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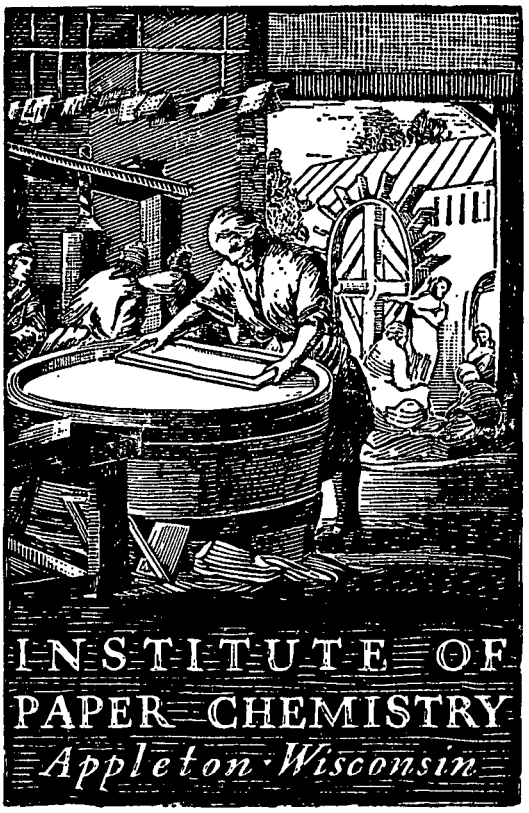

FUNDAMENTAL STUDY OF ADHESION OF CORRUGATED BOARD

Project 2696-4

Report One

A Progress Report

to

FOURDRINIER KRAFT BOARD INSTITUTE, INC.

January 15, 1969

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Corrugating mediums differing in surface roughness and receptivity have been utilized to examine the effects of these properties on adhesion. Initially, starch corrugating adhesive of essentially constant surface tension and viscosity was applied to rough receptive, rough nonreceptive, and smooth receptive mediums. Conditions were selected which eliminated metering but which permitted measurement of the adhesive volumes taken up by roughness and by penetration. Analysis of the treated mediums indicated that the starch adhesive was held primarily in surface roughness in all cases but the extent to which the surface roughness was filled varied with the magnitude of the roughness and receptivity. Of the three surfaces studied, the rough receptive medium accepted the most adhesive and showed the deepest penetration. The rough nonreceptive medium accepted less adhesive in its surface and showed lower penetrability than its receptive counterpart. As would be expected, the smooth receptive medium retained less adhesive in its surface compared to the rough receptive medium and showed marked penetration. Stained tapered sections of the aforementioned mediums confirmed these findings and further indicated that surface roughness was essentially filled only in the case of the smooth medium. The stained sections also indicated that the deepest starch penetration was probably not much in excess of 43% of the total thickness.

Determination of the adhesive distribution within the medium again confirmed that most of the starch applied is held within surface roughness but very little starch was actually retained in the outer extremes of roughness (the high points of the surface in contrast to the valleys). At a contact (application)

time of 0.06 sec. the greatest concentrations of adhesive were generally found at depths of 1.2-3.6 mils and, with increased time, the greatest concentrations shifted to the 2.4-4.8 mil intervals. The starch content dropped off sharply beyond a depth of 4.8 mils although a small amount was indicated to penetrate beyond the 6-mil depth, particularly at the longer contact times. The adhesive within the nonreceptive medium showed less tendency to shift or migrate with time than that within the receptive medium.

Preliminary tests concerned with the extent of water component migration indicate that water does not penetrate beyond what is considered the cooked primary starch, however, these are tentative results subject to confirmation.

Pin adhesion tests on samples prepared on the Institute's corrugator indicated the smooth medium to provide the best overall adhesion followed in order by the rough receptive and the rough nonreceptive mediums. These results were interpreted in terms of the analytical data.

INTRODUCTION

This is Progress Report One on Project 2696-4 established in cooperation with the Fourdrinier Kraft Board Institute, Inc. for the purpose of studying the fundamental aspects of adhesion of corrugated board. The broad objective of the present program is to obtain an understanding of the variables which are important to adhesion in the practical corrugating operation. More specifically, the investigation is directed at elucidation of the interrelationships between the sizing, smoothness, and porosity of the corrugating medium and the role of starch in the adhesion process with particular emphasis on the migration and distribution of starch adhesive components.

One of the requirements of an adhesive is that it spreads on the surface to which it is applied, i.e., it must have a positive spreading coefficient which may be expressed as follows:

$$S = W_A - W_C \qquad (1)$$

where W_A is the work of adhesion and W_C is the work of cohesion. W_A and W_C, in turn, are commonly expressed in terms of surface energies or the numerically equivalent surface tension values as follows:

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \qquad (2)$$

and

$$W_C = 2\gamma_L \qquad (3)$$

where γ_S and γ_L are the surface tensions of the solid and liquid and γ_{SL} is the solid-liquid interfacial tension.

Substitution of Equations (2) and (3) into Equation (1) yields

$$S = \gamma_S - \gamma_L - \gamma_{SL} \qquad (4)$$

Hence, for spreading to occur, the surface tension of the solid must be greater than the sum of the liquid surface tension and the interfacial tension. It has also been shown that

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta_A \tag{5}$$

or

$$\cos \theta_A = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \tag{6}$$

where θ_A is the advancing contact angle formed by the liquid on the solid surface. Substitution of Equation (5) into Equation (2) yields

$$W_A = \gamma_L (1 + \cos \theta_A) \tag{7}$$

which now defines the work of adhesion in terms of only the surface tension of the liquid adhesive and the contact angle. The contact angle is useful as a means of defining the degree of wettability of the solid and the conditions under which the liquid will spontaneously spread. For example, if θ is greater than zero the liquid is nonspreading but partially wets the solid. If θ is zero, the liquid will wet the solid completely and spread at a rate determined by viscosity, surface tension, and surface roughness. The effect of surface roughness on contact angle is indicated by modifying Equation (6) as follows:

$$\cos \theta_{AA} = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \sigma_1 = \sigma_1 \cos \theta_A \tag{8}$$

where θ_{AA} is the apparent advancing contact angle and σ_1 is a roughness factor equal to the ratio of the actual surface area to the geometric surface area. When the solid surface is rough, Equation (8) predicts that θ_{AA} will be greater than θ_A if θ_A is obtuse and θ_{AA} will be less than θ_A if θ_A is acute. In other words, roughness of the solid surface magnifies the wetting or nonwetting property

of the surface depending upon the magnitude of the real contact angle θ_A. For composite heterogeneous surfaces such as prevail on paper and board, Equation (8) may be modified further to yield

$$\text{Cos } \theta_{AA} = \sigma_1 \text{ Cos } \theta_A - \sigma_2 \qquad (9)$$

where, for fibrous structures, σ_1 becomes the solid fiber surface area and σ_2 represents the area of air spaces per unit geometric area. Equation (9) shows that whereas the roughness factor σ_1 may either increase or decrease θ_{AA}, depending upon whether θ_A is obtuse or acute, the porosity factor σ_2 always increases θ_{AA}. Due to the porosity factor, it is possible to have an obtuse apparent advancing contact angle when the real advancing contact angle is acute. Under certain definable conditions of roughness and void fraction (porosity), the surface of the solid may be wettable by the adhesive on a small scale but under the dynamic conditions of conventional adhesive application, the effective contact angle would become obtuse and much poorer wetting may occur than would be the case if the surface were smooth and continuous. In other words, these effects are magnified in short-time intervals and high-speed applications.

In the corrugating operation, the film thickness on the applicator or transfer roll is metered; however, the exact amount transferred depends on instantaneous absorption and film splitting. In general, the total volume of coating or starch adhesive, V, which is retained by paper or board is dependent on the surface roughness (V_R), the volume which penetrates during the interval of contact prior to metering (V_P), and an amount which is characteristic of the metering conditions (V_M). Hence,

$$V = V_R + V_P + V_M \qquad (10)$$

where these quantities represent volumes of fluid coating per unit area. In order to determine the volumes of starch taken up by surface roughness and by porosity through measurement of the total volume consumed, it is necessary to eliminate or at least minimize V_M. This is best accomplished with a thin blade applicator set nearly perpendicular to the sheet. V_M is also minimized by operating at high blade pressure.

Consideration of permeation theory leads to the following relationship for V_P, the volume of adhesive taken up by the porous structure of the medium,

$$V_P = 2\left(\frac{K'\gamma_L \cos\theta\, t}{\eta}\right)^{1/2} \qquad (11)$$

where K' is a constant characteristic of the substrate, γ_L is the surface tension of the adhesive, θ is the contact angle, t is time of contact, and η is the viscosity of the adhesive. Since $t = S/V$ where S is the span between application of the adhesive and final metering and V is velocity it is possible to rewrite Equation (11) as

$$V_P = 2\left(\frac{K'\gamma_L S \cos\theta}{\eta V}\right)^{1/2} \qquad (12)$$

Hence, by eliminating V_M, Equation (10) becomes

$$V = V_R + 2\left(\frac{K'\gamma_L S \cos\theta}{\eta V}\right)^{1/2} \qquad (13)$$

and if Cos θ is constant, a plot of the total volume of adhesive consumed versus $(\gamma t/\eta)^{1/2}$ or $(\gamma S/\eta V)^{1/2}$ should be linear with intercept at V_R and slope of $2(K'\cos\theta)^{1/2}$.

Equation (13) assumes a homogeneous Newtonian fluid whereas the corrugating adhesive represents a heterogeneous system comprised of uncooked starch and bentonite suspended in the cooked starch carrier. In this regard the corrugating adhesive resembles a pigment coating. By design, the suspended starch particles would tend to be filtered out at the surface forming a filter mat which will increase in thickness with time. Further, the viscosity of the excess adhesive which must be removed by metering will tend to increase. In spite of these obvious deviations from ideality, application of this concept has provided a means of determining $\underline{V_R}$ and $\underline{V_P}$ utilizing other heterogeneous systems. This was considered justification for adopting the aforementioned approach.

EXPERIMENTAL PROCEDURES

SELECTION OF CORRUGATING MEDIUMS

The first step in the experimental program on Project 2696-4 involved the selection of corrugating medium to provide distinct differences in surface wettability, porosity, and smoothness. Candidate 26-lb. semichemical corrugating mediums were tested for basis weight, caliper, apparent density, moisture content, water drop, initial contact angle (water and starch corrugating adhesive), Bendtsen porosity and smoothness, nip spreader roughness and receptivity, I.G.T. surface bonding strength, Z-tensile, pin adhesion, and mercury intrusion pore size and pore-size distribution. (A description of these tests is given in Report Two on Project 2696-3.) The results, with the exception of the mercury intrusion data, are recorded in Table I. The mercury intrusion data are recorded separately in Table II. Cumulative pore volume — pressure relationships and volume frequency curves for these substrates are presented in Fig. 1-8. (Note: Mercury enters progressively smaller pores with increase in pressure.)

It will be noted that No. 5162 has a higher frequency of large pores but a generally lower frequency of small pores (Fig. 6), such that the total accumulative pore volume for this substrate (Fig. 3) is slightly lower than that of the others. While some other differences among substrates are indicated by the mercury intrusion data a more obvious difference is indicated in air permeability (Bendtsen porosity, Table I). On the basis of the information in Table I, No. 5111 and 5196 were selected for adhesion studies. By including both sides of 5196, comparisons could be made at approximately equal receptivity and porosity (air permeability) but differing roughness, and at equal roughness but differing porosity and receptivity.

TABLE I

PROPERTIES OF CANDIDATE CORRUGATING MEDIUM

Test	Corrugating Medium No. 5103 Wire	No. 5111 Felt	No. 5162 Felt	No. 5196 Felt	No. 5196 Wire
Basis weight, lb./1000 ft.^{2}	27.1	28.5	27.2	26.3	26.3
Caliper, mils	10.6	10.3	10.5	9.9	9.9
Apparent density	2.6	2.8	2.6	2.7	2.7
Moisture, %	5.3	5.9	7.1	8.0	8.0
Water drop, sec.	154	600+	244	18.7	18.7
Contact angle, degrees					
Starch	91	114	91	86	61
Water	92	104	99	--[a]	--[a]
Bendtsen porosity, ml./min.	950	970	894	1770	1750
Bendtsen smoothness, ml./min.	2750	2700	2700+	2290	2650
Nip spreader					
Roughness	20.3	14.3	15.7	4.9	14.6
Receptivity	4.3	1.2	2.5	12.4	14.5
I.G.T. bonding strength, kp.-cm./sec.	50	83	81	57	51
Z-Tensile, kg./cm.^{2}	10.6	9.3	9.9	7.6	--
Pin adhesion, lb.	57.3	68.0	81.4	68.6	57.0

[a]Penetrated too rapidly for measurements to be made.

Note: The pin adhesion tests were not necessarily run at the same time. Hence, differences in the pin adhesion values may reflect differences in the starch adhesive as well as differences in the substrate.

TABLE II

MERCURY INTRUSION PORE VOLUME DATA FOR CORRUGATING MEDIUMS

Medium No. 5103		Medium No. 5111		Medium No. 5162		Medium No. 5196	
Pressure, p.s.i.	Volume, cc./g.	Pressure, p.s.i.	Volume, cc./g.	Pressure, p.s.i.	Volume, cc./g.	Pressure, p.s.i.	Volume, cc./g.
1.83	0.000	1.81	0.000	1.81	0.000	1.81	0.000
3.26	0.022	3.25	0.020	3.24	0.017	3.24	0.018
4.38	0.033	4.38	0.033	4.35	0.024	4.36	0.029
6.00	0.044	5.99	0.040	5.98	0.038	5.98	0.039
7.02	0.052	7.00	0.047	6.99	0.045	7.00	0.050
8.53	0.059	8.53	0.056	8.52	0.059	8.52	0.061
11.06	0.077	11.06	0.070	11.06	0.079	11.06	0.083
14.15	0.136	14.11	0.104	14.1	0.121	14.2	0.180
16.23	0.187	16.23	0.164	16.2	0.156	19.4	0.247
19.36	0.256	19.36	0.230	19.3	0.224	21.5	0.308
21.5	0.307	21.46	0.282	21.5	0.334	24.6	0.369
24.6	0.369	24.60	0.349	24.6	0.340	26.7	0.422
26.6	0.414	26.68	0.391	26.6	0.373	31.8	0.484
31.8	0.483	31.79	0.449	31.7	0.440	36.9	0.529
36.9	0.537	36.9	0.499	36.8	0.482	41.9	0.558
41.9	0.567	42.0	0.527	41.9	0.512	47.0	0.592
50.0	0.590	47.0	0.555	46.9	0.538	52.0	0.617
52.0	0.614	52.1	0.575	52.0	0.563	62.1	0.653
62.1	0.648	62.1	0.614	62.1	0.600	72.1	0.678
72.1	0.672	72.2	0.637	72.1	0.624	82.0	0.693
82.1	0.696	82.2	0.657	82.1	0.641	92.0	0.707
92.0	0.713	92.2	0.677	92.0	0.660	107	0.727
102.2	0.725	104.2	0.687	102	0.672	122	0.742
112	0.737	112	0.700	112	0.682	137	0.747
120	0.755	122	0.715	122	0.697	150	0.764
150	0.777	137	0.731	132	0.700	175	0.783
175	0.795	150	0.748	150	0.720	200	0.789
200	0.807	175	0.755	175	0.730	210	0.800
250	0.821	200	0.771	200	0.743	250	0.816
300	0.830	250	0.784	250	0.760	300	0.824
350	0.835	300	0.794	300	0.768	350	0.832
400	0.837	350	0.800	350	0.776	595	0.838
450	0.843	420	0.803	400	0.783	760	0.838
700	0.849	500	0.803	450	0.787	870	0.840
900	0.851	625	0.806	870	0.792	1,100	0.844
1,000	0.854	800	0.808	2,000	0.794	2,000	0.847
3,000	0.859	900	0.808	2,200	0.795	6,000	0.847
6,500	0.859	1,300	0.811	4,000	0.796	7,000	0.847
7,000	0.860	2,700	0.813	5,800	0.797	7,200	0.847
9,000	0.860	4,000	0.813	7,700	0.797	8,400	0.850
11,000	0.860	6,500	0.814	9,200	0.798	10,000	0.853
13,000	0.860	8,000	0.814	11,600	0.798	12,700	0.853
15,000	0.861	10,200	0.814	12,600	0.798	15,000	0.853
		12,300	0.814	15,000	0.798		
		13,000	0.814				
		15,000	0.814				

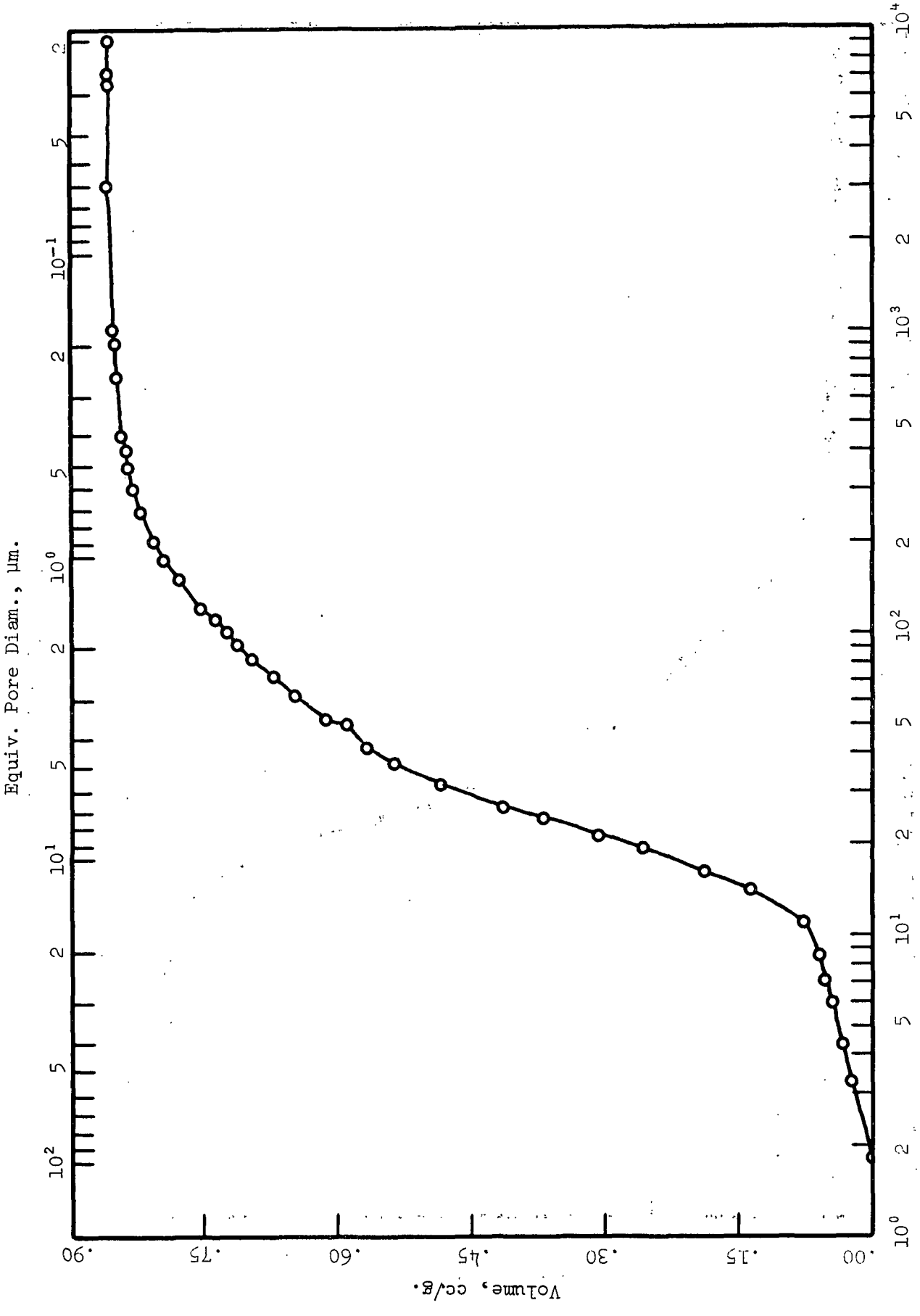


Figure 1. Cumulative Pore Volume – Pressure Relationship for Medium No. 5103

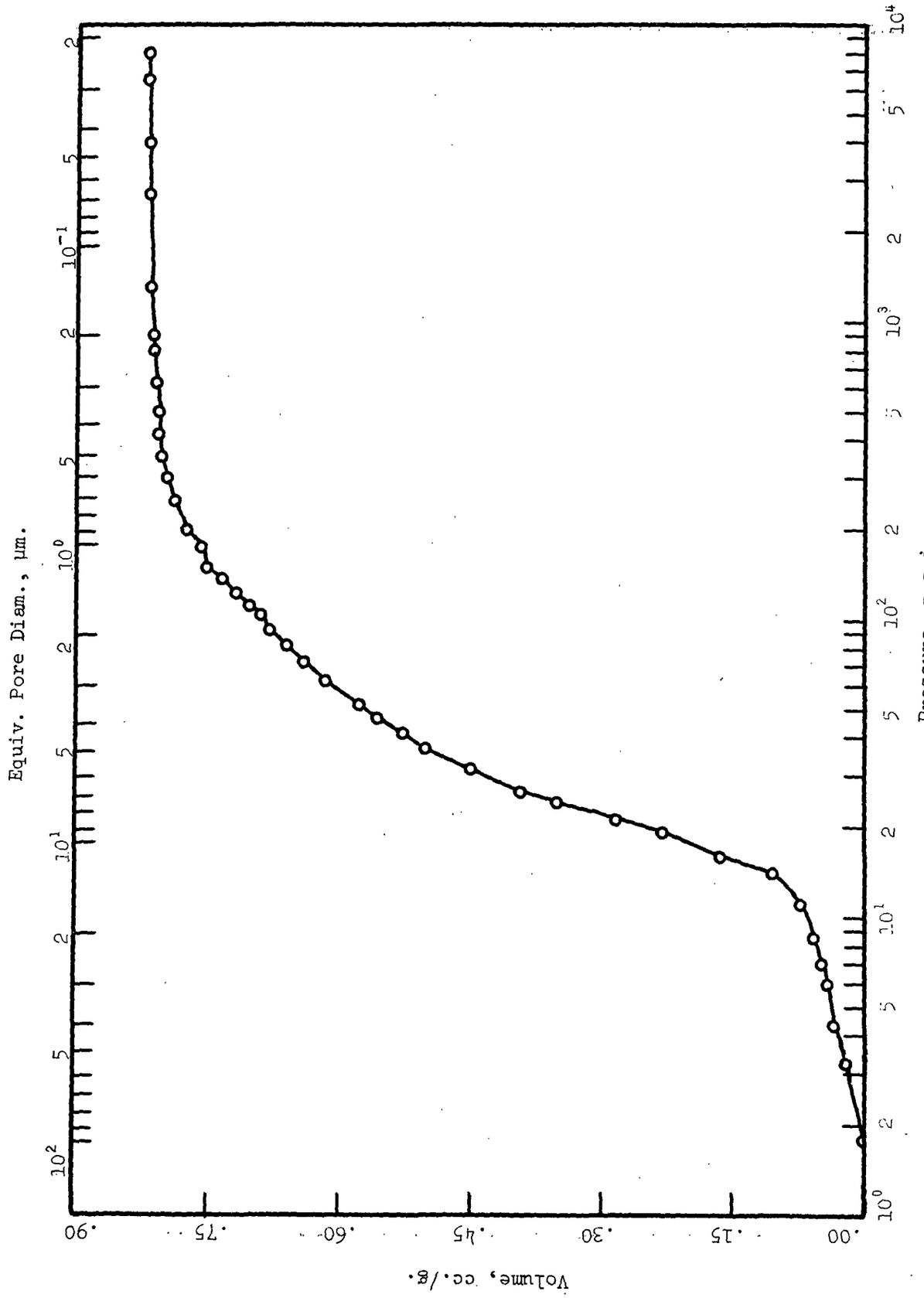


Figure 2. Cumulative Pore Volume — Pressure Relationship for Medium No. 5111

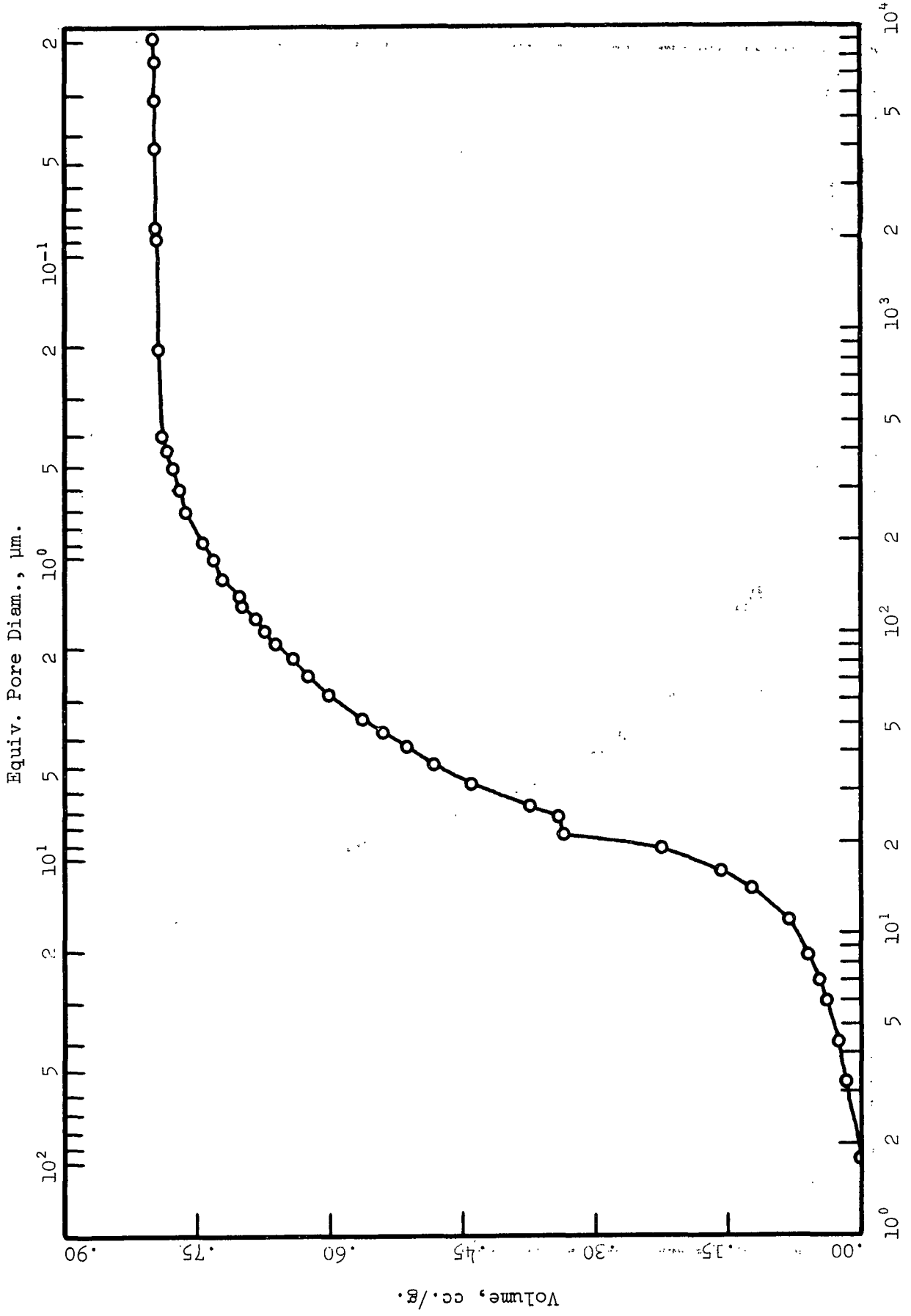


Figure 3. Cumulative Pore Volume — Pressure Relationship for Medium No. 5162

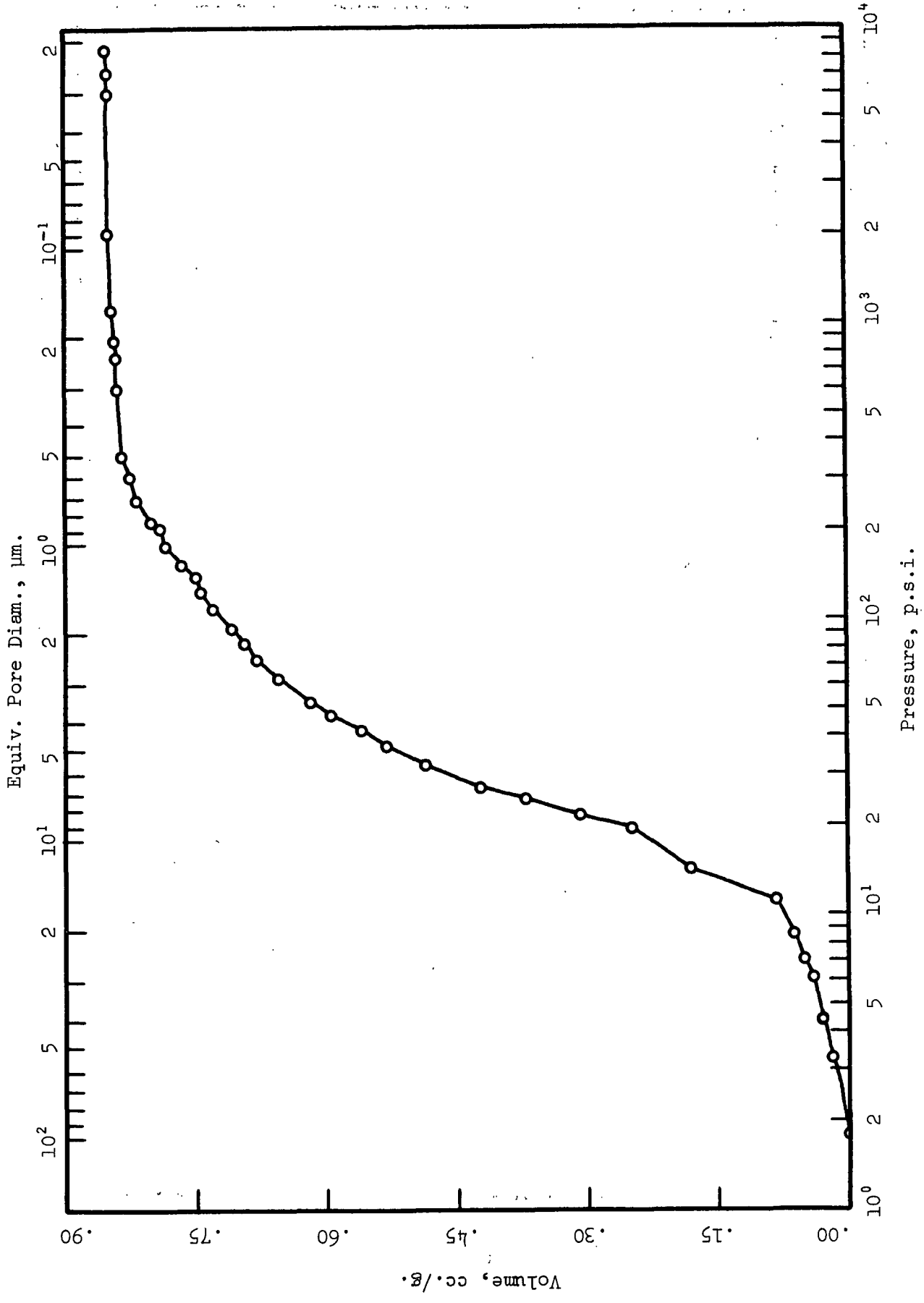


Figure 4. Cumulative Pore Volume — Pressure Relationship for Medium No. 5196.

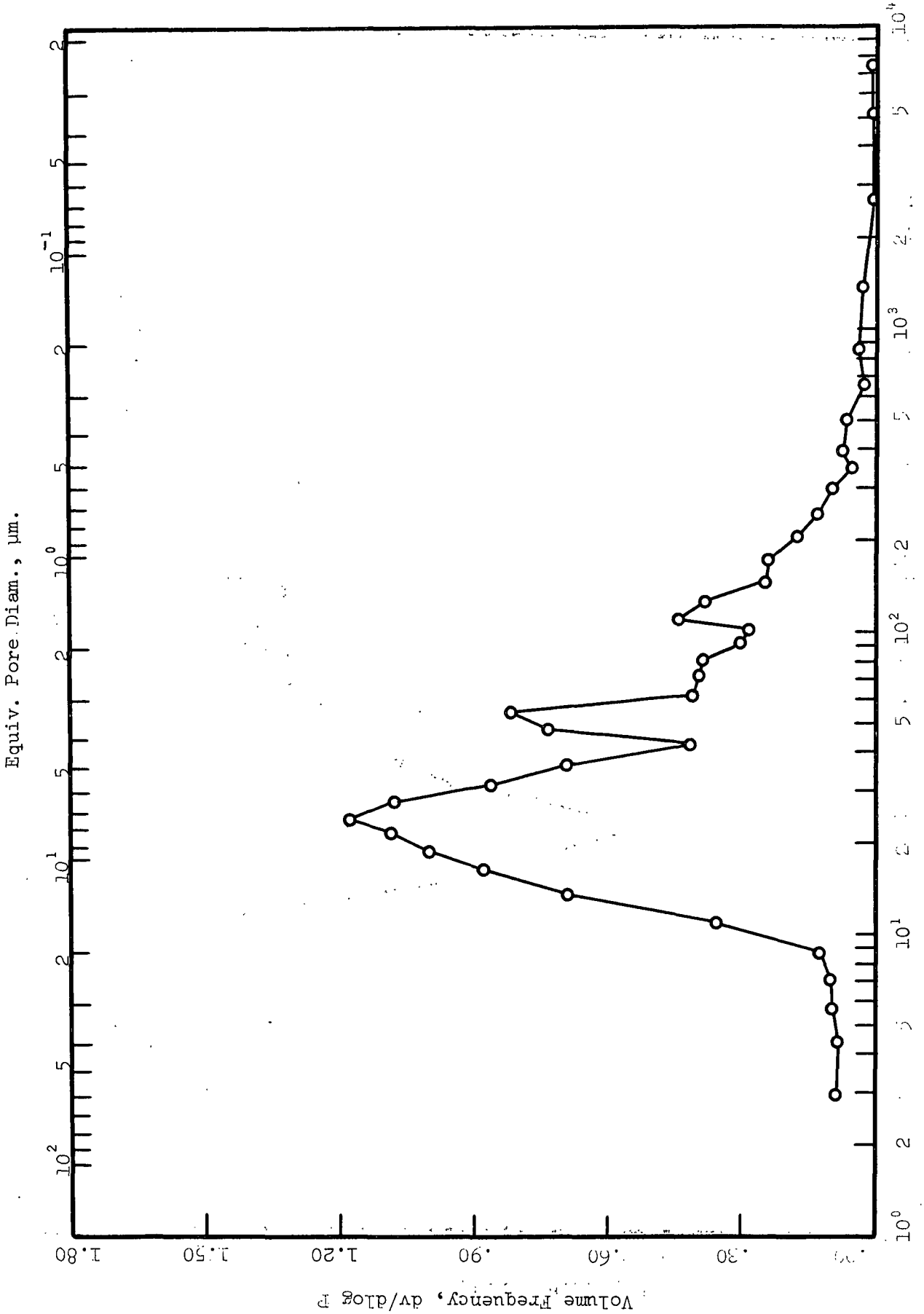


Figure 5. Volume Frequency Curve for Medium No. 5103

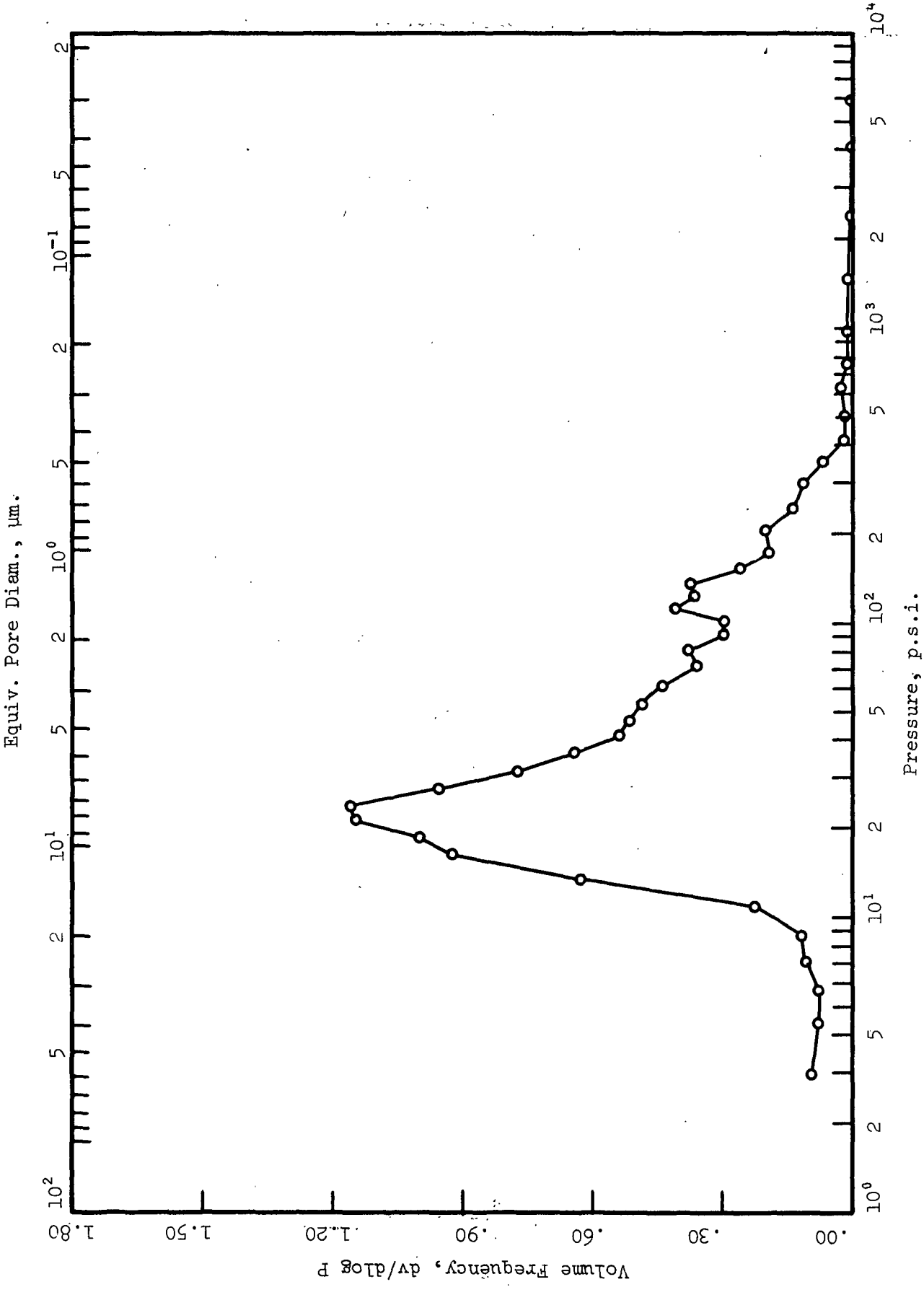


Figure 6. Volume Frequency Curve for Medium No. 5111

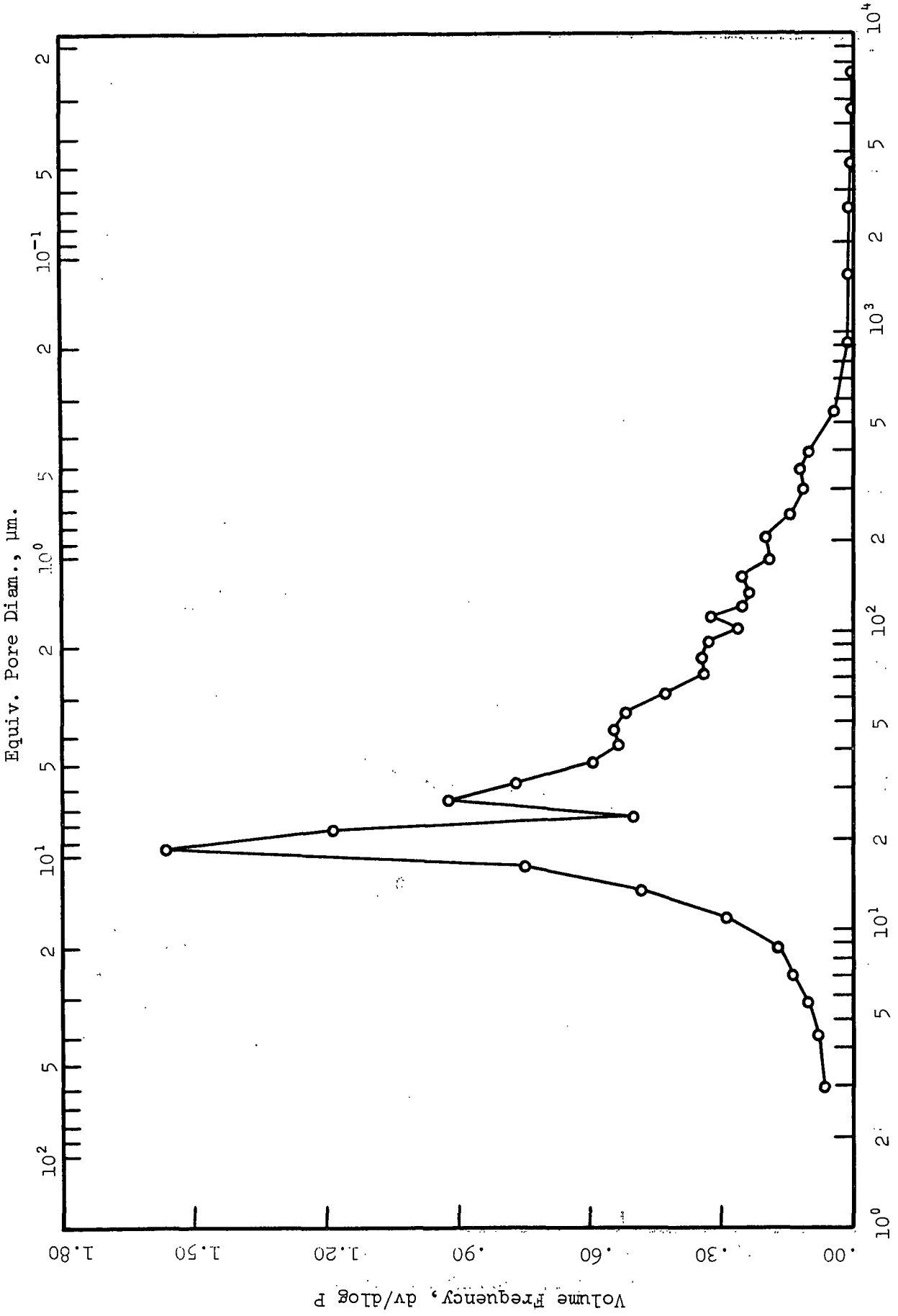


Figure 7. Volume Frequency Curve for Medium No. 5162.

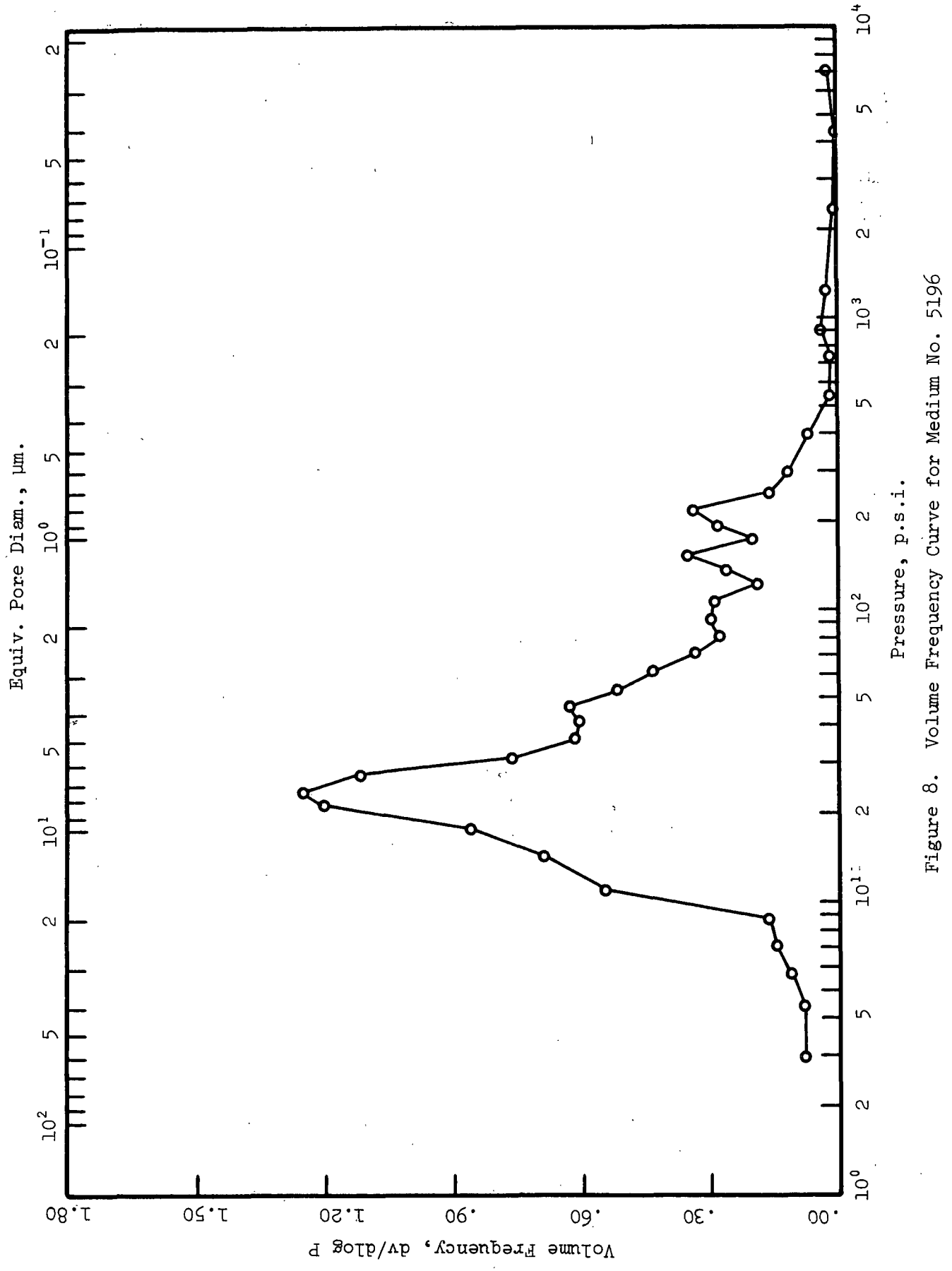


Figure 8. Volume Frequency Curve for Medium No. 5196

PREPARATION OF STARCH CORRUGATING ADHESIVE

A two-mix starch corrugating adhesive was prepared in laboratory-size batches for use on the project. The primary was prepared in a 1-liter stainless steel beaker as follows: 72.6 g. of Bondcor-C starch (Stein-Hall & Co.) was stirred into 363 g. of water utilizing a Lightnin' mixer. The beaker was placed in a water bath at 180-185°F. and caustic solution comprised of 16.0 g. of sodium hydroxide in 71.8 g. of water was added (temperature 90-100°F.). The rate of stirring was increased to maximum while adding the alkali. The beaker was then covered. Approximately four-minutes time was necessary to raise the starch to 170°F., which was maintained for 15 minutes. The starch dispersion was then removed from the water bath and 200 ml. of room-temperature water was added. This lowered the temperature to 135-140°F. The dispersion was then stirred for five minutes before addition to the secondary.

The secondary was prepared in a 3-liter stainless steel beaker at room temperature by stirring 9.1 g. of bentonite into 1200 g. of distilled water, followed by 13.3 g. of borax and 458.2 g. of starch. The bentonite and borax were blended in for five minutes each before addition of the starch. The starch slurry was then stirred for 30 minutes before addition of the primary.

The primary was then slowly added to the secondary while stirring at medium-high speed with two Lightnin' stirrers. After a part of the primary had been added and the viscosity had increased somewhat, the rate of agitation was increased to maximum. The remainder of the primary was then added, followed by 150 ml. of rinse water. The stainless steel beaker was placed in a 100°F. water bath and the starch suspension was stirred for one hour at top speed. The beaker was covered as much as possible during the one-hour stirring period.

Initial batches of adhesive were tested for Stein-Hall viscosity at 100°F. and Brookfield viscosity at 73°F. (Spindle No. 2; 12 r.p.m.). Subsequent batches were also tested for pH, surface tension, solids content, and alkalinity. Brookfield viscosity was also measured after aging five hours at room temperature (five hours was considered the maximum holding time). Surface tension was measured with a du Nouy Interfacial Tensiometer and the readings were corrected for the Harkins-Jordan correction factors (1). Alkalinity was determined by titrating 50 grams of the starch dispersion with 0.1N HCl to the phenolphthalein end point and to pH 7.

Since surface tension and viscosity play an important role in the adhesion process the reproducibility of these properties in the corrugating starch batch preparation is an important consideration. With experience, factors controlling these properties, and especially viscosity, were reasonably well established. These were largely concerne tion of the primary to the secondary and the stirring the addition period. Data for adhesive batches typical of ving established suitable conditions are given in Tab

METHOD FOR ANALYZING STARCH CONTENT OF MEDIUM

Several colorimetric methods for measuring the total starch and starch distribution in corrugating medium were considered. Included among these were an acid dye (tartrazine) and two methods based on the starch-iodine reaction, i.e., the TAPPI method and the method of Browning, Bublitz, and Baker (2). The acid dye method was considered objectionable because of the color interference from the corrugating medium blank controls. The TAPPI method was abandoned because of difficulties concerned with filtering of the extracted adhesive. The method of Browning, Bublitz, and Baker was subsequently found to be suitable and was

TABLE III

REPRODUCIBILITY IN LABORATORY PREPARATION OF STARCH CORRUGATING ADHESIVE

Batch No.	Stein-Hall Viscosity, sec. at 100°F.	Brookfield Viscosity cp. at 73°F.; 12 r.p.m. initially	Brookfield Viscosity cp. at 73°F.; 12 r.p.m. after aging 5 hr.	pH	Alkalinity, ml. 0.1N HCl to phenolphthalein end point	Alkalinity, ml. 0.1N HCl to pH 7	Surface Tension (γ_L), dynes/cm.	Solids, %
1	31	325.0	--	--	--	--	--	--
2	33	347.5	367.5	--	--	--	--	--
3	31	332.5	332.5	--	--	--	--	--
4	31	342.5	337.5	12.2	63.6	85.9	58.9	20.2
5	32.5	352.5	352.5	12.2	64.4	85.9	59.7	20.2
6	33.6	360.0	392.5	12.2	63.8	85.0	60.2	20.2

adopted. A starch calibration curve was prepared utilizing a sample of corrugating adhesive prepared in the manner previously described. The calibration curve is shown in Fig. 9.

In subsequent analyses of treated mediums, duplicate starch determinations were made on 1 x 6-inch specimens cut in the cross-machine direction. The average values were converted to adhesive volumes per unit area in order to conform with the theory advanced in the Introduction.

APPLICATION OF ADHESIVE TO MEDIUM

The corrugating adhesive was applied to the selected mediums on a modified Keegan Coater under conditions which eliminated or at least minimized the volume of adhesive due to metering (V_M). This was accomplished by utilizing a thin blade applicator set nearly perpendicular to the sheet while operating at high blade pressure. A sketch of the arrangement is given in Fig. 10. In operation, adhesive is fed to the medium at the applicator blade and the excess (adhesive which is not taken up by roughness and penetration) is removed with the metering blade. The applicator blade can be moved to any of the pivot positions shown in Fig. 10, thereby providing a range in span (distance from point of application to point of metering). Hence, by changing span and web speed, a relatively wide range in contact time can be achieved.

The pressure required to minimize metering was determined by measuring the amount of starch retained by the medium as a function of the weight on the metering blade. In this direction, starch adhesive was applied at room temperature to the felt side of No. 5196 at a span of 24.45 cm. and a velocity of 15.49 cm./sec. (t = 1.57 sec.). Weights ranging from 2400 to 3900 grams were suspended from the metering bar pivot arm. Samples of treated medium, representative of each weight

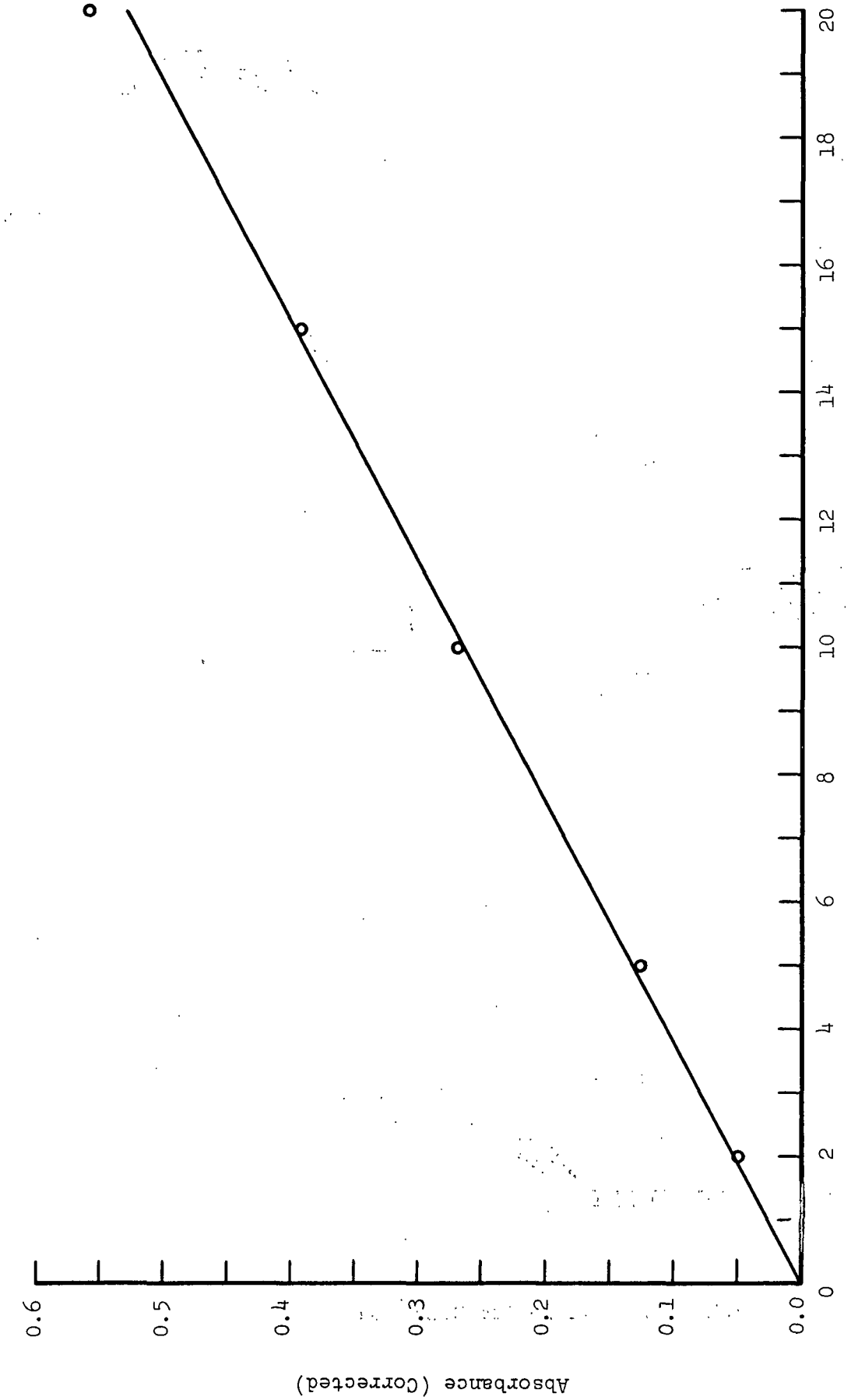


Figure 9. Starch Calibration Curve

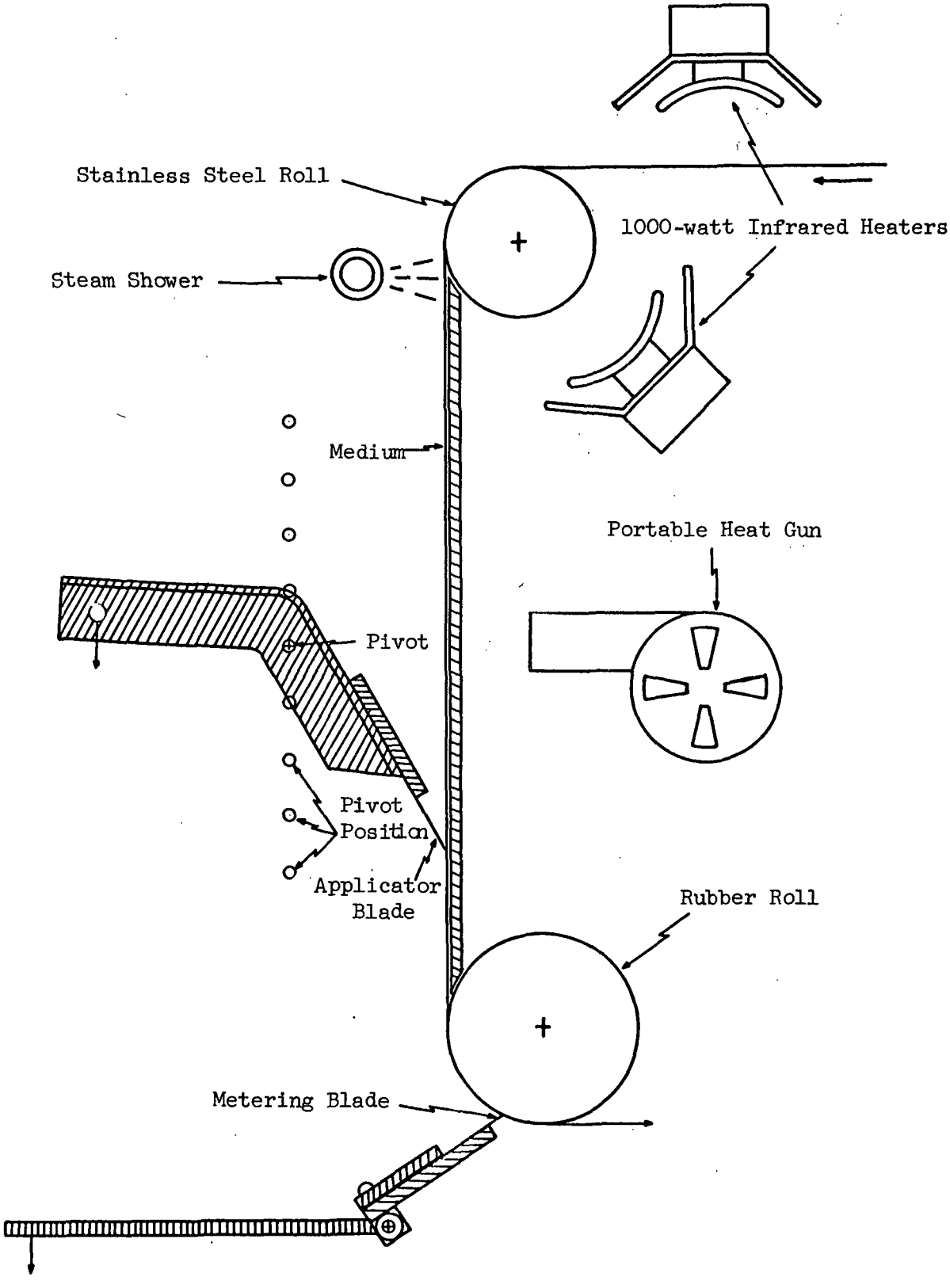


Figure 10. Corrugating Starch Application System

condition, were subsequently analyzed for adhesive content, the results of which are recorded in Table IV. Adhesive volume as a function of weight on the metering bar is shown graphically in Fig. 11.

TABLE IV

THE EFFECT OF METERING BLADE PRESSURE ON ADHESIVE TRANSFER

(Medium 5196, Span 24.45 cm., Velocity 15.49 cm./sec.)

Weight on Metering Bar, g.	Absorbance Due to Starch per $3.87 \times 10^{-3} M^2$	Adhesive Volume, cc./m.^{2}
2400	0.333	16.0
2900	0.303	14.4
3400	0.269	12.9
3900	0.256	12.3

While a slight decrease in adhesive volume is indicated by increasing the weight from 3400 to 3900 g., some deflection of the blade was noted at the higher pressure. Hence, a maximum weight of 3400 g. was adopted for all subsequent applications.

Initial Keegan coater applications were made at room temperature to test the validity of applying the concept to the corrugating adhesive — medium system. The adhesive was applied at three spans and several speeds at each span so as to provide adhesive contact times ranging from approximately 0.03 to 2.5 sec. Samples of medium representative of each condition were subsequently analyzed for starch content. Results are recorded in Table V and the adhesive volume-time relationships are presented in Fig. 12.

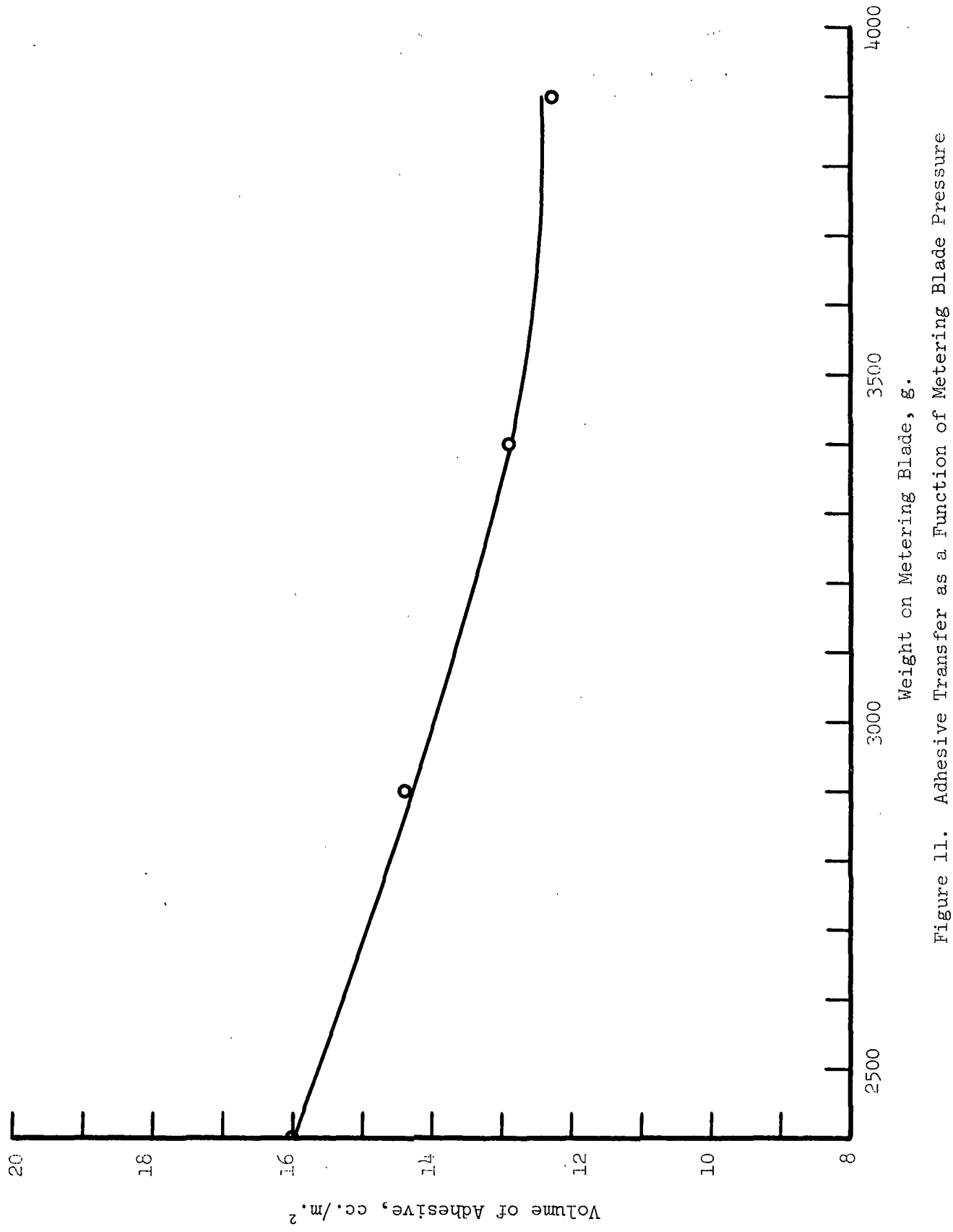


Figure 11. Adhesive Transfer as a Function of Metering Blade Pressure

TABLE V

STARCH CONTENT OF MEDIUM TREATED AT ROOM TEMPERATURE

Corrugating Medium	Span, S, cm.	Velocity, V, cm./sec.	Contact Time, t, sec.	$t^{1/2}$, sec.$^{1/2}$	Absorbance due to Starch per 3.87×10^{-3} m.^{2}	Adhesive Volume, cc./m.^{2}
5196 Felt	1.27	10.16	0.125	0.35	0.297	14.3
		15.24	0.083	0.29	0.306	14.7
		32.51	0.039	0.20	0.278	13.3
	11.75	5.08	2.31	1.52	0.352	16.9
		9.40	1.25	1.12	0.305	14.6
		14.22	0.826	0.91	0.322	15.5
		22.61	0.520	0.72	0.300	14.4
		40.89	0.287	0.54	0.308	14.8
	34.61	8.64	4.01	2.00	0.397	19.1
		22.10	1.57	1.25	0.350	16.8
		51.05	0.678	0.82	0.344	16.5
5196 Wire	1.27	9.65	0.132	0.36	0.425	20.4
		16.51	0.077	0.28	0.421	20.2
		25.65	0.050	0.22	0.430	20.6
		35.05	0.036	0.19	0.412	19.8
	11.75	9.40	1.25	1.12	0.475	22.8
		16.26	0.722	0.85	0.417	20.0
		21.84	0.538	0.73	0.460	22.1
		35.81	0.328	0.57	0.421	20.2
	34.61	14.22	2.43	1.56	0.459	22.0
		17.78	1.95	1.39	0.435	20.9
		41.91	0.826	0.91	0.468	22.5
5111 Felt	1.27	9.40	0.135	0.37	0.325	15.6
		25.4	0.050	0.22	0.308	14.8
		41.66	0.030	0.17	0.296	14.2
	11.75	4.57	2.57	1.60	0.368	17.7
		8.64	1.36	1.17	0.315	15.1
		24.38	0.481	0.69	0.311	15.0
	34.61	14.22	2.43	1.56	0.379	18.2
		21.84	1.58	1.26	0.368	17.7
		35.56	0.973	0.99	0.332	15.9

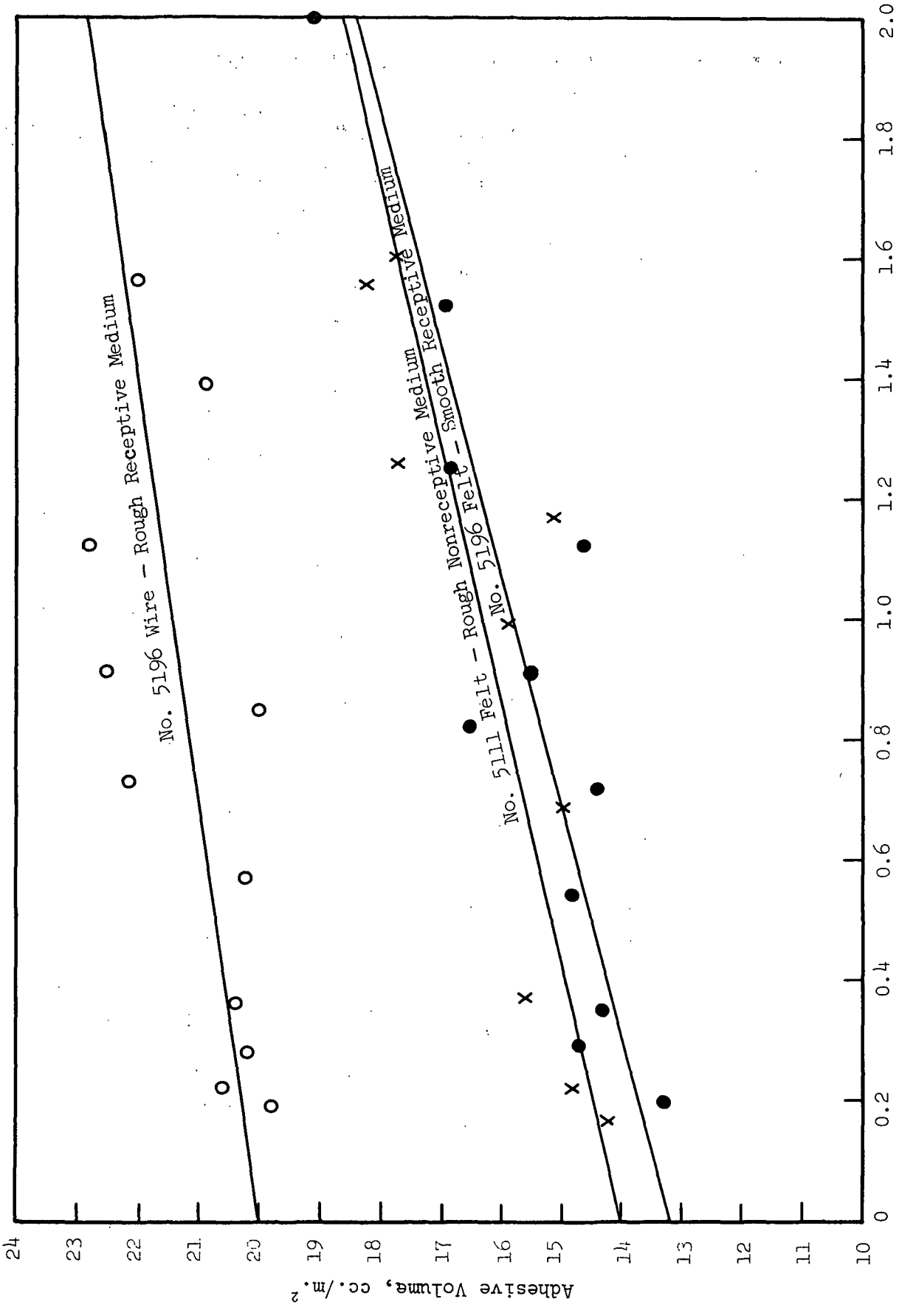


Figure 12. Adhesive Volume – Time Relationships for Room Temperature Applications

Subsequent applications were made to the same mediums under more realistic temperature conditions in terms of corrugating practice. This involved installation of 1000-watt infrared heaters and a steam shower on the Keegan Coater ahead of the applicator blade (refer to Fig. 10). In this manner the medium could be heated to 190-200°F., followed by steam treatment which served to replace most of the moisture lost in heating. In order to maintain the temperature of the medium above the gel point of the starch when operating at long spans and low speed it was necessary to heat the backing plate. A heat gun was used for this purpose. Application of adhesive to the heated absorbent substrate was restricted to contact times of one second or less because of pronounced tracking at the longer times. Results of the starch analyses for this series are given in Table VI and the adhesive volume vs. contact time relationships are given in Fig. 13.

PENETRATION OF STARCH ADHESIVE INTO MEDIUM

Analyses were subsequently initiated to determine quantitatively the starch distribution within the roughness and body of the mediums which were heated and steamed during the adhesive applications. The procedure adopted for this purpose consisted in surface grinding samples from the Keegan Coater to fixed depths and analyzing the starch content left in the specimen at each depth interval. This was accomplished with a Covel Surface Grinder consisting of a grinding wheel 7 inches in diameter and 3/4 inch in width which operates at 3600 r.p.m. The paper or board specimens to be ground are held on a flat surface which can be adjusted with respect to height. The sides of the specimens are held by vacuum; the leading and receding edges are taped. In operation, the specimen is moved into contact with the wheel after adjusting the height to provide the desired depth of grind. The depth can be controlled to within 0.1 mil.

TABLE VI

STARCH CONTENT OF HEATED MEDIUM

Corrugating Medium	Span, S, cm.	Velocity, V, cm./sec.	Contact Time, t, sec.	$t^{1/2}$, sec.$^{1/2}$	Absorbance due to Starch per 3.87×10^{-3} m.^{2}	Adhesive Volume, cc./m.^{2}
5196 Felt	1.27	5.08	0.250	0.50	0.278	13.4
		14.73	0.086	0.29	0.270	13.0
		23.11	0.055	0.24	0.279	13.4
		31.50	0.040	0.20	0.253	12.3
		44.20	0.029	0.17	0.267	12.8
	11.75	10.67	1.10	1.05	0.343	16.5
		15.49	0.759	0.87	0.320	15.4
		25.91	0.453	0.67	0.332	15.9
		37.34	0.315	0.56	0.306	14.7
	29.53	39.37	0.750	0.87	0.338	16.2
5196 Wire	1.27	6.35	0.200	0.45	0.389	18.7
		9.14	0.139	0.37	0.368	17.7
		12.70	0.100	0.32	0.379	18.2
		20.32	0.0625	0.24	0.354	17.0
		55.88	0.0227	0.15	0.366	17.6
	11.75	18.80	0.625	0.79	0.409	19.6
		23.37	0.503	0.71	0.405	19.4
		35.05	0.335	0.58	0.391	18.8
		46.48	0.253	0.50	0.378	18.2
	14.29	27.94	0.511	0.72	0.422	20.3
5111 Felt	1.27	14.99	0.085	0.29	0.246	11.8
		23.11	0.055	0.23	0.233	11.1
		37.34	0.034	0.18	0.221	10.6
	11.75	6.10	1.93	1.39	0.249	12.0
		14.48	0.811	0.90	0.240	11.5
		23.37	0.503	0.71	0.262	12.6
		39.88	0.295	0.54	0.252	12.1
	29.53	7.37	4.01	2.00	0.270	12.9
		14.99	1.97	1.40	0.269	12.9
		22.86	1.29	1.14	0.262	12.6
		37.08	0.80	0.89	0.262	12.6

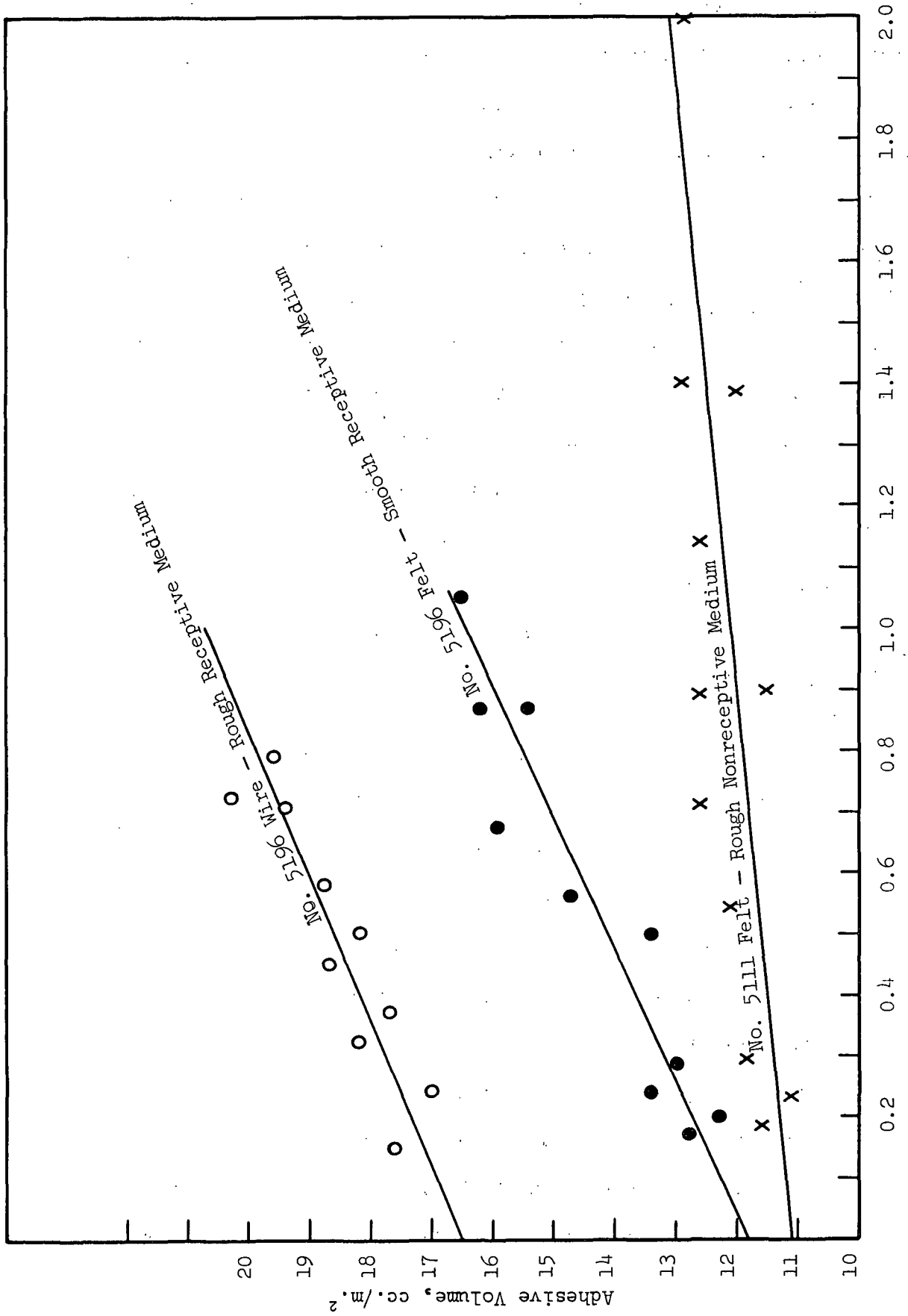


Figure 13. Adhesive Volume — Time Relationships for Heated Medium

In order to establish suitable depth intervals for analysis, samples from short and moderately long contact times were prepared by grinding to increasing depths at a fixed rate of 1.17 mils per inch of length over a total length of six inches. Under these conditions, approximately one-half of the thickness of the medium was removed. (In so far as the grinding technique is concerned, the actual thickness of the medium was approximately 14 mils instead of 10 since the initial point of contact with the grinding wheel would be only the tips of the surface roughness.) The depth of adhesive penetration into the roughness and into the body of the sheet was indicated by staining the tapered specimens with iodine in KI solution. The characteristic blue starch-iodine color was found to fade rather rapidly, hence photographs of the tapered sections were prepared for permanent record. Typical stained sections for the three substrates are presented in Fig. 14. An estimate of the depth of surface roughness was gained by noting the point at which the ground section of the sheet becomes continuously uniform. These depths are indicated in Fig. 14.

On the basis of the stained tapers it was decided to prepare six sections (including the whole medium) at 1.2-mil depths (0, 1.2, 2.4, 3.6, 4.8 and 6.0 mils) from each specimen for starch analysis. The available evidence indicated that very little, if any, adhesive would be found beyond the last interval (6.0-mil depth). A schematic diagram of the grinding interval arrangement is given in Fig. 15. The medium left after each interval was analyzed for starch content which was converted to adhesive volume. The adhesive volume at a given interval was then determined by the difference between the initial volume and that left after grinding. These results are recorded in Table VII. The percentage of adhesive removed at a given interval is listed in Table VIII. Bar graphs showing the amount of adhesive held at given depth intervals are presented in Fig. 16 and 17.

ERRATA SHEET

Project 2696-4

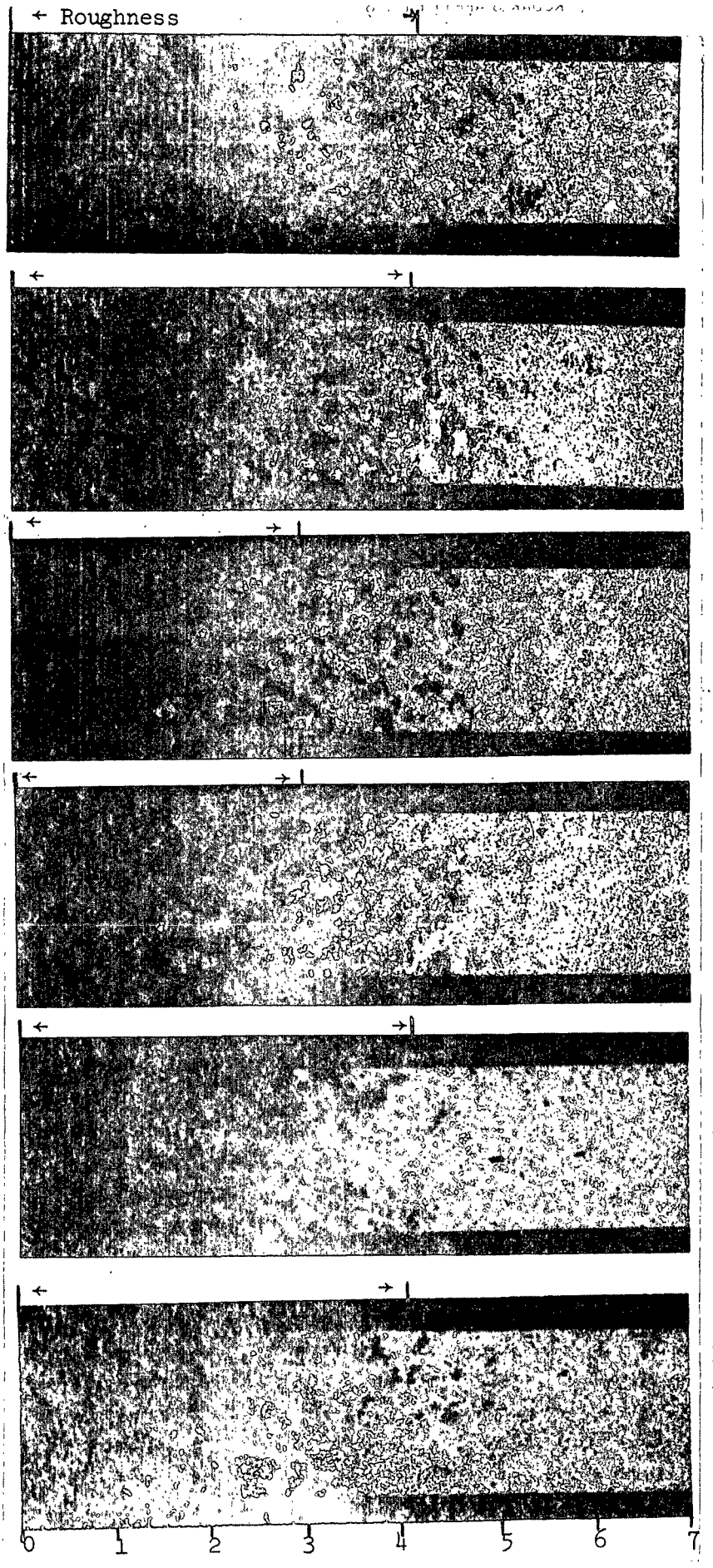
Report One

The following description should appear between the arrows at the top of Fig. 14:

"Approximate Depth Due to Roughness"

The following description should appear immediately below the numbers at the bottom of Fig. 14

"Depth, Thousandths of an Inch"



Rough Receptive Medium
Adhesive Contact Time,
0.62 sec.

Rough Receptive Medium
Adhesive Contact Time,
0.022 sec.

Smooth Receptive Medium
Adhesive Contact Time,
1.1 sec.

Smooth Receptive Medium
Adhesive Contact Time,
0.029 sec.

Rough Nonreceptive Medium
Adhesive Contact Time,
0.79 sec.

Rough Nonreceptive Medium
Adhesive Contact Time,
0.032 sec.

Figure 14. Depth of Starch Adhesive Penetration in Heated Mediums

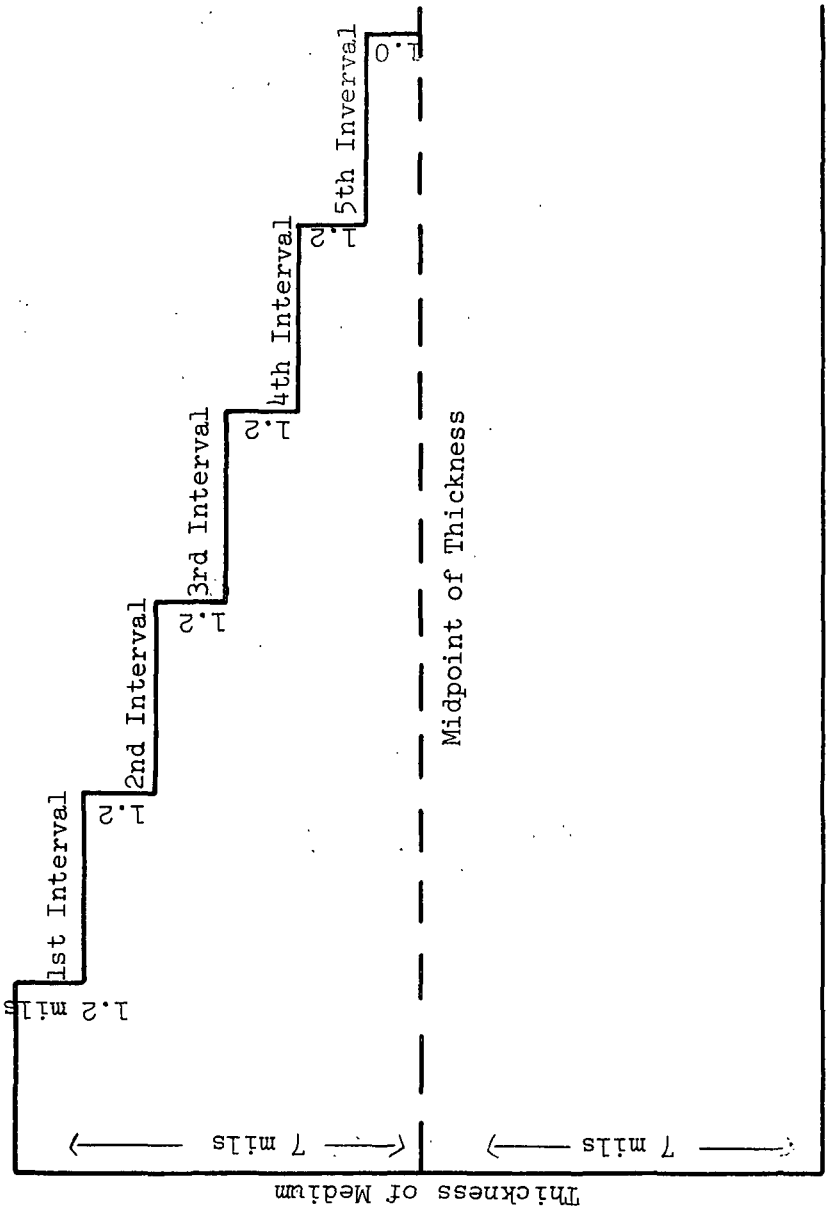


Figure 15. Cross-sectional Diagram of Grinding Intervals for Starch Distribution Analysis

TABLE VII

ADHESIVE VOLUME DISTRIBUTION IN TREATED MEDIUMS

Medium	Description	Contact Time, sec.	Total Adhesive Volume, cc./m.^{2}	Adhesive Volume at Given Depth Intervals, cc./m.^{2} 0-1.2 Mils	1.2-2.4 Mils	2.4-3.6 Mils	3.6-4.8 Mils	4.8-6.0 Mils	6.0+ Mils[a]
No. 5196 felt	Smooth receptive	0.06	13.4	0.6	2.0	5.6	3.9	1.3	0.0
		0.76	16.2	1.9	2.8	4.3	4.2	1.6	1.4
No. 5196 wire	Rough receptive	0.06	17.0	0.3	5.6	4.8	3.8	1.7	0.8
		0.63	19.6	1.4	1.4	6.4	7.1	1.7	1.6
No. 5111 felt	Rough nonreceptive	0.06	11.1	0.7	1.5	4.7	3.1	1.1	0.0
		0.81	11.5	0.2	1.4	4.3	3.8	0.9	0.9

[a]The volume of adhesive attributed to the 6.0+ mil depth was obtained by subtracting the sum of the volumes for the other intervals from the total volume.

TABLE VIII

PERCENTAGE ADHESIVE DISTRIBUTION IN TREATED MEDIUMS

Medium	Description	Contact Time, sec.	Total Adhesive Volume, cc./m.^{2}	Percentage of Adhesive at Given Depth Intervals					
				0.0-1.2 Mils	1.2-2.4 Mils	2.4-3.6 Mils	3.6-4.8 Mils	4.8-6.0 Mils	6.0+ Mils[a]
No. 5196 felt	Smooth receptive	0.06	13.4	4.5	15.0	41.8	29.1	9.7	0.0
		0.76	16.2	11.7	17.3	26.5	25.9	9.9	8.6
No. 5196 wire	Rough receptive	0.06	17.0	1.7	32.9	28.2	22.4	10.0	4.7
		0.63	19.6	7.1	7.1	32.6	36.2	8.7	8.2
No. 5111 felt	Rough nonreceptive	0.06	11.1	6.3	13.5	42.3	27.9	9.9	0.0
		0.81	11.5	1.7	12.2	37.4	33.0	7.8	7.8

[a]The percentage of adhesive attributed to the 6.0+ mil depth was obtained by subtracting the sum of the percentages for the other intervals from 100%.

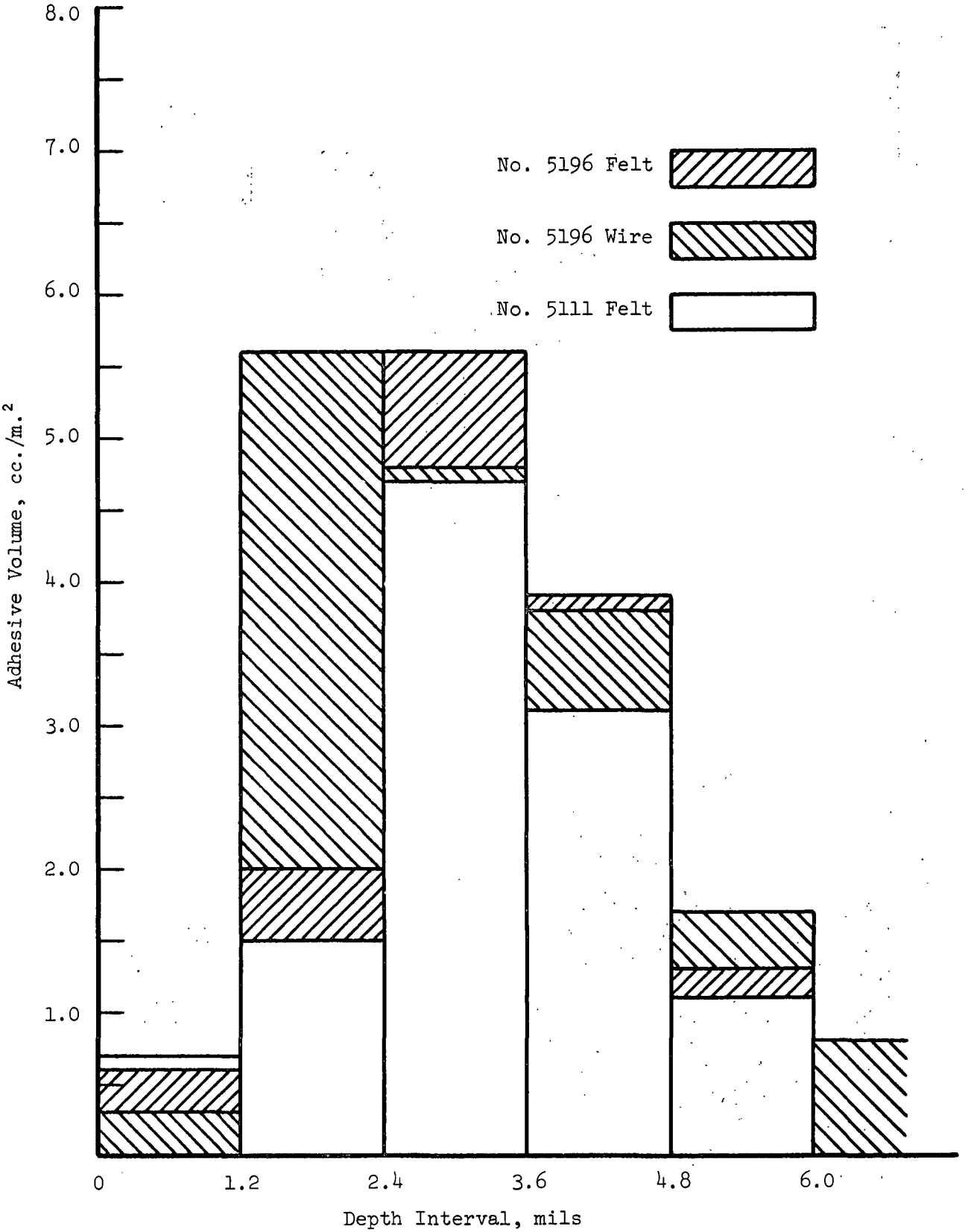


Figure 16. Volume of Adhesive at Given Depth Intervals
(Contact Time ≃ 0.06 sec.)

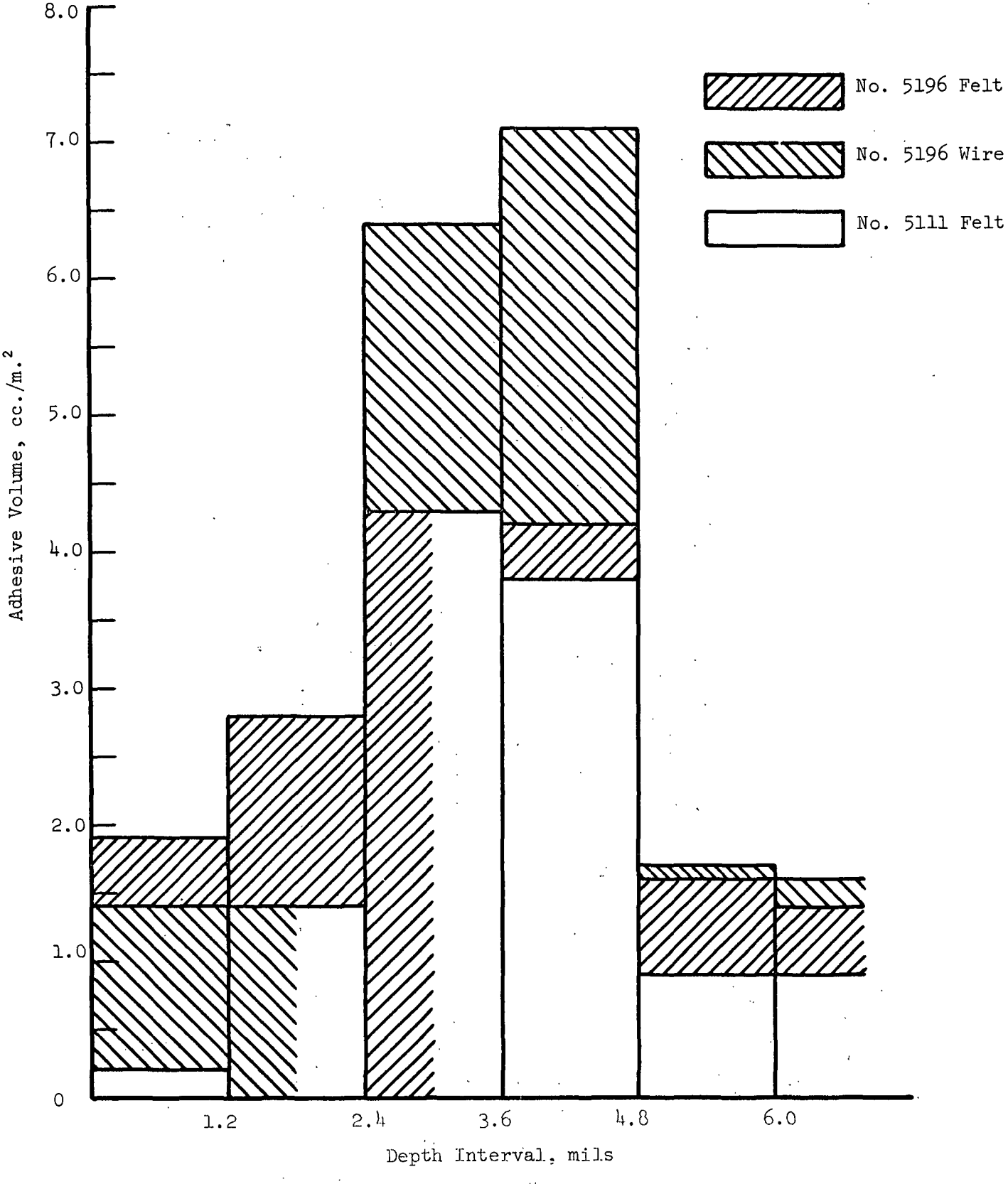


Figure 17. Volume of Adhesive at Given Depth Intervals (Contact Time 0.63-0.81 sec.)

ADHESION AS A FUNCTION OF CONTACT TIME

In an effort to correlate the analytical data with practical adhesion values, starch corrugating adhesive was applied to the selected mediums on the Institute corrugator at a 9-mil transfer roll clearance over a range in speed so as to provide contact times roughly comparable to those utilized on the Keegan Coater, i.e., 0.05 to 2.0 sec. The corrugator was operated without the medium pre-heater at speeds under 63 ft./min. in order to maintain reasonably constant surface temperatures. All applications were made on the same day from the same batch of adhesive thereby eliminating changes in those properties of the adhesive which would be expected to influence wetting and penetrating ability. Pin adhesion values for the corrugated board are recorded in Table IX. Pin adhesion — time relationships are presented graphically in Fig. 18.

WATER COMPONENT MIGRATION

The extent of penetration by the water component of the adhesive into the corrugating mediums is currently under investigation. In order to study this effect it was necessary to assemble a device which would immobilize the water within short but well-defined contact times. An arrangement which has proved quite successful in this respect is shown in Fig. 19. The equipment consists of a pair of applicator rolls driven by a 1/3 h.p. motor with transmission, a source for heating the medium, and a liquid nitrogen trap fitted with a metal rack. A 4 x 11-inch strip of the medium (cut grain long) is held over the nip of the applicator rolls which are driven at a predetermined speed. A stainless steel plate (0.030 in. in thickness) is attached to the base of the sheet to add weight and to help guide the specimen into the liquid nitrogen trap. An aluminum foil pouch, which serves as a reservoir for the corrugating

TABLE IX

THE EFFECT OF ADHESIVE CONTACT TIME ON PIN ADHESION

Medium	Corrugating Speed, f.p.m.	Adhesive Contact Time, sec.	Pin Adhesion, lb.	Predominant Type of Failure
5196 Felt	17.5	2.0	64.7	Medium-adhesive interface
	34.0	1.05	64.5	Medium-adhesive interface
	62.5	0.56	65.4	Within medium
	143	0.24	68.9	Within medium and at liner-adhesive interface
	320	0.109	67.4	Within medium
	460	0.076	53.0	Within adhesive
	574	0.063	57.4	Medium-adhesive interface
	669	0.052	58.0	Medium-adhesive interface
5196 Wire	17.5	2.0	50.4	Within adhesive and at liner-adhesive interface
	34.0	1.05	58.9	Medium-adhesive interface
	62.5	0.56	64.3	Within medium
	143	0.24	64.3	Within medium
	320	0.109	63.8	Within medium
	460	0.076	59.2	Within medium and at medium-adhesive interface
	574	0.063	57.3	Within medium
	669	0.052	56.2	Within medium
5111 Felt	17.5	2.0	48.3	Medium-adhesive interface
	34.0	1.05	45.6	Medium-adhesive interface
	62.5	0.56	51.2	Medium-adhesive interface
	143	0.24	55.0	Medium-adhesive interface
	320	0.109	54.4	Medium-adhesive interface
	460	0.076	52.6	Medium-adhesive interface
	574	0.063	54.2	Medium-adhesive interface
	669	0.052	55.5	Medium-adhesive interface

Note: The clearance on the corrugator was 0.009 inch in all cases.

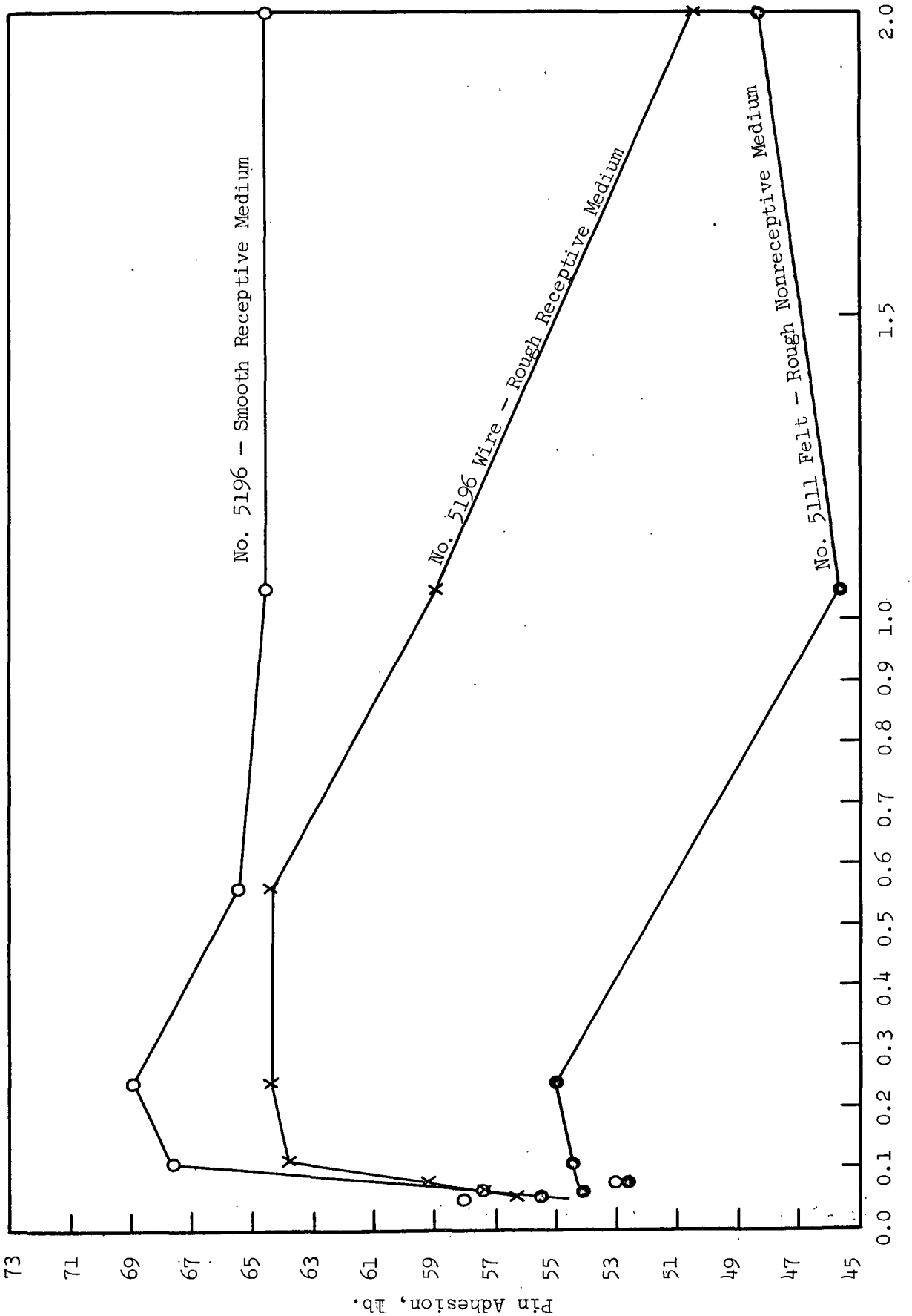


Figure 18. Pin Adhesion as a Function of Contact Time

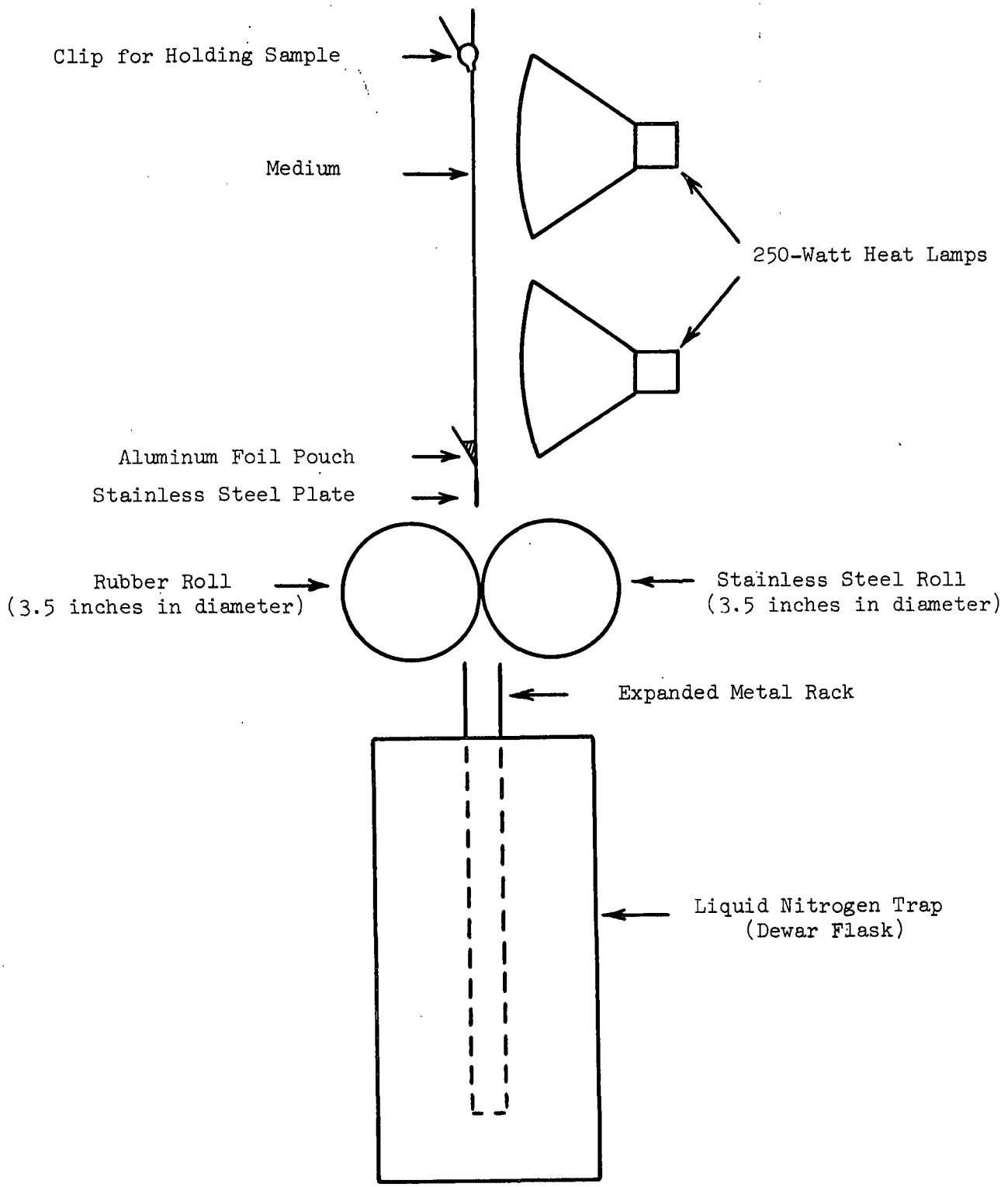


Figure 19. Device for Applying and Immobilizing Corrugating Starch in Short Time Intervals

adhesive, is fastened to the medium above the steel plate. In operation, the medium is heated to 160°F., 2 ml. of adhesive is metered into the pouch, and the specimen is dropped into the nip and on into the liquid nitrogen. In passing through the nip, the adhesive spreads over the surface and is then immobilized (frozen) by the liquid nitrogen. The speed of the rolls and the distance from the nip to the surface of the liquid nitrogen determine the adhesive contact time. The frozen specimens are removed from the liquid nitrogen trap, quickly trimmed to 4 x 6 inches, and then stored in a second liquid nitrogen reservoir. After a series of applications has been completed, the samples are freeze dried. Freeze drying serves to remove the water by sublimation, leaving the nonaqueous components in place. Preliminary tests indicated that no starch or water was lost to the liquid nitrogen in this operation in which approximately 0.02 cc./in.^{2} of adhesive was applied to the medium. This amount of adhesive is less than that applied in practical corrugating but more than that applied on the Keegan Coater.

Thus far, two sets of exploratory tests have been conducted in which the three selected mediums were treated with corrugating adhesive. In the first series the adhesive was used as is; a fluorescent dye (Uranine B) was added to the prepared adhesive in the second series. The fluorescent dye is assumed to migrate with the water and should be detected by examination under U.V. light. Sheets from both series were taper ground in the manner previously described. Specimens from the first series were stained with iodine in KI solution; samples from the second series were examined under U.V. light. The iodine-stained sections showed that starch had penetrated to about the same extent under these conditions as had been found earlier in the Keegan Coater applications, indicating that starch afterflow had not occurred in the Keegan Coater applications. Examination of the specimens from the second series indicated that starch had penetrated

to about the same extent as the water. This was subsequently confirmed by marking the deepest water penetration as shown by U.V. light on a given specimen and then staining the same section with iodine. In all cases examined thus far, the deepest water penetration coincided with the starch penetration. These results are considered tentative, however, since it has not been firmly established that the fluorescent dye is not preferentially sorbed by the medium or the starch.

DISCUSSION OF RESULTS

The room-temperature Keegan Coater results (Table V, Fig. 12) served to demonstrate the feasibility of the method for studying the effects of surface roughness and receptivity on adhesive acceptance and penetration. As would be expected, surfaces of approximately equal receptivity but differing roughness (two sides of No. 5196) are shown to have notably different intercepts or, in other words, marked differences in the amount of adhesive held within the roughness. The results also show that surfaces of approximately equal roughness but differing receptivity (No. 5111 felt and 5196 wire) retain very different amounts of adhesive in their roughness. Since the nonreceptive medium retained substantially less adhesive it was assumed that its roughness was not filled with adhesive. Marked differences in slope (extent of penetration) were not apparent in the room-temperature applications but the total volume of adhesive held by the rough absorbent medium is indicated to be notably higher than that held by either of the other two substrates within the contact times studied.

Subsequent applications at higher temperature showed somewhat similar trends (Table VI and Fig. 13) although less adhesive was retained at short contact times in all cases. The higher temperature applications also resulted in greater slopes for the receptive surfaces indicating that the adhesive was able to penetrate these surfaces to a greater extent than at room temperature. Presumably lower viscosity facilitated the greater penetration at the higher temperature. The nonreceptive medium, on the other hand, is shown to have a very low slope, indicating a low level of adhesive penetration. Once again most of the adhesive was indicated to be held within surface roughness, and, as before, the rough receptive medium accepted more adhesive in its surface voids than the equally rough nonreceptive medium.

The stained tapered sections (Fig. 14) confirm the aforementioned indications and further reveal that surface roughness was probably not completely filled in any case within short contact times. The relatively shallow roughness of the smooth receptive surface appears to be nearly filled, but considerable unfilled space is indicated in the rough surface and, in particular, the non-receptive surface. This applies to the longer contact times as well as the short times. On the basis of the stained tapers the deepest penetration was estimated to be about six mils or 43% of the sheet thickness considering a total thickness of 14 mils. However, most samples showed little penetration beyond 4.7 mils or 33% of the thickness. It is also apparent from Fig. 14 that surface roughness constitutes a very sizeable percentage of the total thickness of the medium. For example, roughness accounts for approximately 50% of the total thickness of the receptive medium (No. 5196) considering both surfaces. Hence, the volume required to fill these surface interstices would be fairly substantial and the ability of the adhesive to enter and occupy all of the void spaces would be a limiting factor particularly at high corrugating speeds.

The distribution of adhesive within surface roughness and the body of the medium (Tables VII and VIII; Fig. 16 and 17) again confirms that most of the adhesive is retained in surface roughness within short time intervals. This assumes that roughness ends within the 2.4-3.6-mil interval in the smooth medium and within the 3.6-4.8-mil interval in the rough surfaces. However, the distribution data also show that a relatively small amount of adhesive is actually held within the outermost interval (0-1.2 mils) and some penetration occurs beyond the 6-mil depth with time. Comparison of Fig. 16 and 17 shows the effect of time and penetration on adhesive distribution. At the short contact time (0.06 sec.), the greatest concentration of adhesive was found within the 1.2-3.6-mil intervals but with time and

penetration the greatest concentration shifted to the 2.4-4.8 mil intervals with a very pronounced decline beyond the 4.8-mil depth. It will be noted that the adhesive volumes for No. 5111 (rough nonreceptive medium) are generally lower and do not shift to the same extent with time as was found with the receptive surfaces. This is in keeping with the earlier Keegan Coater results which showed a low slope for the nonreceptive surface.

Pin adhesion values (Table IX; Fig. 18) for the three surfaces were not markedly different at very short contact times but became more significant within 0.1 sec. (400-500 f.p.m.) and quite pronounced at 0.1 to 1.0 sec. contact (30-320 f.p.m.). The smooth receptive medium is shown to provide the best overall adhesion followed by the rough receptive medium and, finally, by the rough nonreceptive medium. It would be expected that the starch adhesive begins to set up at the longer contact times before contact with the liner is made; hence, the pin adhesion values under these conditions may not be meaningful. It is noteworthy that the predominant type of failure (Table IX) in the rough nonreceptive medium was at the medium adhesive interface, whereas that for the rough receptive medium was generally within the medium. The point of failure was found to vary considerably in the case of the smooth receptive medium.

Interpretation of these results in terms of the Keegan Coater and adhesive distribution data suggests that the best adhesion was afforded by the substrate having the most <u>complete</u> and <u>continuous</u> contact with the adhesive throughout surface roughness, i.e., by the smooth medium. While the starch distribution data show that relatively little starch is held in the outer extremes of roughness, the pressure involved in corrugating would tend to force contact with the available adhesive deeper within the roughness. Samples tested for pin adhesion were prepared on the experimental corrugator where the medium was effectively calendered and where

considerably more adhesive was applied than on the Keegan Coater and, therefore, more adhesive was probably available at the outer surface. Hence, the observed differences in pin adhesion presumably stem, at least in part, from differences that exist deeper within the roughness and the body of the medium. The smooth receptive medium was the only substrate whose surface was essentially filled and, therefore, capable of providing intimate contact through its roughness into the body of the medium. Because of its greater smoothness less adhesive was required to fill its roughness and, at longer contact times, more adhesive was available at the outer extremes of roughness (0-2.4 mils). Also, because it was a receptive medium, adhesive was able to penetrate beyond roughness within a relatively short time. The rough surfaces, on the other hand, and, in particular, the nonreceptive surface were not filled and, therefore, contained unoccupied void spaces which are frequently points of failure in adhesive joints because of localized stress concentrations.

The fact that the pin adhesion values tend to converge to a relatively low level at higher corrugating speeds and the fact that the receptive surfaces show markedly reduced values under these conditions suggest that dynamic contact angle and wettability are critical factors in practical corrugating operations. On this basis it might be expected that less penetration into roughness actually occurred than is indicated by the current starch distribution data. However, the stained tapered sections of samples drawn from the liquid nitrogen trap indicate that adhesive afterflow did not occur on the Keegan Coater. Conceivably, starch is forced into surface cavities under these conditions, but because of a high dynamic contact angle, poor wetting of the pore walls occurs with the result that the bond fails except in those areas where mechanical anchoring occurs.

The current results pose a means of improving adhesion through the use of a relatively smooth receptive medium, i.e., a medium which would accept the adhesive at high speed and which contains only enough roughness to provide "tooth" in the final adhesive bond. The "smooth" medium used in this study was smooth only in relation to the other surfaces examined. The depth of the roughness in this medium was approximately 0.003 inch, which is possibly more than adequate. This assumes adequate internal bonding strength in both the medium and the liner. If failure occurs within one of these members it is not considered adhesional failure since, strictly speaking, adhesion refers to the interface. The roughness and receptivity of the liner would also be expected to play an important role in the adhesion of that member in the same manner in which they apply to the medium. In fact, the receptive properties of the liner may even be more critical than those of the medium since the adhesive may be partially set up by the time contact is made with the liner.

FUTURE WORK

While the information reported herein indicates that the water component of the corrugating adhesive does not penetrate the medium beyond the starch, these results are at best qualitative and should be confirmed under better defined conditions. Acid dyes, in addition to the fluorescent dye, will be considered for this purpose. Having established the feasibility of the method, the ratio of starch:water will be determined at several depth intervals in order to establish whether or not water migrates from the uncooked adhesive and is thereby unavailable for gelling of the starch at or near the surface. The medium will be calendered prior to these applications in order to better approximate the conditions existing on the corrugator. Photomicrographs of the adhesive at the surface and within the medium will be prepared in conjunction with this work. The information derived from this part of the program, together with that presented in this report should form the basis for defining the critical conditions for adhesion in corrugated board.

Although not part of the present program, it may subsequently be desirable to obtain corroborative evidence for the effects of smoothness, porosity, and sizing on adhesion. For this purpose, medium would be formed from a given fiber furnish under well-defined conditions on an experimental paper machine. This approach should permit optimization of bonding strength by making available a wider range in smoothness, sizing, etc. than was available in the commercial papers.

LITERATURE CITED

1. Harkins, W. D., and Jordan, H. F., J. Am. Chem. Soc. 52:1751(1930).

2. Browning, B. L., Bublitz, L. O., and Baker, P. S., Tappi 35, no. 9:419-20 (Sept., 1952).

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