by qualitative means that elimination or minimization of surface tension forces are important in creating aerogels from any liquid.

Shutt and Mack (18) worked with cellophane and natural celluloses which had been impregnated with glycerol and several glycols. They analyzed for the amounts of these materials which could not be removed by prolonged drying at 88°C. They concluded that the residual glycerol and glycols were held by physical adsorption forces.

Stamm and Hansen (19) liquid exchanged water-swollen wooden blocks. They replaced all but 0.1% (or less) of the water by distilling with cellosolve, alcohol-acetone, or diacetone alcohol and displaced these respectively with benzene, petroleum ether and toluene. Stamm and Hansen concluded from shrinkage measurement that about 19% of the intermediate polar liquid was not replaced by the final nonpolar liquid. From this conclusion Stamm and Tarkow (20) proposed that nonpolar liquids would replace all of the intermediate polar liquid except for a monomolecular layer of the polar liquid. This effect, it was further suggested, always causes structural shrinkage upon evaporation of the final liquid and means that it should not be possible to obtain a fully expanded aerogel by the method of Kistler (10).

The most extensive work with fibers dried from organic liquids has been reported by Staudinger and Döhle (9). These workers were interested in the relative ease of acetylation of a variety of mercerized and non-mercerized cellulose fibers. The fibers were moistened with water and then exchanged with methanol, ether, and a selected final organic liquid. This liquid was removed by vacuum drying under 0.1 mm. of mercury pressure at 100°C. for two days. Drying was carried out from some fifteen different organic liquids. All liquids were retained in the dried structures. The residuals were measured by gravimetric means and chemical analyses. It was thus established that the retained liquid could be completely displaced by rewetting the dried fibers with water, and that the residual liquid was solely that used as final liquid.

In reference to the residuals, Staudinger and Döhle reasoned that when cellulose is dried from water, the water molecules may move along the polyglucose chain by way of auxiliary valence bonds between water molecules and hydroxyl groups of the cellulose. Thus, when the outer regions of a fiber have lost surface-bound water, the internally held water can move along the cellulose structure to hydrate the outer regions and subsequently evaporate. However, if before drying, the water is replaced with a water-soluble organic liquid and this replaced with a water-insoluble organic liquid, the cellulose hydroxyls are no longer associated by coordinative auxiliary valences with the liquid. Staudinger and Döhle observed that without such association the organic molecules should be more easily removed from the fiber than water. Since such is not the case and since there is no chemical bond between the organic liquid and cellulose, the investigators postulated that the liquid molecules are held tightly between the cellulose chains and cannot emerge for steric reasons. The absence of auxiliary valence forces between the organic liquid and the cellulose deprives the liquid molecules of a mechanism for moving from the internal to the external surfaces.

Staudinger and Döhle further believed that the trapping of liquid molecules between cellulose molecules makes hydrogen bonding between neighboring hydroxyl groups impossible.

GAS ADSORPTION TECHNIQUES APPLIED TO FIBERS DRIED FROM ORGANIC LIQUIDS

Recently several investigations have been reported where gas adsorption techniques were used in conjunction with WAN-dried fibers. These studies were not specifically directed toward explaining any of the WAN-drying phenomena, but the results are noteworthy for the sake of comparisons.

Gas adsorption techniques have been used primarily to determine total specific surface areas by the Brunauer, Emmett, and Teller (B.E.T.) method (21). Haselton (14, 22, 23) has reviewed in detail this method and its application to cellulose. Assaf, Haas, and Purves (11) determined B.E.T. areas by nitrogen adsorption methods on cotton linters swollen in a 10% caustic solution. An exchange method replaced the water of the swollen fibers by successive treatments with absolute methanol, magnesium-dried methanol and sodium-dried benzene. The benzene was removed by intermittent vacuum applications. The fibers dried from benzene were flame sealed in glass adsorption bulbs. Assuming the nitrogen molecule to have a cross-sectional area of 17.0 sq. A., two of the WAN-dried samples gave areas of 53.0 and 64.6 sq. m. per gram.

Hunt, Blaine and Rowen (24) used the WAN-drying method of Assaf, Haas and Purves (11). From nitrogen adsorption data, they obtained B.E.T. areas as high as 71.3 sq. m. per gram for cotton linters treated with 10% caustic and 47.3 sq. m. per gram for nontreated linters. The adsorption isotherm for the treated fibers showed appreciable hysteresis whereas that for the untreated displayed much less. The isotherm for water-dried linters showed no hysteresis. Pore volume distribution curves were determined from the isotherms of the WAN-dried fibers and indicated a preponderance of pores of 24 to 60 A. diameter for the caustic-treated sample and of 16 to 56 A. for the untreated sample with peaks of the distribution curves occurring at 40 and 32 A., respectively.

Haselton (14, 22, 23) also used the WAN-drying procedures of Assaf, Haas, and Purves to prepare samples from a water-swollen sprucewood meal, from a chlorite holocellulose, and from a KOH-extracted holocellulose of the same meal. The B.E.T. areas of these samples were 4.0, 61.3, and 62.2 sq. m. per gram, respectively. Haselton calculated pore volume distribution curves for the latter two samples. The pore sizes ranged from 10 to 100 A. in diameter with a peak of the distribution curve at about 40 A. for both samples.

Escard, Saulquin and Girardy (25) studied the development of surface area of linters during beating. These workers liquid exchanged water-swollen fibers with alcohol and then with benzene, drying the fibers from the latter. The B.E.T. areas from gas adsorption data were 0.47 to 22.1 sq. m. per gram, for unbeaten and beaten fibers, respectively.

Grotjahn and Hess (26) prepared cellulose samples by dewatering fibers with pyridine, ethanol-ether, ethanol, or butanol by azeotropic distillation or by a replacement method. The final solvents were removed by vacuum drying. Azeotropic distillation with butanol gave a surface area of 37.7 sq. m. per gram for a sulfite alpha pulp and 207 sq. m. per gram for the same pulp highly refined.

Forziati, Brownell, and Hunt (27) exchanged water-swollen cotton with methanol, then with benzene or n-pentane and removed the final solvent by vacuum drying or with a stream of dry nitrogen. For cottons differing in variety and maturity or chemical treatment, B.E.T. areas ranged from 4 to 148 sq. m. per gram. These workers noted that different B.E.T. areas could be achieved with the same fiber sample by drying at different temperatures. Their limited data suggested that an optimum temperature of drying existed for obtaining a maximum surface area.

DETERMINATION OF PORE SIZE DISTRIBUTION FROM GAS ADSORPTION DATA

In the preceding section it was noted that Hunt, Blaine and Rowen (24) and Haselton (22, 23) had established pore size distribution curves from gas adsorption isotherms. The method used to establish these curves was developed by Shull (28) whose work was based on the earlier theories of Wheeler (29). Hunt and co-workers applied this method to the desorption branch of the isotherms whereas Haselton applied it to the adsorption branch. The Wheeler-Shull method is based on the assumption that all pore distributions are of a Gaussian or Maxwellian type. Barrett, Joyner and Halenda (BJH) (30) stated that Shull's assumption of a simple Gaussian or Maxwellian distribution of pore sizes is not justified for many adsorbents. These workers, in turn, provided a method for calculating pore volume distribution curves, which required no assumptions such as those made by Shull.

Wayne (31) thought the BJH method was inconveniently elaborate, and so proposed a rapid graphical approximation of the pore volume distribution curves. Pierce (32) adopted the essential features of the BJH method but modified the computations into a more simplified and straightforward method. The method of Pierce was used in this thesis.

The method of Pierce employs the desorption branch of the isotherm in establishing the pore volume distribution curves. Not all investigators have agreed as to whether the adsorption or desorption branch should be used in pore distribution computations. Recently, some convincing data have been presented to show that the desorption branch should be used (33, 34, 35).

PRESENTATION OF THE PROBLEM

The purpose of this thesis is to gain information which will provide a better understanding of the processes of liquid exchange of water-swollen cellulose fibers and the drying of these exchanged fibers from hydrocarbons.

The preceding literature survey indicates that the present understanding of WAN-dried fibers is limited primarily to data on the amounts of liquids retained in these fibers and to some observations on the increased porosity and accessibility of these fibers compared to water-dried fibers. The simple measurement of the quantity of residual liquid is insufficient to elucidate any mechanisms of WAN-exchanging and WAN-drying. In this respect, it has not been demonstrated that there are any consistent relationships between the large areas of WAN-dried fibers and their residuals of liquids. Nor has it been proved that development of larger surface areas is limited because it is not possible to replace less than a monomolecular layer of an intermediate polar exchange liquid with a final nonpolar liquid. In fact, there is no evidence relating the properties of the organic exchange liquids and conditions for removal of those liquids to any properties of the WAN-dried fibers.

To achieve the purpose of this thesis, gas adsorption techniques will be used. Such techniques will evaluate total surface areas, or accessibility to gaseous molecules, and total pore volumes of WAN-dried fibers.

It is known that some polar organic liquids can swell cellulose fibers, whereas nonpolar liquids do not. Thus, when fibers are dried from polar liquids, there may be effects which would not arise when drying is done from a nonpolar liquid. To eliminate such effects, this study, therefore, will be primarily devoted to drying from hydrocarbons. The knowledge gained by study of drying from nonpolar liquids should contribute to a better understanding of the more complex drying from polar liquids.

To achieve an understanding of the liquid exchange process, water-swollen fibers will be enchanged with methanol and various hydrocarbons of different molecular size and shape and of different solubility in methanol. The quantities of exchange liquids and the length of exchange time needed to achieve reproducible surface areas will be determined. Exchanges will also be made using different alcohols as intermediate exchange liquids but the same hydrocarbon for final exchanges. All drying from the final hydrocarbons will be done under a set of standard conditions. The results of such investigations may provide evidence for or against the proposal that intermediate polar exchange liquids, which cannot be replaced by a nonpolar liquid, control the development of WAN-dried fiber areas.

To obtain an understanding of the WAN-drying process, water-swollen fibers exchanged with methanol will be exchanged with different hydrocarbons and each hydrocarbon will be evaporated from the fibers at several different temperatures. These experiments will be evaluated by measurements of B.E.T. areas, amounts of residual hydrocarbons, and adsorption isotherms. These results should provide an insight into relations between area development, fiber porosity, residual hydrocarbons, and properties of the exchange liquids.

To this point all work will have been done with fibers which previously had never been dried. If these fibers are dried from water, the well-known phenomenon of irreversible bonding occurs. When these water-dried fibers are reswollen in water and liquid exchanged, the exchange process occurs in a structure of less specific surface area than for fibers never water-dried. The results for fibers which have been once-dried from water before reswelling and WAN-drying should establish the importance that fiber structure has in the retention of liquids in fibers dried from organic liquids.

A complete analysis of all results should contribute much to the understanding of phenomena related to the exchanging and drying processes.

DESCRIPTION OF APPARATUS

LIQUID EXCHANGE APPARATUS

Water has a great affinity for cellulose and its presence during the final stage of a WAN-drying process should decrease fiber surface area. Therefore, experimental equipment and procedures were designed to keep moisture to a minimum when cellulose was being WAN-dried.

The liquid exchange apparatus shown in Figure 1 was constructed entirely of pyrex glass and consists of three separate units: a distillate receiving flask (C), a liquid storage and metering unit (B), and a sample bulb (A).

The distillate receiving flask is basically a 250-ml. globe separatory funnel. To the stem of the funnel, an inner glass joint is sealed. A special assembly for conducting distillate into the receiving flask is attached to the mouth of the funnel. The side-arm of this assembly is an outer ground-glass joint which fits to a condenser during distillation or which holds a plug (E) during other operations.

The liquid storage and metering unit (B) constructed of 39-mm. pyrex test tubes has an outer joint at the top end for holding the distillate receiving flask. Also, near the top, a side arm is connected to either vacuum or pressure. The vacuum line was used when liquid was transferred from the distillate receiving flask into the metering unit. The pressure line was used when liquid was moved out of the metering unit and through the sample bulb. Air from the pressure line was dried by passage through a tube (D) filled with Anhydrone. The vent shown in Figure 1 permitted flushing out of the metering unit with new or fresh liquid without removing the attached sample tube.

The sample bulb was constructed by the following series of glass blowing operations: To a hole blown in the bottom of a 25-mm. test tube, there was sealed a 1-mm. capillary stopcock, the length of the capillary stem between the stopcock and the bottom of the test tube being 5 to 8 cm. At a point 5 to 8 cm. from this connection, the test tube was necked down to a 10-mm. diameter. At the 10-mm. diameter, the tube was broken and the rimmed section of the original test tube was discarded. The remaining structure is shown in Figure 1 as that part of bulb (A) below the dotted line S_1. The section above S_1 was made by sealing a 10/30 inner joint to one stem of a 2-mm. capillary stopcock. The end of the 10/30 joint was about 4 cm. from the center of the stopcock plug. On the other stem and at a distance of about 10 cm. from the center of the stopcock plug, a 10-mm. tubing was sealed. At a point 0.5 cm. from this latter seal, the 10-mm. tubing was broken, leaving that section of bulb (A) shown above line S_1 in Figure 1. After water-wet fibers were put into the lower section of the bulb through the opening at the 10-mm. neck, the two sections were sealed together at point S_1 in Figure 1. For exchange purposes, the sample bulb was attached to the metering unit through the 10/30 joint shown in Figure 1.

APPARATUS FOR EVAPORATION OF ORGANIC LIQUIDS FROM FIBER SAMPLES

Figure 2 shows the experimental setup for evaporating the final organic liquid from an exchanged fiber sample at room temperature. Prepurified nitrogen passes through drying tubes D_1 of Anhydrone, and D_2 of phosphoric

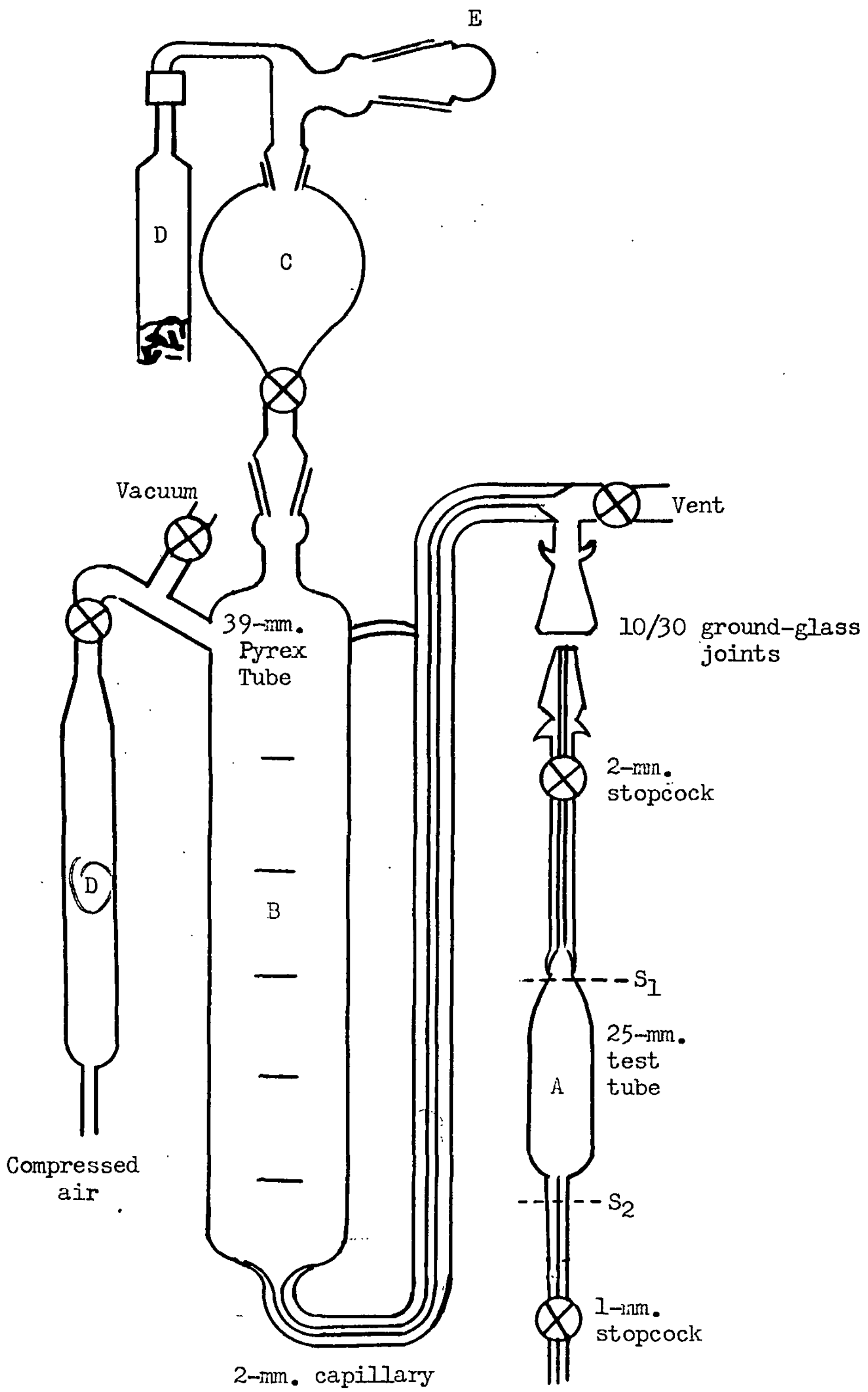

Figure 1. Liquid Exchange Apparatus

anhydride mixed with glass wool, and through a flow meter before passing through the sample bulb (A). The rate of gas flow as indicated by the flow meter is controlled by a stopcock (G). The vent shown in Figure 2 permits continuous flow of gas through the system when the bulb is attached to the apparatus and before drying has started.

When drying is to be done at temperatures near or above room temperature, an attachment to the sample bulb is made as shown in Figure 3. This attachment consists simply of a 50-mm. pyrex tube 13 cm. long with a 10-mm. side arm. This tube is held around the sample bulb by a split No. 10 rubber stopper. The stopper fits snugly around the lower capillary stem of the sample bulb and carries a glass tubing connected to a circulating pump and water reservoir of constant temperature. The entire assembly of Figure 3(a) adapts to the drying apparatus of Figure 1 through the 10/30 ground-glass joints and is held there by metal springs or rubber bands and hooks.

For drying at temperatures below 0°C., the sample bulb (A_1) shown in Figure 3(b) is used. This bulb is an obvious modification of sample bulb (A). Drying is carried out with bulb (A_1) immersed in a cold bath to some level below the stopcocks, the bulb assembly being connected to a drying apparatus identical to that in Figure 2.

GAS ADSORPTION APPARATUS

The gas adsorption apparatus is of the volumetric type shown in Figure 4. Description of this apparatus may be obtained by reference to Haselton (<u>22</u>). The designations of structural components in Figure 4 are identical with those in Haselton's description and the changes in design should be

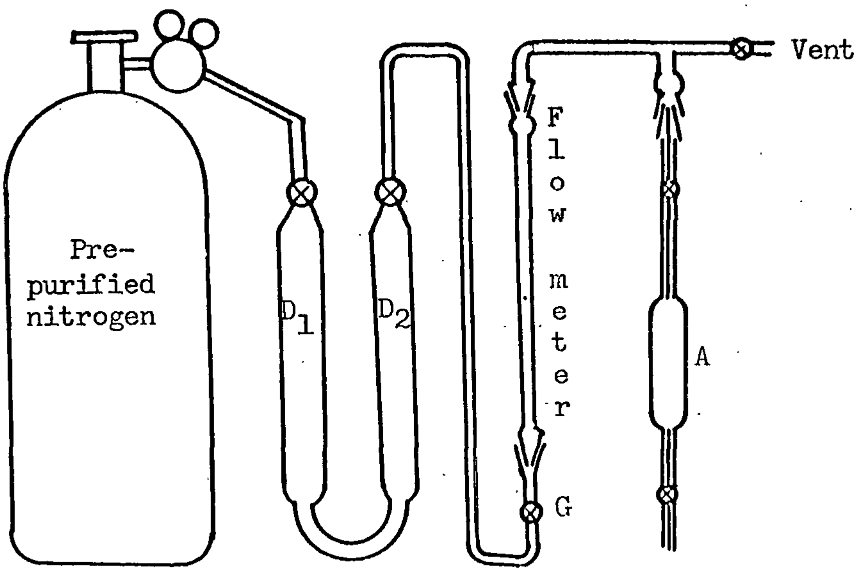

Figure 2. Drying Apparatus

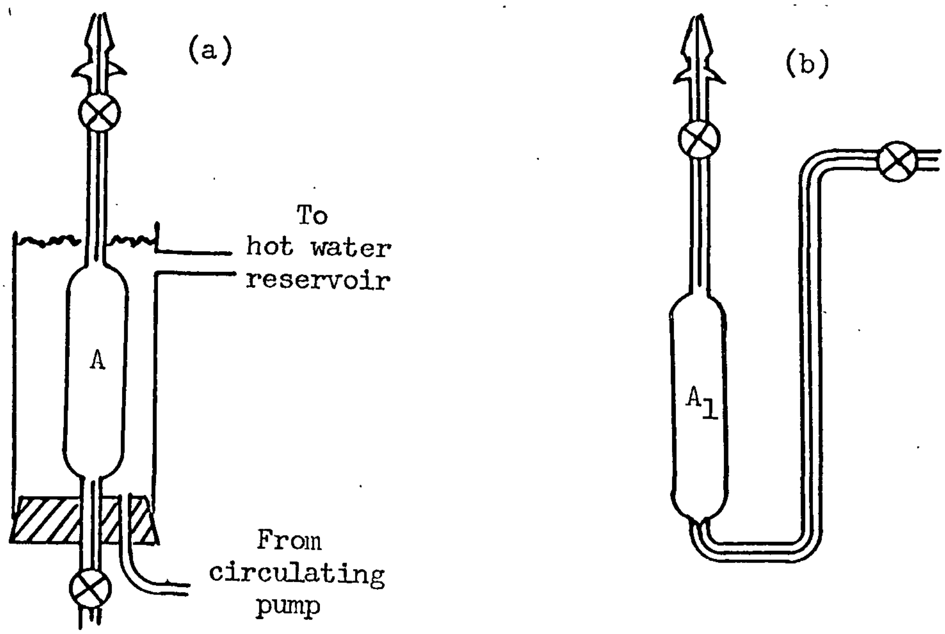

Figure 3. Special Drying Assemblies

obvious. The most significant change is the method of attaching the sample bulb to the adsorption apparatus. By the new method the sample bulb has an inner 10/30 ground-glass joint (G) which fits an outer joint of the adsorption apparatus. Formerly the sample bulb was flame sealed to the apparatus.

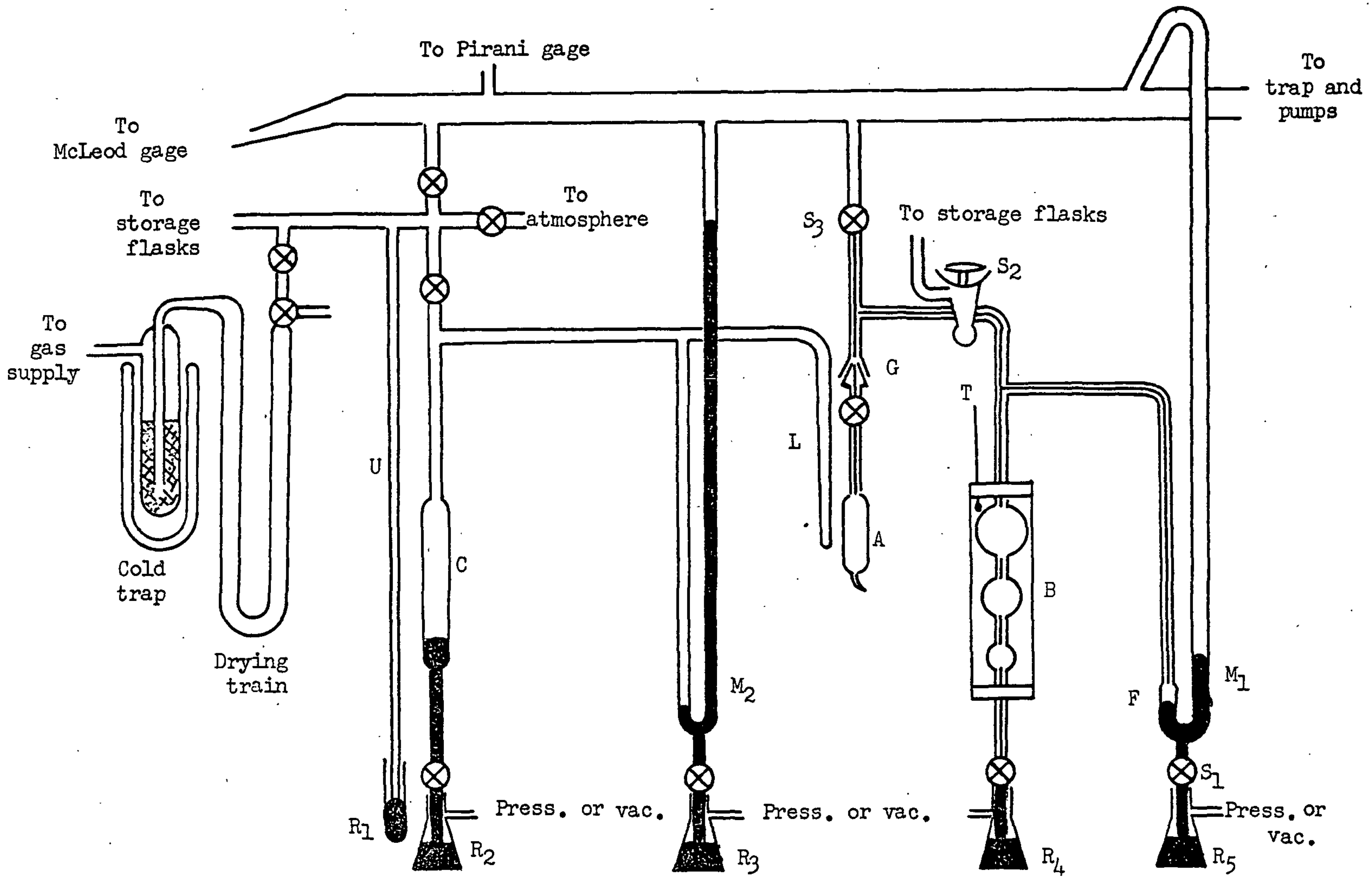

Figure 4. Gas Adsorption Apparatus

GENERAL EXPERIMENTAL PROCEDURES

PREPARATION OF PULP

All experiments were made with a commercial fully bleached Mitscherlich spruce sulfite pulp which was obtained at a nearby mill. The pulp of about 25% solids was collected at a roll press of a wet-lap machine and quickly stored in four Pliofilm bags. In the Institute laboratory, the pulp from each bag was torn into small pieces, soaked in distilled water for 0.5 hour, and slurried with a Lightnin' stirrer. The slurry was drained on a cloth wash box and the resulting thickened pulp was thoroughly washed with filtered tap water. The pulp was soaked once more in distilled water for 10 to 15 minutes before it was drained and given a final washing with distilled water. Thereafter, the pulp was centrifuged, and broken up into small pieces. Each bag of pulp weighing about 2500 grams was treated with 75 ml. of a 0.2% solution of Lignasan, and placed in cold storage in Pliofilm bags. This pulp was of about 29% solids content. The pulps from each of the orignial four bags were handled separately but given similar treatments.

The experimental pulp was analyzed for Klason lignin (Institute Method 13) and alpha-cellulose (Institute Method 421a). The results of these analyses are given in Table I. The data of Table I show that the experimental pulp had a negligible lignin content.

TABLE I

ANALYSIS OF PULP

Klason lignin, %	0.2	Sample no. 1
	-0.1	Sample no. 2
Alpha-cellulose, %	83.4	
Extractives, %	0.55	

PREPARATION OF ANHYDROUS EXCHANGE LIQUIDS

DRYING OF ALCOHOLS

Methanol, ethanol and propanol were used in the course of the investigations and all three were dried by the method which employs magnesium turnings and iodine (36).

After the alcohol had been dried by the chemical reaction and just minutes before it was to be used in the exchanging process, it was distilled from the reaction flask to the distillate receiving flask. The latter flask held 250 ml. of liquid. When this flask was filled, it was removed from the distilling apparatus and its receiving opening quickly plugged as shown in Figure 1. To achieve optimum anhydrous conditions, the first 200 ml. of dry distillate was used to flush the walls of the condenser and receiving flask before collection of the exchange portion was started. Furthermore, all distillations were timed so that they were completed within five minutes of the start of the exchange process.

Using Institute Method 615, dried methanol which had stood in the receiving flask for several hours was analyzed for moisture. The alcohol contained 0.0079% of water or approximately 0.000063 grams of water per milliliter of alcohol.

DRYING OF HYDROCARBONS AND MISCELLANEOUS ORGANIC LIQUIDS

All hydrocarbons were dried by refluxing with ribbons of freshly extruded sodium. Refluxing was usually carried out overnight. The conditions of distillation were the same as for the alcohols.

Acetone was dried by storage over anhydrous calcium sulfate; whereas, tetrahydrofuran and ethyl ether were both dried in the same manner as the hydrocarbons, that is, by refluxing with sodium ribbon.

LIQUID EXCHANGE PROCEDURES

The first objective of the experimental program was to establish a liquid exchange procedure which would give reproducible surface areas for a selected drying method. This exchange procedure will now be described and from hereon referred to as the "standard method of exchange". The experiments which led to the standard method of exchange will be described later. In giving details of experiments, it will be noted if procedures differ from the following standard method.

A six-gram sample of the experimental pulp was uniformly dispersed in 250 ml. of distilled water by stirring gently for a few seconds. The pulp was not given any further agitation during a 48-hour soaking period. After soaking, the pulp was drained on a coarse fritted-glass funnel just until there was no free water standing above the pulp. In this dripping-wet state, the pulp was transferred by fingers to the sample bulb through the opening of the necked-down portion of the lower half of the bulb shown in Figure 1. The wet pulp was loosely packed in the bulb. Free water always stood above the fibers after loading of the bulb.

The next step was to flame-seal the upper part of the sample bulb to the lower. While this was being done, the fibers were protected from the heat by wrapping a piece of water-soaked paper towel around the lower half of the bulb. Blowing of the softened glass during sealing was done through rubber tubing connected to the 10/30 ground-glass joint. With the stopcock plug removed from the upper section of the bulb, and corks inserted in the plug openings, a chamber for condensed steam from the liquid above the sample was provided. Although the free water above the pulp sample usually boiled away, the top fibers were thoroughly wet during and after the glass blowing operations. After the sealing procedures, the stopcock plug was reinserted, and the completed sample bulb was attached to the liquid exchange apparatus.

The sample was liquid exchanged by the following standard schedule:

1. The first exchange was with 400 ml. of absolute methanol. With a pressure of 5 p.s.i., as a driving force, a 40-ml. quantity of methanol was passed through the sample in approximately one minute. Thereafter, every 10 minutes a 40-ml. quantity of methanol was forced through the sample, until the 400 ml. had been used. The exchange was completed in 100 minutes.

40ml every 10 min

2. The second exchange was by the same procedures as above except that 200 ml. of dried methanol was the exchange liquid. This exchange was completed in 50 minutes.

5 exchanges, 50 min

3. The third exchange was carried out as in the foregoing but with 200 ml. of a hydrocarbon dried over sodium. This exchange was completed in 50 minutes.

4. The fourth exchange was identical to the third but is designated separately because a freshly distilled 200-ml. quantity of hydrocarbon was used.

The manipulations required to operate the exchange apparatus should be obvious by reference to Figure 1. With the metering unit under vacuum, the exchange liquid was permitted to flow from the receiving flask into the metering unit. Pressure was then admitted to the metering unit. With pressure on the liquid level in the metering unit, and the upper stopcock of the sample bulb opened, the flow of exchange liquid was controlled by the lower stopcock of the sample bulb.

When the sample bulb was placed on the exchange apparatus, the upper stopcock of the bulb was not lubricated. When the final quantity of liquid had been exchanged through the sample, and with the bulb still attached to the exchange apparatus, the plug of the upper stopcock was removed and lubricated with Silicone vacuum grease. While the plug was out, dry compressed air flowed out of the plug openings and thus prevented moisture from reaching the contents of the bulb. After the lubricated plug was replaced and the stopcock closed, the sample bulb was transferred to the drying apparatus.

PROCEDURES FOR EVAPORATING ORGANIC LIQUIDS FROM LIQUID-EXCHANGED FIBERS

The sample bulb containing fibers immersed in a final exchange liquid was held with rubber bands to the drying apparatus as shown in Figure 2. After attachment of the bulb to the apparatus and with the vent on the apparatus opened, the rate of flow of dry nitrogen at room temperature and atmospheric pressure was set at 50 ml./min. Next the vent was closed and the upper stopcock of the bulb opened. When the lower stopcock of the bulb was opened, the free liquid around the sample drained from the bulb and thereafter drying commenced, the evaporating organic liquid being carried out of the sample bulb by the flow of the dry nitrogen. Drying was continued until after an eight-hour period, the sample bulb showed no loss in weight. This constant weight was noted on a balance accurate to 0.5 mg. Drying times were established for each liquid and thereafter samples were not weighed for a constant weight but left on the drying apparatus for the predetermined time and assumed to be then dried. For drying at room temperature, the drying times are given in Table II.

TABLE II

TIME ALLOWED FOR DRYING OF VARIOUS ORGANIC LIQUIDS FROM CELLULOSE

Liquid	Drying Time[a] hrs.
Ethyl ether	18 - 24
N-pentane	18 - 24
N-hexane	36 - 44
Cyclohexane	44 - 48
Benzene	44 - 48
Toluene	44 - 48
Acetone	48
Tetrahydrofuran	48

[a] A rate of 50 ml./min. of dry nitrogen was maintained during drying, and all samples were dried at room temperature.

When evaporation of the organic liquid was to be at temperatures above room temperature, the experimental arrangement of Figure 3(a) was attached to the drying apparatus. When the temperature of the bulb contents equalled that of the circulating water, drying proceeded in the same manner as previously described.

For drying at temperatures below 0°C., the sample bulb shown in Figure 3(b) was immersed in a cold bath to some point above the liquid level in the bulb. The 10/30 ground-glass joint was attached to a drying apparatus, and when the sample had reached the lower temperature, drying proceeded in the manner previously described.

Drying at lower temperatures required longer times which varied for different liquids. Again, the completion of drying was determined by drying to constant weight of the sample bulb. If the sample weight did not change after a 24-hour period, drying was considered completed.

A sample which was not completely dried could be readily detected by the gas adsorption apparatus. For such samples, the outgassing period to achieve the required pressure for adsorption measurements was several hours long. A thoroughly dried sample could be outgassed to the required pressure in a few minutes.

Before drying was completed, the lower stopcock of the sample bulb was removed and relubricated with Silicone vacuum grease. At the completion of drying, the lower stopcock was closed first and the upper one next. The sample bulb was then removed from the drying apparatus.

PREPARATION OF SAMPLE BULB FOR ADSORPTION MEASUREMENTS

The sample bulb as removed from the drying apparatus was not immediately ready for the adsorption measurements. There was no longer a need for the lower stopcock of the bulb so it was removed. This was done by first attaching the ground-glass joint to a rubber hose of a vacuum pump and then opening the upper stopcock to evacuate the bulb. After evacuating for about a minute, the upper stopcock was closed again. When a torch was applied at a point on the lower capillary stem of the bulb, the vacuum permitted the softened capillary walls to collapse and fuse together. The capillary tubing was severed at a point about 1 cm. from the bottom of the bulb. The fibers were protected from the heat by wrapping wet paper around the body of the bulb. The dry fibers sealed in the sample bulb and under vacuum were then ready for the adsorption measurements.

GAS ADSORPTION MEASUREMENTS

The sample bulb was attached to the adsorption apparatus by the ground-glass joint as shown in Figure 4. Before the stopcock of the sample bulb was opened for outgassing, the capillary sections of the apparatus and bulb which were exposed to the atmosphere during attachment of the bulb were outgassed for about one hour. The sample was then outgassed for at least four hours after a pressure of 10^{-6} mm. of mercury was reached. More commonly, the sample was outgassed overnight.

The procedures for obtaining the adsorption measurements need not be detailed here as they have been set forth by Haselton (22). The general requirements were that four equilibrium adsorption points be obtained between the relative pressures (P/P_o) of 0.05 to 0.30. These points were used to calculate B.E.T. areas.

When it was required to establish both adsorption and desorption branches of an isotherm, two procedures could be followed: The isotherm could be determined in one continuous experimental run of 16 to 20 hours. Another attack would be to complete the isotherm in two separate runs. Large adsorption and desorption increments could be carried out one day and the following day new data would provide the isotherm detail not achieved by the previous run. This latter attack was employed because, in effect, it offered a duplication of the isotherm.

DETERMINATION OF SAMPLE WEIGHT AND THE AMOUNT OF RESIDUAL ORGANIC LIQUID

It was desirable to know the weight of a WAN-dried sample before adsorption measurements were made. This knowledge permitted the B.E.T. area to be calculated while the sample bulb was still on the adsorption apparatus. If inconsistencies appeared in the calculations, the experimental data could be redetermined.

An approximate fiber weight was obtained before the sample bulb was attached to the adsorption apparatus. Before the fiber sample was put into the sample bulb, the two parts of the bulb were weighed. Prior to this weighing, the two stopcocks had been lubricated. (This lubricant was removed prior to WAN-exchanging and replaced prior to WAN-drying.) After the lower stopcock had been cut from the sample bulb, the weight of the bulb filled with dried fibers under vacuum and the weight of the severed stopcock were obtained. The total of these two weights plus a correction for buoyancy effects, minus the previous weight of the empty bulb gave an approximate fiber weight. The buoyancy correction was determined by multiplying the density of air at 70°F. (0.0012 gram. per ml.) by the volume of the empty bulb. This volume was determined by measuring the volume of water required to fill the bulb before it was loaded with fibers.

After the sample bulb was removed from the adsorption apparatus, the exact sample weight was determined. The stopcock on the bulb was briefly opened to equilibrate pressures inside and outside of the bulb. A file scratch was made on the large diameter of the bulb. The bulb was then weighed to the nearest 0.1 mg. A hot wire was used to break open the bulb and after removing the fiber sample the weight of the empty bulb was determined. This weight subtracted from the former gave the most accurate weight of fibers dried from an organic liquid. This value was used to calculate B.E.T. areas. This value was not the ovendry weight of the original fibers because the WAN-dried fibers had retained a quantity of organic liquid which was not removed during drying.

The quantity of residual organic liquid was obtained as follows: The fiber sample removed from the broken bulb was placed in a tared weighing bottle. The sample was covered with distilled water and permitted to soak overnight. Upon wetting, the sample gave off a strong odor of the liquid from which it was dried. The water-soaked sample was dried to a constant weight on a 105°C. oven. By subtracting the weight of the weighing bottle from this constant weight, the oven-dried weight of the fibers was obtained. The weight of the cellulose plus organic liquid less the oven-dried weight gave the weight of residual liquid. The weight of residual liquid divided by the oven-dried fiber weight gave the percentage residual.

STUDIES OF LIQUID EXCHANGE VARIABLES

The process of replacing one liquid by another in a cellulose fiber involves a number of variables. Amoung these are the quantity of the new liquid required to replace the old and the time required for a given quantity of the new to replace the old. The temperature of exchange, the molecular sizes and purity of the exchanging liquids, whether or not agitation is used during exchange, and the distribution of pore sizes in which exchange occurs are also involved. In the latter case, many small pores may hold molecules which cannot be replaced by larger molecules unable to enter the small pores. If the new liquid is not completely miscible with the old, there is an uncertainty of whether replacement of the old is complete. The degree of fiber swelling is a variable if any exchange liquid can swell the cellulose. Furthermore, biologists have noted that tissues undergo shrinkage and distortion upon immersion in alcohol, and it has been suggested that cellulose might behave similarly when dehydrated with alcohol (10, 27).

In order to control some of these variables or to determine their relative importance, a series of experiments were carried out which related the numerous variables to the development of fiber surface areas. The WAN-dried fibers received different treatment during the exchange process but all were dried under the same conditions.

EFFECT OF RATE OF LIQUID EXCHANGE AND OF FIBER SOAKING TIME

If the standard exchange rate described in the Procedures Section is too fast to permit the most complete replacement of the old liquid by the new, an increase or decrease of that rate should, respectively, increase or decrease the amount of unexchanged old liquid. In this work, varying the amount of water replaced by methanol should affect the area developed upon drying. Haselton (23) showed that fibers WAN-dried from benzene decreased in area from about 65 to 25 sq. m. per gram when exposed to a relative humidity of 22.9% and redried. At this low relative humidity no capillary condensation of water has occurred that would bring the high surface tension effects of water into play; moreover, at this relative humidity, even the presence of a complete monomolecular layer of water is questionable. Upon WAN-drying, therefore, if traces of water are present on fibers because of incomplete removal by liquid exchange, decreasing areas with increasing amounts of residual water should be found. Varying amounts of unexchanged methanol should be expected to cause a similar effect.

In the first series of experiments, effects of WAN-exchanging at different rates with constant quantity of exchange liquid and effects of water-soaking the experimental pulp for different times before exchanging were studied. In these experiments, the final exchange liquid was benzene unless otherwise noted.

Sample E-1[1] was uniformly dispersed in 250 ml. of water by gentle stirring and soaked for 48 hours. The fibers for Sample E-2 were sealed into a bulb and soaked therein for 48 hours without agitation. E-1 and E-2 were WAN-exchanged by the standard method described in the section of General Procedures. The exchange rate for this method was 40 ml./10 min.

[1] The sample designation E-1 means that it is the first experiment performed on the given sample. E-1R means that a repeat surface area determination has been made on the Sample E-1. The designation E-1A means that Sample E-1 has received some treatment which may modify it. If a duplicate experiment is made with a new fiber sample, the duplicate is designated as E-1D.

Sample E-6 and all later samples were stirred into a uniform dispersion with 250 ml. of water. E-6 and E-6D were soaked for 48 hours but unlike the previous samples were WAN-exchanged at the rate of 40 ml./20 min. with the standard quantities of 400 ml. of absolute methanol, 200 ml. of dried methanol, and 400 ml. of benzene. For comparison with the above experiments, two samples, E-3 and E-4, were soaked for only 24 hours and exchanged at the rate of 40 ml./10 min. and 40 ml./5 min., respectively. In addition, Samples E-9 and E-10 were soaked for 12 and 81 hours, respectively, and WAN-exchanged at the standard rate.

Because of the relatively large size of its molecules, benzene was selected for the above series of experiments. For comparison, some of the above experiments were repeated with n-pentane, a smaller and linear molecule. In these experiments the soaking times were 10 minutes (E-21), 24 hours (E-32, E-37) and 48 hours (E-17, E-17D, E-31, E-44). For this series the standard methods of exchanging and drying were used.

The results presented in Table III show that the time allowed for the standard exchange was sufficient. Two samples (E-6 and E-6D) which were exchanged in 500 minutes showed no significant differences in areas when compared with two other samples (E-1 and E-3) which were exchanged in 250 minutes, when all four samples were exchanged with the same quantities of liquids.

The choice of 48 hours as a standard time for soaking fibers is justified by the results of Table III. Comparing Sample E-9 with E-10 and Sample E-17 with E-21, no significant change in area is noted with considerable differences in soaking times. This result was to be expected.

The fibers had never been dried and therefore it was unlikely that any bonding had occurred which might have been disrupted to different extents by resuspension in water for different lengths of time.

TABLE III

EFFECTS OF LIQUID EXCHANGE RATES AND FIBER SOAKING TIMES

Sample No.	Exchange Rate, ml./min.	Time of Water-Soaking, hrs.	B.E.T. Area, sq. m./g.[1]	Final Exchange Liquid
E-1	40/10	48	43.0	Benzene
E-2	40/10	48	43.7	Benzene
E-3	40/10	24	44.3	Benzene
E-6	40/10	48	42.6	Benzene
E-6D	40/10	48	44.6	Benzene
E-9	40/10	12	46.2	Benzene
E-10	40/10	81	46.7	Benzene
E-31	40/10	48	122	Matheson practical grade n-pentane
E-32	40/10	24	119	Same as E-31
E-17	40/10	48	129	Viking n-pentane (grade unknown)
E-17D	40/10	48	128	Same as E-17
E-21	40/10	10 min.	129	Same as E-17
E-37	40/10	24	133	Phillips pure grade n-pentane
E-44	40/10	48	129	Phillips pure grade n-pentane, repurified

[1] All samples were dried at room temperature.

The results of Table III show that two samples (E-31 and E-32) dried from Matheson practical grade n-pentane had areas of 122 and 119 sq. m. per gram. Two additional experiments (E-27 in Table IV and E-34 in Table VIII) using this same grade of n-pentane resulted in areas of 122 and 121 sq. m. per gram. Thus, Matheson practical grade of n-pentane consistently gave fiber areas of about 121 sq. m. per gram; however, on comparable experimental bases as shown in Table III (and Table IV), several samples dried from Viking and Phillips pure grade of n-pentane had areas of about 129 sq. m. per gram. There apparently were two levels of fiber areas depending on the source of supply of the n-pentane. It was concluded that such variation could be attributed to difference in purity of the hydrocarbon from different sources.

Thereafter, all samples were treated with Phillips pure grade of hydrocarbons. As shown by the results in Table III, the additional purification of Phillips pure grade of n-pentane by treatment with an acidic permanganate solution did not result in a change in fiber surface area.

An idea of the reproducibility of the standard method of exchanging and drying can be gained from the data of Table III. The standard deviation of the data for samples dried from benzene is 1.51 sq. m. per gram, (3.4%). For the data of fibers dried from Viking or Phillips n-pentane, the standard deviation is 1.9 sq. m. per gram, (1.4%). The greater variation of the data for the samples dried from benzene may be attributed partly to the matter of chemical purity mentioned above. The samples dried from benzene were exchanged with a c.p. grade of the liquid from the two different suppliers; but at that stage of the work, no attempt was made to keep the results separated on the basis of source of chemical.

The data of Table III show that there is agreement within 5 sq. m. per gram of five samples dried from Phillips and Viking n-pentane at room temperature. This agreement is even better when it is considered that no attempt was made to control the temperatures of drying. These temperatures may have varied from 23 to 33°C. Subsequent investigations revealed that this range of temperatures could easily account for an area variation of 5 sq. m. per gram.

EFFECTS OF TOTAL QUANTITY OF EXCHANGE LIQUID AND RATE OF DEHYDRATION

To determine whether the quantities of liquids used in the standard exchange method were sufficient to give reproducible surface areas, samples were exchanged with increased amounts of methanol, or the final exchange liquid and dried at room temperature. For Sample E-5, the first exchange step was done in 50 minutes with 1800 ml. of dried methanol; the remaining steps followed the standard method, using benzene as the final liquid. The standard exchange method was also modified for Sample E-50. In this case, after the exchange with 400 ml. of absolute methanol, 200 ml. of dried methanol in 20-ml. portions were passed through the sample at intervals during an eight-hour period after which exchanging continued by the standard method with more dried methanol and finally _n_-pentane.

To note whether the rate at which water was removed from fibers caused a shrinkage of the fiber structure, Sample E-7 was exchanged with 200-ml. quantities of a series of solutions of methanol in water. The series included concentrations of 5, 10, 20, 30, 50, 70 and 90% by volume of methanol in water. These exchanges were followed by the additional exchanges of the entire standard exchange method. It was felt that the replacement of water by the gradual exchange with increasing concentrations of methanol in water was slow enough to inhibit any tendency for fiber structure collapse by rapid dehydration. Benzene was the final liquid of Sample E-7 but the procedures were repeated for Samples E-8 and E-27 for which the final liquid was _n_-pentane. The above procedures of Sample E-7 were slightly modified for Sample E-41. For the latter, fibers were water-soaked for 36 hr., exchanged at standard rates with 200 ml. of 5% solution, and permitted to remain in contact with the 5% methanol solution for 12 hours; thereafter, the exchange continued as in the case of E-7, starting with the 10% solution. For E-41, n-pentane was the final exchange liquid.

Any effects which might arise as a result of rapid removal of alcohol from fibers was tested in the experiment with Sample E-8. For this sample, after the standard exchanges with methanol, exchanges were made with 200 ml. each of 5, 10, 15, 20, 30, 50, 70 and 90% by volume of benzene in methanol followed by exchange with 400 ml. of dried benzene. All exchanges were at the standard rate.

The results of Table IV show that when the areas of samples exchanged with increased amounts of liquids are compared with those of samples exchanged with the standard amounts, one finds no significant difference. This means that the standard exchange method gave complete removal of water and methanol, or that these liquids had been displaced to a constant amount which could not be decreased by further exchanges.

The data given in Table IV also confirm the observations of others (10, 27) that rapid dehydration of fibers with alcohol does not result in fiber shrinkage; at least over a considerable range of rate of dehydration, no change in fiber area was observed. The area of Sample E-7 appears to be comparatively large as a result of slow dehydration, but Samples E-27 and E-41 which were in essence duplicates of the former did not show such an effect.

TABLE IV

EFFECTS OF LIQUID QUANTITIES AND RATE OF DEHYDRATION

Sample No.	B.E.T. Area, sq. m./g.	General Experimental Procedures[1]
E-5	43.5	Exchanged with increased amounts of methanol, and WAN-dried from benzene
E-7	48.2	Dehydrated slowly, WAN-dried from benzene
E-8	42.9	Methanol replaced slowly, WAN-exchanged from benzene
E-1[2]	43.0	Standard exchange, compare with E-5, E-7, and E-8
E-27	122	Dehydrated slowly, WAN-dried from Matheson n-pentane
E-31[2]	122	Standard exchange, compare with E-27
E-50	127	Exchange with increased amounts of methanol, and WAN-dried from Phillips n-pentane
E-41	126	Dehydreated slowly, WAN-dried from Phillips n-pentane
E-44[2]	129	Standard exchange, compare with E-50 and E-41

[1] All samples were dried at room temperature.

[2] Data taken from Table III.

EFFECTS OF FINAL EXCHANGE LIQUID

It is conceivable that during the liquid exchange process internal parts of the cellulose fibers act as sieves for the exchange molecules. There could be pores into which a small molecule like methanol might diffuse and replace water but into which a bulky hydrocarbon could not diffuse to replace the methanol. Staudinger and Döhle (9) classified fibers dried from methanol or water as inactive celluloses. These celluloses were difficult to acetylate because the drying from water or methanol had brought about the well-known effects of hornification. The degree of acetylation of these water-dried and methanol-dried fibers were 0.43 and 1.1% respectively; whereas for the same ramie fibers soaked in water, liquid exchanged, and dried from benzene the degree of substitution was 19.9%. Therefore, if methanol is not displaced from fibers as completely with a bulky cyclic hydrocarbon as with a linear hydrocarbon, greater areas should be consistently developed from the latter. This effect would suggest two results; (1) that incomplete removal of methanol would control the extent of fiber area development, and (2) that molecules of different size or bulkiness could be used to achieve different fiber areas and thus give an indication of the extent of pores of various molecular dimensions in fibers. To investigate these possibilities, fibers were WAN-dried at room temperature from a series of hydrocarbons of different size and shape. The results of these experiments are given in Table V.

TABLE V

EFFECT ON SURFACE AREA OF FINAL EXCHANGE LIQUID

Sample No.	B.E.T. Area, sq. m./g.[1]	Final Exchange Liquid	Molecular Shape
E-1	43.0	Benzene	Cyclic
E-57	48.1	Toluene	Cyclic and branched
E-51	88.5	Cyclohexane	Cyclic
E-29	108	n-Hexane	Linear
E-44	129	n-Pentane	Linear

[1] All samples were dried at room temperature.

Of the liquids listed in Table V, toluene is perhaps the bulkiest molecule, with cyclohexane, benzene, n-hexane, and n-pentane following in decreasing order of bulkiness. Although cyclohexane can assume "boat" and "chair" structural configurations, it is doubtful that this property appreciably lessens its effective minimum cross-sectional area for entering molecular-size pores; moreover, this molecular area should be greater than that of the unsaturated benzene molecule. On this basis of molecular size, the results of Table V permit some interesting speculations on the exchange process.

Toluene is a larger molecule than benzene yet Table V shows that fibers WAN-dried from toluene had a greater area than those dried from benzene. On the bases of molecular size and solubility in methanol, toluene probably did not remove more methanol from the fibers than benzene; thus, the two apparently removed methanol to the same extent. Thus, methanol had to be in pores of such a size that either benzene or toluene could enter for equally effective replacement of the alcohol. On this basis, two conclusions may be drawn from the fact that fibers dried from toluene had a larger area than those dried from benzene. These conclusions are: (1) that the hydrocarbons completely replaced methanol from the fibers or replaced it to an amount which did not control the magnitude of the fiber areas developed, and (2) that a property of the final liquid was responsible for the development of different areas.

Fibers dried from cyclohexane had an area nearly double the area of fibers dried from either of the aromatics. Cyclohexane is a slightly larger molecule than benzene; moreover, unlike benzene, cyclohexane is not completely miscible with methanol. If cyclohexane did not replace as much methanol as benzene, a smaller surface area would have been expected. Thus, the effectiveness with which methanol can be replaced must not depend on complete miscibility of the hydrocarbon with methanol. Furthermore, n-hexane and n-pentane should have been expected to be equally effective in replacing methanol since they are nearly equal in size and both are completely miscible with methanol; yet fibers dried from n-pentane had a 20% greater area than those dried from n-hexane.

The above comparisons cast doubt upon the idea that the hydrocarbons replaced all but a monomolecular layer of methanol (19). This is supported by the previous statement that traces of water affect fiber area and of how methanol and water decrease the reactivity of fibers dried from them; therefore, it seems that a momomolecular layer of alcohol would have controlled the development of fiber areas and thus the areas achieved by use of different hydrocarbons would have been nearly equal. However, the areas developed from different hydrocarbons varied greatly. Such variation can not be attributed to different amounts of unreplaced methanol; because, as previously discussed. conditions for at least equal replacement of methanol gave different areas. Therefore, it seems likely that the variations in fiber areas were the result of differences in properties of the different hydrocarbons.

THE EFFECT OF THE ALCOHOL

Methanol was selected as the intermediate exchange liquid for the standard method because it is the smallest molecule miscible with water and many hydrocarbons. It was expected that the small molecule would give the most complete removal of water by virtue of its ability to enter very small pores. However, it has been shown that molecular sieves (structures with pores of molecular size) occlude equal volumes of molecules of different chain lengths but of the same minimum cross-sectional area (37). Thus, ethanol and n-propanol with the same minimum cross-sectional area as methanol should be able to remove as much water from fibers as methanol. To support this reasoning, Samples E-17, E-20, and E-22 were exchanged with standard quantities of methanol, ethanol, and n-propanol, respectively, and subsequently WAN-dried at room temperature from n-pentane. Table VI shows that these three samples did not develop the same area; thus, the effectiveness of water removal must not have been equal for the three alcohols.

TABLE VI

THE EFFECT ON SURFACE AREA OF THE ALCOHOL

Sample No.	B.E.T. Area, sq. m./g.	Intermediate Exchange Liquid	Final Exchange Liquid[1]
E-17	129	Methanol	n-Pentane
E-20	108	Ethanol	n-Pentane
E-22	103	n-Propanol	n-Pentane
E-46[2]	109	Ethanol	n-Pentane

[1] All samples were given standard exchange and were dried at room conditions.

[2] Water was exchanged by ethanol at 40° C. and at a slow rate.

It could be reasoned that the samples exchanged with ethanol or n-propanol would have replaced as much water as methanol if more time had been allowed for these longer molecules to diffuse into the smaller pores. This reasoning was not supported by the data of Sample E-46 in Table VI. A sample exchanged with the standard quantities of ethanol at 40°C. and at a rate of 40 ml. quantities every 15 minutes did not develop a greater area than did a sample exchanged at room temperature and at the standard rate.

There are two possible factors that may be responsible for the lower areas of the ethanol and n-propanol-exchanged samples. First, there is the possibility that the method of water removal from ethanol and n-propanol was not as effective as for methanol. This method was the same for all three alcohols but it was observed that for both ethanol and n-propanol the reaction of the magnesium turnings to the corresponding magnesium alkoxide was never complete even after hours of refluxing, whereas for methanol the reaction was always completed in about 15 minutes. It was assumed that the reaction had advanced far enough that complete drying of the ethanol or propanol was realized. The second possibility rests upon the fact that the alcohols are known to associate with themselves and, thus, effectively form larger molecules. Therefore, it is conceivable that the water removal was not controlled by the minimum cross-sectionsl area of single molecules but by the larger dimensions of associated molecules. It would be expected that associated ethanol and n-propanol molecules would be more bulky than those of methanol; thus, less water would be replaced with ethanol and n-propanol; and as a result, lower fiber areas would be developed.

The results made methanol the logical choice as best of the three alcohols to use as the intermediate liquid in the exchange process.

AN INVESTIGATION OF INTERNAL BONDING OF WAN-DRIED FIBERS

It is known that considerable irreversible bonding occurs when fibers are dried from water the first time. That is, bonds are formed which cannot be disrupted by reswelling in water. Whether or not similar bonding results to a lesser degree from the WAN-drying of fibers has never been demonstrated. To make such a demonstration, Sample E-38 was WAN-dried from benzene. Without removing these dried fibers from the sample bulb, n-pentane was flushed onto the sample and a standard exchange was made with 400 ml. of the n-pentane. The sample was dried a second time and its B.E.T. area was then determined. After this area determination, the sample bulb was broken open and the fibers were soaked in 250 ml. of distilled water for 48 hours. These fibers were designated as Sample E-38A. They were sealed in a new sample bulb and WAN-dried by the standard methods with pentane as the final liquid.

The results given in Table VII show that fibers WAN-dried from n-pentane had an area nearly three times that of fibers dried from benzene. Moreover, if a sample of fibers WAN-dried from benzene was soaked in n-pentane, given a standard exchange with this liquid and dried therefrom, an area decrease resulted. However, when this sample, which had been dried twice, once from benzene and once from n-pentane, was soaked in water and then given a standard exchange and WAN-dried from n-pentane, the area was nearly 4 times what it was after the second drying.

Treatment with n-pentane did not increase the area of the fibers previously dried from benzene because the pentane could not swell the WAN-dried structure. The structure was swollen by water. These effects suggest that if any hydrogen bonds were formed during the WAN-drying of fibers they could be broken in water. The lower areas of Samples E-38 and E-40 as compared with E-1 and E-17, respectively, may have been the result of the second drying given the sample (E-38). The treatment with n-pentane may have introduced traces of moisture to the fibers. Also, some bonds formed upon drying from hydrocarbons may not be broken.

TABLE VII

THE CHANGE OF AREA OF WAN-DRIED FIBERS BY IMMERSION IN A HYDROCARBON OR WATER

Sample No.	B.E.T. Area, sq. m./g.	Remarks[1]
E-17	129	WAN-dried from n-pentane
E-1	43	WAN-dried from benzene
E-38	34	WAN-dried from benzene followed by n-pentane exchange and drying thereafter
E-40	119	Sample E-38, water-soaked and then WAN-dried from n-pentane

[1] All samples were dried at room temperature.

These interpretations explain some experimental results of Assaf, Haas, and Purves (11). These workers WAN-dried alkali-swollen linters from benzene. A substitution reaction was carried out on these linter in different media. When the reactions were in alcohols or ethers the degree of substitution increased with decreasing molecular volume of the medium. However, the degree of substitution was independent of molecular volume when the medium was a hydrocarbon. In light of the interpretation of the data in Table VII, the same degree of substitution in different hydrocarbon media was to be expected. The hydrocarbons did not swell the WAN-dried fibers; thus, the reactions in different hydrocarbons proceeded to the same extent. However, alcohols and ethers are known to swell cellulose fibers whereas the hydrocarbons may not swell cellulose (6). Therefore, when the reactions were carried out in these polar media the WAN-dried fibers were swelled to different extents and the degree of substitution varied accordingly.

EFFECTS OF DRYING EXCHANGED FIBERS FROM VARIOUS HYDROCARBONS AT DIFFERENT TEMPERATURES

Significant differences were noted when fibers were WAN-dried from various hydrocarbons at room temperature. It was suggested that such differences might have been the result of some property or properties of the final exchange liquid. Since many properties of liquids change with temperature, it was logical to study the effect of WAN-drying at different temperatures. It was hoped that the extent or manner of fiber area changes with changes in temperature of drying would reflect a comparable change in some liquid property common to all final hydrocarbons.

For each of five different hydrocarbons, fiber samples were WAN-exchanged by the standard method. Replicate samples were dried at various temperatures below the boiling point of each hydrocarbon. The procedures and apparatus used were described in the Section on General Experimental Procedures.

The results of WAN-drying from various hydrocarbons at different temperatures are plotted in Figure 5. Because of a lack of knowledge of the WAN-drying process, it was not possible to anticipate the results shown in Figure 5. The work of Forziati, Brownell and Hunt (<u>27</u>) suggested that a maximum area would be obtained by WAN-drying at some temperatures and that for fibers dried from <u>n</u>-pentane the maximum area would develop near 0°C. However, for fibers dried from five different hydrocarbons over temperature ranges as great as 100°C., no maximum area was found. With certain few exceptions, fiber areas increased linearly with increasing temperatures.

Although it was not anticipated that fiber areas would increase linearly with increased drying temperatures, there was reason to anticipate

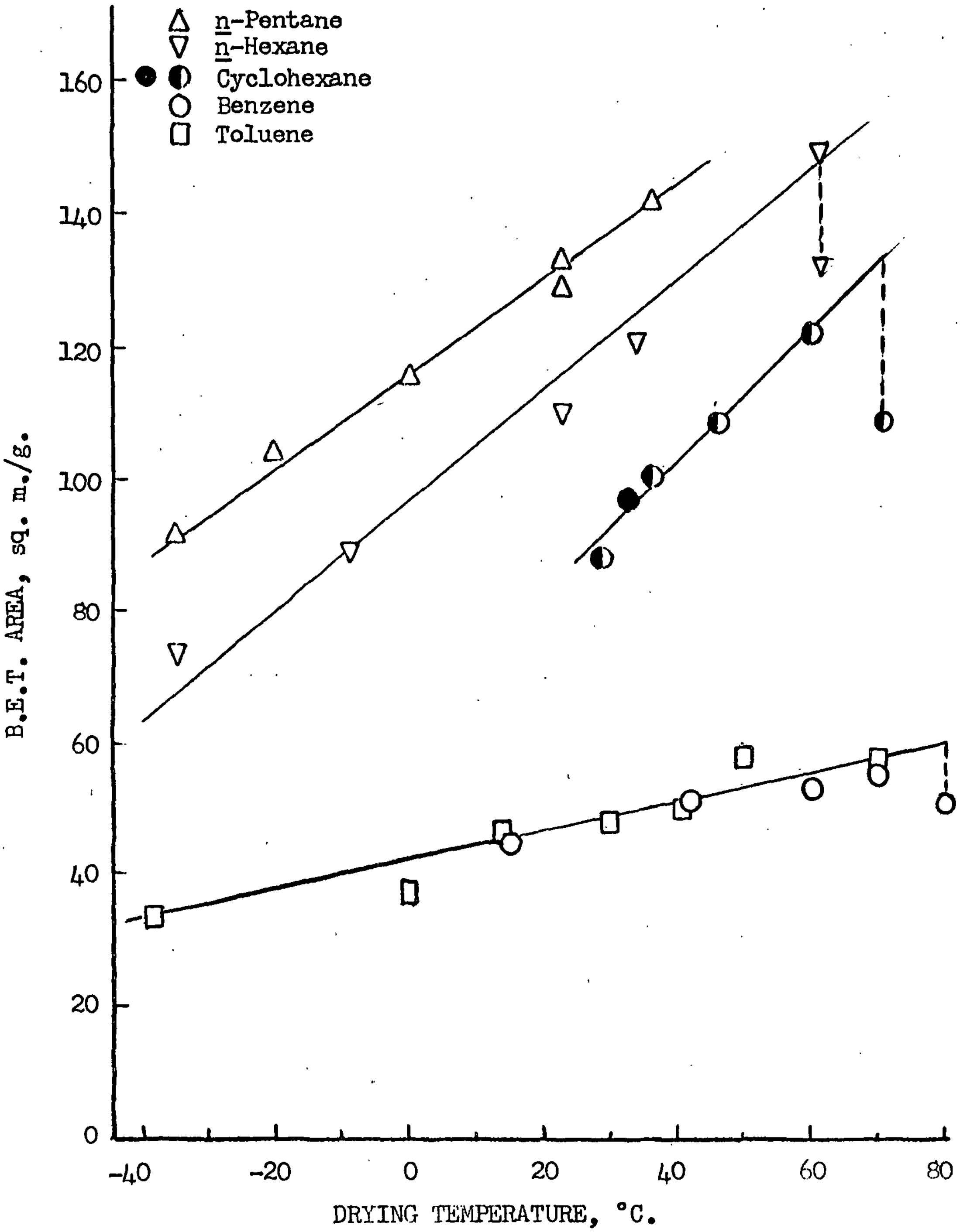

Figure 5. Effects of WAN-drying from Various Hydrocarbons at Different Temperatures

that the response of fiber areas to changes of drying temperatures might show the same trends for the different hydrocarbons. This followed from the observation that many physical properties of the simple hydrocarbons undergo nearly equal numerical changes with the same change in temperature. Therefore, if a physical property of the hydrocarbons was controlling fiber area development, similar trends of changes in areas might result from equal changes in WAN-drying temperatures for different hydrocarbons. Since such relationships did occur, there was added reason for believing that a hydrocarbon property was instrumental in creating fiber accessibility.

Figure 5 reveals that fibers dried from the aromatics did not show the same area response to drying temperatures as those dried from the other hydrocarbons. The difference might be attributed to a marked difference in the magnitude of some physical property of the two groups of hydrocarbons. Also, it may be that the aromatics are capable of some unique relationship with cellulose. These possibilities will be given further consideration.

With one exception, the samples represented by the data of Figure 5 were exchanged at room temperature. The exception was a sample for which the exchange of methanol by cyclohexane was done at 69°C. Inasmuch as methanol boils at 64.65°C. the exchange at the elevated temperature was not started immediately after the standard exchange of water by methanol. After this exchange was completed, two 40-ml. quantities of cyclohexane were passed through the sample bulb at the standard exchange rate and at room temperature. Following these two exchanges, the sample bulb was surrounded with a water bath at 69°C. as shown in Figure 3(a). The liquid metering unit of Figure 1 was immersed in a bath at the same temperature. Thus, the cyclohexane was heated to 69°C. before passage through the sample, and held at that temperature while in contact with the fibers. The remaining exchanges of methanol by cyclohexane proceeded at the standard rate. After this special exchange, the sample was permitted to cool at room temperature before drying was started. The result of this experiment is represented by the solid point on the plot for cyclohexane in Figure 5. Exchanging at the elevated temperature did not result in a fiber area different than what might have been expected for fibers exchanged at room temperature.

Figure 5 shows that some samples dried above 60°C. did not follow the established trends of increasing areas with increasing temperatures of drying. The area of a sample dried from cyclohexane at 70°C. did not increase over that of a sample dried from the same liquid at 60°C.; instead, it was lower by 23 sq. m. per gram. Similar results were obtained with samples dried from benzene at 81°C., and n-hexane at 61°C. These results are shown in Figure 5 as the points connected to the linear lines by dotted lines. These results were obtained when the drying times were extended beyond the point where an odor of the hydrocarbon was coming from the sample during the drying step. It thus appeared that the lower areas might reflect a temperature effect upon the cellulose.

To check this possibility, a second sample was WAN-dried from n-hexane at 61°C. for 1.5 hours. The specific surface was found to be 18 sq. m. per gram greater than that of the previous sample which was dried at 61°C. for 4 hours. Thus, the time of drying at this elevated temperature had an effect on the specific surface.

It was obvious that drying times should decrease as temperatures of drying increased. Thus, it was necessary to find a way of judging when the samples were dry so that the drying periods would not be needlessly prolonged. It seemed possible that the fibers were dry when an odor of the hydrocarbon could not be detected in the stream of dry nitrogen leaving the bottom of the sample bulb. A series of experiments were carried out to check this possibility.

n-Hexane was used as the final exchange liquid for five separate samples. These samples were dried by the standard method which varied only in the length of time of drying. This method used the bulb assembly shown in Figure 3(a). With the upper and lower stopcocks closed, water at 60°C. was circulated around the sample bulb. It had been determined separately that the WAN-exchanged fibers would rise to the elevated temperature in 8 to 10 minutes. Thus, the standard procedure was to allow 15 minutes for the sample to attain the bath temperature. After this period of time, the upper and then the lower stopcock were opened to permit the dry nitrogen to pass through the sample. The five samples were dried for five lengths of time; 28 minutes, 0.75, 1.5, 4.0 and 8.0 hours. The odor of n-hexane could not be detected after 28 minutes of drying.

Two additional samples were added to the above series. These samples were duplicates and were dried in a manner different from the standard procedure. After the 15-minute period for temperature equilibrium, the lower stopcock of the sample bulb was rapidly opened and the n-hexane permitted to surge from the sample under its own pressure. The discharging vapors were bubbled through a small amount of n-hexane in a 50-ml. beaker. When the rate of bubbling slowed to about one per second, the upper stopcock of the bulb was opened and drying was continued with nitrogen. The total drying time for these samples was 18 to 20 minutes from the moment the lower stopcock was opened.

When it was felt that drying at elevated temperatures was completed, the circulating hot water was rapidly replaced with water at room temperature. Thereafter, the nitrogen flow was continued at room conditions for the standard time.

The experiments in which samples were WAN-dried from n-hexane for different lengths of time at 69°C. provided more detailed data on this effect of drying time. The results of these experiments are shown in Figure 6. When the standard drying procedure was followed, there was an area decrease of 19 sq. m. per gram when the drying time was lengthened from 28 minutes to 8 hours. Since time of exposure of the fiber system to the elevated temperature was the only thing that varied in the experiments, and since the effect of incomplete drying for the shorter times would have worked against the development of larger areas, the results must reflect the effect of the time of exposure at the elevated temperature.

The areas of these samples dried at 69°C., as well as those of the previous samples dried at 61°C. showed much greater variation with different drying times than did the areas of fibers dried at room temperature. The samples dried from n-pentane at room temperature had minimum drying times of 18 to 24 hours (Table II). Sometimes these samples dried at room temperature would remain on the drying apparatus for 30 or more hours; thus,

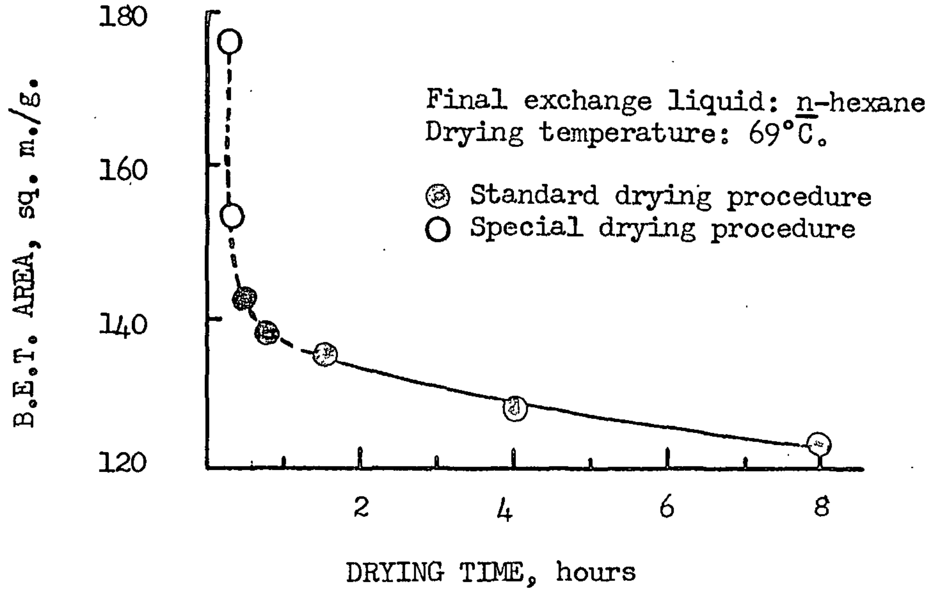

Figure 6. Effects of Drying For Different Times

the drying times varied as much as 12 hours. These samples showed little variation in area (Table III). On the other hand, the samples dried at 61 and 69°C. from n-hexane were very sensitive to drying times which varied from minutes to a few hours. Because of the pronounced difference in the dependence on drying times at the different levels of temperature of drying, it must be concluded that there was a temperature effect upon cellulose. This effect was most pronounced above 60°C.

It was unexpected that temperatures as low as those employed in this work would have an effect upon cellulose. An explanation of the effect may be offered when it is considered, that for any increase in temperature, the molecular energy of vibration of cellulose hydroxyl groups may influence hydrogen bonding. The nature of this influence for a given temperature increase is unknown. However, if more hydrogen bonding occurred at higher temperatures, lower surface areas would be expected.

If hydrogen bonding is influenced by temperature changes, the relative positions of fiber structural units may be disturbed; the spaces between these structural units may become smaller or some units may come into contact for the first time. For either case, the accessibility to area measuring-nitrogen molecules would be decreased.

The two experiments in which fibers were WAN-dried from n-hexane in 18 to 20 minutes were essentially duplicates and should have given the same result. However, Figure 6 shows that the areas of these two samples were different by more than 20 sq. m. per gram. Since the special procedure of sudden release of n-hexane from the sample may have introduced complications into the mechanisms of the drying, further work was done on such procedures and the effects will be discussed later (see page 90).

The rate of 50 ml./min. of dry nitrogen was arbitrarily chosen for evaporation of the hydrocarbons. If this rate was greatly increased, it seemed possible that the temperature of drying might be effectively decreased. This might occur because the rapidly evaporating hydrocarbon would extract its heat of evaporation from the surroundings; thus, the temperature of the cellulose and unevaporated liquid would decrease. To note if such an effect was critical, samples were WAN-dried from n-pentane at increased rates of dry nitrogen flow.

The results given in Table VIII indicate that there was no difference between drying at a nitrogen flow of 50 ml./min. or 85 ml./min. However, when comparative samples were dried at the rates of nitrogen flow of 50 and 125 ml./min., the fiber area decreased for the increased rate, as shown by the data in Table VIII. Apparently, the larger rate of flow of nitrogen caused evaporative cooling and effectively lowered the drying temperature. Included in Table VIII are the results of two samples WAN-dried by the techniques of Assaf, Haas, and Purves (11). Both samples were dried in a vacuum desiccator and then sealed in adsorption bulbs. However, one sample was dried slowly by intermittent evacuation of the desiccator and the other was rapidly dried by a rapid and continuous evacuation of the desiccator. The faster drying caused evaporative cooling which resulted in a lowered area. These effects explain why Assaf, Haas, and Purves (11) could not get reproducible results with a chemical reaction on fibers WAN-dried in a nonuniform manner.

TABLE VIII

EFFECT OF RATES OF DRYING

Sample No.	B.E.T. Area,[1] sq. m./g.	Nitrogen Flow Rate, ml./min.	Final Exchange Liquid
E-31	122	50	Matheson n-pentane
E-34	121	85	Matheson n-pentane
E-17	129	50	Viking n-pentane
E-24	121	125	Viking n-pentane
SD-2[2]	41.6	—	Benzene
SD-5[2]	27.4	--	Benzene

[1] All samples were dried at room temperature.

[2] Dried by the procedures of Assaf, Haas, and Purves (11).

RELATIONSHIP BETWEEN AMOUNT OF RETAINED HYDROCARBON AND FIBER AREA

The details of the method used to determine the amount of residual liquid held in WAN-dried fibers were given in the Section on General Experimental Procedures. The method had one main source of error. When the sample bulb was broken with a hot wire, glass fragments were sometimes lost. This loss would make the values of percentage of residual high.

The data concerning residual liquids were obtained from the experiments on removal of hydrocarbons at different temperatures.

To this point all WAN-drying experiments were carried out with fibers which had never been dried by any means. Samples of these water-saturated fibers were dried by two different methods. One method was to dry the fibers in air at room conditions which meant that these fibers had a moisture content of 8 to 10%. The other method was to first air dry the fibers at room conditions and then to store these fibers over phosphorus pentoxide for several weeks; these fibers had a negligible moisture content. Samples of the fibers dried by the two different methods were resuspended in water and WAN-dried. For these fibers the exchange process occurred on less surface area per unit weight of fibers than for the fibers never water-dried. Therefore, it was possible to note how the amount of residual liquid would vary as the fiber area available for WAN-exchanging was decreased. To check if the relationships between area and residuals showed the same trends for water-dried fibers as well as for never-dried fibers, one sample of air-dried pulp was resoaked in water for 48 hours, stirred for 28 hours, then WAN-dried from _n_-hexane at -20°C.

Samples of the above-mentioned fibers which were water-dried in air at room conditions were placed in 250 ml. of distilled water and gently stirred with an electric stirrer until the fiber clumps were separated and a uniform fiber suspension was obtained. To note if the stirring action was influencing the areas developed, samples were stirred for 10 to 11 hours, for 24 hours or were given no stirring. All samples were water-soaked 48 hours, including the stirring times. Three separate samples of the fibers which were dried over phosphorus pentoxide were soaked in 250 ml. of distilled water for 4, 14, and 41 days before they were WAN-dried from n-pentane.

The experimental pulp had been stored in four Pliofilm bags. The contents of each bag had been treated separately. To note if the pulp was essentially the same in at least two different bags, four samples from a bag designated as Batch no. 2 were WAN-dried at 36 and 37°C. from n-pentane and at 0 and -36°C. from n-hexane. The data from these samples should confirm any relationship between fiber areas and residuals of hydrocarbons which were found for the pulp designated as Batch no. 1. With the exception of these four experiments, all other work was done with pulp from Batch no. 1.

Whether the samples were taken from different batches of the experimental pulp, or were air-dried from water before they were WAN-dried, the relationship between fiber areas and the amount of hydrocarbon retained showed the same trends. As fiber areas increased, there was a decrease in the percentages of retained liquid. Furthermore, this relationship held for the five different hydrocarbons which were used as final exchange liquids. These results are shown in Figures 7 and 8.

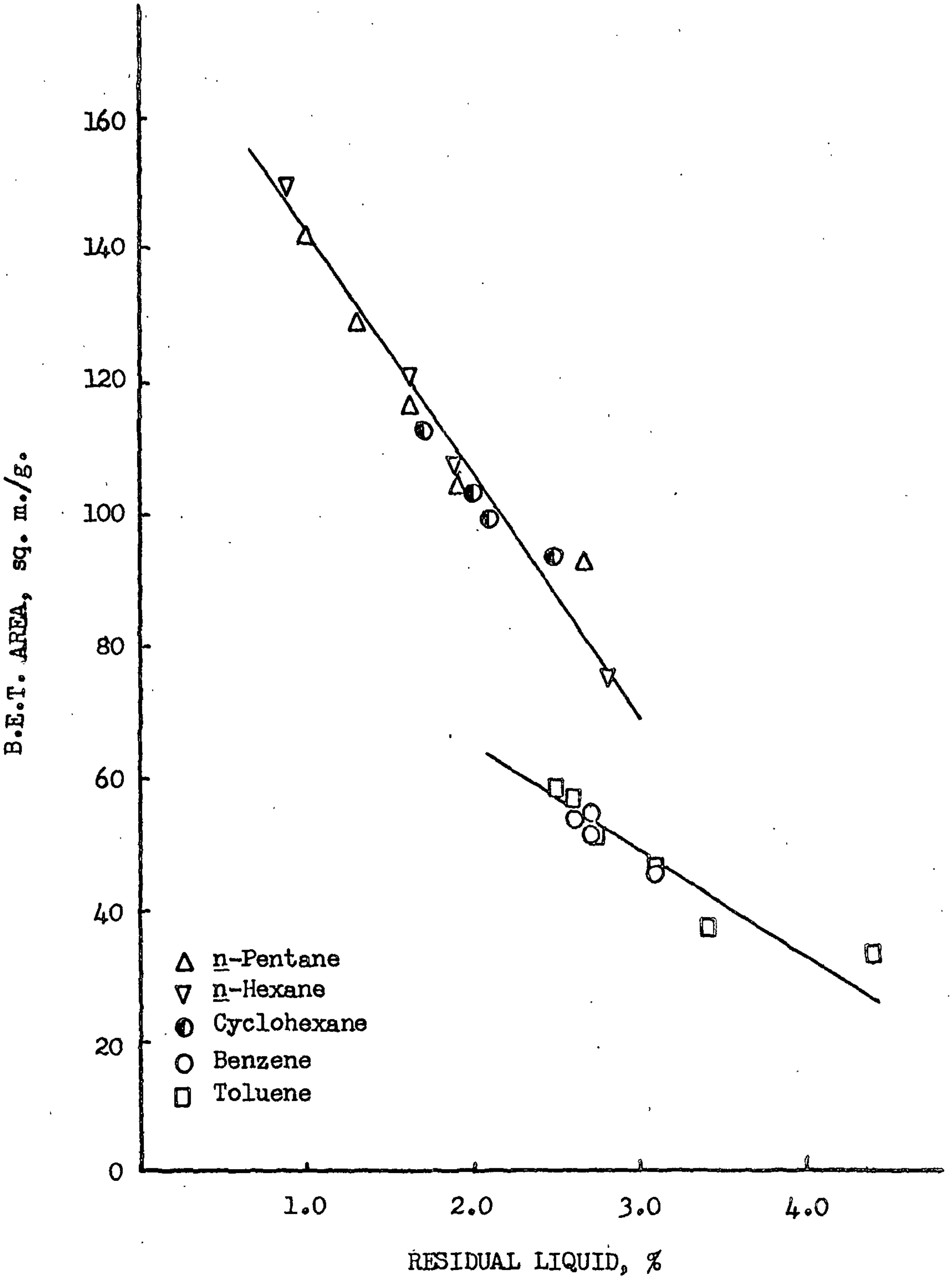

Figure 7. Relationships Between Fiber Area and Residual Liquid

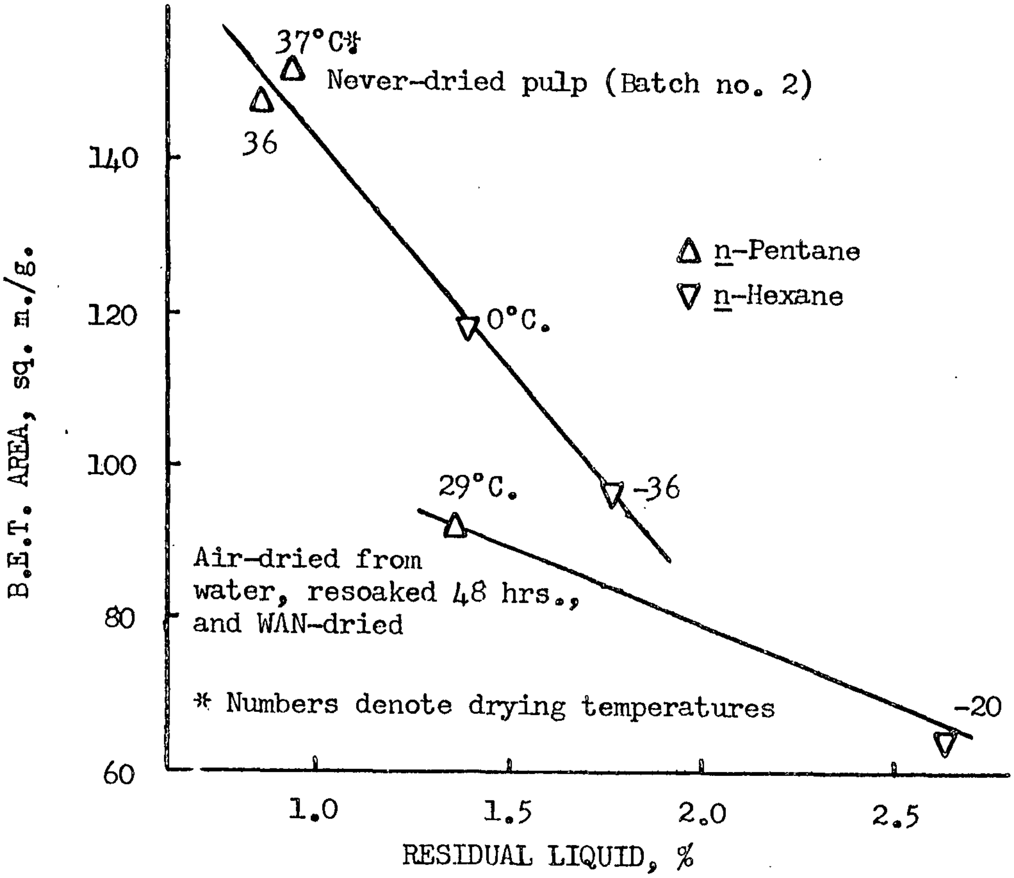

Figure 8. Relationships Between Fiber Area and Residual Liquid

Figure 7 reveals the interesting result that at equal areas there was a nearly equal amount of residual liquid held in fibers dried from n-pentane, cyclohexane, and n-hexane. For example, at an area of 110 sq. m. per gram, these liquids were held in the respective percentages of 1.9, 1.7, and 1.9. At a given area the residuals for these liquids usually agreed within 0.2% of each other. This phenomenon of nearly equal residuals for equal fiber areas suggests that the mechanism of area development was the same for all three of the hydrocarbons although the temperatures of WAN-drying were different for the three different liquids. Fibers dried from benzene and toluene also showed nearly equal amounts of residuals at equal areas.

In Figure 8, the data for the never-dried pulp of Batch no. 2 showed the same trend of increased residuals with decreased areas as was previously noted for pulp from Batch no. 1, (Figure 7). Also, for this pulp, fiber areas decreased for decreased temperatures of drying. The pulp of Batch no. 2 had an area of 96.3 sq. m. per gram when dried from n-hexane at -36°C. whereas that of Batch no. 1 had an area of 74.6 when dried from n-hexane at -38°C. (Figure 5). At comparable conditions of drying, pulp of Batch no. 2 had consistently higher surface areas than pulp of Batch no. 1. This difference between these pulps suggests that, when the pulp was slurried by the Lightnin' stirrer, one batch received different mechanical treatment than the other.

In Figure 8, the data of water-dried fibers showed that fiber area decreased with drying temperatures and that as area decreased the amount of residual increased. These trends were the same for fibers never dried from water.

In Table IX there are tabulated data on fiber areas and percentage of residual hydrocarbon for fibers air-dried from water, fibers water-dried over phosphorus pentoxide and fibers never dried from water. These data show that fiber areas may be changed considerably by a mild mechanical action. Comparing Samples E-49 and E-94 in Table IX it is seen that there is an area loss of about 8 sq. m. per gram (12%) when fibers dried in air to a moisture content of 8 to 10% are dried further to a negligible moisture content over phosphorus pentoxide.

TABLE IX

AMOUNT OF RETAINED LIQUID IN DIFFERENT FIBER STRUCTURES

Pulp History[1]	Sample No.	Residual Hydrocarbon, %	B.E.T. Area, sq. m./g.	Drying Temp., °C.
Never-dried from water	E-75	1.0	142	36
Water-dried in air, water-soaked 48 hrs., stirred 10 hrs.	E-26	1.8	85.1	23 to 28
Ditto except stirred 11 hrs.	E-30	1.7	84.3	23 to 28
Ditto except stirred 24 hrs.	E-97	1.4	91.9	23 to 28
Ditto except not stirred	E-49[2]	1.2	66.7	23 to 28
Water-dried over P_2O_5, water-soaked 4 days	E-94	1.5	58.5	36
Ditto except soaked 14 days	E-96	1.4	56.3	36
Ditto except soaked 41 days	E-106	1.3	50.6	36

[1] Final step was to WAN-dry all samples from n-pentane.

[2] This sample was water-soaked 6 days. After tabulated area was determined, sample was outgassed at 100°C. for 16 hours; thus, the percentage residual was low.

The first desorption of water from a wood pulp which has never been dried always lies above the second desorption values for the pulp after it has been dried once and resaturated (38). This irreversibility is commonly accepted to reflect the failure of water, during resaturation, to rupture secondary cellulose-cellulose bonds formed during primary desorption (39). Moreover, the adsorption of water after primary desorption is considered to occur in the amorphous or disordered regions of fibers (40). The data from Samples E-75 and E-94 given in Table IX show that upon primary desorption the fibers lost 59% of their surface areas. It would be interesting to be able to compare such area losses with other fiber properties such as accessibility to reactants, reaction rates, strength properties, etc. Such comparisons are not a part of this work, but it is interesting to note that these techniques of WAN-drying and gas adsorption offer a method of relating changes in accessible fiber area with those fundamental changes which occur during primary desorption.

A surprising result of Table IX is that fibers dried over phosphorus pentoxide and then resoaked in water for 41 days before WAN-drying had an area 8 sq. m. per gram less than like fibers water-soaked only 4 days. It was expected that longer soaking times would increase the extent of disruption of hydrogen bonds which had been formed during the original drying from water. Perhaps the speculations of Magne and Skau (41) explain the area decrease with prolonged swelling. These workers noted that since the lumen of a cellulose cell increases in size during swelling there might be a decrease in the size of some very small pores in the cell. Any decrease in pore size would of course decrease accessible surface area. There is the other possibility that bacterial attack during the prolonged soakings had an effect upon the fiber surface. Furthermore, hemicelluloses in the experimental pulp may create an effect; conceivably with long soaking times, the hemicelluloses could diffuse into the pore structure of the cellulose fiber.

Perhaps the most important information in Table IX lies in the fact that the fibers which were completely dried from water retained a greater amount of residual liquid after WAN-drying than did fibers which had never been dried. This result is important for it reveals something about a mechanism of the retention of liquids in WAN-dried fibers.

The fiber area accessible to liquid exchange was much greater for the never-dried pulp than for the pulp with a history of being dried from water. Thus, for the same conditions of WAN-drying, it was reasoned that the fibers with a smaller area for exchange purposes would probably retain less residual liquid. Since this was not the case, and since the only difference between the pulps which had been water-dried and never dried was a probable difference in fiber structure, the retention of liquids in WAN-dried fibers must not be mainly dependent on total fiber area, but must be a function of the porous structure of the fibers. These observations lead to the conclusions (1) that forces of physical adsorption do not hold residual hydrocarbons in cellulose because physical adsorption would rely on total surface area and thus amounts of residual would decrease with decreasing area; (2) that if a fiber structure is changed during the WAN-drying process by changing the conditions of drying, the amount of liquid retained in the dried structure would be expected to change; and (3) since drying of cellulose from water would not be expected to increase the number of pores in a fiber, the retention of liquid must rely on the size or shape of pores instead of their total number.

Physical adsorption of any liquid on cellulose would decrease with increased temperatures. Thus, it could be reasoned that as the temperature of WAN-drying increased there were fewer molecules of hydrocarbons retained on the cellulose and the areas would always increase with increased temperatures. Also, for any given temperature and liquid, the amount of liquid physically adsorbed on cellulose would increase with increased areas of cellulose. Contrary to this requirement of physical adsorption, the results of Table IX show that a fiber of less area held more residual liquid than a fiber of greater area. Therefore, physical adsorption could not be a primary mechanism for retention of liquids and cannot explain why larger areas were developed at increased drying temperatures.

It is doubtful that physical adsorption is even a secondary mechanism for retained liquids. Haselton (14) established an isotherm for the adsorption of n-butane on water-dried cellulose. A very slight hysteresis was observed but the loop closed and the latter part of the desorption curve retraced the initial adsorption curve. If physical adsorption forces had retained some of the butane the hysteresis loop would never have closed.

Furthermore, if forces of physical adsorption were holding hydrocarbon molecules in the WAN-dried fibers, the relationship shown in Figures 7 and 8 between fiber area and percentage of retained liquid would have been different. All fiber samples regardless of drying temperature were outgassed at room conditions for many hours on the adsorption apparatus. For the fibers which had been dried at conditions below room temperature, the outgassing would remove the liquid retained at lower temperatures if the liquid was physically adsorbed. Thus, the amount of residual liquid would be expected to be constant for all samples dried at room temperature or below. Likewise, the corresponding fiber areas would have been equal. In addition, it will be shown later that when samples were outgassed for days at room temperature the fiber areas never increased; in fact, they always decreased. This effect is inconsistent with any theory of physical adsorption to account for residual liquids in WAN-dried fibers.

Aside from the foregoing evidence against physical adsorption as a mechanism for retention of liquids, the results of Table IX focus attention upon the porous nature of cellulose. The porosity of the fibers which had never been dried is the only fiber property which could have changed when the fibers were water-dried. Thus, the change in porosity is the only effect to account for increased amounts of residual liquids held in the water-dried fibers.

THE POROUS NATURE OF WAN-DRIED FIBERS

The use of gas adsorption techniques to investigate the structures of porous materials is quite common. The adsorption isotherms of such adsorbents always show hysteresis. The size and shape of the hysteresis loop has provided both qualitative and quantitative information about porous adsorbents. Thus, adsorption isotherms of WAN-dried fibers should provide useful information of these structures.

The procedures for obtaining the adsorption isotherm were discussed in the General Experimental Procedures Section. In establishing the isotherms, the problem arose as to how complete the isotherm should be made in the range of high relative pressures (P/P_o). The isotherms were always of the Type II designation (21) and thus had an asymptotic approach to saturation pressures. With this type of isotherm, which is common to finely divided adsorbents, it is difficult to determine the total pore volume of the adsorbent. This difficulty arises from the fact that as the saturation pressure is approached the adsorbate begins to condense between the porous adsorbent particles as well as continues to fill up the largest pores within the adsorbent. The problem is to separate the two effects so that a reasonable value of the total pore volume of the adsorbent is obtained.

To meet this problem, Barrett suggests carrying the isotherm determinations to $P/P_o = 0.99$ then to repeat the determination to $P/P_o = .97$. If the shapes of the two isotherms are in good agreement and their desorption points fall upon a common line near the start of desorption at the lower P/P_o, the true saturation volume may be assumed to be at some point just below $P/P_o = 0.99$ (42). Apparently this approach is based upon the fact that if the internal pores of the finely divided adsorbent have not become filled at $P/P_0 = 0.97$ but are filled at $P/P_0 = 0.99$, scanning of the hysteresis loop occurs and the desorption branches from the two different relative pressures will not coincide (43). This approach has been supported by some experimental evidence. Ries and co-workers (44, 45) found isotherms of Type II, for finely divided adsorbents, to have a break in the curve between the P/P_0 values of 0.970 and 0.985. These workers (44) believed the break occurred at the saturation volume and confirmed their beliefs with an independent determination of that volume. For one sample of WAN-dried fibers, two separate determinations showed a slight break in the isotherm at a relative pressure of 0.975. It was therefore decided to accept the relative pressure of 0.97 for determining the total pore volumes of WAN-dried fibers.

STRUCTURES NEVER DRIED FROM WATER

The isotherms for fibers WAN-dried from benzene, cyclohexane, and n-pentane are shown in Figure 9 and have the same shape as nitrogen isotherms for certain finely divided catalysts (44, 45). The closure of the hysteresis loop at $P/P_0 = 0.40$ to 0.42 is in good agreement with the catalyst isotherms (44, 45), and with the prediction of Cohn (46) for nitrogen adsorption on rigid porous adsorbents. It can be seen in Figure 9 that the isotherms were reproducible and that the hysteresis loops always closed. Thus, it may be concluded that the cellulose fibers are behaving as rigid structures during low temperature nitrogen adsorption and desorption. If any swelling of the fibers occurred, it was reversible; otherwise the hysteresis loop would not have closed.

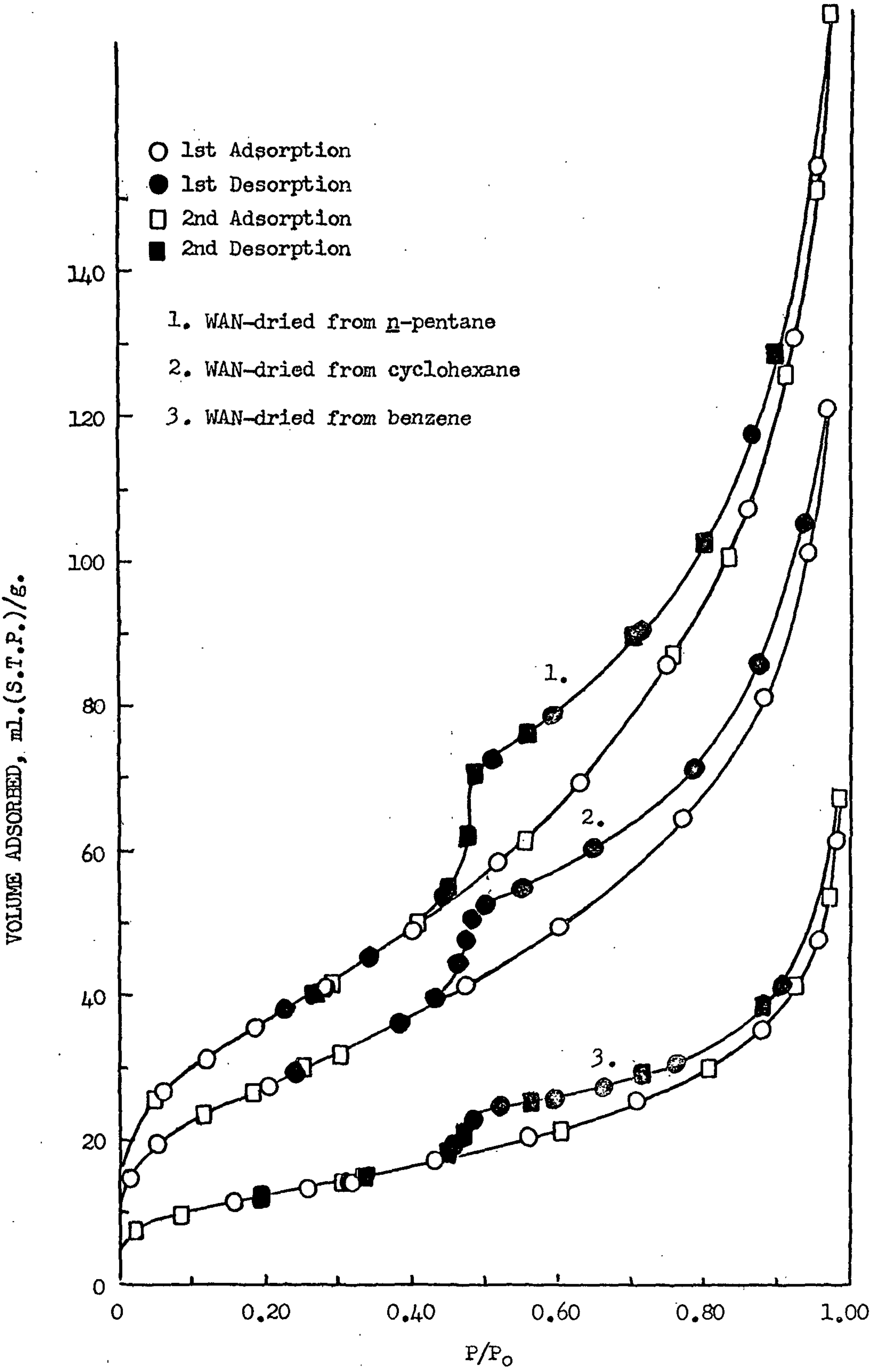

Figure 9. Adsorption of Nitrogen on WAN-dried Fibers

The isotherms of the three different WAN-dried samples are of the same type. Moreover, all of the isotherms have an inflection point on the desorption curve at $P/P_o = 0.475$, indicating that all three samples have the same mean ~~near~~ pore diameter. From these observations, it appears that the only difference between the three samples was the total number or length of a given pore size, which accounted for the different total fiber areas.

However, it has been shown that the three samples held different amounts of retained hydrocarbons; but it has not been shown whether or not the retained liquids account for the differences in fiber areas. That is, if the retained liquids could be removed without disturbing the structure, it is not known if the remaining cellulose structures would be identical in every respect. To learn if the residual-free cellulose structures were identical for the three samples, the total pore volume available to nitrogen molecules was obtained from the isotherms of Figure 9; and these volumes were corrected for the corresponding volume of retained liquid to give a corrected total pore volume. These corrected pore volumes are listed in Table X.

TABLE X

RELATIONSHIPS OF RETAINED LIQUIDS AND WAN-DRIED FIBER STRUCTURES

Sample no.	E-3	E-42	E-37
Final exchange liquid	Benzene	Cyclohexane	n-Pentane
B.E.T. area, sq. m. per gram	44.3	103	133
Actual residual, %	2.4	2.0	1.3[1]
Volume of residual (% residual/density) cc./g. fibers (I)[2]	.028	.025	.021
Total pore volume from isotherm (N_2 vol. at $P/P_o = 0.97$) x .00155 (II)	.082	.188	.260
Corrected total pore volume (I) + (II) cc./g. fibers	.110	.213	.281
Theoretical residual, assuming N_2 adsorption on monomolecular layer of residual liquid, %[3]	2.2	3.7	3.1

[1] An assumed value because E-37 was given special outgassing after its isotherm was established. This value is the average of two similarly WAN-dried samples (E-21 and E-44) with areas nearly equal to that of E-37.

[2] The densities used were those of hydrocarbons at 20°C. instead of at -195°C. This simplification should be acceptable for the comparative results.

[3] It was assumed that benzene molecules were packed with the longest molecular dimension perpendicular to the pore wall, whereas for cyclohexane and n-pentane the shortest dimensions were assumed to be perpendicular to the pore wall. Molecular cross-sectional areas were taken as 26, 39, and 52A.^{2} for benzene cyclohexane, and n-pentane, respectively.

The corrected total pore volumes given in Table X reveal that the fibers WAN-dried from the three different liquids have different structures irrespective of the retained liquids. Since the original water-wet fibers were identical and since these fibers were treated alike except for the final exchange liquid, the different total pore volumes must be attributed to some differences in the properties of the final exchange liquids. Furthermore, whatever property is different for the three liquids, it must provide a mechanism for changing the fiber structure.

It should be apparent that fiber areas do not differ solely because the fibers hold various amounts of retained liquids. Instead, the fiber areas differ because of changes in the fiber structure, and the magnitude of these changes may account for the inclusion of different amounts of liquids.

It could be assumed that the retained liquid molecules are held on the pore walls of the fiber structure and that nitrogen adsorption takes place on the retained hydrocarbon molecules. Thus, different fiber areas would be expected to reflect different amounts of residual liquids, depending on the size, density and packing of the liquid molecules. By starting with the area of a WAN-dried fiber, it is possible, by assuming a type of molecular packing, to calculate an approximate theoretical value of a residual liquid. When this was done, as shown by the results of Table X, the theoretical residuals were much larger than the actual residuals, except when the fibers had been WAN-dried from benzene. If the original assumption had been true, it seems that there should have been better agreement between the theoretical and the actual values, or that all theoretical values would disagree in the same manner with the actual values.

However, it may be recalled that benzene did not develop fiber areas in the same manner as cyclohexane or n-pentane when drying was done at different temperatures. Perhaps then, since there is fair agreement between the theoretical and actual residual of benzene, the differences noted by drying from the aromatics can be attributed to the retention of aromatic molecules on the pore walls of the WAN-dried fibers. In an attempt to learn something of these possibilities for retention of residual molecules

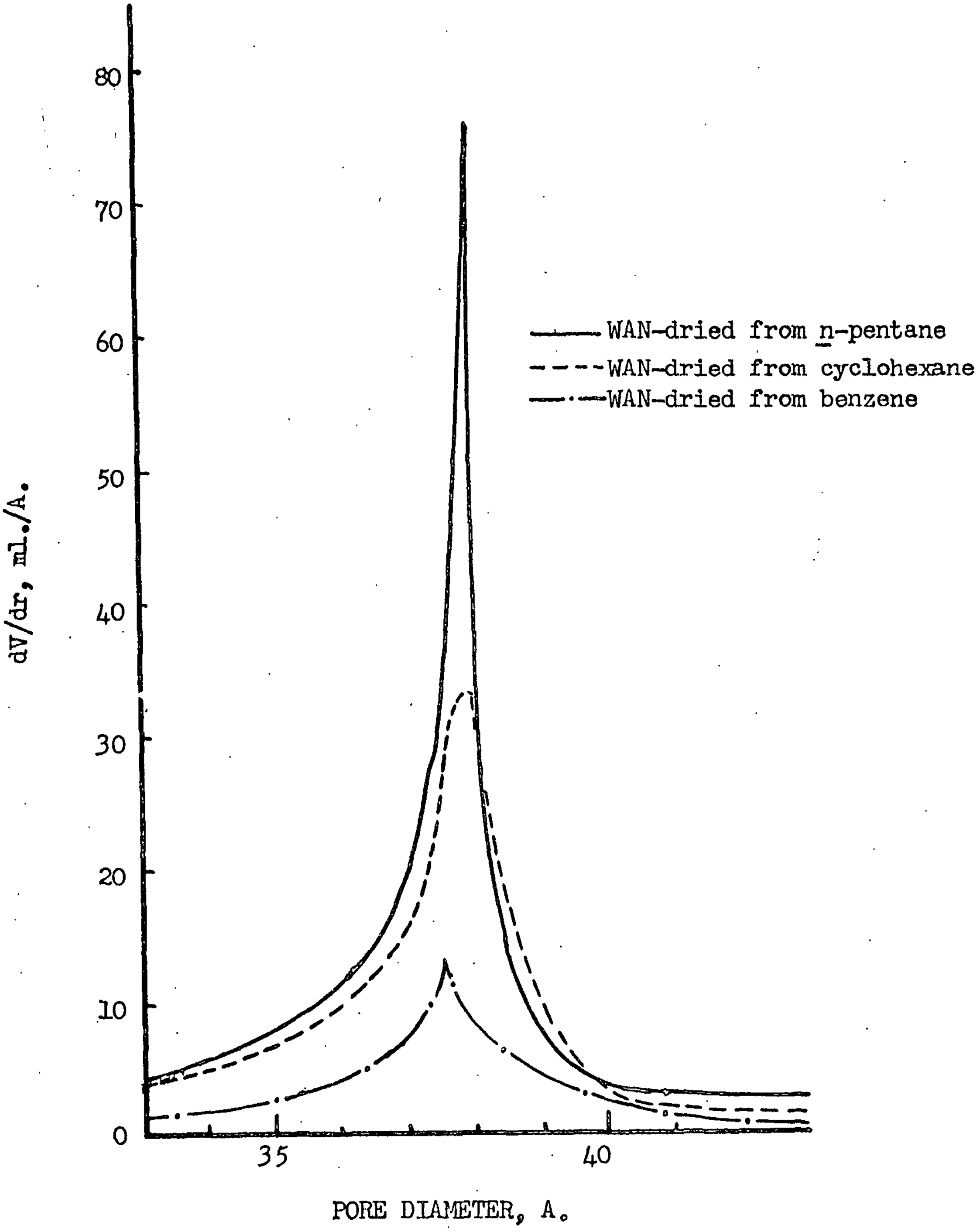

Figure 10. Pore Volume Distributions of WAN-dried Fibers

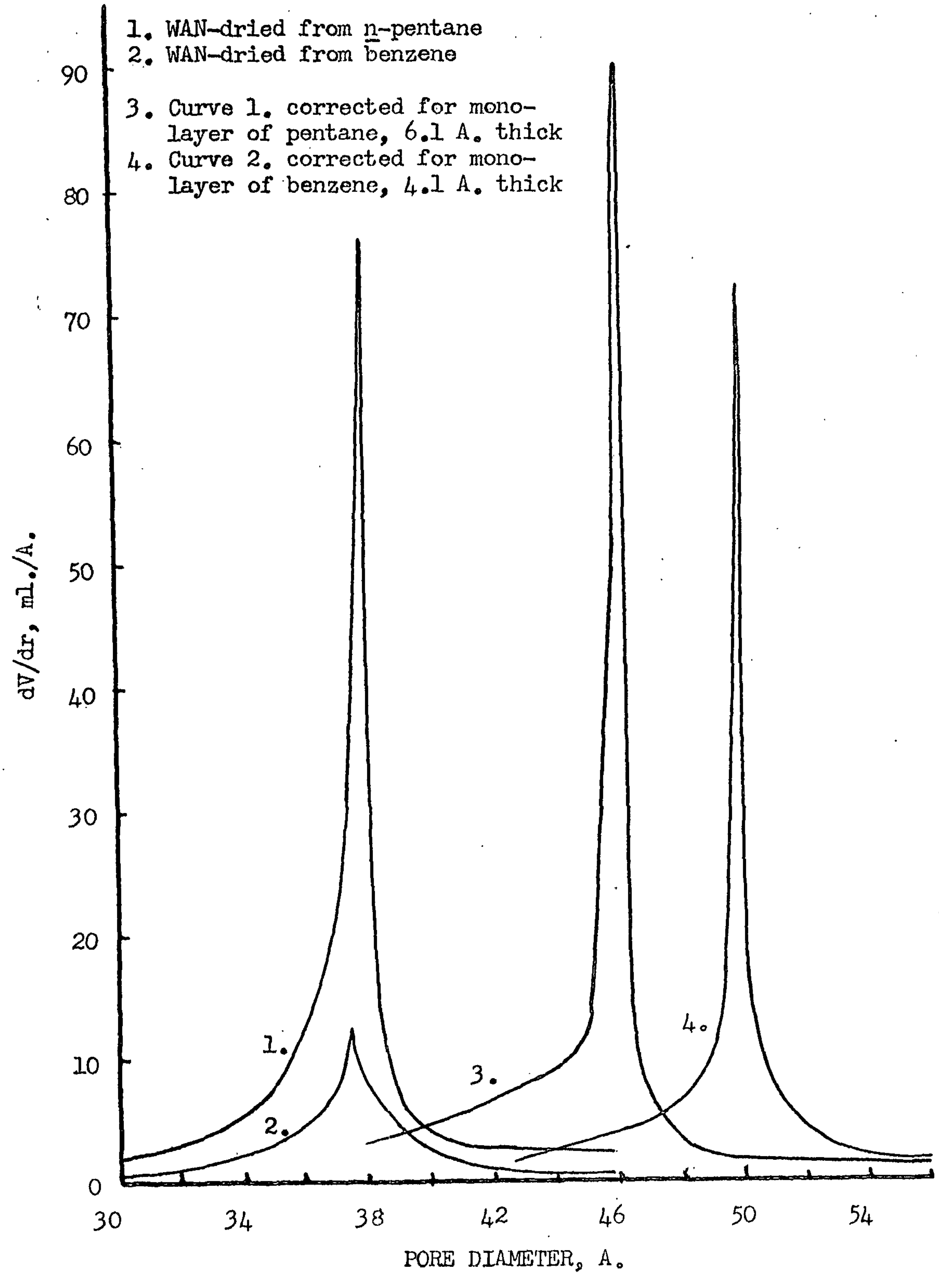

Figure 11. Pore Volume Distribution Curves Corrected and Uncorrected for Monolayer of Residual Liquid

on pore walls, pore volume distribution curves were calculated for the three isotherms of Figure 9. These distribution curves are shown in Figure 10 where V is pore volume for pore radius r and dV/dr is relative pore volume.

If benzene were held on the walls of pores, it would be possible to compensate for a thickness of benzene molecules on all surfaces and thus get a picture of the residual-free cellulose structure. This was done by using the isotherm data to calculate a distribution curve for the pores filled by nitrogen, and this calculated data was then adjusted to correct for a monomolecular thickness of benzene. The same corrections were made for the fibers WAN-dried from n-pentane and the results of the corrections are shown in Figure 11.

From the pore volume distribution data it was possible to determine a fiber area. Of course, this method was independent of the B.E.T. method but the results should show agreement. The areas calculated from the distribution curves of Figure 11 are given in Table XI along with the corresponding B.E.T. areas.

TABLE XI

A COMPARISON OF B.E.T. AREAS AND AREAS CALCULATED FROM PORE VOLUME DISTRIBUTION DATA

Final Exchange Liquid	B.E.T. Area, sq. m./g.	Area from Uncorrected PVD[1] Data, sq. m./g.	Area from Corrected PVD Data, sq. m./g.
Benzene	43	39	52
Pentane	129	127	154

[1] Pore volume distribution

Some interesting interpretations may be developed from the results of Figures 10 and 11, Table XI and the concept of residual liquids held on the accessible pore walls. If residual benzene were held on the pore walls but residuals of cyclohexane or n-pentane were not, the pore volume distribution curve of the sample dried from benzene should have been displaced from the other curves in Figure 10. This seems a logical conclusion because the effect which might hold benzene on the pore walls would be in addition to an effect which changed the structures of fibers dried from cyclohexane, and n-pentane but which gives them the same pore volume distributions, as shown in Figure 10. On the other hand, if an added effect accounted for benzene being held on the pore walls, compensation for this effect should make the corrected pore volume distribution curve coincide with the curves for cyclohexane and n-pentane, as in Figure 10. However, the results of Figure 11 show that such compensations would always make the corrected distribution curves shift to new mean pore diameters. Thus, it appears that the differences between fibers dried from the aromatics and the other hydrocarbons are not the result of residual aromatics held on pore walls.

The results of Table XI and Figure 11 show that when compensation is made for molecules assumed to be retained on the pore walls the lower fiber areas from benzene cannot be adjusted to the higher areas from n-pentane. This is further evidence against any concept of residuals being held on pore walls, and is further support for the observation that WAN-dried fibers of different areas had different pore structures.

WATER-DRIED STRUCTURES

It has been stated that only a change in pore structure could account for the retention of greater amounts of residual liquid in WAN-dried fibers previously dried from water than in like fibers never dried from water. The fact that drying from water does alter the pore structure of fibers is shown in Figure 12.

The shapes of the two isotherms in Figure 12 are similar but are definitely different in the high relative pressure range. The isotherm of the water-dried sample shows a much more rapid approach to saturation pressures than does the other isotherm. The finally determined adsorption point for the water-dried sample was at $P/P_o = .996$ and at $P/P_o = .973$ for the never-dried sample. This rapid approach to saturation pressures indicates the pore structure of the water-dried sample is definitely different from the other sample and is different primarily by virtue of fewer large pores. Thus, water-drying of the fibers resulted in a loss of large pores as well as a decrease in fiber area. Such results suggest that for fiber structures of equal areas but of different pore structures, the fibers with larger pores would be expected to retain a smaller amount of residual liquid.

STABILITY OF STRUCTURES

Hunt, Blaine and Rowen (24) observed that the B.E.T. areas of their WAN-dried fibers decreased when repeat adsorption measurements were made. Such instability of the WAN-dried structure was observed in the present work. To gain insight into this effect, sample bulbs were removed from the adsorption apparatus and stored for different lengths of time and returned to the apparatus for repeat area determinations. Other samples were left on the apparatus and outgassed for several days before repeat

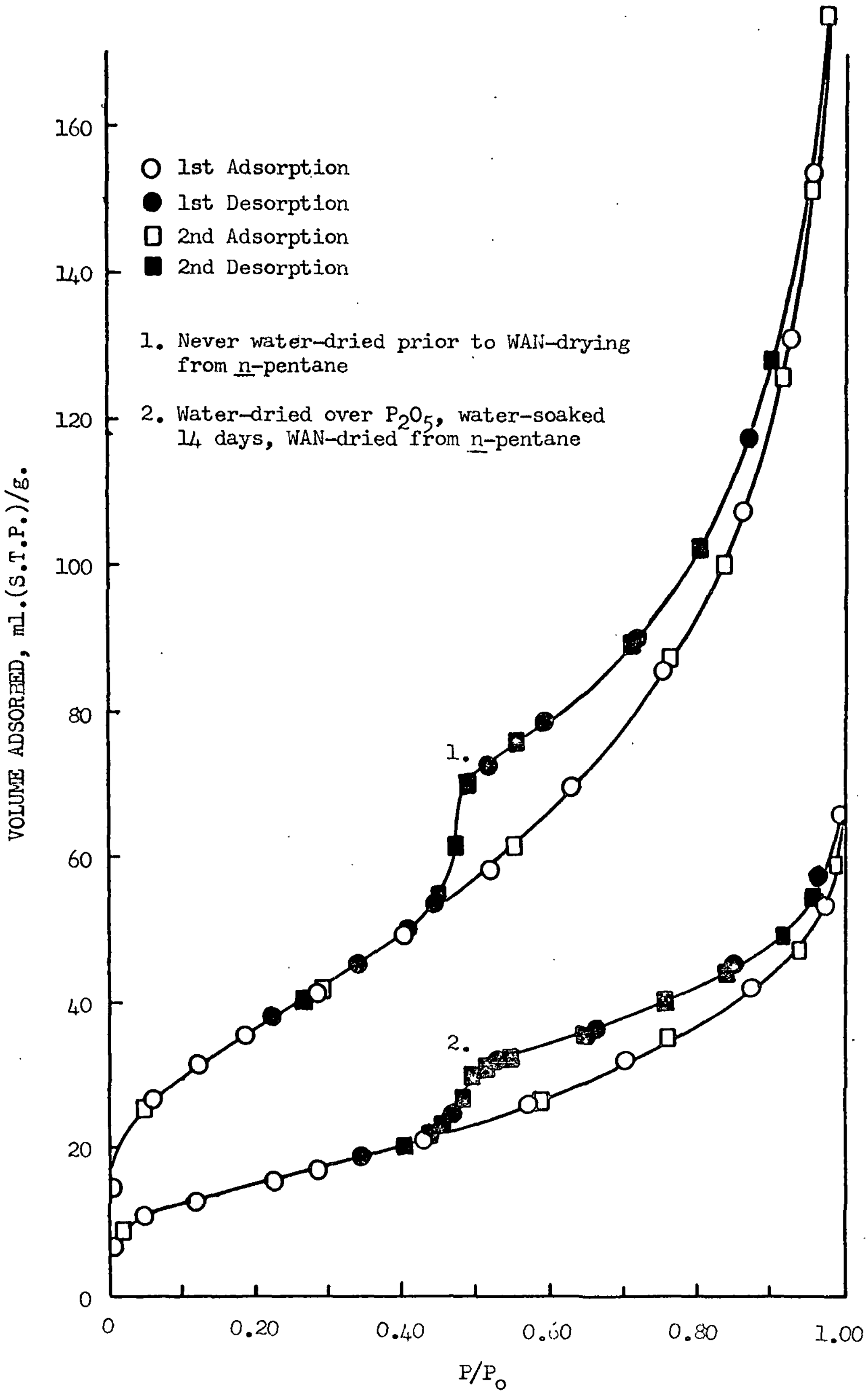

Figure 12. Nitrogen Adsorption on WAN-dried Fibers

determinations were made. Still other samples were removed from the adsorption apparatus, and connected to another vacuum system; a steam jacket was placed about the sample bulb, and outgassing of the sample at 100°C. for 16 hours was carried out. These samples were returned to the adsorption apparatus for a repeat area determination.

Whether WAN-dried samples were outgassed at room temperature for several days or were stored away for different times, the redetermined fiber areas were smaller, as is shown by the data of Table XII. When the temperature of outgassing was raised to 100°C. for 16 hours, the redetermined fiber areas decreased 33 to 37% whether the fiber sample had been WAN-dried from benzene, cyclohexane, or n-pentane; and whether or not the fibers had been dried once from water.

The data presented in Table XII reveal that when fiber areas were redetermined a day later than the initial determination there was little or no change in areas. However, if the redetermination was made several days or weeks later, the area decreases were from 2 to 12 sq. m. per gram. These results indicated that the area losses were time dependent. The gradual but steady area decreases suggested that the fiber structure was slowly changing, perhaps by the gradual formation of hydrogen bonds between neighboring hydroxyl groups. If this were the case, temperature increases should affect the rate of such bond formations. Therefore, samples were outgassed at 100°C.; the fiber areas showed a marked decrease as a result of the treatment.

It could be pointed out that traces of residual water or alcohol not removed by the WAN-drying process might account for gradual area decreases

TABLE XII

STABILITY OF WAN-DRIED STRUCTURES

Sample No.	B.E.T. Area, sq. m./g.	Final Exchange Liquid	Remarks[1]
E - 3	44.3	Benzene	
E - 3R2	43.0	Benzene	Aged 16 days
E - 4	50.1	Benzene	
E - 4R1	49.1	Benzene	Aged 1 day
E - 6D	44.6	Benzene	
E - 6DR1	44.6	Benzene	Aged 1 day
E - 17	129	*n*-Pentane	
E - 17R1	122	*n*-Pentane	Aged 15 days
E - 17R2	122	*n*-Pentane	Aged 16 days
E - 17R3	116	*n*-Pentane	Aged 33 days
E - 17R4	117	*n*-Pentane	Aged 43 days
E - 17A[1]	115	*n*-Pentane	
E - 12	93.7	Cyclohexane	
E - 12R1	89.5	Cyclohexane	Aged 25 days
E - 12R3	87.4	Cyclohexane	Aged 42 days
E - 32	119	*n*-Pentane	
E - 32R1	119	*n*-Pentane	Aged 1 day
E - 10	47.9	Benzene	
E - 10R1	38.4	Benzene	Aged 7 weeks
E - 36	57.4	Ether	
E - 36R1	55.4	Ether	Outgassed 6 days
E - 16	89.7	*n*-Hexane	
E - 16R1	87.6	*n*-Hexane	Outgassed 5 days
E - 1	43.0	Benzene	
E - 1A	28.9	Benzene	Outgassed 16 hrs. at 100°C.
E - 12D	94.9	Cyclohexane	
E - 12DA	59.5	Cyclohexane	Outgassed 16 hrs. at 100°C.
E - 37	133	*n*-Pentane	
E - 37A	88.1	*n*-Pentane	Outgassed 16 hrs. at 100°C.
E - 49	66.7	*n*-Pentane	
E - 49A	44.3	*n*-Pentane	Outgassed 16 hrs. at 100°C.

[1] After determination E - 17R4, the fiber sample was resoaked in water, then exchanged and WAN-dried as before.

as drying was continued on the adsorption apparatus. However, this seems unlikely because the area decrease continued after lengthy and repeated outgassings at room temperature, whereas water or alcohol should have been completely removed during the outgassing which preceded the initial area determination. This latter observation is based on results from freeze-drying experiments. These experiments to be described later showed that fibers completely saturated with water, and contained in sample bulbs of the same dimensions used for the WAN-dried fibers, were dried in 50 hours at -5°C. Thus, if the removal of residual water caused a 33% area loss in 16 hours of outgassing at 100°C., then a comparable loss should have been expected for those samples continually outgassed for 5 and 6 days at room temperature. However, those samples did not show such a loss.

The substantial area lost by outgassing at 100°C. must occur by the same mechanism that accounted for lower areas when fibers were WAN-dried at temperatures above 60°C. The apparent area losses by drying at such temperatures were not as great as those realized by outgassing at 100°C., but they were greater than the losses by outgassing several days at room temperature. The consistent dependence of the stability of the fiber areas upon time and temperature is good evidence for the proposal that the stability of the WAN-dried fiber structures is a function of the rate of formation of hydrogen bonds between neighboring hydroxyl groups within the structures.

It is important to note that the samples outgassed repeatedly, at room temperature, or at 100°C. had less residual liquids than samples not given such treatment. Since the outgassing treatments resulted in a loss of surface area it must be concluded that the residual liquids were not held in a manner such that their loss made new area accessible to nitrogen adsorption.

THE RELATIONSHIPS BETWEEN WAN-DRYING PHENOMENA AND SURFACE TENSION OF THE FINAL EXCHANGE LIQUID

It has been shown that the amount of residual liquid held in WAN-dried fibers is related to the fiber pore structure, and that irrespective of retained liquids, fibers which have been WAN-dried to achieve different areas have different pore structures. It follows that the change of pore structure may in itself be responsible for the retention of various amounts of residuals and for the development of different surface areas. It was suggested that a property of the final hydrocarbon was responsible for the different areas of WAN-dried fibers. If this is true, that property must be such that it can alter the fiber pore structure. The liquid property of surface tension meets the requirement of being capable of changing a fiber structure.

Campbell (4) explained how surface tension effects of water could collapse a cellulose structure and be responsible for strength development in a sheet of paper. Van den Akker (47) confirmed this interpretation with experimental evidence. The surface tensions of liquids used in this thesis were about one-fifth that of water. However, one of Campbell's (4) classical analyses shows that these smaller forces are still adequate for distortion of the microscopic structural units of a fiber. A fiber unit of 1-mm. length and .003-mm. diameter pictured as a beam supported at the ends and uniformly loaded by the surface tension force of 30 dynes per cm. would deflect 4 mm. at the center. Certainly a fibril of this size would undergo a considerable distortion as a result of surface tension. Thus, as the hydrocarbons begin to evaporate and form menisci in the fiber pores, surface tension forces act upon the structural units and in distorting or moving them bring about changes in the structure of the fiber.

There were several approaches which could be used to test the importance of surface tension effects in developing different fiber areas by WAN-drying. First, it was possible to test the existing data for consistencies which should be expected from such effects. Second, since surface tensions continue to decrease above the boiling points of hydrocarbons, the trend of area development at lower temperatures of drying should continue at the higher temperatures above the boiling points. Third, if surface tension effects could be completely eliminated, the largest fiber areas should be achieved and perhaps no residual liquid would remain. This last approach could be carried out by subliming water from the saturated fibers, and this method was attempted. Also, Kistler's method of preparing fully expanded aerogels could be used. The method was not used because of certain anomalies; (1) at the critical temperature of propane (95.6°C.), the already described temperature effects upon cellulose would be uncertain, and (2) liquids in capillaries have elevated boiling points (48); therefore, the critical temperature or point of zero surface tension would be unknown.

To relate surface tension effects to the experimental results, it was necessary to know the magnitude of this liquid property at different temperatures. It was possible to obtain values of surface tension for the different hydrocarbons at various temperatures from the literature. However, the values in the literature were usually for highly purified hydrocarbons. Therefore, surface tension measurements were made at different temperatures for the liquids used in this work.

Surface tensions were measured with a stalagmometer. The instrument was arranged so that the hydrocarbon was dropped from the stalagmometer into an enclosure saturated with vapors of the hydrocarbon. The stalagmometer and the enclosure were situated in a controlled temperature medium. Measurements were made at three or more different temperatures below the boiling point of the hydrocarbon.

It was discovered that the surface tensions of the hydrocarbons used in this work had values which agreed within a dyne per cm. over a wide temperature range with the values reported in the literature. Therefore, the literature values were used in the interpretation of the data (49, 50). Surface tension measurements were made of hydrocarbon samples which had passed through the exchanged fibers. These samples were taken from the final portion of exchange liquid. They showed no consistent or appreciable change in surface tension for having passed through the sample.

THE EFFECT OF SURFACE TENSION ON SURFACE AREA AT TEMPERATURES BELOW THE BOILING POINTS OF HYDROCARBONS

The experiments needed to evaluate the surface tension effects at temperatures below the boiling points of hydrocarbons have already been described. The data obtained by WAN-drying at different temperatures were simply related to the corresponding surface tensions.

If the classical interpretations by Campbell (4) concerning the importance of surface tension in the water-drying of cellulose can be applied to the comparatively small surface tension involved in WAN-drying, there are certain results which may be predicted for the WAN-drying process. Since a decrease of surface tension would lessen the forces producing structural changes and since surface tensions decrease with increasing temperatures, fiber areas should increase as WAN-drying temperatures increase. Such an effect has already been shown by the results presented in Figure 5.

Also, if the forces of surface tension are primarily responsible for area development in WAN-dried fibers, the magnitude of area increase for a given decrease in surface tension should be the same for all liquids. Of course, this requirement can only be met if areas develop linearly with changes in surface tension. Since all ordinate increments are equal in Figure 13, it can be seen that the slopes of the three upper lines are nearly equal; thus, Figure 13 shows that the magnitude of area increase for a given increment of surface tension was the same for at least three different liquids.

Furthermore, if surface tension is a primary mechanism in developing WAN-dried fiber structures, the prediction can be made that at equal surface tensions equal fiber structures and areas could be achieved by drying from different hydrocarbons. This is another way of stating that any physical property of the hydrocarbons which is responsible for producing different WAN-dried fiber areas must respond to temperature as described by the results of Figure 5; and the transposition from the WAN-drying temperatures to the physical property should result in the resolution of the three widely spaced lines of Figure 5 into a single line. As shown in Figure 14, the transposed data of Figure 5 for fibers WAN-dried from <u>n</u>-pentane, <u>n</u>-hexane, and cyclohexane fall about a single line; and equal surface tensions result in nearly equal surface areas.

If no effect other than surface tension were responsible for differences in WAN-dried fibers, equal fiber areas should be achieved at equal surface tensions of all hydrocarbons. The fact that the areas of fibers dried from the aromatics fall upon a common line in Figures 13 and 14 suggests that surface tensions are partly responsible for the development of those areas. However, the deviation of the data for the

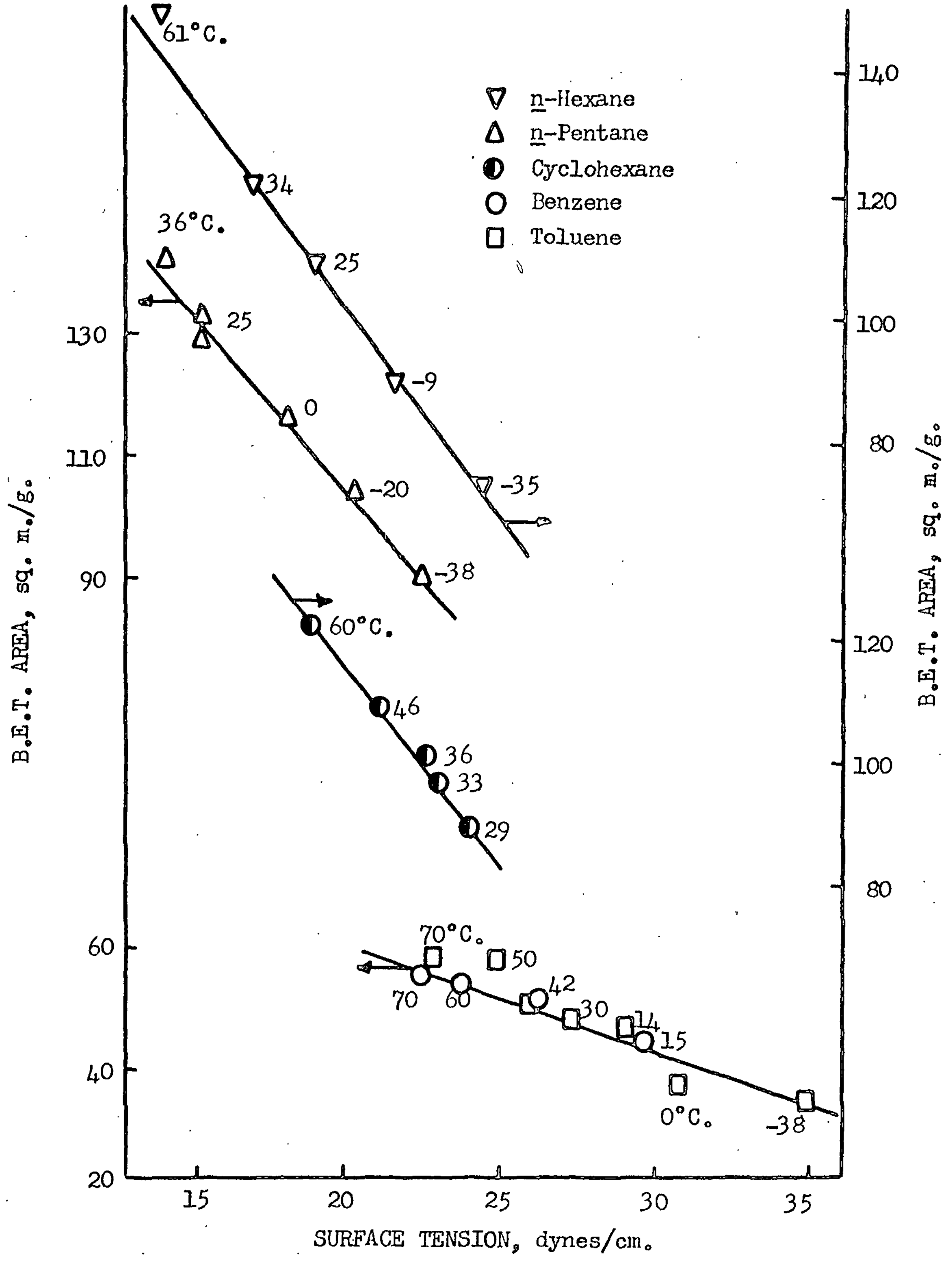

Figure 13. The Relationship Between Surface Area of WAN-dried Fibers and Surface Tension of Final Exchange Liquid

aromatics from the data for the nonaromatics suggests that another effect has been imposed upon the fiber-hydrocarbon system. Without additional investigations it seems most logical to assume that these different trends were caused by some unique relationship between the aromatics and the cellulose. Whether such relationship arises from the unsaturated and resonant structure of the aromatics or from some unique physical dimension in the aromatic-cellulose system is unknown.

However, there is another aspect of the data for the aromatics. At surface tensions less than 25 dynes per cm., drying occurred at 60°C. or greater as shown in Figure 13. Thus, in Figure 14, the apparent deviation of the data for the aromatics from the data for the nonaromatics, might be attributed in part to the previously noted temperature effects.

The data of Figure 14 also lead to the suggestion that an effect other than surface tension arose when fibers were WAN-dried from cyclohexane. The dotted line which connects the points for fibers dried from cyclohexane indicates that at equal surface tensions fibers dried from this hydrocarbon have greater areas than fibers dried from the other hydrocarbons. An explanation to account for the larger areas will be offered in a subsequent discussion (see page 100).

Conceivably, for large surface tension values, the fiber structure may respond differently than was the case for lower values. Indeed, there has to be a finite area regardless of how great the forces of surface tension may be. Thus, it may be assumed that the lower end of the line of the nonaromatic data in Figure 14 would asymptotically approach some fixed surface area.

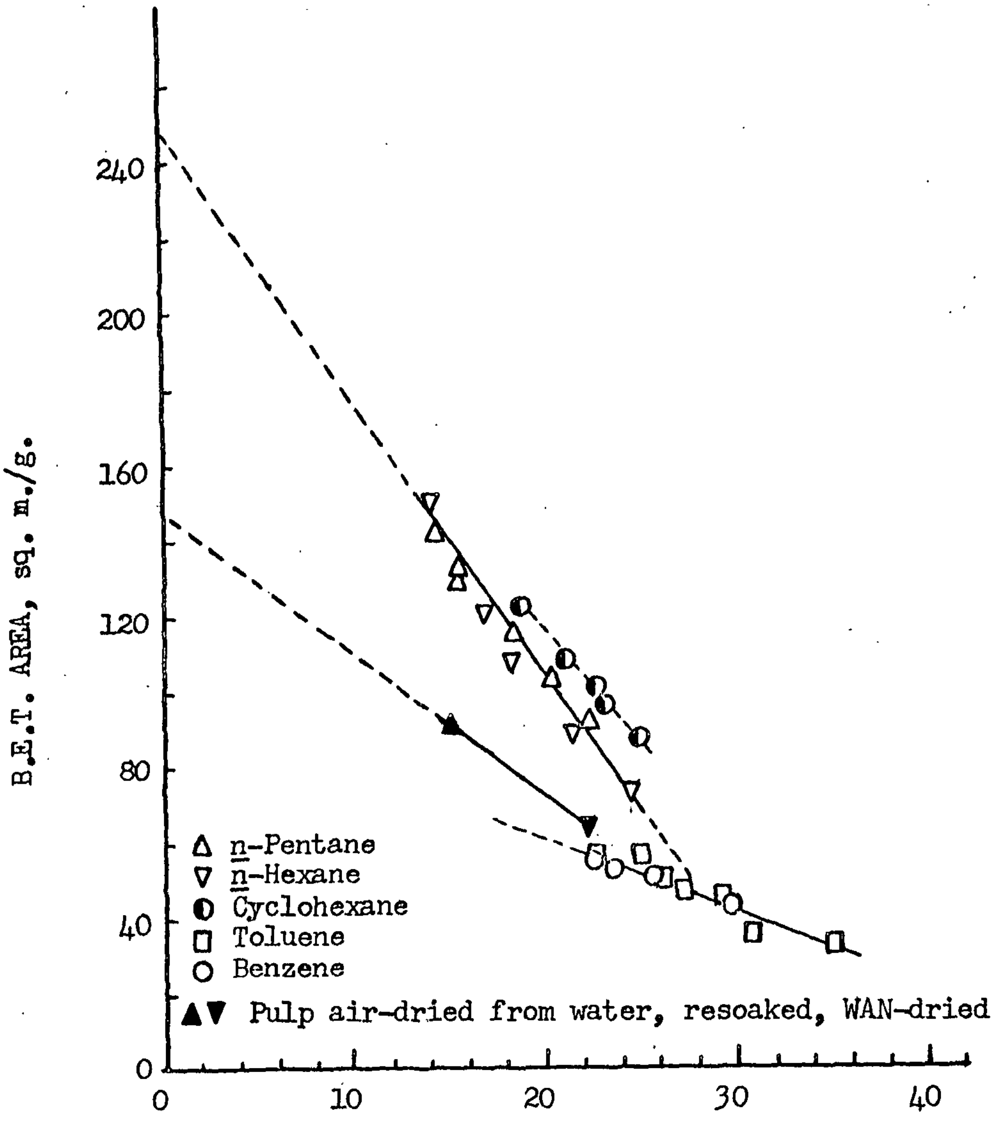

Figure 14. The Relationship Between Surface Area of WAN-dried Fibers and Surface Tension of Final Exchange Liquid

It is interesting to speculate on the significance of the extrapolation to zero surface tension of the data for the nonaromatic hydrocarbons of Figure 14. The reliability of the extensive extrapolation is questionable. The surface area of about 247 sq. m. per gram at zero surface tension compares with an area of 202 sq. m. per gram determined by Stamm (51) for water adsorption on a bleached spruce sulfite pulp. Since the latter area was for fibers which had been water-dried before the adsorption measurements were made, and since, as previously noted, drying from water may decrease accessible surface area as much as 60%, the area from the extrapolated data seems a bit small. However, it should be noted that Stamm used in his calculations the value of 14.7 sq. A. as the cross-sectional area of the water molecule. It has not been shown that this is the correct molecular area to use for water molecules adsorbed on cellulosic surfaces.

If Stamm had used the molecular cross-sectional area of 10.5 sq. A. as used by Lange and Lindvall (52) the fiber area would have been about 145 sq. m. per gram. This nearly equals the value of 147 sq. m. per gram obtained by extrapolating to zero surface tension the data presented in Figure 14 for fibers which had been dried from water. The revised area of 145 sq. m. per gram makes the area of 247 sq. m. per gram from Figure 14 more plausible.

The data of Figure 14 provide still another expected result if the forces of surface tension are dominant in developing area of WAN-dried fibers. It may be reasonably assumed that the water-dried fibers have a more compact and rigid structure than the original never-dried fibers. Figure 14 shows that for the fibers which had been dried from water the magnitude of area increase for surface tension decrease was noticeably less than for never-dried fibers.

THE EFFECT OF SURFACE TENSION ON SURFACE AREA AT TEMPERATURES ABOVE THE BOILING POINTS OF HYDROCARBONS

It was possible to provide additional tests for surface tension effects by removing the hydrocarbons from the fiber structure at temperatures above their boiling points. Katz and Saltman (53) have shown that surface tensions of all linear hydrocarbons when plotted against reduced temperatures fall upon a single straight line. The data of these investigators were used to obtain surface tensions of n-pentane and n-hexane at temperatures above their boiling points.

In WAN-drying fibers at temperatures above the boiling point of the hydrocarbon, it was necessary to keep both stopcocks of the sample bulb in Figure 3(a) closed when the sample was being brought to temperature; otherwise there would have been localized boiling in the sample bulb. During the rise to temperature, the hydrocarbon increased the pressure inside the bulb. After 15 minutes, the lower stopcock of the bulb was quickly opened and the pressure immediately forced liquid and vapors out of the bulb. While vapors were being blown out of the lower capillary stem, the end of the stem was immersed in some of the discharging liquid held in a 25-ml. beaker. By this means, the rate of vapor discharge could be followed. Within 3 to 5 minutes of the initial release of pressure, hydrocarbon vapors were discharging at about one bubble per second. At this point, the upper stopcock of the bulb was opened and dry nitrogen at the standard rate was passed through the bulb until drying was complete. Drying was considered complete when no odors of the final hydrocarbon could be detected. Thereafter, the hot water circulating about the bulb was immediately replaced with water at room temperature. Dry nitrogen continued to flow through the bulb at room temperature for the standard drying time.

Because it was felt that the rate of vaporization of the hydrocarbons above their boiling points might influence the experimental results, several sample bulbs were constructed with a 2-mm. capillary stem for discharging of vapors. Normally, that stem was 1-mm. capillary. It was reasoned that the larger capillary would bring about a more rapid pressure release and, thus, a more rapid removal of hydrocarbons.

The results presented in Figure 15 show that considerable variation in area was observed when fibers were WAN-dried at temperatures above the boiling points of n-hexane or n-pentane. The largest area resulting from these experiments was 196 sq. m. per gram. The areas were sometimes much greater, and other times lower, than the values expected from the established trends. Furthermore, it was not always possible to reproduce an area at a given temperature. The data of Figure 15 also show that discharging the hydrocarbons through a 1-mm. capillary or a 2-mm. capillary caused no consistent trends in area development. It was thought that by enlarging the discharge capillary from 1 mm. to 2 mm. the rate of liquid blow-off and evaporation would be increased and some consistent effect might emerge.

It seems reasonable to assume that several different and sometimes opposing effects contributed to the erratic results presented in Figure 15. First, at such temperatures, the liquids were held under pressure. A

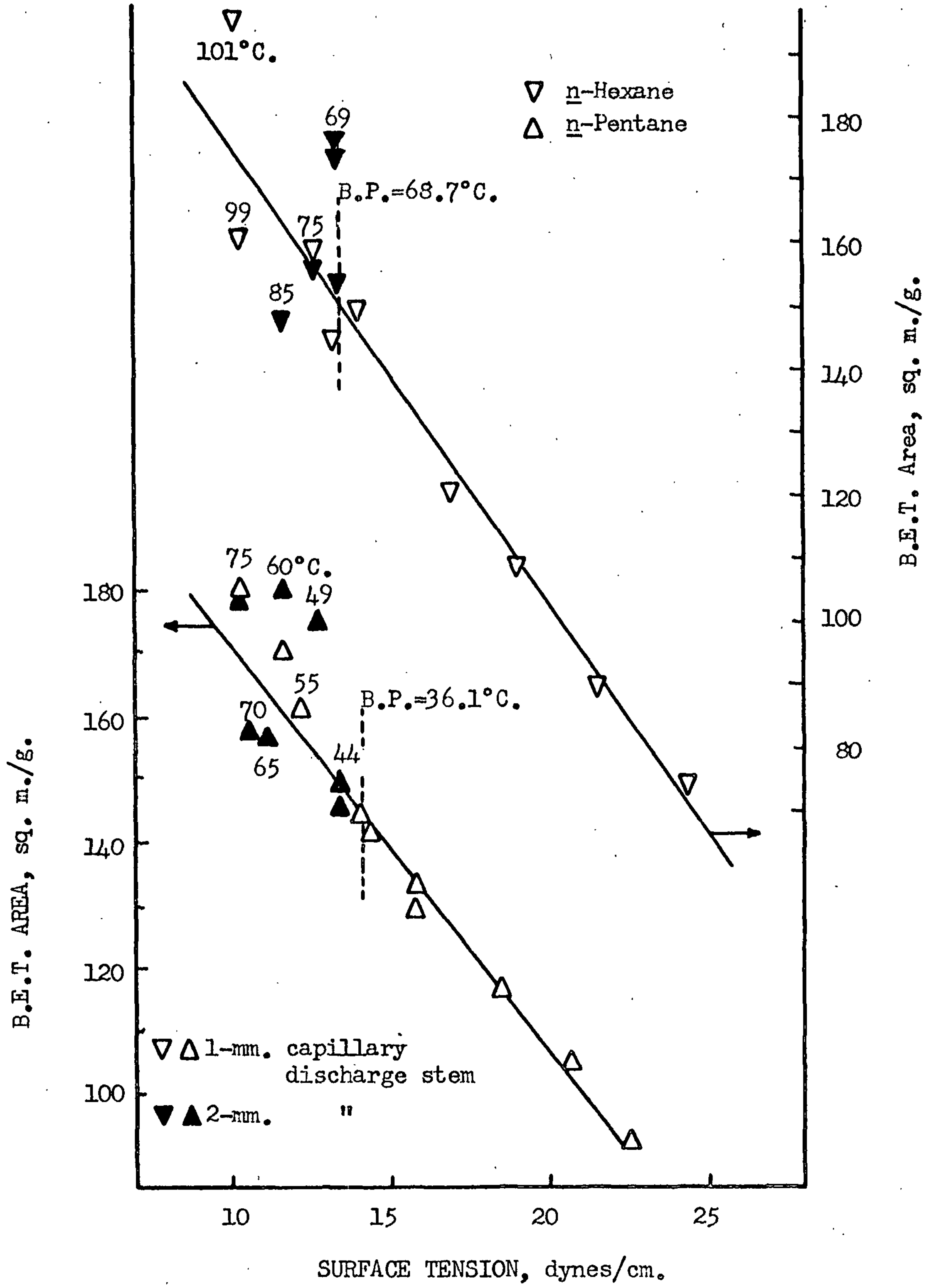

Figure 15. The Effect on Surface Area of WAN-drying Fibers Above and Below Boiling Points of Hydrocarbons

sudden release of pressure would cause evaporative cooling. Such cooling should have made the actual drying temperatures lower than the apparent temperatures and led to surface areas below those expected on the basis of the trend previously established. Second, at temperatures above 60°C., the previously described temperature effects (see page 52) would favor lower areas. As the temperature of drying increases, there should be a greater influence on hydrogen bonding and, thus, a greater effect upon the fiber structure. Third, considering the effects of surface tension as a force applied to the fiber structure, the application of this force for a short time would probably result in less structural change than if an equal force were applied for a longer time. In the latter case, the structural units would have more time to undergo creep and permanent deformation. Furthermore, when the pressure is released from the liquid hydrocarbons there is the possibility of nucleate boiling occurring within the fiber structure. Conceivably, such boiling might disrupt some parts of the fiber structure and make new regions accessible to gas adsorption.

It is not known to what extent any of the above effects were responsible for the varied results of Figure 15. However, it is apparent that effects other than those of surface tension were involved. Further evidence of the variation of results from these experiments is presented in Table XIII. The results of table XIII reveal that although the areas of fibers dried above the boiling points of the respective hydrocarbons varied over a wide range, the percentages of residual liquid did not follow the trends previously shown where larger fiber areas were accompanied by lower amounts of residual liquid.

TABLE XIII

RESIDUAL HYDROCARBON IN FIBERS DRIED ABOVE THE BOILING POINTS OF n-PENTANE AND n-HEXANE

Sample No.	B.E.T. Area, sq. m./g.	Residual Liquid, %	Temperature of Drying, °C.	Final Exchange Liquid
E-98	181	1.1	60	n-Pentane
E-119	170	1.0	60	n-Pentane
E-99	176	1.1	69	n-Hexane
E-99D	154	1.4	69	n-Hexane
E-100	148	1.3	85	n-Hexane
E-102	156	1.4	75	n-Hexane
E-103	157	1.2	70	n-Pentane
E-105	144	1.0	37	n-Pentane
E-108	156	1.0	65	n-Pentane
E-109	145	1.0	44	n-Pentane
E-110	149	1.0	44	n-Pentane
E-111	162	1.1	55	n-Pentane
E-112	178	0.6	75	n-Pentane
E-113	180	0.8	75	n-Pentane
E-114	161	1.4	99	n-Hexane
E-116	196	1.0	101	n-Hexane

FREEZE-DRYING OF WATER-SWOLLEN FIBERS TO ELIMINATE THE EFFECTS OF SURFACE TENSION

Samples of the original water-saturated experimental pulp were sealed into glass bulbs of approximately the same dimensions as the bulb shown in Figure 1. The fibers were sealed in the bulbs by the same techniques used by Haselton (22) to seal water-dried fibers in adsorption bulbs. The water-saturated samples were frozen at -20, -80 and -195°C., and dried at -5 or -20°C.

The "freeze-drying" apparatus was of a design by Flosdorf (54), except that connections between the sample bulb and the drying apparatus were made with ground-glass joints. The essentials of the drying procedures were (1) the immersion of the previously frozen sample bulb in a cold bath,

(2) connection of the bulb to a vacuum header, and (3) collection in a cold trap of water vapors from the sample. Experiments were run to determine the length of time required to achieve complete dryness at a given temperature. Thereafter, the dried fibers were transferred to the adsorption apparatus for an area determination.

The results of the "freeze-drying" experiments are given in Table XIV. They reveal that very little water was <u>sublimed</u> from the structures. Apparently, the water was not in the solid state as drying occurred, because such low fiber areas are about what would be expected by drying from water at room conditions (<u>22</u>). Most unbeaten water-dried fibers have an area of about 1 sq. m. per gram as measured by nitrogen adsorption.

TABLE XIV

SURFACE AREAS OF FIBERS DRIED BY LOW TEMPERATURE SUBLIMATION OF WATER

Sample Designation	Freezing Temp., °C.	Drying Temp., °C.	B.E.T. Area, sq. m./g.
FD-20-5-1	-20	-5	1.20
FD-80-5-1	-80	-5	1.62
FD-80-20-6p	-80	-20	1.81
FD-195-20-1	-195	-20	3.17

Table XIV shows that as the temperature of drying decreases there is a trend to larger areas. Also, as the temperature of freezing was decreased the areas increased for a given temperature of drying. These results indicate that for the most part water was unfrozen at the drying temperatures of -5 and -20°C. and may not have frozen at -80 and -195°C. Apparently, the water is held in the fibers as a supercooled liquid. The lowering of the freezing points of liquids held in fine capillary systems has been reported in the literature (55-57). Thus, the unfrozen water evaporates from the fibers by the same mechanisms prevailing at room conditions. Some of the water was frozen as indicated by the noted trends. Furthermore, the results of Van den Akker (47) show that water held between fibers can be frozen and sublimed. Thus, the low surface areas of Table XIV are the result of internal collapse of the fiber structure due to surface tension effects of the unfrozen water.

THE EFFECT OF DRYING LIQUID-EXCHANGED FIBERS FROM POLAR ORGANIC LIQUIDS

In this work, hydrocarbons were selected as the liquids from which to dry fibers because it was felt that polar organic liquids might contribute additional effects to the development of accessible fiber area. To give support to this feeling, several samples were dried from polar organic liquids.

Fiber samples were given a standard methanol exchange which was followed by an exchange with a polar organic liquid. The fibers were dried from the polar liquid by the standard procedures. The polar liquids used were acetone, tetrahydrofuran and ethyl ether.

TABLE XV

THE EFFECT ON FIBER SURFACE AREA OF DRYING FROM POLAR ORGANIC LIQUIDS

Sample No.	B.E.T. Area, sq. m./g.	Final Exchange Liquid	Surface Tension, dynes per cm.
E-11	21.7	Acetone	23.7 (50)
E-14[1]	20.5	Acetone	26.2 (50)
E-18	19.5	Tetrahydrofuran	26.4 (58)
E-36	57.4	Ethyl ether	17.0 (50)

[1] This sample was dried at 0°C. whereas all others were dried at room conditions

The results in Table XV show that even for the polar liquids the larger areas were developed at lower surface tensions. At surface tensions equal to those in Table XV the nonaromatic hydrocarbons developed much larger surface areas. At comparable surface tensions of those in Table XV, fibers dried from the aromatics had areas twice as large as the fibers dried from acetone and tetrahydrofuran but had areas only slightly larger than the fibers dried from ethyl ether. With these comparisons it is interesting to note that, on the basis of dipole moment and dielectric constant, ethyl ether is a much less polar liquid than either acetone or tetrahydrofuran.

It is not known what added effect the polar liquids impose upon the surface tension effects. However, the effects may be related to the phenomena of fiber swelling in different liquids. Thus, fibers swell greatly in water and slightly less in acetone but swell very slightly in ether and still less in the hydrocarbons (6). Thus, those polar liquids which show little tendency to swell fibers might be expected to develop fiber areas substantially greater than polar liquids which swell cellulose much more. Without further information these possibilities must be left to speculation.

INTERPRETATIONS OF THE WAN-EXCHANGE AND WAN-DRYING PROCESSES

In light of the experimental data compiled in this work, it is possible to offer several interpretations of the WAN-exchange and WAN-drying processes. An attempt will be made to unify the variables of the two processes into a series of interpretations which will be consistent with all available experimental data.

THE EXCHANGE FROM WATER TO ALCOHOL

The formation of structural units of a cellulose fiber in a growing tree occurs in an aqueous medium. Therefore, all spaces between the structural units are filled with water. Some of these spaces are no doubt of the order of a few diameters of a water molecule. In spaces or pores of this size, there may not be complete replacement of the water by the alcohol, during the alcohol exchange. When the entire exchange process is finished and drying of the exchanged fibers is started, any unexchanged water will evaporate during the drying process. The evaporation of this water will bring about some hydrogen bonding and thereby cause some change in the fiber structure. In this work, if any such change occurred, it was assumed to be constant because the process for removal of water was standardized. In addition to changes caused by evaporation of nonreplaceable water, other changes are brought about by other effects of the exchange and drying processes. It should be expected that these latter effects will cause different responses or magnitudes of changes in different type of fibers which do not contain the same amount of unexchangeable water.

THE EXCHANGE FROM ALCOHOL TO HYDROCARBONS

On the bases of molecular size and solubility, the evidence presented in this work gave no indication that replacement of methanol by hydrocarbons was any less complete than replacement of water by the alcohol. All hydrocarbons irrespective of molecular size were apparently equally effective in replacement of the alcohol. Therefore, prior to drying, the fiber structures are saturated with a hydrocarbon and contain equal amounts of unexchanged traces of water and methanol.

There arises the question as to whether or not there is a fiber structure change as a result of the fibers being saturated with different hydrocarbons. That is, do fibers WAN-exchanged and saturated with a n-pentane have a different structure than the same fibers saturated with n-hexane or cyclohexane?

The answer to the above question is not given by this work. Any change in the fiber structure as a result of contact with different liquids would probably arise from the electrostatic fields set up at the numerous molecular centers of the polyglucose units in cellulose and the molecular properties of the liquids. Such properties might include dielectric constant, dipole moment, the ability to undergo induced polarization, and the relative ability to swell cellulose. These properties represent several fields of investigation which were not a part of this work. The complex structure and strongly polar nature of cellulose make the isolation and evaluation of any effects arising from the foregoing liquid properties very difficult, especially with our limited knowledge of such systems. Still other effects such as changes in the modulus of elasticity of cellulose at different drying temperatures may also play a role in the WAN-drying process. These various effects may be of importance during WAN-drying but were not evaluated in this work; thus, they must be left to speculation and future investigations.

Also, surface tension as a molecular property is a measure of the free surface energy of liquids. Conceivably, the free energy of the molecules of liquid and cellulose help to determine the structure of saturated fibers before WAN-drying occurs. The interrelationship of such free energies remains yet to be determined.

THE EVAPORATION OF HYDROCARBONS FROM WAN-EXCHANGED STRUCTURES

Using the concepts of surface tension, it is possible to offer the following general interpretations of the WAN-drying process: Before a liquid hydrocarbon evaporates from a fiber pore, a meniscus forms at the pore entrance and thus the internal tension of the liquid tends to collapse the pore. These pores, or capillaries, have neighboring structural units, such as fibrils or microfibrils, as boundaries or walls. Where these structural units touch to form the pore wall, there are nips or corners. In a saturated fiber, these nips are filled with nonpolar liquid. Some structural units are likely to be independent of any pore wall and are separated from other units by layers of liquid molecules. As surface tension forces move any of the structural units into closer contact or into contact for the first time, there is every opportunity for liquid molecules to become enmeshed in the nips of the structural units of contracting pore walls and at the new points of contact. The chains of molecules forming the surface of the structural units provide the irregularities which hold the liquid molecules.

The extent to which the pores collapse or new contacts between structural units are made will be a function of surface tension, other factors remaining constant. Thus, in support of the experimental evidence, as surface tension increases, the total pore volume of fibers will decrease along with accessible surface area, whereas the amount of enmeshed or retained liquid will become greater. It follows from this interpretation that if liquid molecules are trapped between structural units, they hold those units apart. Thus, large molecules will hold the structures farther apart than small molecules. This can explain why at equal surface tensions slightly larger fiber areas were obtained from bulky cyclohexane than from n-hexane.

The foregoing interpretations do not rest upon any concept of unique pores with entrances available to liquids during liquid exchange but which close during the drying step, thereby entrapping molecules. Such a concept is not inconsistent with the view already expressed. Where surface tension forces are moving structural units with respect to each other, there is the possibility of distorting or closing pore openings to entrain liquid molecules.

There are certain objections to the above concept: (1) Surface tension forces as a direct mechanism for closing pore openings is difficult to defend when referring to pores of the size of a few molecular diameters. The existence of menisci of a diameter of a few molecules is difficult to visualize. (2) Experimental evidence showed that, with prolonged outgassing, fibers lost residual liquids but also lost surface area. If liquids were held in pores, the gradual escape of molecules might not result in less fiber area. On the other hand, if molecules were clamped between structural units, their eventual escape for kinetic reasons might permit the entraining units to come closer together into a less strained condition. (3) It seems most likely that the fiber pores are interconnected and that each pore has several openings; thus, it is improbable that all openings would be distorted or closed before the liquid held within could escape. These objections, however, are not sufficient to eliminate completely the possibility of some entrainment of liquid in pores.

THE WAN-DRYING OF DIFFERENT CELLULOSE STRUCTURES

During WAN-drying, the extent of collapse and the quantity of retained liquid of any fiber structure will be determined by fiber plasticity, number and size of pores, dimensions of fiber structural units, and surface tension. These factors can explain why fibers of smaller specific surface can retain equal or greater amounts of residual liquids than fibers of larger area, and why some structures will respond differently to changing surface tensions.

In this work, fibers dried once from water prior to resoaking and WAN-drying had an area 60% less than fibers never water-dried; yet the water-dried fibers held a slightly greater quantity of residual liquid. This latter effect must be related to the change of fiber structure by water-drying. The amorphous regions were still accessible after drying from water and reswelling in the same medium; however, the structural units in these regions were brought into a more compact arrangement. Thus, these structural units were nearer to each other and had less space in which to move. This meant that an increased number of new contacts between structural units could arise during drying. A greater number of such contacts will mean a greater quantity of retained liquid in the amorphous region. This effect must have been large enough to compensate for the loss of pores related to the areas made inaccessible by water-drying.

The foregoing interpretation suggests that, for the comparisons of WAN-dried structures, knowledge of fiber area and amounts of retained liquids would be most helpful.

SUGGESTIONS FOR FUTURE WORK

TEMPERATURE EFFECTS UPON CELLULOSE

This work has shown that at moderate temperatures (about 70°C.) and above there is a strong temperature effect upon WAN-dried structures. This phenomenon merits additional investigation. It would be worthwhile to know if the temperature effects are reversible and if they arise only when the fibers are dry as opposed to a liquid saturated state. Such an investigation might provide worthwhile information on the development of strength in paper during drying at various temperatures.

FIBER STRUCTURAL CHANGES FROM MECHANICAL AND CHEMICAL TREATMENT

The techniques used in this work may be applied to investigate the manner in which fiber structures respond to surface tension after they have been mechanically or chemically treated. The accumulated information of change of slope of the curve for the area vs. surface tension plot, of quantity of residual liquids, and of the change in shape of the adsorption isotherm should give an insight into the various treatments to cellulose.

HIGH PRESSURE RELEASE OF HYDROCARBONS FROM CELLULOSE STRUCTURE

A more elaborate control of the release of low boiling hydrocarbons from exchanged fibers at high temperatures and pressures should complement the work of this thesis. Development of techniques for creating fully expanded aerogels would provide useful information on the most probable accessible area of fibers in a water suspension.

WAN-DRYING OF CELLULOSE FROM AROMATIC HYDROCARBONS

There is some reason to believe that cellulose responds differently to WAN-drying from the aromatic hydrocarbons than from the nonaromatics. Further, investigations could be directed at proving or disproving this possibility. The investigation might involve use of linear unsaturated hydrocarbons of conjugated and unconjugated bonds. The results of such investigations might determine if types of bonds in hydrocarbons cause effects which are additive to surface tension effects in determining area development and the amount of liquid retained in WAN-dried fibers.

SUMMARY AND CONCLUSIONS

An apparatus was designed and techniques were developed for the liquid exchange of water-swollen fibers. The exchange was from water to methanol to a hydrocarbon. The fibers were dried from the latter liquid by a stream of dry nitrogen. These fibers were described as having been WAN-dried. Nitrogen adsorption techniques were used to measure the total areas and pore volumes of these fibers. In addition, the amounts of residual hydrocarbons held in the fibers were determined.

Preliminary work established the reproducibility of the techniques of exchanging and drying. Some of the more important results led to the following general observations on WAN-dried fibers.

1. For the final exchange liquids studied, the fiber surface areas were not controlled by the molecular size or shape of the final liquid or its solubility in methanol. Thus, fibers dried from cyclohexane developed areas twice as large as those dried from benzene, yet the former molecule may be slightly larger than benzene and is less soluble in methanol. Also, by a slight increase in the drying temperature, cyclohexane-dried fibers could be made to exceed in areas those dried from the linear molecule _n_-hexane.

2. Fibers dried from _n_-pentane at room temperature had an area triple that of fibers dried from benzene. However, if fibers dried from benzene were resoaked in water, then liquid exchanged and dried from _n_-pentane, they developed an area almost equal to that of fibers dried only once from _n_-pentane. Thus, WAN-drying creates very few bonds of the irreversible type common to water-drying.

3. It was also established that areas of WAN-dried fibers were not controlled by the rate of exchange of water by methanol. However, the areas were influenced by the choice of alcohol for the water replacement; methanol gave the best results. Moreover, for reproducible results the purity of the exchange liquids had to be the same and the drying rate had to be fixed at a constant value.

4. Because such notable differences in fiber areas could be achieved by WAN-drying from different hydrocarbons, it seemed unlikely, as suggested by others (19), that the final exchange with hydrocarbons removed all of the methanol but a nonexchangeable monomolecular layer. A residual monolayer of methanol or water would probably control the development of fiber areas.

Further investigations were directed at establishing the following; how or why liquids are held so tenaciously in WAN-dried fibers, the role of the fiber structure in the retention of liquids, and any correlations between liquid proporties and the phenomena of WAN-drying.

Notable effects were observed when fibers were dried from different hydrocarbons at various temperatures. Fibers dried from n-pentane, n-hexane, cyclohexane, benzene and toluene developed increasing areas with increasing temperatures of drying. On a plot of area as a function of temperature, three widely spaced linear lines of nearly equal steep slopes were observed for the first three hydrocarbons, whereas for benzene and toluene all points fell on a common line of gradual slope.

The work on WAN-drying at various temperatures and additional experiments yielded valuable information about liquid retention in WAN-dried fibers.

1. As increased areas were developed at increased drying temperatures, the amounts of retained liquids decreased.

2. At equal areas, fibers dried from n-pentane or n-hexane held approximately equal amounts of liquids.

3. Fibers dried from water then resoaked prior to exchanging and WAN-drying developed an area about one-half that for fibers never water-dried, yet the former retained more residual liquid than the latter, both having been WAN-dried under like conditions.

The experiments on WAN-drying at various temperatures also revealed a temperature effect upon cellulose. Near 70°C., the fiber area decreased with prolonged drying times, whereas at room conditions such sensitivity to drying time was absent. Also, extensive loss of fiber area resulted when WAN-dried fibers were outgassed at 100°C. for 16 hours.

Further information on liquid retention and the porous nature of WAN-dried fibers was derived from gas adsorption isotherms.

1. From the isotherms of fibers dried at room temperature from n-pentane, cyclohexane and benzene, total pore volumes were obtained and corrected for the respective volumes of retained liquids. The corrected total pore volumes were .281, .213 and .110 cc./g., respectively. These corrected pore volumes mean that the fiber structures were different, irrespective of the retained liquids, and that WAN-drying alters the fiber structure.

2. When fibers were water-dried prior to resoaking, exchanging, and WAN-drying, their isotherm was of a different shape than that for fibers never water-dried. This means that the former have a completely different porous structure compared to the latter. It was also noted that the water-dried fibers had 60% less area than the fibers never water-dried; moreover, prolonged soaking times of the former in water resulted in unexpected lower WAN-dried areas.

The results on retained liquid, fiber porosity, and fiber area were best interpreted when related to surface tension of the final exchange liquid.

1. The linear relationships previously cited between areas developed and drying temperatures were upheld when the corresponding surface tensions were substituted for temperatures. However, unlike the temperature relationships, the surface tension relationships when plotted showed that the data for n-hexane, cyclohexane and n-pentane fell about a common line. Lower surface tensions gave higher surface areas.

2. For the previously noted corrected total pore volumes, the greater pore volumes were consistently created from liquids of lower surface tension.

3. Equal surface areas could be developed by drying fibers from n-hexane and n-pentane at temperatures reflecting equal surface tension. At these same surface tensions, cyclohexane appeared to develop slightly greater surface areas. However, all three hydrocarbons developed the same magnitude of increase in area with decrease in surface tension. Benzene and toluene behaved similarly but did not show the same magnitude

of area change. Failure of benzene and toluene to show the same response as the other hydrocarbons may mean that the aromatics are capable of unique relationship.

4. When fiber areas were equal as a result of drying from n-pentane and n-hexane at equal surface tensions, the amounts of residual solvents were nearly equal.

5. n-Pentane and n-hexane were flash evaporated from a fiber system at increasing temperatures above their boiling points. Such techniques introduced complications, since the surface areas showed considerable variation, and the amounts of residual liquids followed no consistent trend. However, the trend continued for greater areas at conditions favoring lower surface tensions.

6. Attempts were made to eliminate surface tension effects by freezing water-saturated fibers and subliming off the frozen water. The results showed that most of the water apparently never froze, because the fiber areas were about the same as for fibers normally water-dried at room conditions. Also, it was shown that fibers dried from polar organic liquids have smaller surface areas than fibers dried from the hydrocarbons at conditions of equal surface tension.

Several major conclusions may be drawn from the above observations and results.

1. Physical adsorption of hydrocarbons on cellulose surfaces is a highly improbable mechanism of liquid retention in WAN-dried fibers. This mechanism relies on total area of contact between liquid and cellulose at

a given temperature, and the magnitude of adsorptive forces which decrease with increasing temperatures. Therefore, physical adsorption could not account for more residual being held on less surface area for the same conditions of WAN-drying, as was the case for fibers once dried from water compared with fibers never water-dried.

2. The only factor which can account for the fact that fibers which have been water-dried then resoaked, exchanged and WAN-dried, retained larger amounts of residual liquids than like fibers never water-dried is a change in the pore structure of the fiber. This change was reflected in the shapes of the gas adsorption isotherms of the two systems.

3. Surface tension emerges as a most important factor in the WAN-drying of fibers. It gives the most consistent relationships with the experimental results. It can account for the noted fiber structural changes, by the well-known effects of the forces of internal liquid tension, and thereby provides a basis for a working concept of the WAN-drying phenomena.

4. Moreover, the change of the fiber structure by the forces of surface tension can account for residual liquids in WAN-dried fibers. Liquid molecules can become enmeshed and trapped in the surface roughness of structural units collapsing or moving together in response to surface tension forces.

This work provides interpretations of WAN-drying which include and support the theory of Staudinger and Döhle (9) that liquid molecules are entrapped between polyglucose chains. It goes further in presenting a mechanism for entrapment which provides a consistent interpretation of all available experimental data on fibers dried from nonpolar liquids.

This work gives a hitherto unprovided insight into WAN-drying and thus should prove of great value to any future investigators desiring to work with WAN-dried fibers. Furthermore, the work provides new and additional interpretations of several different works reported in the literature.

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APPENDIX

TABLE A

EFFECTS OF WAN-DRYING FROM VARIOUS HYDROCARBONS AT DIFFERENT TEMPERATURES

Final Exchange Liquid	Sample No.	B.E.T. Area, sq. m./g.	Temp. of Drying, °C.
n-Pentane	E-75	142	36
	E-17	129	23 to 30
	E-37	133	23 to 30
	E-33	116	0
	E-25	104	-20
	E-86	92.0	-35
n-Hexane	E-62	132	61
	E-65	150	61
	E-53	121	34
	E-29	108	23 to 30
	E-16	89.7	-9
	E-63	74.6	-38
Cyclohexane	E-81	109	70
	E-82	122	60
	E-80	109	46
	E-83	101	36
	E-52	97.0	33
	E-51	88.5	29
Benzene	E-95	51.2	81
	E-79	55.1	70
	E-77	53.9	60
	E-78	51.4	42
	E-84	45.2	15
Toluene	E-88	58.0	70
	E-87	59.1	50
	E-93	50.5	41
	E-57	48.1	30
	E-85	47.2	14
	E-58	37.8	0
	E-66	34.4	-38

TABLE B

EFFECTS OF WAN-DRYING FOR DIFFERENT LENGTHS OF TIME AT A MODERATE TEMPERATURE

Sample No.	B.E.T. Area, sq. m./g.	Drying Time 69°C.	Remarks
E-104	126	8 hrs.	WAN-dried by standard procedures[1]
E-91	129	4 hrs.	WAN-dried by standard procedures
E-90	133	1.5 hrs.	WAN-dried by standard procedures
E-89	138	45 min.	WAN-dried by standard procedures
E-92	142	28 min.	WAN-dried by standard procedures
E-99	176	18 to 20 min.	WAN-dried by special procedures[1]
E-99D	154	18 to 20 min.	WAN-dried by special procedures

[1] All samples were WAN-dried from <u>n</u>-hexane.

TABLE C

RELATIONSHIP BETWEEN FIBER AREA AND RESIDUAL LIQUID

Final Exchange Liquid	Sample No.	B.E.T. Area, sq. m./g.	Residual Liquid, %	Pulp History
n-Pentane	E-75	142	1.0	Never water-dried (Batch no. 1)
	E-44	129	1.3	
	E-33	116	1.6	
	E-25	104	1.9	
	E-86	92.0	2.7	
n-Hexane	E-65	150	0.9	
	E-53	121	1.6	
	E-29	108	1.9	
	E-63	74.6	2.8	
Cyclohexane	E-43	113	1.7	
	E-42	103	2.0	
	E-12D2	99.3	2.1	
	E-12	93.7	2.5	
Benzene	E-77	53.9	2.6	
	E-78	51.4	2.7	
	E-79	55.1	2.7	
	E-84	45.2	3.1	
Toluene	E-87	59.1	2.5	
	E-88	58.0	2.6	
	E-93	50.5	2.7	
	E-85	47.2	3.1	
	E-58	37.8	3.4	
	E-66	33.7	4.4	
n-Pentane	E-74	147	0.9	Never water-dried (Batch no. 2)
	E-73	152	0.9	
n-Hexane	E-70	118	1.4	
	E-69	96.3	1.8	
n-Pentane	E-97	91.9	1.4	Air-dried from water, resoaked, WAN-dried
	E-26	85.1	1.8	
	E-30	84.3	1.9	
n-Hexane	E-45	64.1	2.6	

TABLE D

ADSORPTION OF NITROGEN ON WAN-DRIED FIBERS

Sample E-37
WAN-Dried from
n-Pentane

P/P_o	Volume Adsorbed, ml. (S.T.P.)/g.	
.005	14.83	1st Adsorption
.061	26.89	
.122	31.45	
.188	35.71	
.285	41.34	
.403	49.33	
.521	58.73	
.630	69.83	
.751	86.11	
.861	108.05	
.924	131.45	
.957	154.34	
.870	117.97	1st Desorption
.715	90.36	
.596	79.14	
.513	72.92	
.444	53.91	
.342	45.51	
.225	38.26	
.050	25.75	2nd Adsorption
.289	41.64	
.553	61.57	
.759	87.63	
.833	100.93	
.912	126.02	
.956	151.39	
.974	175.61	
.901	128.57	2nd Desorption
.804	102.55	
.713	89.83	
.558	76.33	
.487	70.59	
.474	61.93	
.449	54.62	
.408	50.20	
.267	40.72	

Sample E-42
WAN-Dried from
Cyclohexane

P/P_o	Volume Adsorbed, ml. (S.T.P.)/g.	
.015	14.93	1st Adsorption
.053	19.70	
.203	27.49	
.476	41.13	
.607	49.80	
.776	64.58	
.887	81.22	
.947	101.29	
.972	121.61	
.943	105.73	1st Desorption
.885	86.04	
.793	71.60	
.656	60.08	
.551	54.68	
.503	52.48	
.484	50.63	
.478	47.87	
.468	44.45	
.437	39.83	
.384	36.22	
.245	29.48	
.114	23.51	2nd Adsorption
.188	26.95	
.255	29.87	
.302	32.06	

TABLE D (Continued)

ADSORPTION OF NITROGEN ON WAN-DRIED FIBERS

Sample E-3, WAN-Dried from Benzene

P/P_o	Volume Adsorbed, ml. (S.T.P.)/g.	
.090	9.92	1st Adsorption
.163	11.49	
.264	13.26	
.320	14.69	
.434	17.21	
.560	20.52	
.712	25.75	
.882	35.36	
.958	47.97	
.981	61.95	
.911	41.51	1st Desorption
.766	30.91	
.666	27.53	
.601	25.89	
.528	24.33	
.487	22.61	
.462	19.31	
.416	17.09	
.305	14.53	
.203	12.48	
.025	7.25	2nd Adsorption
.313	14.39	
.605	21.72	
.811	30.08	
.929	41.25	
.972	53.83	
.985	67.71	
.885	38.68	2nd Desorption
.722	29.24	
.565	25.07	
.491	23.09	
.473	20.50	
.455	18.62	
.334	15.06	
.202	12.41	

TABLE E

PORE VOLUME DISTRIBUTIONS OF WAN-DRIED FIBERS AS DETERMINED FROM NITROGEN ADSORPTION DATA

E-37, WAN-Dried from n-Pentane

Pore Diameter, A.	Relative Pore Volume, dV/dr ml./A.
30.0	2.30
32.0	3.26
34.0	5.59
36.0	12.25
37.0	19.60
37.5	33.80
38.0	75.80
38.5	13.00
39.0	7.53
40.0	3.69
42.5	2.88
46.0	2.53
50.0	2.03

E-3, WAN-Dried from Benzene

Pore Diameter, A.	Relative Pore Volume, dV/dr ml./A.
30.0	0.93
33.0	1.44
35.0	2.72
37.0	7.45
37.5	12.40
38.0	8.40
39.0	4.35
40.0	2.64
41.0	1.45
42.0	0.82
46.0	0.64
50.0	0.61

E-42, WAN-Dried from Cyclohexane

30.0	2.69
32.0	2.81
33.25	3.79
35.0	7.21
36.0	10.00
37.0	16.40
37.5	28.60
38.0	33.00
38.5	17.70
39.0	9.48
40.0	2.92
42.0	1.46
46.0	1.43
50.0	1.50

TABLE F

CORRECTION OF PORE VOLUME DISTRIBUTIONS FOR MONOLAYER OF RESIDUAL LIQUID

E-37, Corrected for Monolayer of n-Pentane, 6.1 A. Thick

Pore Diameter, A.	Relative Pore Volume, dV/dr ml./A.
38.0	2.69
40.0	4.83
42.0	7.15
44.0	8.33
45.0	11.80
46.0	48.00
46.2	90.28
46.5	13.75
47.0	7.13
48.0	3.05
52.0	1.86
56.0	1.30

E-3, Corrected for Monolayer of Benzene, 4.1 A. Thick

Pore Diameter, A.	Relative Pore Volume, dV/dr ml./A.
43.0	1.86
46.0	4.10
48.0	5.90
49.0	9.45
49.5	17.40
50.0	72.00
50.2	20.20
50.5	13.00
51.0	7.35
52.0	4.06
56.0	1.76
60.0	0.84

TABLE G

NITROGEN ADSORPTION ON WAN-DRIED FIBERS

E-96, Water-Dried over P_2O_5, Water-Soaked
14 Days, WAN-Dried from n-Pentane

P/P_o	Volume Adsorbed, ml. (S.T.P.)/g.	
.006	6.50	1st Adsorption
.050	10.75	
.121	13.05	
.228	15.83	
.283	17.26	
.431	21.39	
.577	26.71	
.703	32.44	
.874	42.65	
.970	54.06	
.996	66.64	
.964	57.90	1st Desorption
.848	45.86	
.662	36.86	
.532	32.31	
.468	25.10	
.343	18.86	
.022	9.01	2nd Adsorption
.588	26.94	
.761	35.00	
.938	48.19	
.988	59.81	
.960	55.00	2nd Desorption
.918	49.83	
.840	44.39	
.754	40.23	
.649	36.07	
.547	32.62	
.517	31.58	
.496	30.09	
.483	27.46	
.457	23.57	
.434	22.03	
.406	20.86	

TABLE H

RELATIONSHIPS BETWEEN AREAS OF WAN-DRIED FIBERS AND SURFACE TENSIONS OF FINAL EXCHANGE LIQUIDS

Final Exchange Liquid	Sample No.	B.E.T. Area, sq. m./g.	Temp. of Drying, °C.	Surface Tension, dynes/cm.
n-Pentane	E-75	142	36	14.4
	E-17	129	25	15.5
	E-37	133	25	15.5
	E-33	116	0	18.3
	E-25	104	-20	20.6
	E-86	92.0	-35	22.3
n-Hexane	E-62	132	61	14.1
	E-65	150	61	14.1
	E-53	121	34	17.0
	E-29	108	25	18.1
	E-16	89.7	-9	21.5
	E-63	74.6	-38	24.6
Cyclohexane	E-81	109	70	17.3
	E-82	122	60	18.8
	E-80	109	46	21.2
	E-83	101	36	22.7
	E-52	97.0	35	23.2
	E-51	88.5	29	24.9
Benzene	E-95	51.2	81	21.1
	E-79	55.1	70	22.5
	E-77	53.9	60	23.8
	E-78	51.4	42	25.9
	E-84	45.2	15	29.6
Toluene	E-88	58.0	70	22.7
	E-87	59.1	50	25.0
	E-93	50.5	41	26.0
	E-57	48.1	30	27.3
	E-85	47.2	14	29.1
	E-58	37.8	0	30.7
	E-66	34.4	-38	35.2
Pulp air-dried from water, resoaked, WAN-dried				
n-Pentane	E-97	91.9	29	15.0
n-Hexane	E-45	64.1	-20	22.6

TABLE I

EFFECTS ON FIBER SURFACE AREA OF WAN-DRYING ABOVE THE BOILING POINT OF FINAL EXCHANGE LIQUID

Final Exchange Liquid	Sample No.	B.E.T. Area, sq. m./g.	Temp. of Drying, °C.	Surface Tension, dynes/cm.	Size of Capillary Discharge, mm.
n-Hexane	E-99	176	69	13.5	2
	E-56	173	69	13.5	2
	E-99D	154	69	13.5	2
	E-67	145	69	13.5	1
	E-68	159	75	12.8	1
	E-102	156	75	12.8	2
	E-100	148	85	11.8	2
	E-116	196	101	10.2	1
	E-114	161	99	10.4	1
n-Pentane	E-105	144	37	14.0	1
	E-110	149	44	13.3	2
	E-109	145	44	13.3	2
	E-64	174	49	12.8	2
	E-111	162	55	12.2	1
	E-98	181	60	11.7	2
	E-119	170	60	11.7	1
	E-108	156	65	11.1	2
	E-103	157	70	10.5	2
	E-113	180	75	10.2	1
	E-112	178	75	10.2	1