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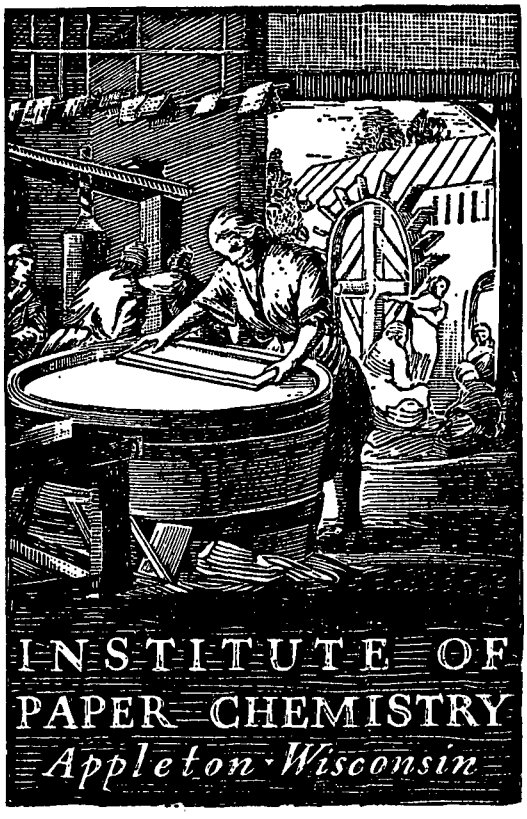

FUNDAMENTAL STUDY OF ADHESION OF CORRUGATED BOARD

Project 2696-4

Report Two

A Progress Report

to

FOURDRINIER KRAFT BOARD INSTITUTE, INC.

September 30, 1969

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The extent of starch- and water-component penetration into calendered mediums has been examined as part of a program concerned with a fundamental study of adhesion of corrugated board. The mediums utilized for this purpose were the same as those used in the earlier study but were machine calendered to effect a reduction of 30-35% in caliper in order to better approach practical corrugating conditions. A reference starch adhesive was applied to the receptive and nonreceptive mediums in a laboratory application which permitted immobilization of the adhesive within 0.06 and 0.6 sec. The extent of starch penetration was measured colorimetrically; the water (liquid) component penetration of the adhesive was followed by incorporating a fluorescent dye into the starch adhesive. The extent to which the uncooked starch granules penetrated the medium and the physical state of the adhesive within the medium were examined by photomicroscopy.

As was found in the earlier study, the volume of adhesive accepted by the mediums in short-time intervals was shown to depend upon the receptive nature of the medium. The nonreceptive medium accepted notably less adhesive than the receptive medium at both contact times. However, regardless of the receptive character of the medium, an initial classification of adhesive components occurred in the application process wherein starch was rejected in favor of water (liquid). Beyond this, a further classification of starch and water occurred as a function of depth of penetration into the medium. Most of the starch was retained within 1.2 mils of the surface regardless of the substrate whereas water (liquid) penetrated in greatest amounts beyond the 1.2-mil depth. Hence, water migrated away from the uncooked starch in all cases leaving the starch in a "starved" condition at the surface.

The nonreceptive medium retained more water in proportion to the starch at the surface than did the receptive surfaces but the amount of adhesive accepted by this substrate was notably less. The receptive medium, on the other hand, retained more starch but less water in proportion to the starch in the surface regions.

Photomicrographs of the treated mediums revealed that the uncooked starch is retained primarily at or near the surface of the medium, although some is lost in large surface irregularities. Most of the starch granules evident in the photomicrographs ranged from 5-15 μm. and were small enough to enter many of the surface cavities. Some cooked starch was associated with the granules at the surface and a small amount penetrated approximately one-third the thickness of the test specimen.

These results were interpreted in terms of the practical corrugating process.

INTRODUCTION

Results described in Progress Report One relating corrugating adhesion to the surface chemical properties of the medium revealed that most of the starch adhesive was retained within surface roughness but the extent to which the roughness was filled and the distribution of starch within the roughness varied with the receptive character of the medium and the speed of application. Of the mediums studied, a relatively smooth receptive medium provided the best overall adhesion when single faced followed in order by rough receptive and nonreceptive mediums. The smooth receptive medium was the only substrate whose "roughness" was essentially filled and therefore capable of providing intimate contact through its surface into the body of the medium. 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 because of localized stress concentrations.

Preliminary tests concerned with the extent of water-component migration indicated that water does not penetrate beyond the starch; however, these were tentative results subject to confirmation. It was shown conclusively that relatively little starch migrated beyond the depth of roughness and, because of the limitation of particle size, this was assumed to be the solubilized portion of the starch in the carrier. Presumably, the migration of water and solubilized carrier away from the uncooked portion would leave unsatisfactory conditions for gelling at the surface where bonding occurs. The aforementioned results were obtained on uncalendered corrugating medium and it is well established that the tips of the flutes, where the adhesive is applied, undergoes transverse compression or "calendering" so as to cause approximately a 35% reduction in caliper in that area. The present report pursues the matter of starch-water migration and starch distribution within calendered medium.

EXPERIMENTAL PROCEDURES

PHYSICAL PROPERTIES OF CALENDERED MEDIUMS

The corrugating mediums utilized in this phase of the experimental program were the same as those used in the initial phase as described in Progress Report One. These were comprised of a rough nonreceptive medium (No. 5111) and a receptive medium (No. 5196) one side of which was smooth, the other side rough. In order to more closely approach practical corrugating conditions whereby the flute tips are effectively reduced in thickness, the medium was hot-roll calendered prior to application of adhesive.

The calendered medium was subsequently tested for basis weight, caliper, apparent density, moisture content, water drop, contact angle, Bendtsen porosity and smoothness, nip spreader roughness and receptivity, I.G.T. surface bonding strength and mercury intrusion pore size and pore size distribution. With the exception of the mercury intrusion data, the test results for both calendered and uncalendered medium are presented in Table I. The mercury intrusion data are listed separately in Table II. The cumulative pore volume-pressure relationship and volume frequency curves are presented graphically in Fig. 1 through 4.

Pin adhesion data for these mediums were given in Progress Report One and are repeated here in Table III for purposes of comparison. Pin adhesion as a function of adhesive contact time is shown graphically in Fig. 5.

PREPARATION OF STARCH CORRUGATING ADHESIVE AND METHODS OF ANALYSIS

In order to differentiate starch- and water-component migration into corrugating medium, consideration was given to the use of a fluorescent dye for tracing water or liquid penetration and to starch-iodine for the starch component migration.

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF UNCALENDERED AND CALENDERED CORRUGATING MEDIUM

Test	Corrugating Medium: Uncalendered No. 5111 Felt	Uncalendered No. 5196 Felt	Uncalendered No. 5196 Wire	Calendered No. 5111 Felt	Calendered No. 5196 Felt	Calendered No. 5196 Wire
Basis weight, lb./1000 ft.^{2}	28.5	26.3	26.3	28.1	26.1	26.1
Caliper, pt.	10.3	9.9	9.9	6.9	6.7	6.7
Apparent density	2.8	2.7	2.7	4.1	3.9	3.9
Moisture, %	5.9	8.0	8.0	7.0	7.1	7.1
Water drop, sec.	600+	18.7	18.7	600+	25	25
Contact angle, degrees						
Starch	114	86	61	115	81	78
Water	104	--[a]	--[a]	104	--[a]	--[a]
Bendtsen porosity, ml./min.	970	1770	1750	339	856	856
Bendtsen smoothness, ml./min.	2700	2290	2650	340	256	363
Nip spreader						
Roughness	14.3	4.9	14.6	5.7	0.0[b]	0.0[b]
Receptivity	1.2	12.4	14.5	2.2	13.6	16.8
I.G.T. bonding strength, kp.-cm./sec.	83	57	51	53	43	26

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

[b] The absorption rate for these surfaces was too high for accurate measurements of the spread pattern to be made.

TABLE II

MERCURY INTRUSION PORE VOLUME DATA FOR UNCALENDERED AND CALENDERED CORRUGATING MEDIUMS

Uncalendered Medium				Calendered Medium			
No. 5111		No. 5196		No. 5111		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.
1.81	0.000	1.81	0.000	1.71	0.0000	1.70	0.0000
3.25	0.020	3.24	0.018	2.75	0.0117	2.75	0.0179
4.38	0.033	4.36	0.029	4.29	0.0235	4.79	0.0313
5.99	0.040	5.98	0.039	7.33	0.0352	8.13	0.0448
7.00	0.047	7.00	0.050	11.1	0.0509	11.1	0.0627
8.53	0.056	8.52	0.061	16.2	0.0716	16.3	0.0873
11.06	0.070	11.06	0.083	21.3	0.0869	21.3	0.1150
14.11	0.104	14.2	0.180	26.4	0.1124	26.5	0.1620
16.23	0.164	19.4	0.247	31.4	0.1433	31.6	0.2108
19.36	0.230	21.5	0.308	36.6	0.1828	36.7	0.2596
21.46	0.282	24.6	0.369	41.7	0.2141	41.8	0.2936
24.60	0.349	26.7	0.422	46.8	0.2474	46.9	0.3245
26.68	0.391	31.8	0.484	51.9	0.2776	51.9	0.3500
31.79	0.449	36.9	0.529	57.0	0.2952	57.1	0.3715
36.9	0.499	41.9	0.558	62.0	0.3120	62.1	0.3894
42.0	0.527	47.0	0.592	67.1	0.3257	67.1	0.4028
47.0	0.555	52.0	0.617	72.1	0.3390	72.2	0.4145
52.1	0.575	62.1	0.653	77.1	0.3492	77.2	0.4239
62.1	0.614	72.1	0.678	82.2	0.3578	82.2	0.4333
72.2	0.637	82.0	0.693	92.2	0.3735	92.3	0.4454
82.2	0.657	92.0	0.707	102	0.3860	102	0.4570
92.2	0.677	107	0.727	112	0.3985	112	0.4673
104.2	0.687	122	0.742	127	0.4103	122	0.4762
112	0.700	137	0.747	142	0.4209	137	0.4856
122	0.715	150	0.764	167	0.4318	157	0.4955
137	0.731	175	0.783	177	0.4416	167	0.5058
150	0.748	200	0.789	197	0.4498	207	0.5161
175	0.755	210	0.800	227	0.4588	242	0.5259
200	0.771	250	0.816	262	0.4671	287	0.5358
250	0.784	300	0.824	300	0.4749	350	0.5425
300	0.794	350	0.832	385	0.4827	450	0.5514
350	0.800	595	0.838	500	0.4851	600	0.5546
420	0.803	760	0.838	650	0.4913	800	0.5590
500	0.803	870	0.840	800	0.4925	1,000	0.5595
625	0.806	1,100	0.844	1,000	0.4945	2,000	0.5608
800	0.808	2,000	0.847	2,000	0.4952	3,000	0.5622
900	0.808	6,000	0.847	3,000	0.4964	5,000	0.5635
1,300	0.811	7,000	0.847	5,000	0.4972	7,000	0.5653
2,700	0.813	7,200	0.847	8,000	0.4972	9,000	0.5662
4,000	0.813	8,400	0.850				
6,500	0.814	10,000	0.853				
8,000	0.814	12,700	0.853				
10,200	0.814	15,000	0.853				
12,300	0.814						
13,000	0.814						
15,000	0.814						

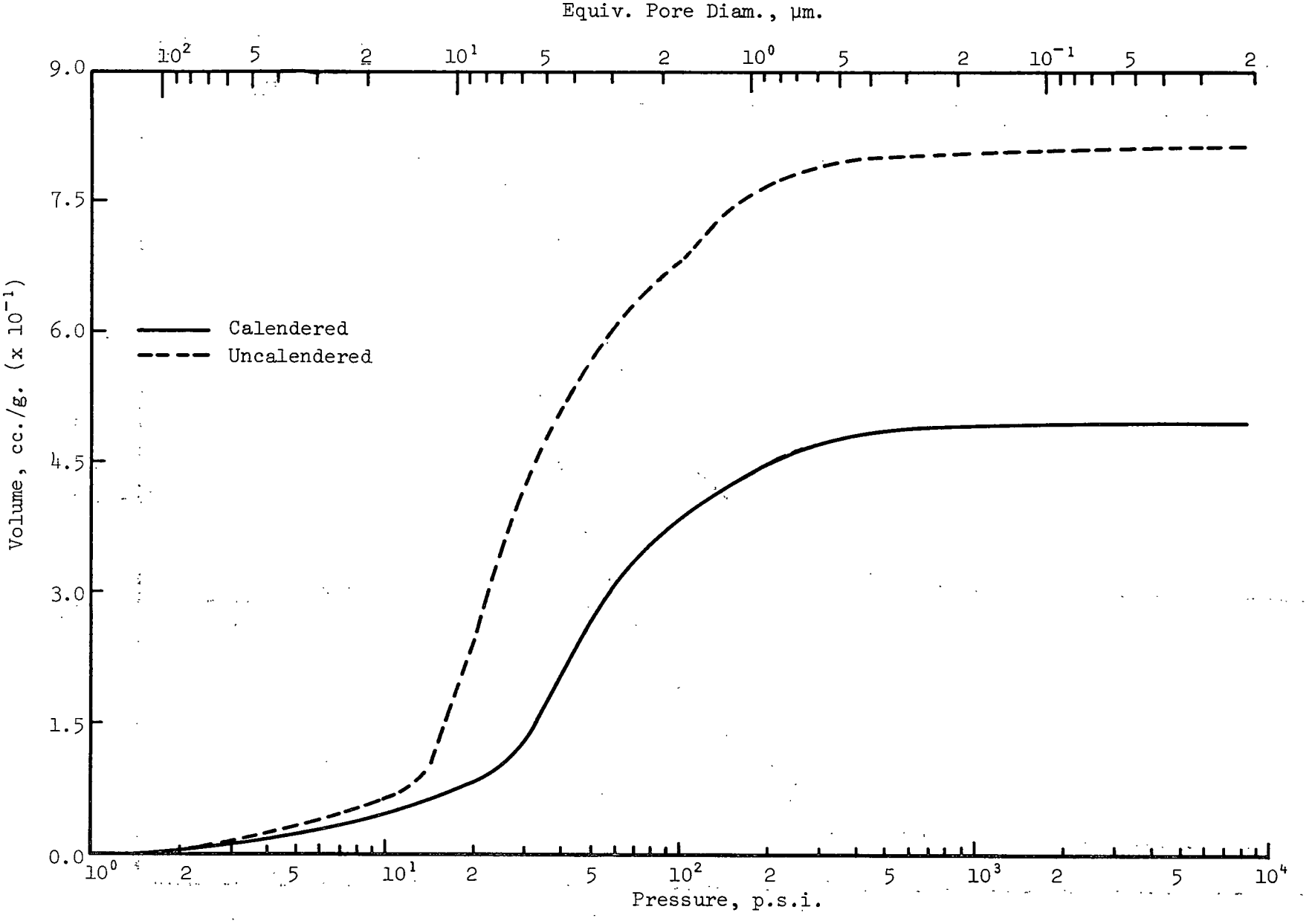


Figure 1. Cumulative Pore Volume — Pressure Relationships for Nonreceptive Medium (No. 5111)

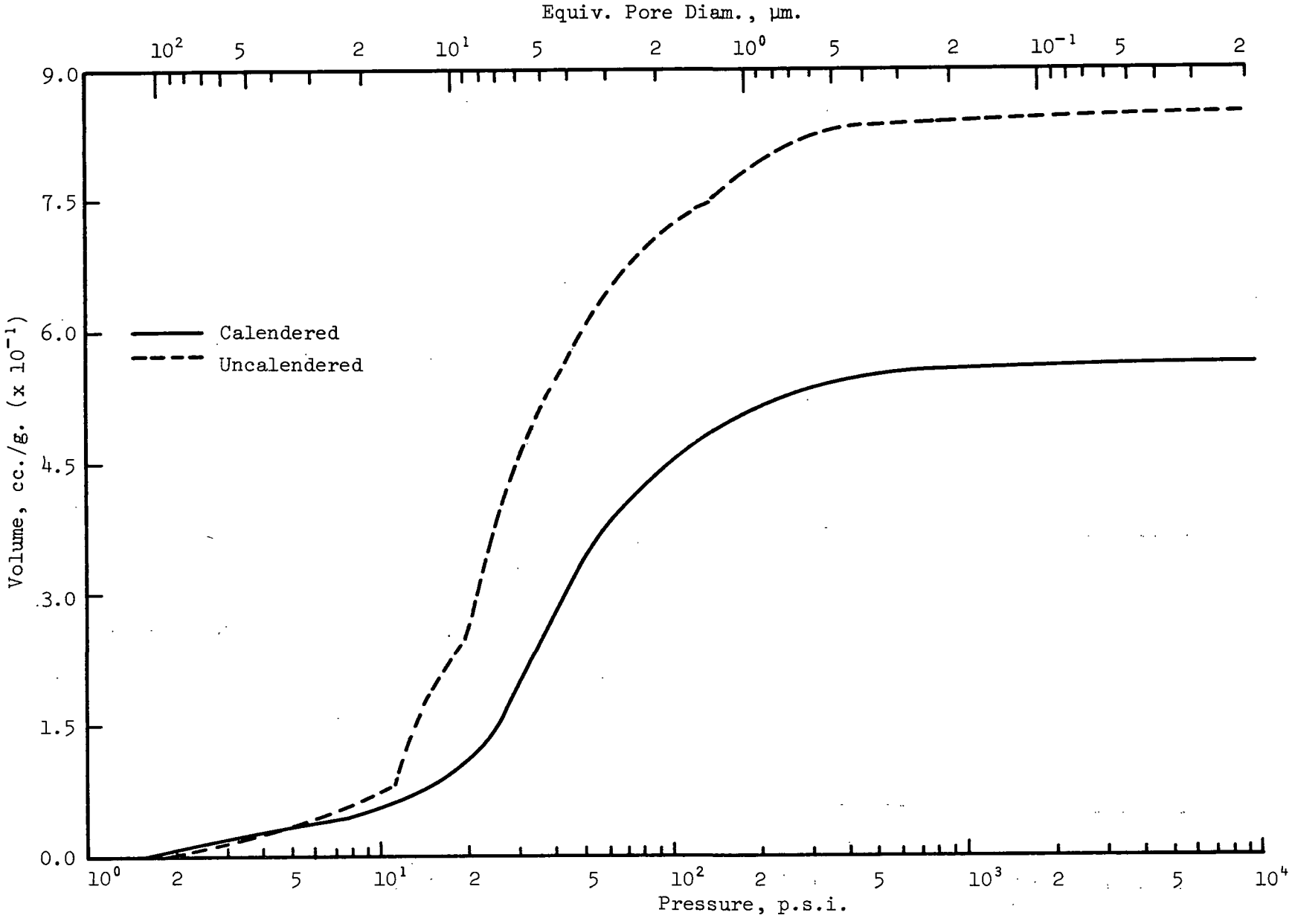


Figure 2. Cumulative Pore Volume — Pressure Relationships for Receptive Medium (No. 5196)

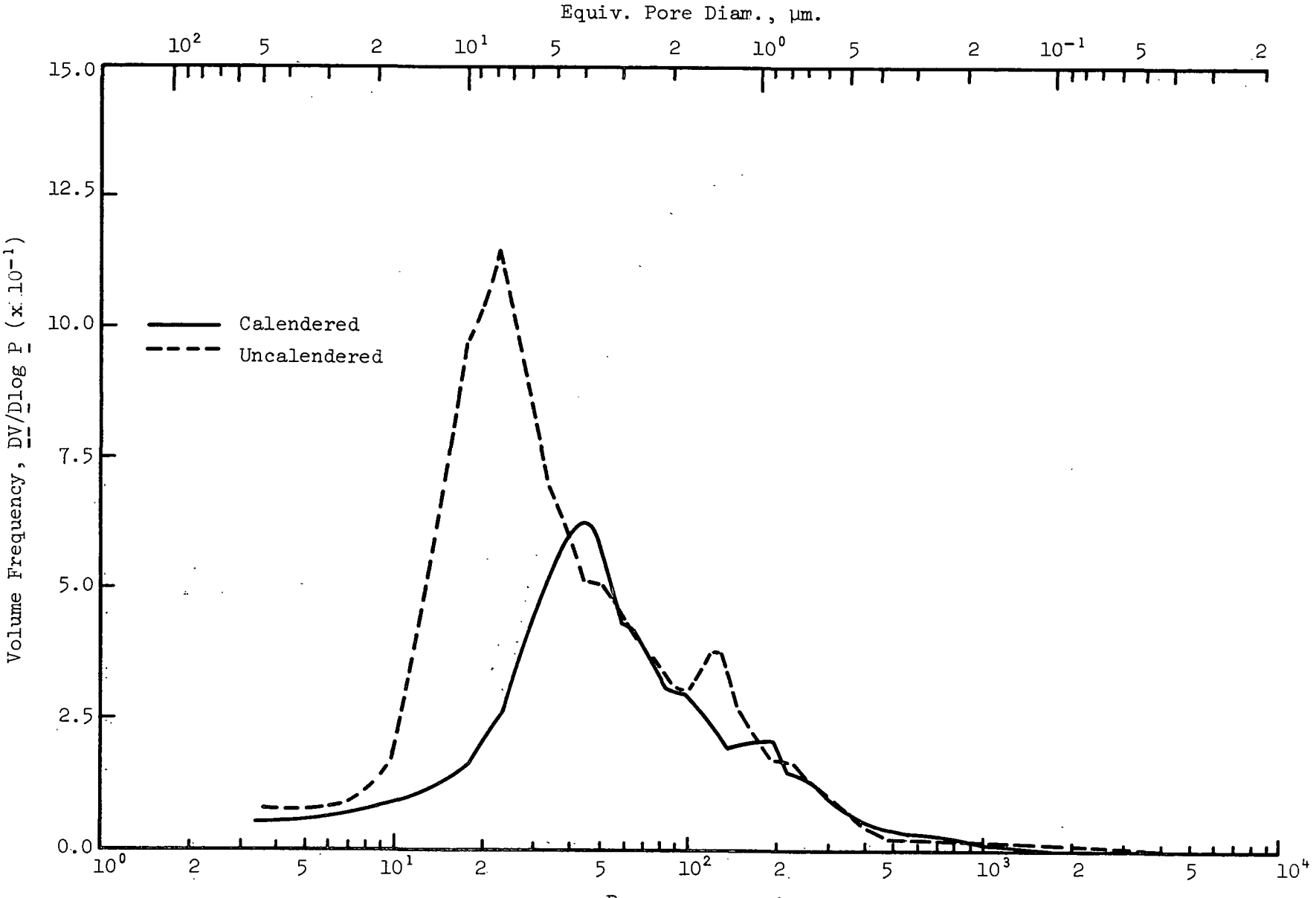


Figure 3. Volume Frequency Curves for Nonreceptive Medium (No. 5111)

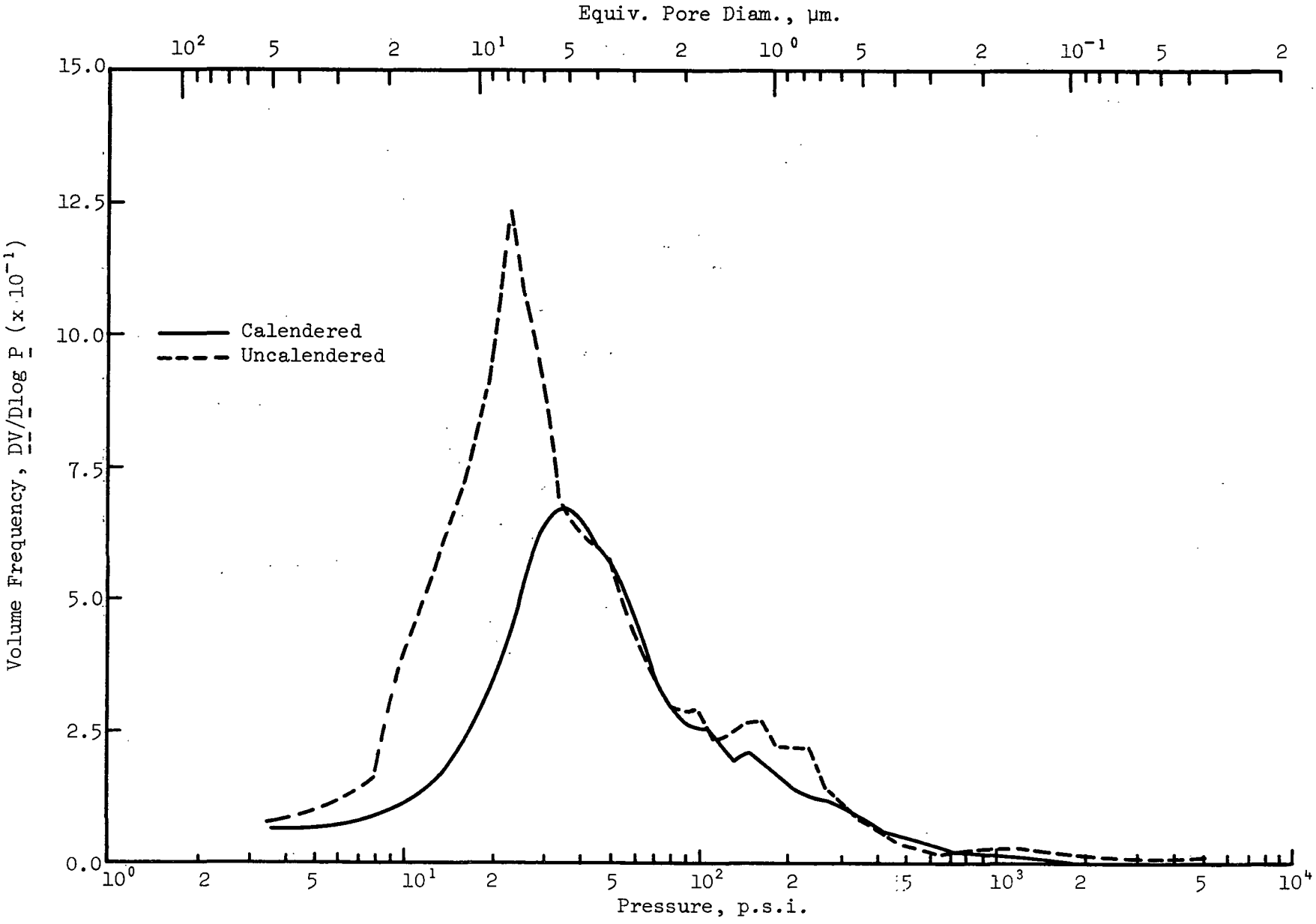


Figure 4. Volume Frequency Curves for Nonreceptive Medium (No. 5196)

TABLE III

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.

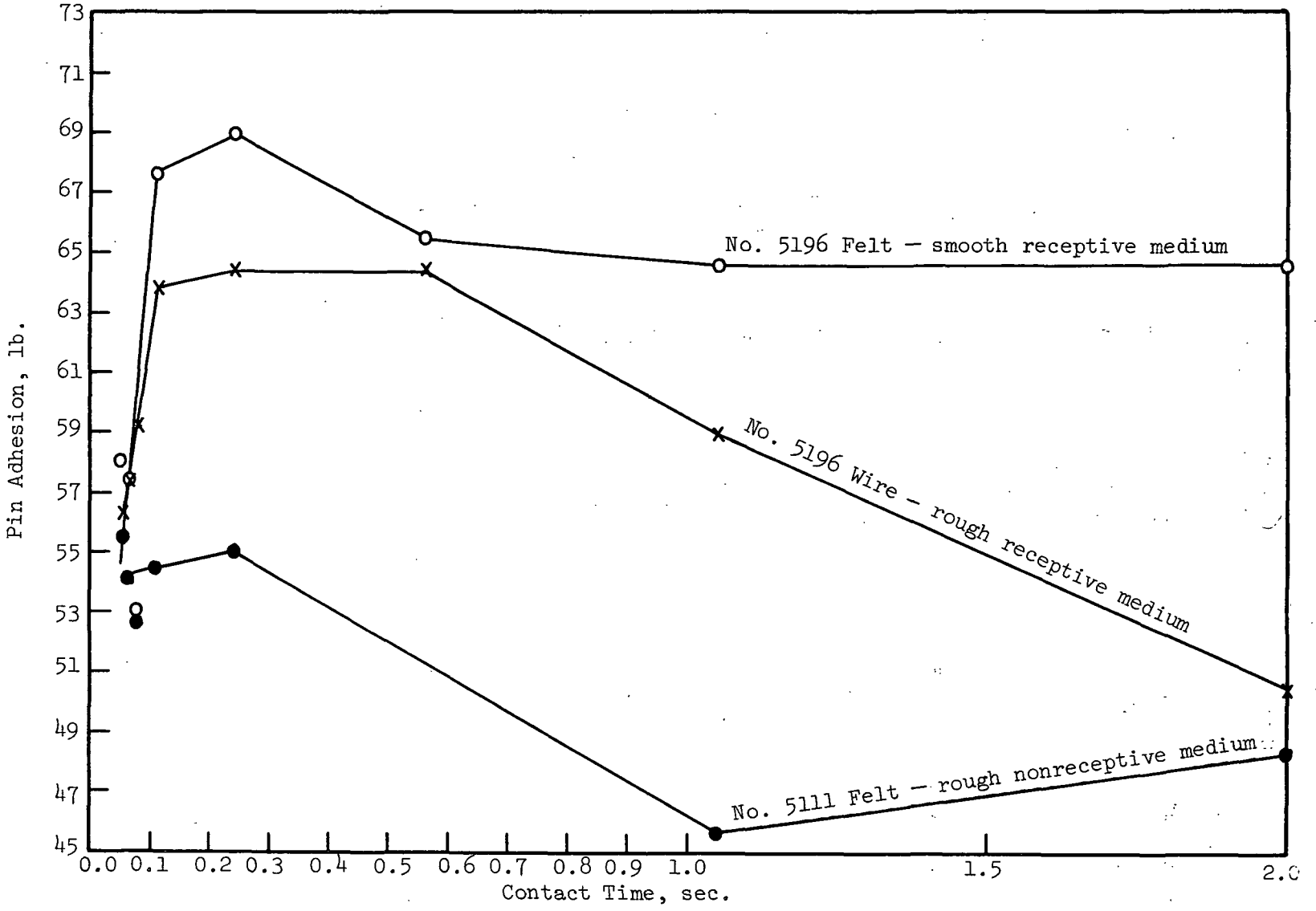


Figure 5. Pin Adhesion as a Function of Contact Time

The two-mix starch corrugating adhesive utilized in this study was prepared in the same manner as described in Report One with the exception that a fluorescent dye, Calcocid uranine B, was added after all other components had been blended. The amount of dye added was 0.3655 g. per 400 g. of starch corrugating adhesive. This relatively large amount of dye was needed for accurate determination of liquid penetration deep within the medium.

In order to determine if the presence of the fluorescent dye interfered with the analysis of starch by the Browning, et al procedure (1), two calibration curves were prepared; one without the dye, the other with the dye. The calibration curves were found to coincide and were the same as that given in Report One.

The fluorescent method involved extraction of the treated medium with hot water and determination of the amount of fluorescence in the extract with a DU spectrophotometer. In this case calibration curves were prepared based on known amounts of corrugating adhesive in reference samples of the medium.

PRELIMINARY CAPILLARY RISE EXPERIMENTS

Qualitative capillary rise tests were subsequently carried out to further test the feasibility of using the fluorescent dye for tracing the extent of the water component migration. This test which eliminates the effect of application pressure was carried out by vertically suspending strips of both the receptive and nonreceptive calendered mediums with the ends dipped in the following three suspensions or solutions: (1) water containing the fluorescent dye (0.3655 g. dye per 400 g. water), (2) adhesive containing the fluorescent dye, and (3) adhesive without fluorescent dye. After a given time the height of rise of liquid was marked as were the boundaries when examined under ultraviolet light and/or when stained with iodine. It was found that the dye followed the liquid boundary in the presence

or absence of starch and the starch and water boundaries coincided in a given medium. While these tests indicate that the starch component migrated as far as the water, they do not indicate the relative amounts or volumes involved.

APPLICATION AND IMMOBILIZATION OF CORRUGATING STARCH ADHESIVE

The equipment utilized for applying and immobilizing the starch adhesive in short time intervals was essentially the same as that described in Report One with a few minor modifications. A schematic drawing of the device is presented in Fig. 6. The equipment consists of a pair of applicator rolls driven by an electric motor with a variable speed 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 inch 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 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 made, the samples are freeze dried which serves to remove the water component by sublimation leaving the nonaqueous components in place. Preliminary tests indicated that neither starch nor fluorescent dye was lost to the liquid nitrogen.

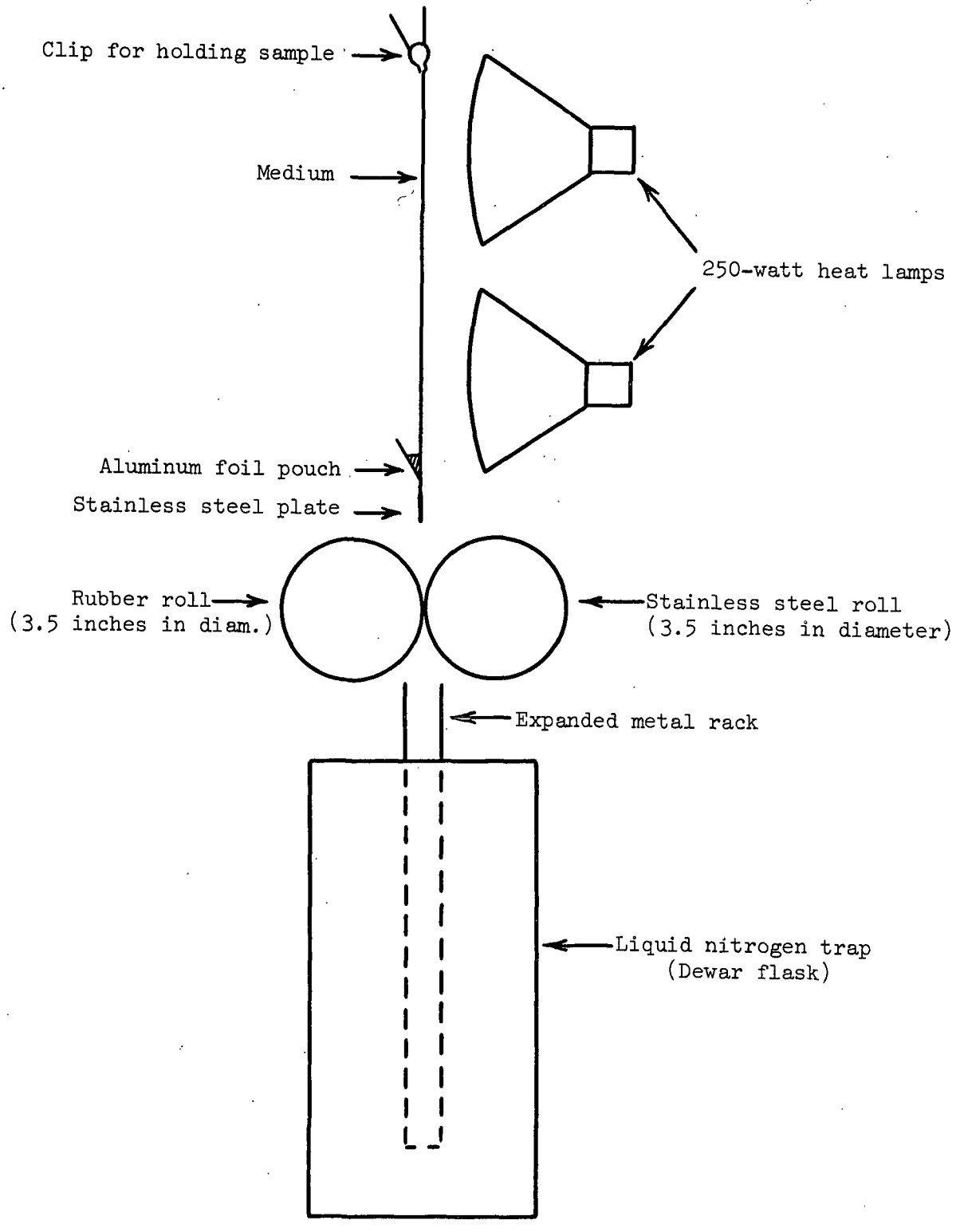


Figure 6. Device for Applying and Immobilizing Corrugating Starch in Short Time Intervals

Initial applications of corrugating adhesive utilizing this device were not satisfactory because the film applied was not uniform across the width of the specimen. The problem stemmed from a hand-adjusted screw system for controlling pressure or gap on the applicator rolls. A spring loading mechanism was tested but was found to be unsatisfactory at high application speeds due to "chattering." Dial distance indicators were subsequently attached to the applicator rolls and these were found to be satisfactory for controlling the uniformity of the starch film. In operation, the gap between the rolls was adjusted to zero and the roll speed was adjusted to 340 or 34 f.p.m. These speeds provided adhesive contact times of 0.06 and 0.6 second prior to immobilization in the liquid nitrogen. The adhesive was applied to the felt side of the nonreceptive medium (No. 5111) and to both sides of the receptive medium (No. 5196).

EXTENT OF ADHESIVE PENETRATION AND COMPONENT DISTRIBUTION

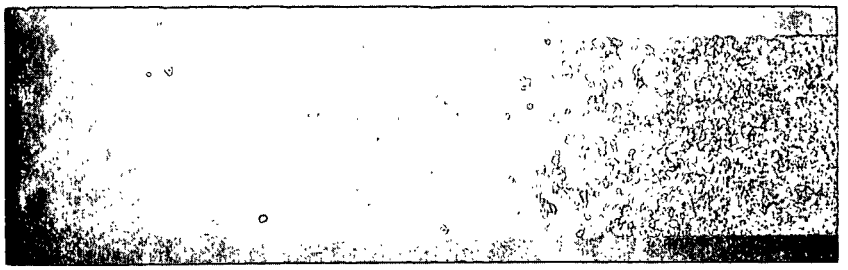
In order to determine the extent of penetration of the adhesive into the calendered medium, sheets of the treated medium were taper-ground at a fixed rate of 0.5 mil per lineal inch over a total length of six inches. For this purpose, the 4 x 6-inch sheets were cut across the width into strips 2 x 4 inches. Two strips were utilized for taper grinding. The first strip was ground from a depth of 8 to 6.5 mils over a three-inch distance and the second from 6.5 to 5.0 mils over an equal distance.

The thickness of the treated sheets after freeze drying was approximately 7 mils as measured with Cady calipers. However, in so far as the grinding technique is concerned, the actual thickness of the treated medium was 8 mils since the initial point of contact with the grinding wheel would be the outermost tips of surface roughness. The depth of starch penetration into the sheet was indicated

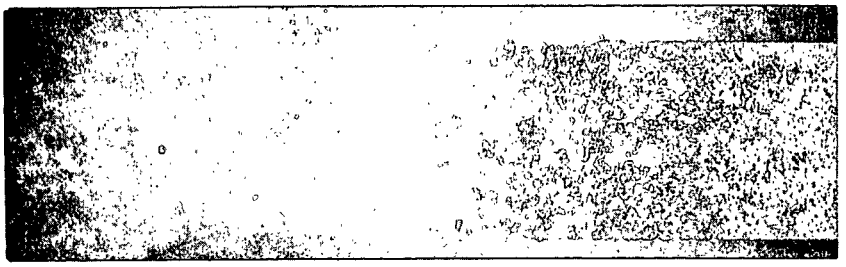
by staining the tapered specimens with iodine in KI solution. The depth of liquid penetration was noted by observation under ultraviolet light. Photographs of the iodine-KI-stained sections are presented in Fig. 7.

From the observations of the stained tapers it was decided to prepare 5 sections at 0.6-mil depth intervals or, in other words, at 0.0, 0.6, 1.2, 1.8, and 2.4-mil depths for analysis. Very little adhesive, if any, was indicated to have penetrated beyond the 2.4-mil depth interval. The grinding interval arrangement is shown schematically in Fig. 8. The medium that remained after grinding was analyzed for starch content by the iodine-KI technique and for liquid content by the fluorescent method. These results were converted into adhesive volumes using an adhesive density of 1.08 g./ml. The difference between the initial volume and that left after grinding was considered to be the adhesive volume at a given depth interval. The difference in adhesive volumes indicated by the two analytical methods was attributed to water since no other liquid form was present. Hence, reference is made to water or liquid component migration as measured by fluorescence. (Note: In preparing samples for analysis, three 1-3/8 x 3-inch specimens were cut across the width of each 4 x 8-inch sheet. The three strips were utilized for a single analysis and, hence, the entire area of the sheet was represented in a given determination. Duplicate determinations were made in all cases.)

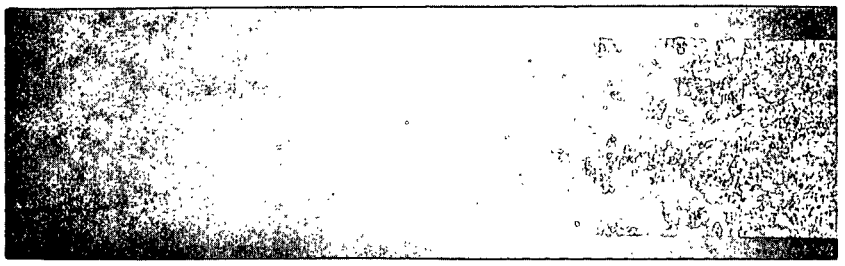
Adhesive volumes based on starch content are recorded in Table IV. Liquid adhesive volumes based on fluorescence are recorded in Table V. The percentage of adhesive based on starch and on fluorescence are presented in Tables VI and VII, respectively. Bar graphs showing the volume of adhesive based on the two analytical methods are presented in Fig. 9-12. A summary of adhesive volume data is given in Table VIII.



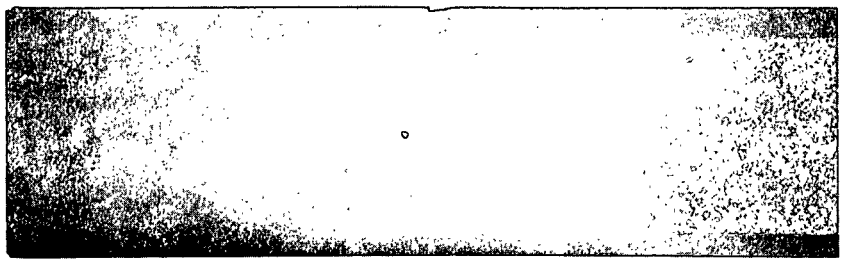
Rough Receptive Medium
Adhesive Contact Time,
0.6 sec.



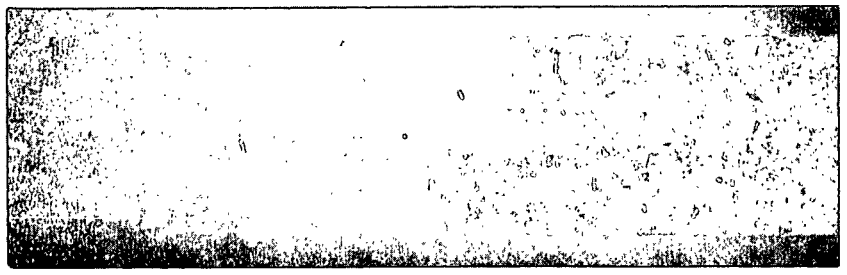
Rough Receptive Medium
Adhesive Contact Time,
0.06 sec.



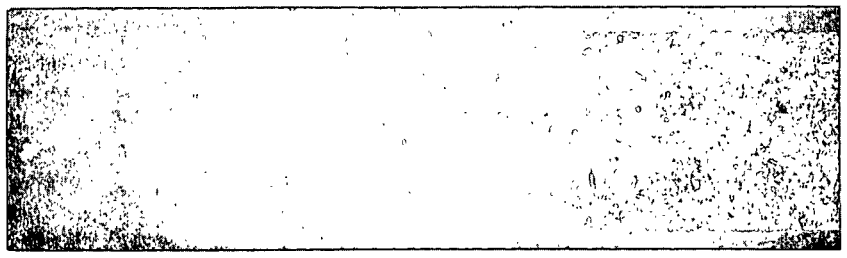
Smooth Receptive Medium
Adhesive Contact Time,
0.6 sec.



Smooth Receptive Medium
Adhesive Contact Time,
0.06 sec.



Rough Nonreceptive Medium
Adhesive Contact Time,
0.6 sec.



Rough Nonreceptive Medium
Adhesive Contact Time,
0.06 sec.

0.0 0.6 1.2 1.8 2.4 3.0

Depth, mils

Figure 7. Depth of Starch Adhesive Penetration in Heated Calendered Mediums

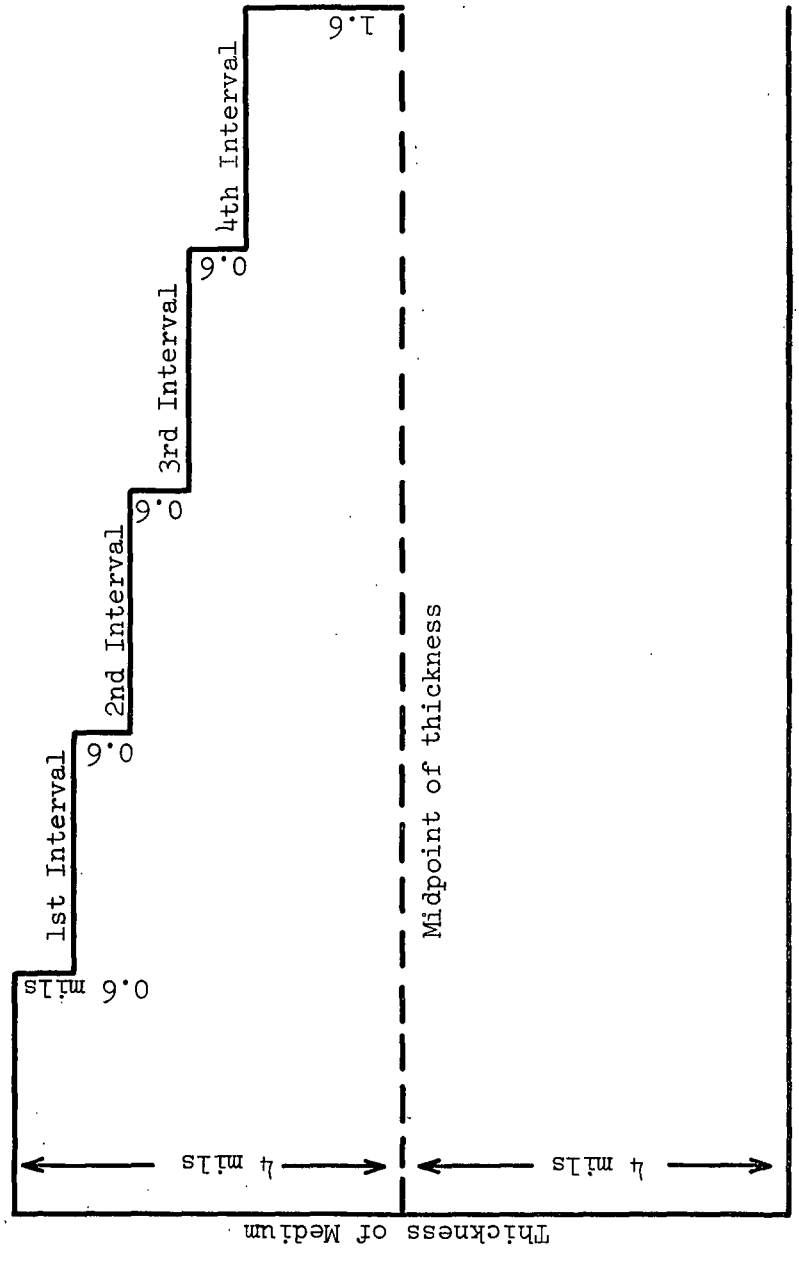


Figure 8. Cross-Sectional Diagram of Grinding Intervals for Starch and Water Distribution Analyses

TABLE IV

ADHESIVE VOLUME DISTRIBUTION IN CALENDERED MEDIUMS BASED ON STARCH

Medium	Description	Contact Time, sec.	Total Adhesive Volume, cc./M²	Adhesive Volume at Given Depth Intervals, cc./M²				
				0.0-0.6 Mils	0.6-1.2 Mils	1.2-1.8 Mils	1.8-2.4 Mils	2.4+ Mils
No. 5196 felt	Smooth receptive	0.06	13.24	7.82	2.83	1.51	1.08	0.00
		0.60	12.81	3.82	5.53	0.78	2.68	0.00
No. 5196 wire	Rough receptive	0.06	12.93	7.10	1.39	2.50	0.82	1.12
		0.60	13.13	6.09	2.63	1.32	1.79	1.30
No. 5111 felt	Rough nonreceptive	0.06	7.91	2.14	2.34	2.14	1.05	0.24
		0.60	8.25	1.92	3.09	2.07	0.41	0.76

TABLE V

LIQUID ADHESIVE VOLUME DISTRIBUTION IN CALENDERED MEDIUMS BASED ON FLUORESCENCE

Medium	Description	Contact Time, sec.	Total Liquid Volume, cc./M²	Liquid Volume at Given Depth Intervals, cc./M²				
				0.0-0.6 Mils	0.6-1.2 Mils	1.2-1.8 Mils	1.8-2.4 Mils	2.4+ Mils
No. 5196 felt	Smooth receptive	0.06	19.92	2.52	1.83	3.51	9.62	2.44
		0.60	19.28	1.65	3.77	3.33	9.71	0.82
No. 5196 wire	Rough receptive	0.06	19.83	1.91	4.43	0.85	11.59	1.05
		0.60	21.08	2.40	4.99	6.64	5.77	1.28
No. 5111 felt	Rough nonreceptive	0.06	13.98	1.28	0.70	4.14	7.80	0.06
		0.60	15.43	1.75	1.73	4.76	6.96	0.23

TABLE VI

PERCENTAGE ADHESIVE DISTRIBUTION IN CALENDERED MEDIUMS BASED ON STARCH

Medium	Description	Contact Time, sec.	Total Adhesive Volume, cc./M^2	Percentage of Adhesive at Given Depth Intervals				
				0.0-0.6 Mils	0.6-1.2 Mils	1.2-1.8 Mils	1.8-2.4 Mils	2.4+ Mils
No. 5196 felt	Smooth receptive	0.06	13.24	59.07	21.37	11.40	8.16	0.00
		0.60	12.81	29.82	43.17	6.09	20.92	0.00
No. 5196 wire	Rough receptive	0.06	12.93	54.91	10.75	19.33	6.34	8.66
		0.60	13.13	46.38	20.03	10.05	13.63	9.90
No. 5111 felt	Rough nonreceptive	0.06	7.91	27.05	29.58	27.05	13.27	3.03
		0.60	8.25	23.27	37.45	25.09	4.97	9.21

TABLE VII

PERCENTAGE LIQUID ADHESIVE DISTRIBUTION IN CALENDERED MEDIUMS BASED ON FLUORESCENCE

Medium	Description	Contact Time, sec.	Total Liquid Volume, cc./M^2	Percentage of Liquid at Given Depth Intervals				
				0.0-0.6 Mils	0.6-1.2 Mils	1.2-1.8 Mils	1.8-2.4 Mils	2.4+ Mils
No. 5196 felt	Smooth receptive	0.06	19.92	12.65	9.19	17.62	48.29	12.25
		0.60	19.28	8.56	19.56	17.27	50.36	4.25
No. 5196 wire	Rough receptive	0.06	19.83	9.63	22.34	4.29	58.45	5.30
		0.60	21.08	11.39	23.67	31.50	27.37	6.07
No. 5111 felt	Rough nonreceptive	0.06	13.98	9.16	5.01	29.61	55.79	0.43
		0.60	15.43	11.34	11.21	30.85	45.11	1.49

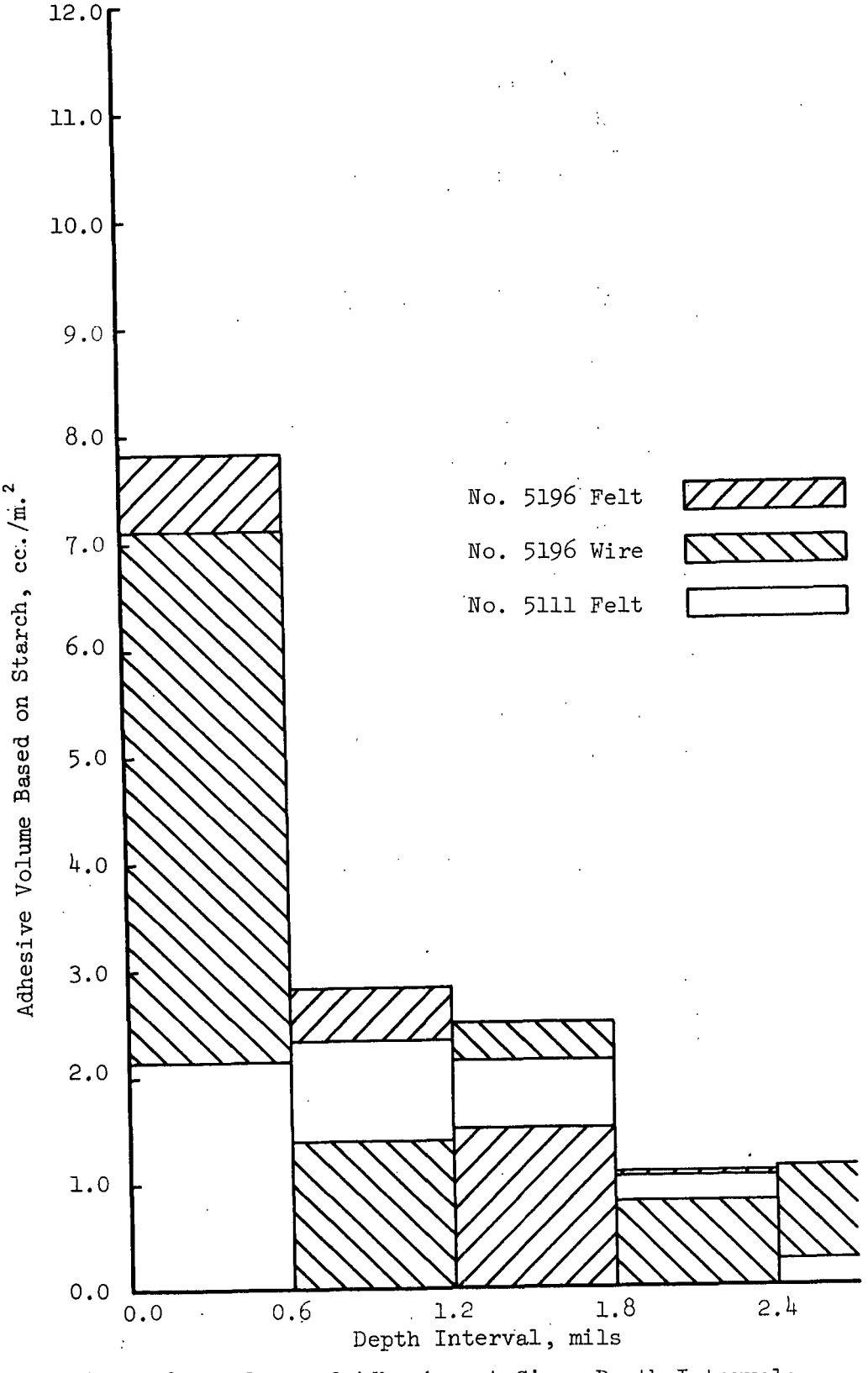


Figure 9. Volume of Adhesive at Given Depth Intervals (Contact Time, 0.06 sec.)

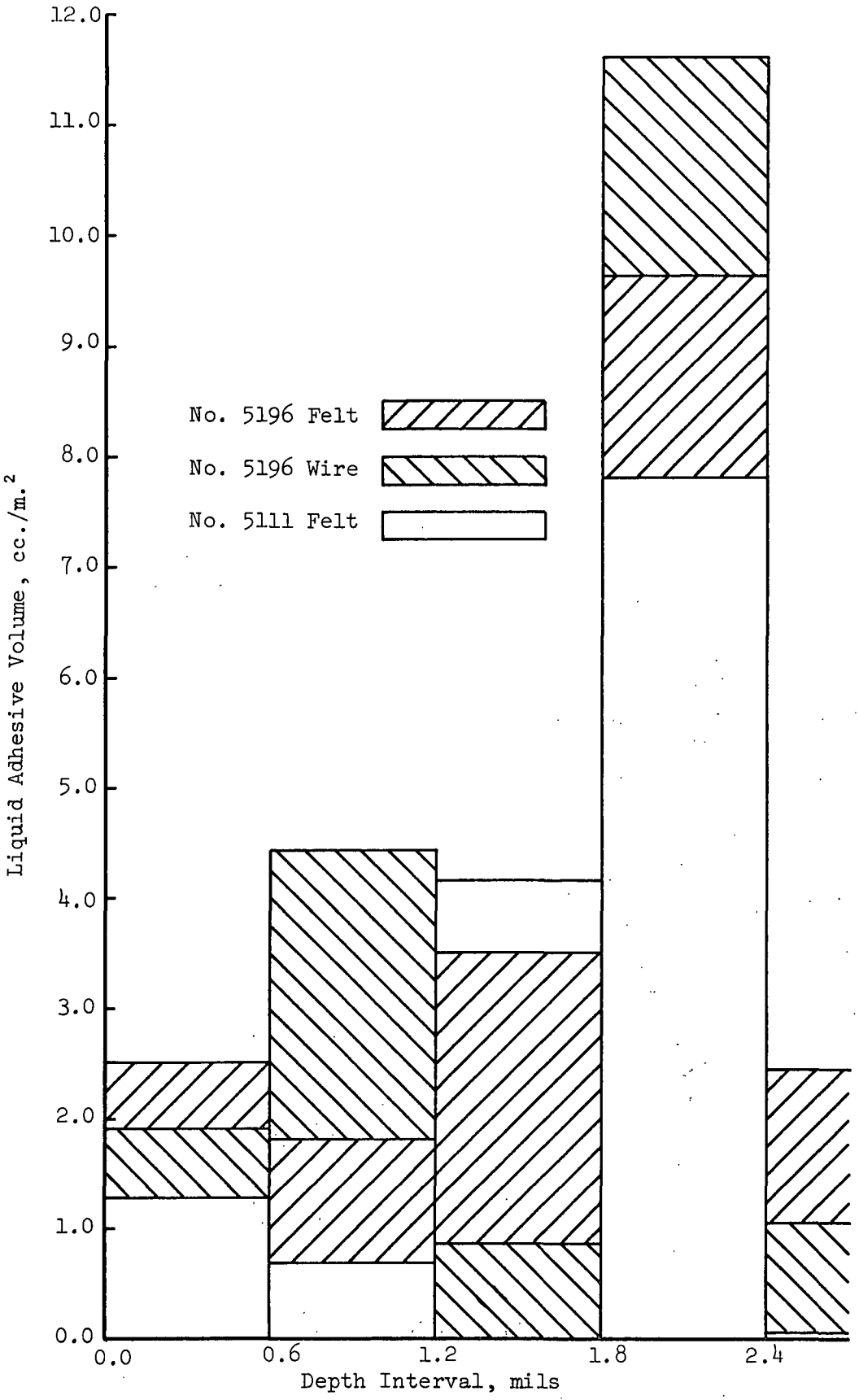


Figure 10. Volume of Liquid at Given Depth Intervals (Contact Time, 0.06 sec.)

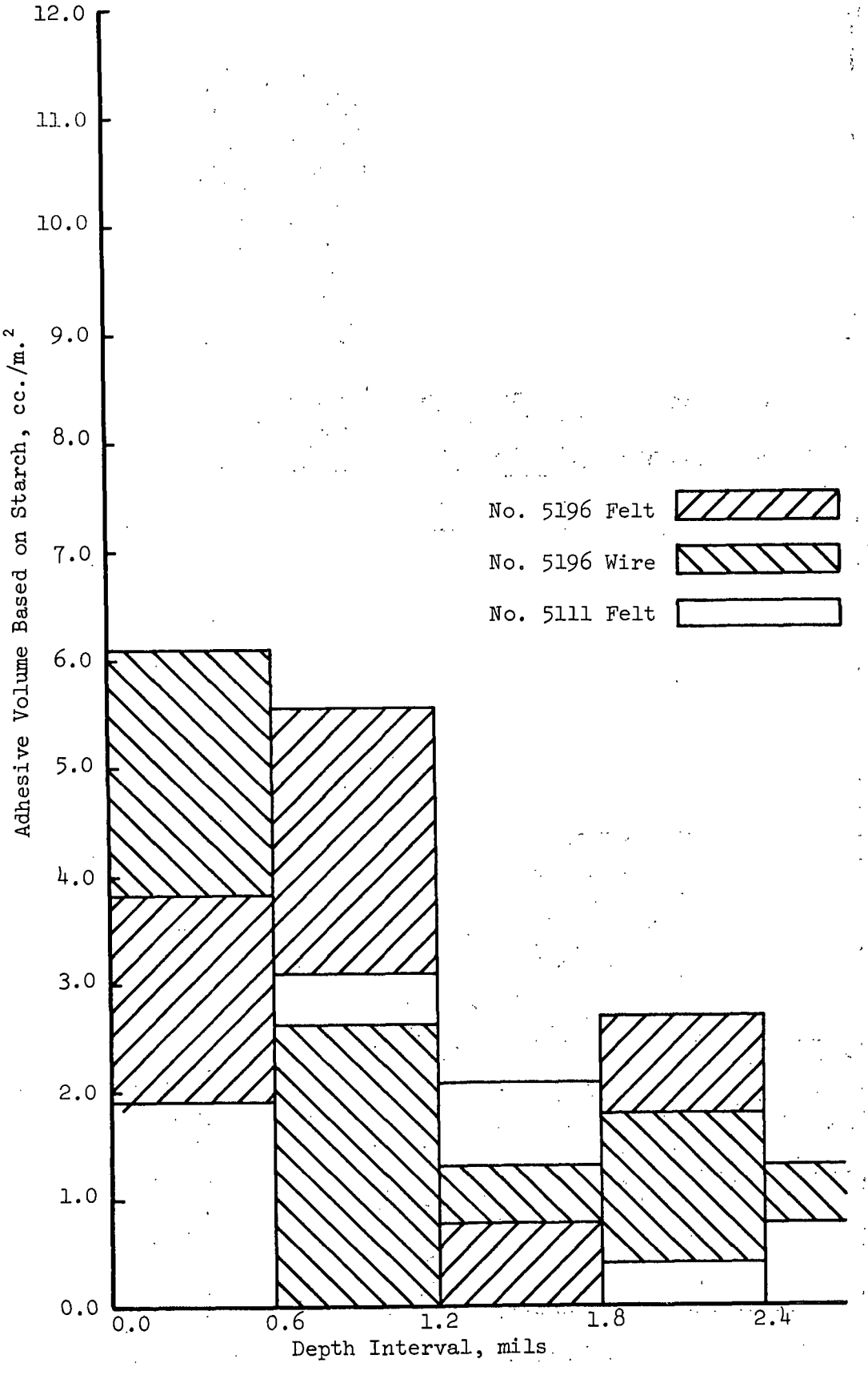


Figure 11. Volume of Adhesive at Given Depth Intervals (Contact Time, 0.6 sec.)

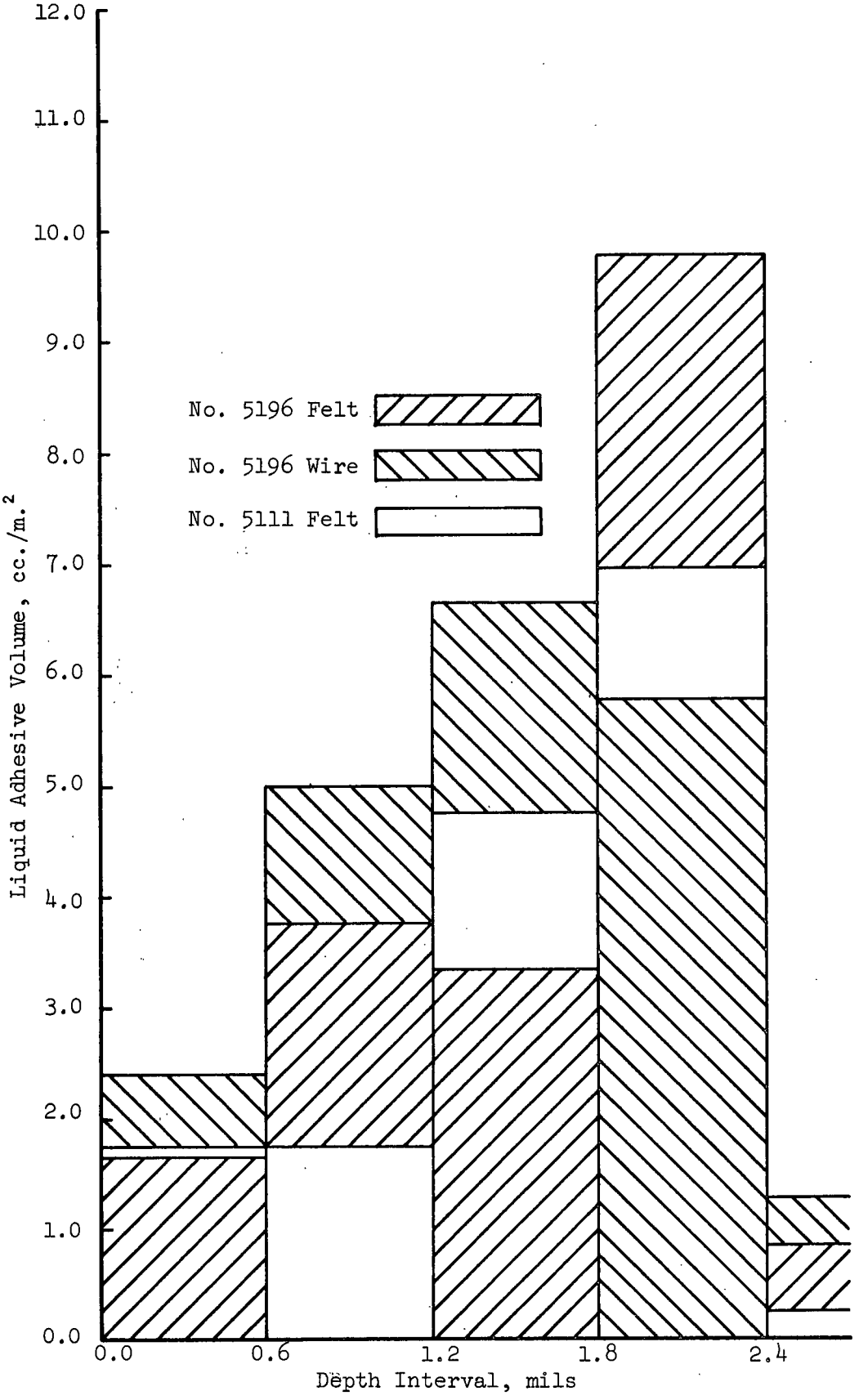


Figure 12. Volume of Liquid at Given Depth Intervals (Contact Time, 0.6 sec.)

TABLE VIII

A SUMMARY OF ADHESIVE VOLUME DATA

Medium	Description	Contact Time, sec.	Adhesive Volume, cc./M^2 based on starch-iodine	Liquid Volume, cc./M^2 based on fluorescence	$\Delta\underline{V}$, cc./M^2	Ratio of Volumes Fluorescence/ Starch-Iodine
5196 felt	Smooth receptive	0.06	13.24	19.92	6.68	1.50
		0.60	12.81	19.28	6.47	1.50
5196 wire	Rough receptive	0.06	12.93	19.83	6.90	1.53
		0.60	13.13	21.08	7.95	1.60
5111 felt	Rough nonreceptive	0.06	7.91	13.93	6.07	1.77
		0.60	8.25	15.43	7.15	1.88

PHYSICAL FORM OF THE STARCH ADHESIVE IN TREATED MEDIUM

Photomicrographs were prepared of medium treated on the adhesive immobilization device at a contact time of 0.06 sec. in an effort to establish the physical form of the starch at the surface and within the medium. For this purpose photomicrographs were prepared of microtome cross sections and of surface views at various depth intervals. Specimens for the surface views were first stained with iodine in KI solution and then photographed at 230X utilizing Epi-illumination and polarized light.

Microtome sections were prepared as follows. Strips of the sample approximately 1/4 x 1/2 inch were placed in No. 00 gelatin capsules containing inhibitor-free butyl methacrylate resin plus catalyst (benzoyl peroxide). The capsules were placed in an oven overnight at 45-50°C. for polymerization of the resin. The gelatin was removed from the embedded sample and the hardened methacrylate specimen placed in the microtome holder. Cross sections were prepared at a thickness of 10 to 12 μm. The sections were then mounted on glass slides in iodine-KI solution in preparation for viewing under the microscope. Photomicrographs were prepared at 185X.

Photomicrographs of the receptive medium are presented in Fig. 13-24. Photomicrographs of the nonreceptive medium are presented in Fig. 25-30.

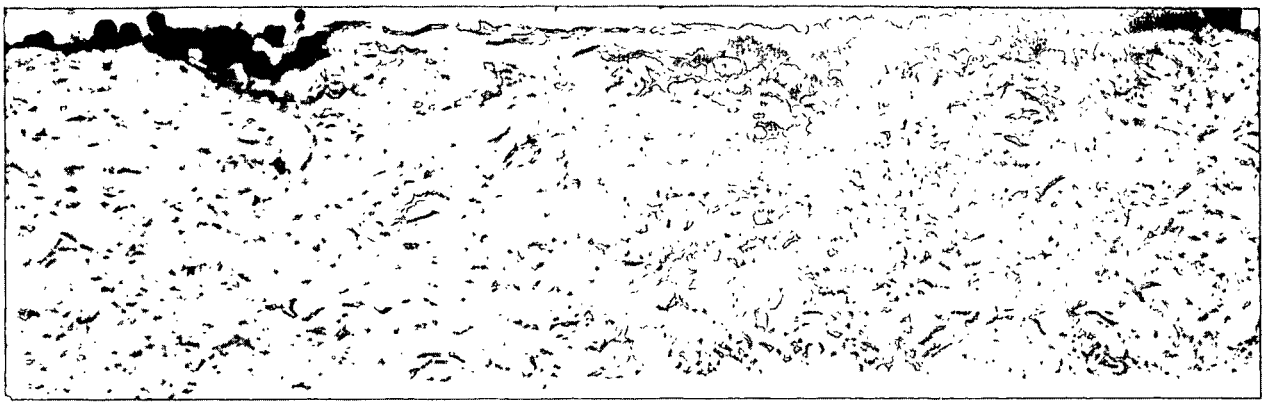


Figure 13. Cross Section, Smooth Receptive Medium, 185X

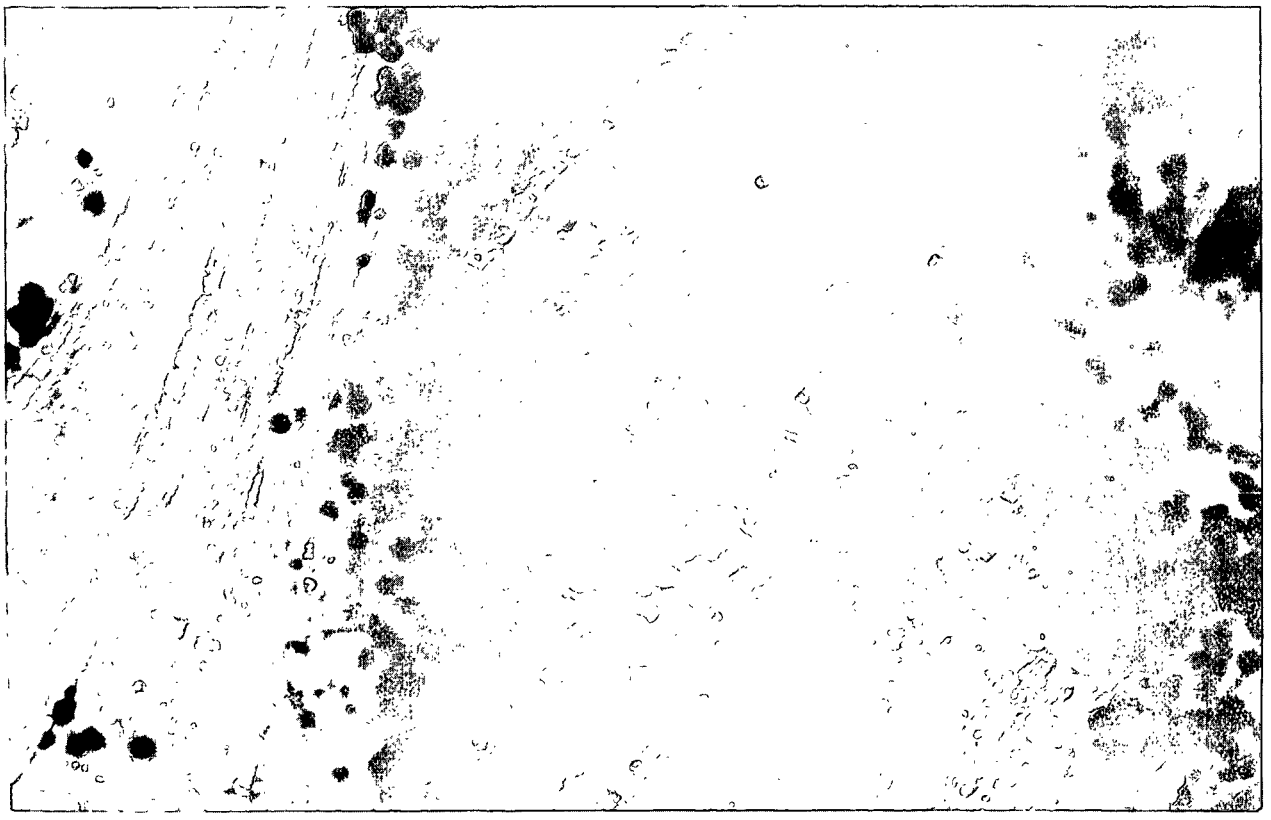


Figure 14. Surface View, Smooth Receptive Medium, Full Thickness, 230X

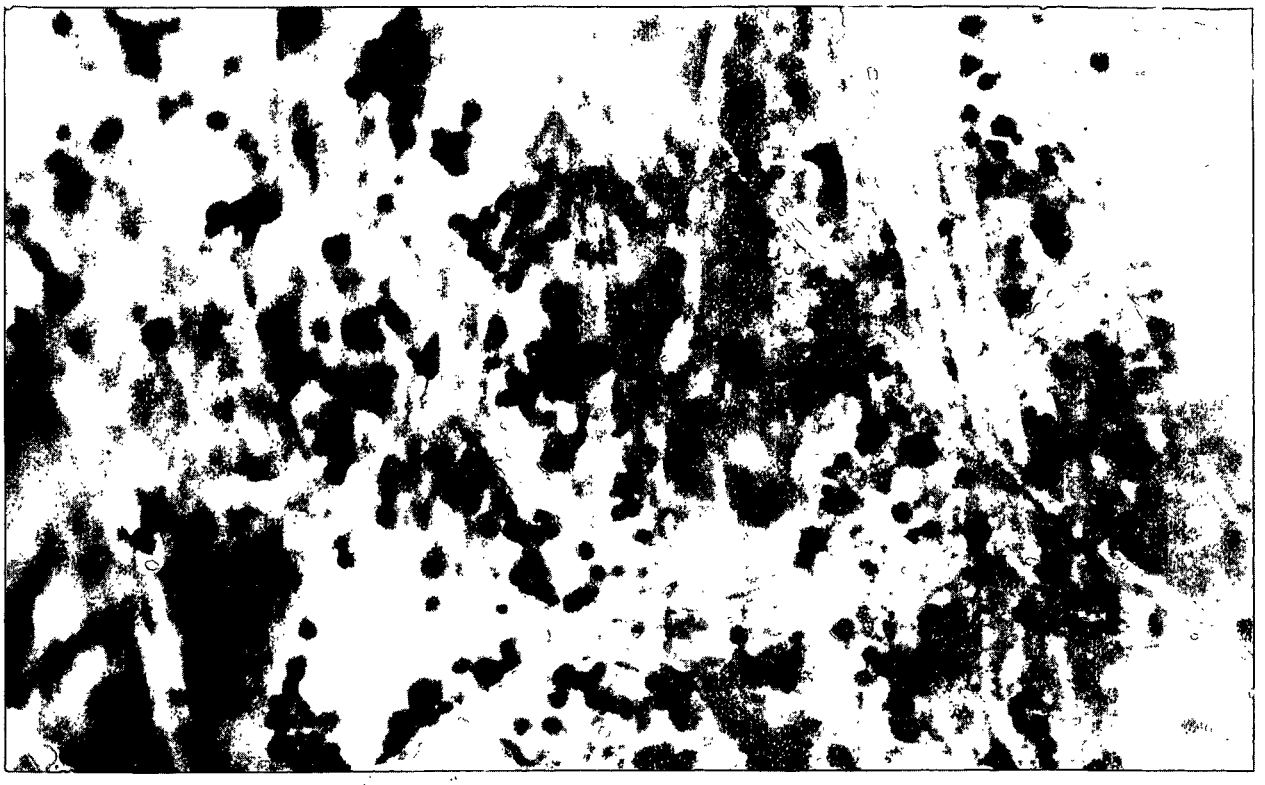


Figure 15. Surface View, Smooth Receptive Medium, 0.6-Mil Depth, 230X

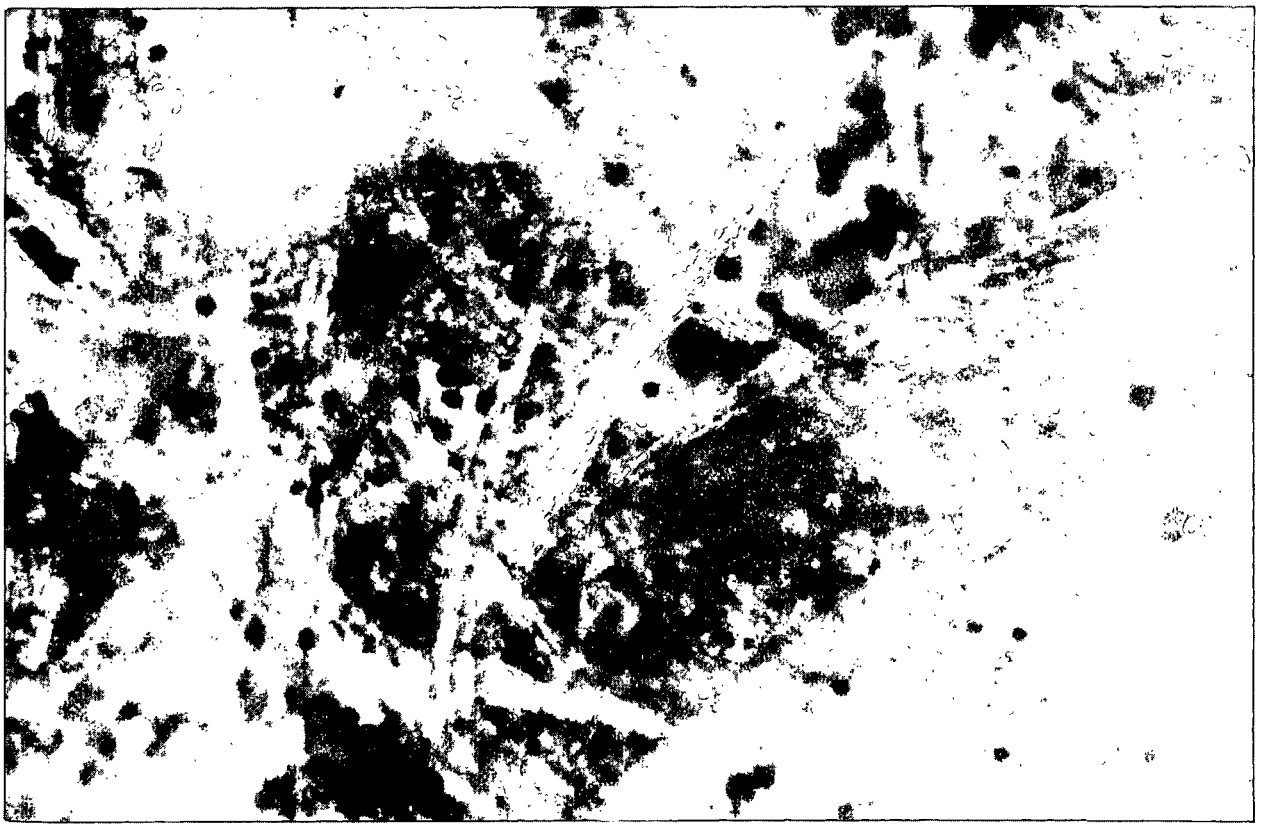


Figure 16. Surface View, Smooth Receptive Medium, 1.2-Mil Depth, 230X

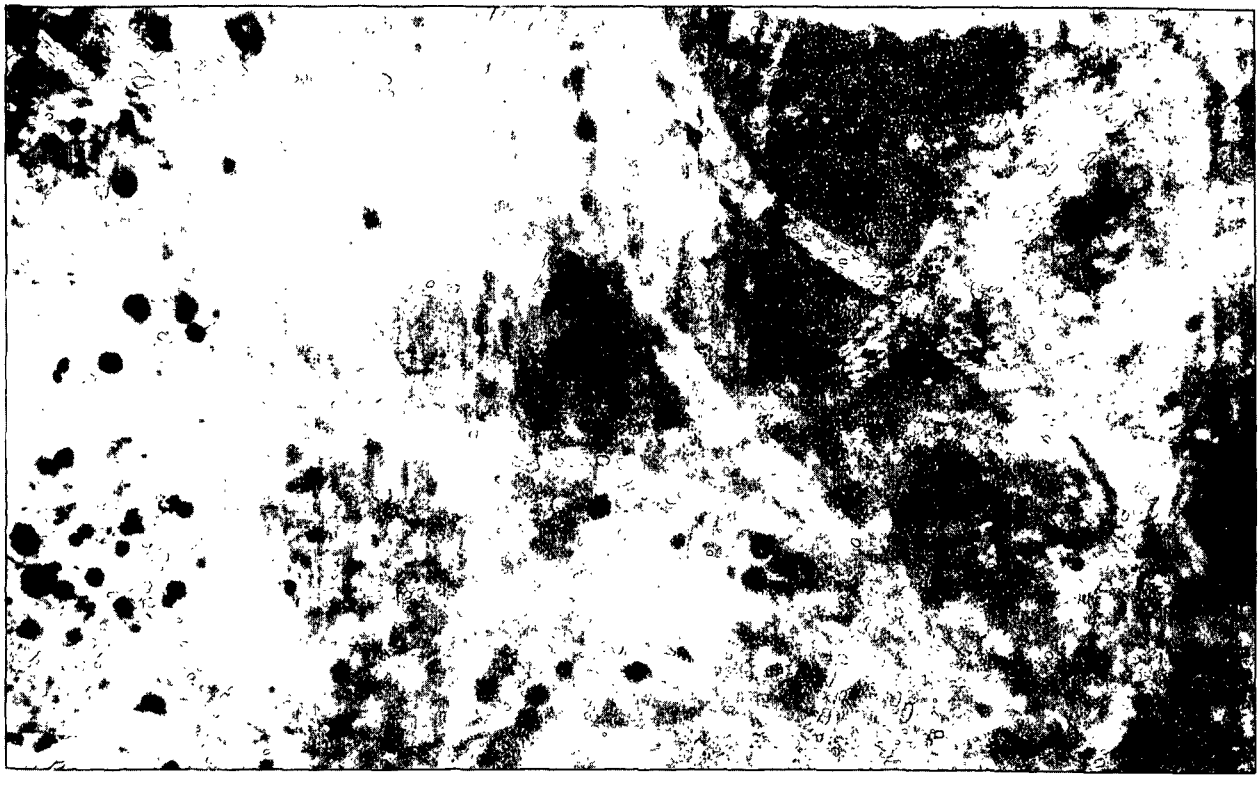


Figure 17. Surface View, Smooth Receptive Medium
1.8-Mil Depth, 230X

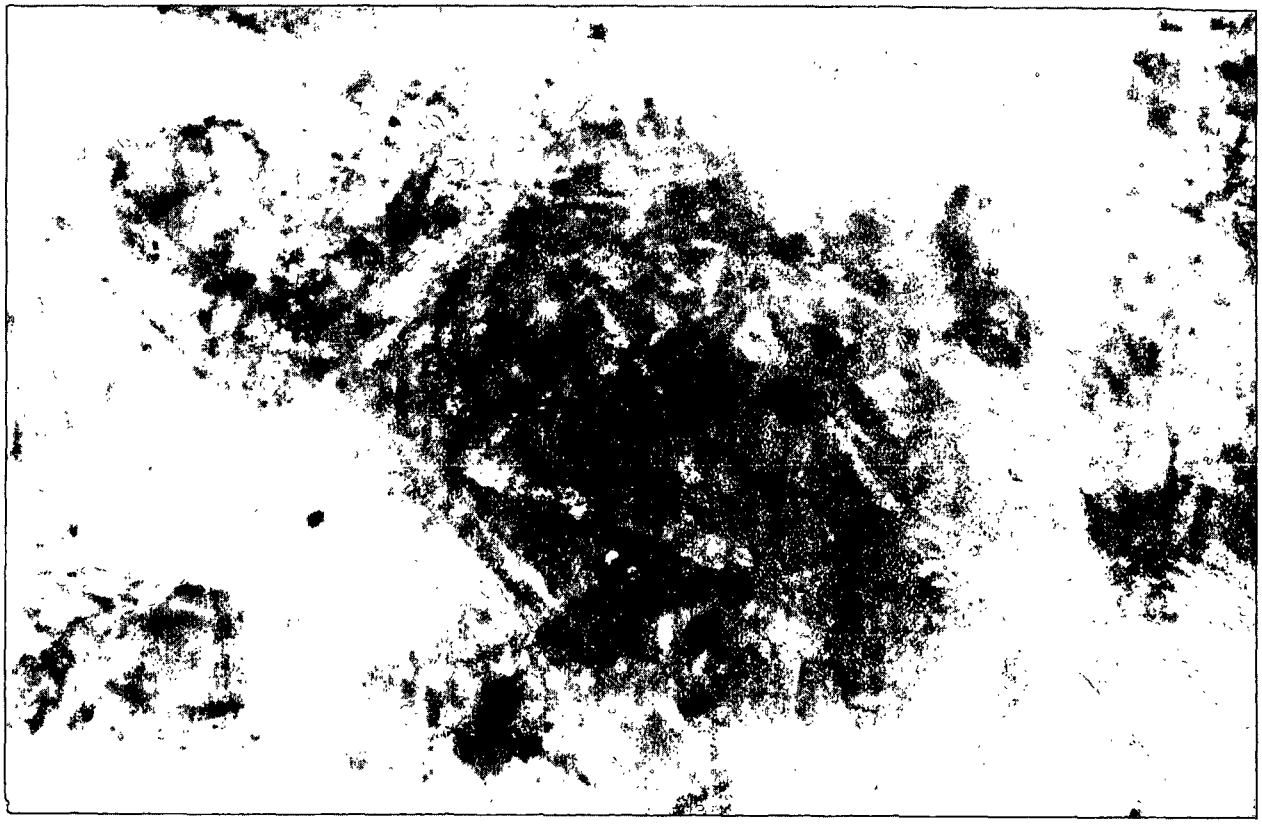


Figure 18. Surface View, Smooth Receptive Medium,
2.4-Mil Depth, 230X

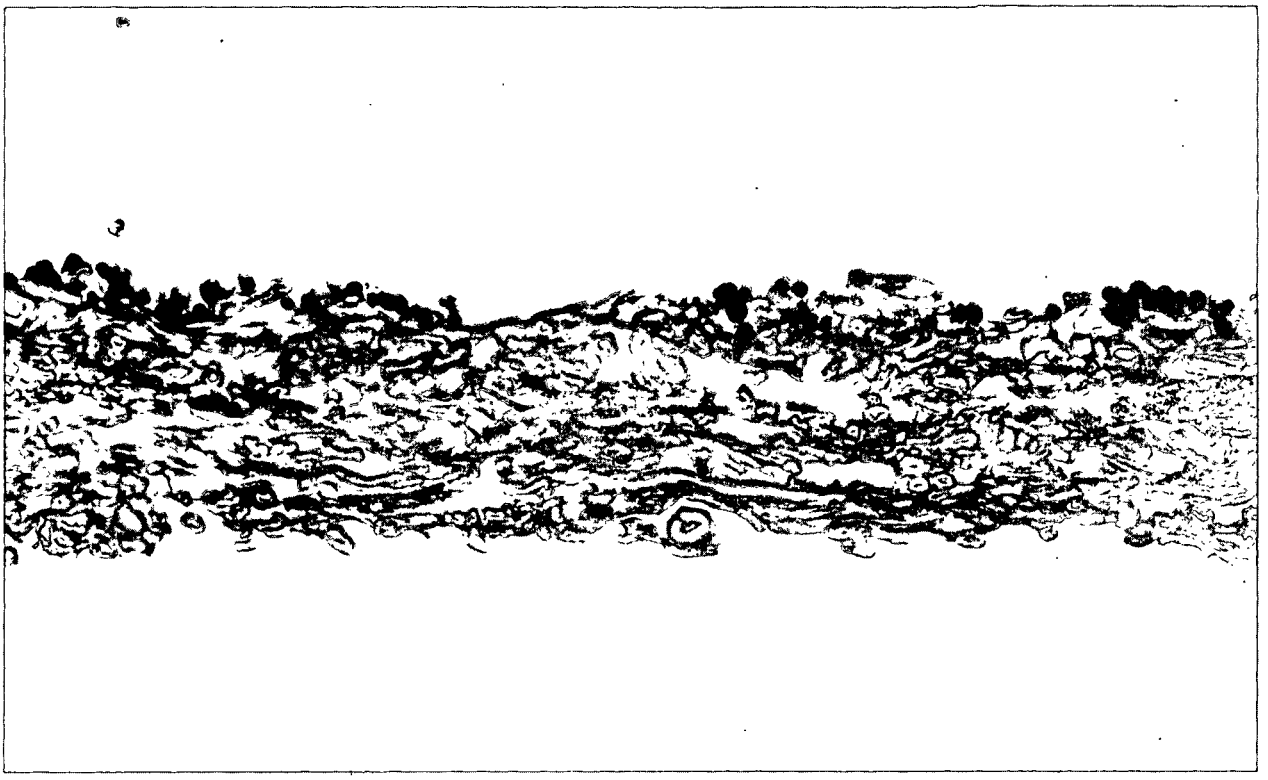


Figure 19. Cross Section, Rough Receptive Medium, 185X

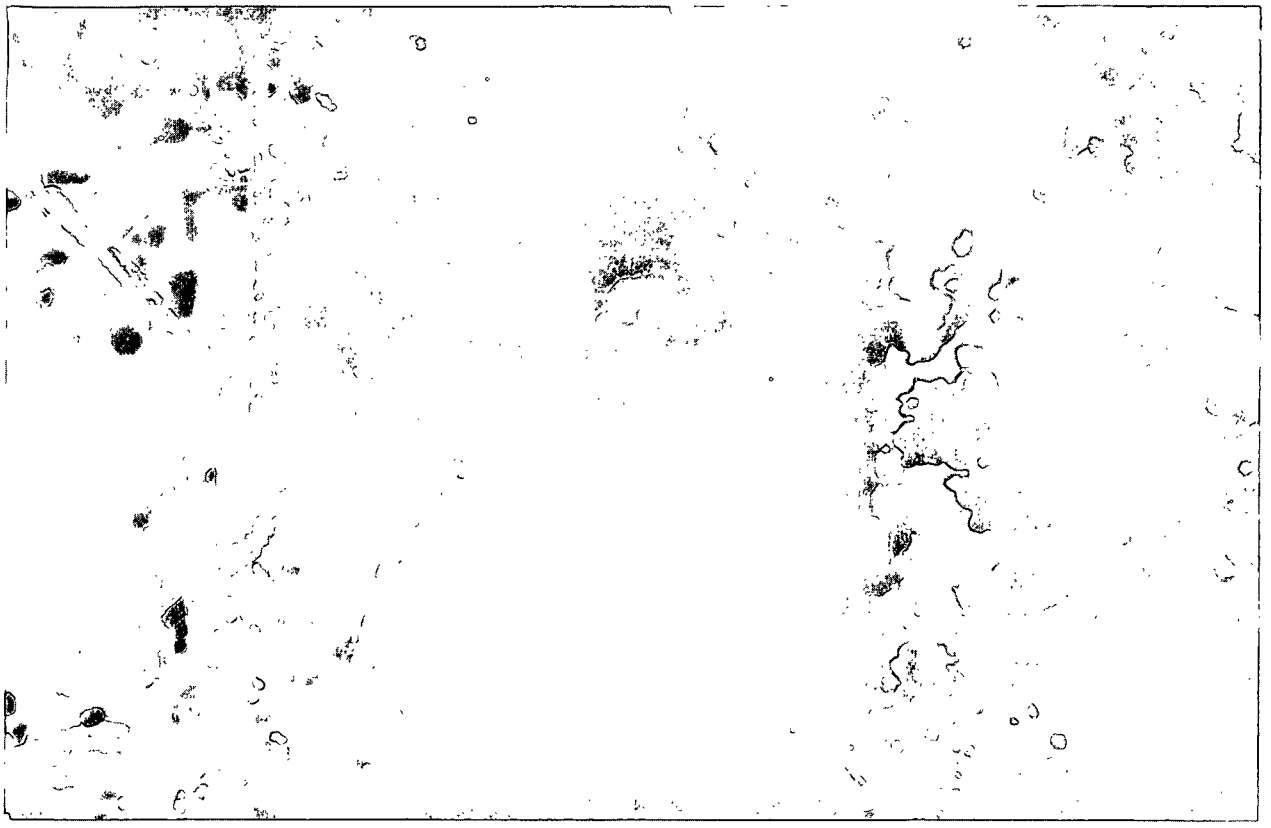


Figure 20. Surface View, Rough Receptive Medium, Full Thickness, 230X

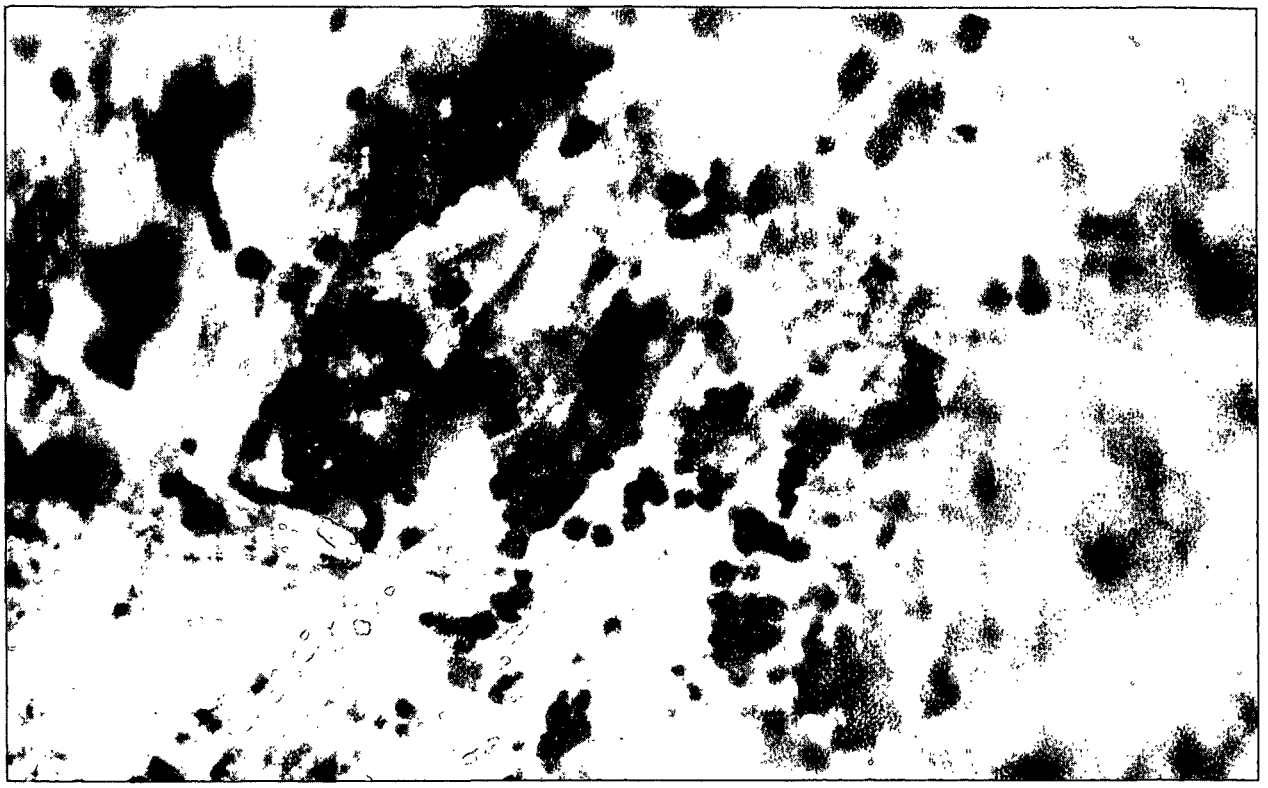


Figure 21. Surface View, Rough Receptive Medium, 0.6-Mil Depth, 230X

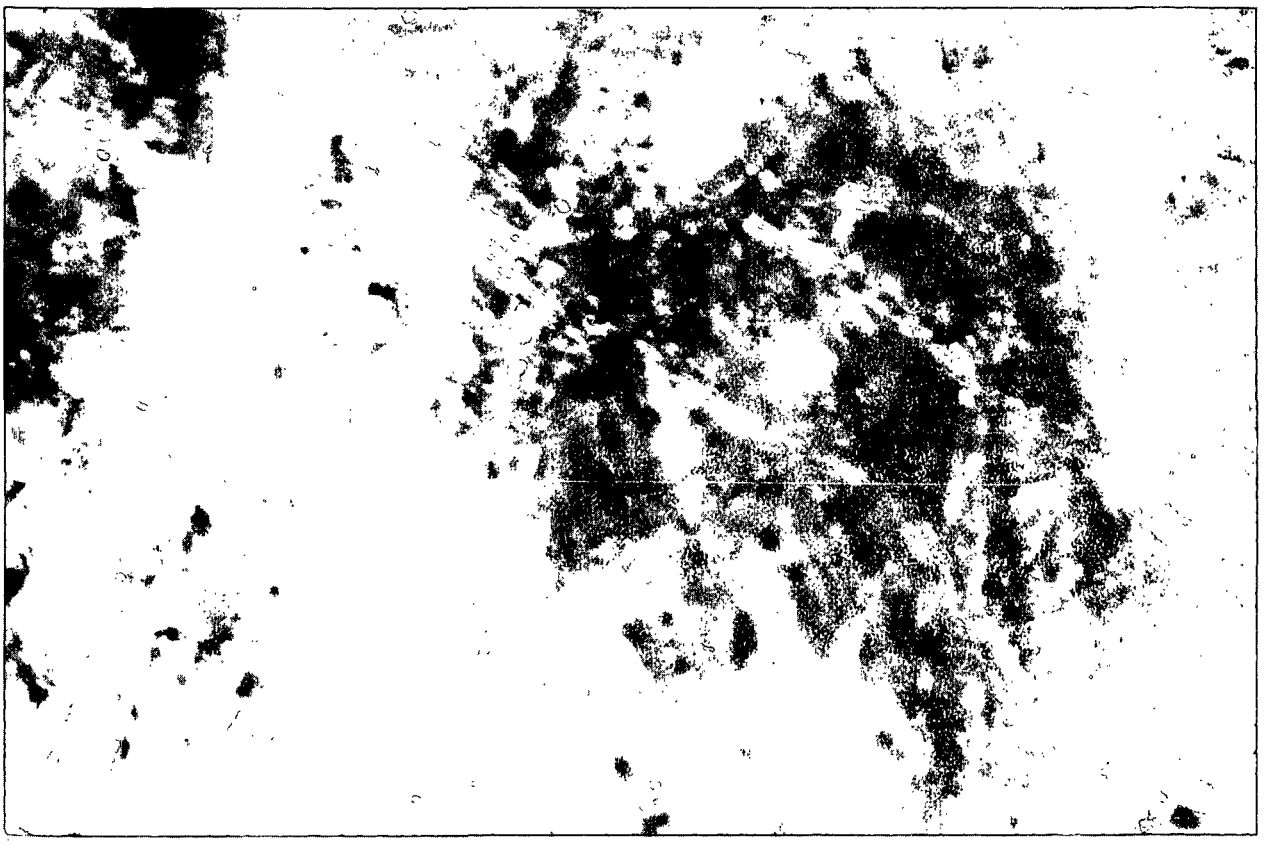


Figure 22. Surface View, Rough Receptive Medium, 1.2-Mil Depth, 230X

Figure 23. Surface View, Rough Receptive Medium, 1.8-Mil Depth, 230X

Figure 24. Surface View, Rough Receptive Medium, 2.4-Mil Depth, 230X

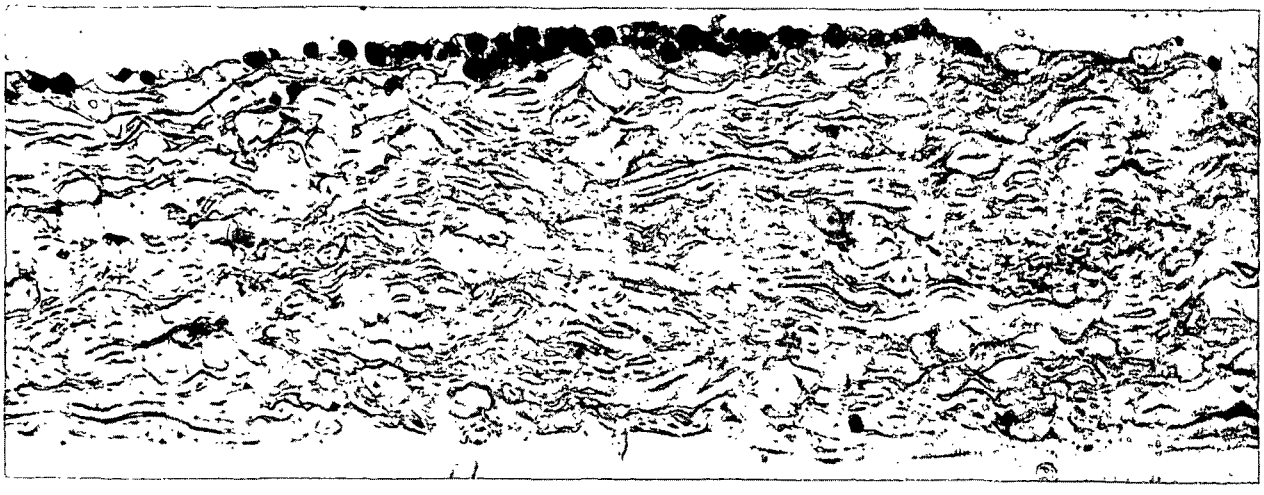


Figure 25. Cross Section, Rough Nonreceptive Medium, 185X

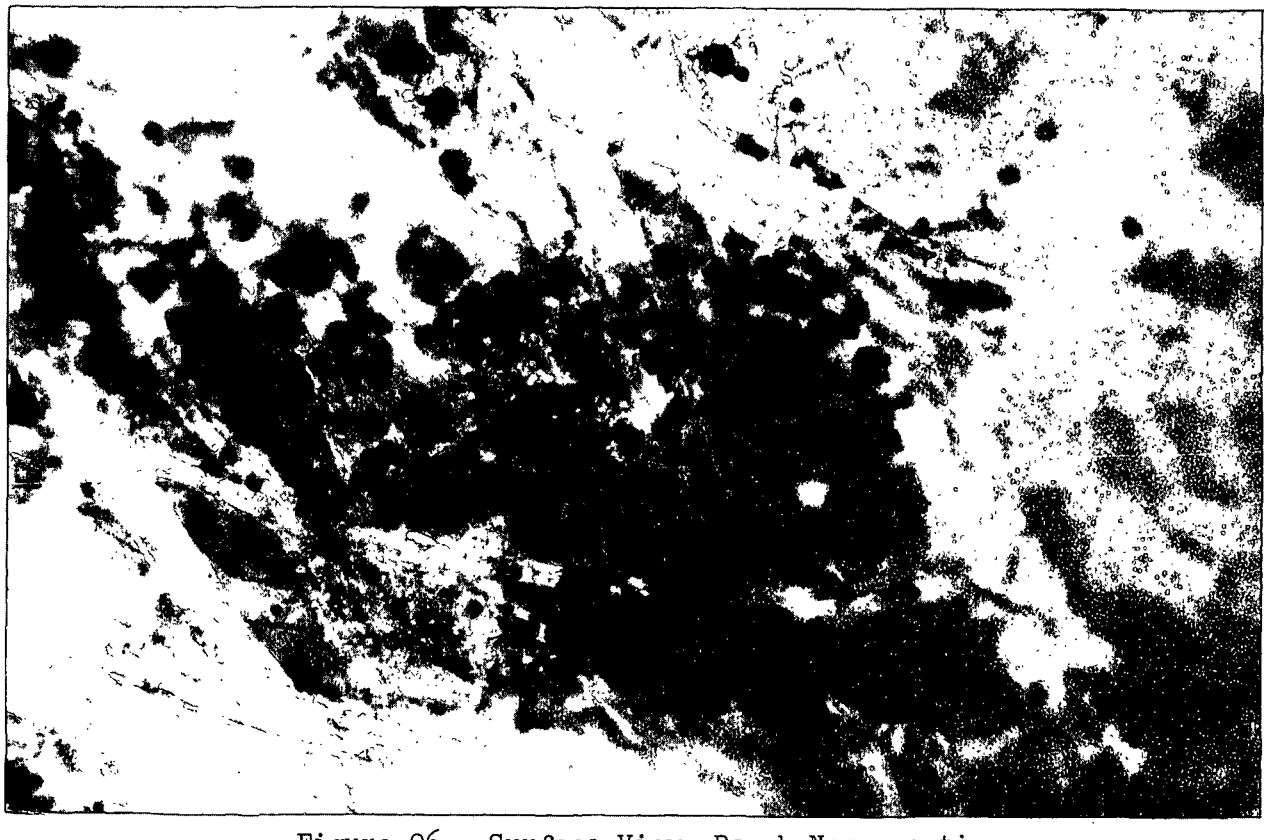


Figure 26. Surface View, Rough Nonreceptive Medium, Full Thickness, 230X

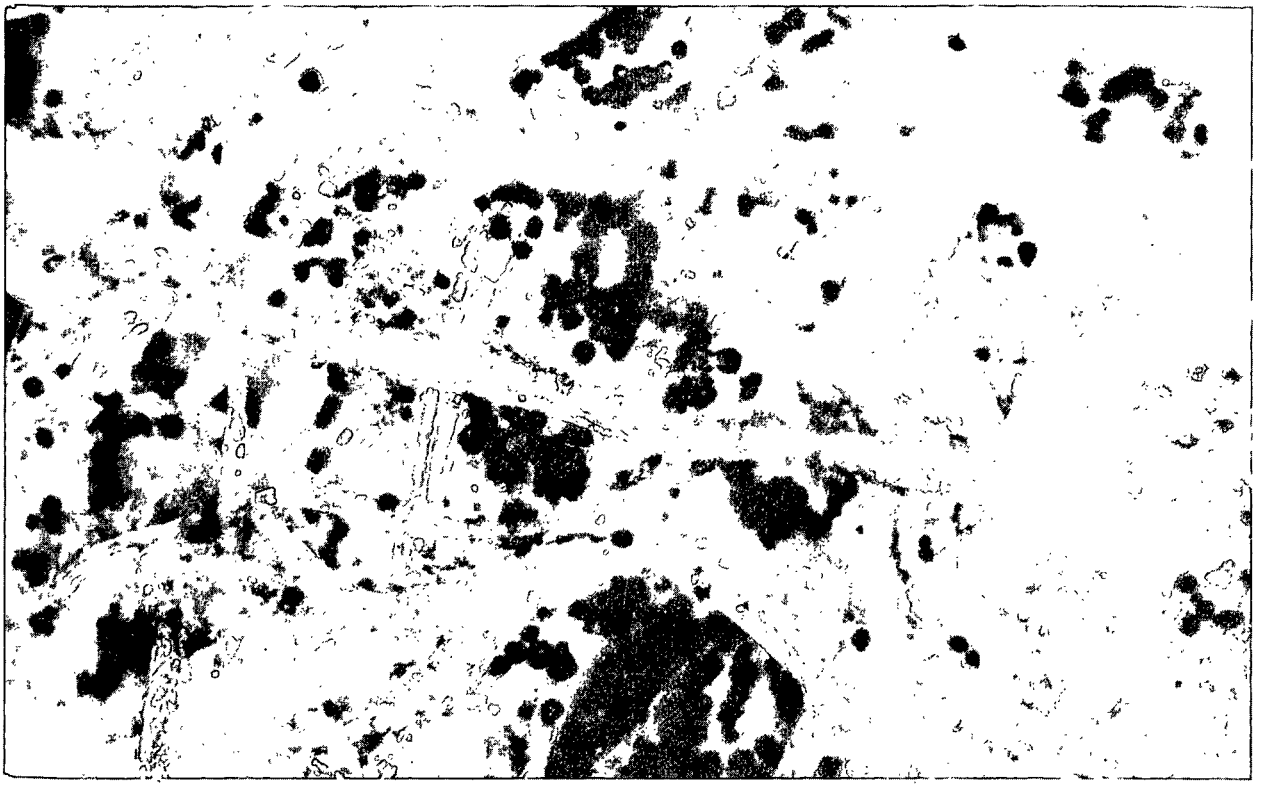


Figure 27. Surface View, Rough Nonreceptive Medium, 0.6-Mil Depth, 230X

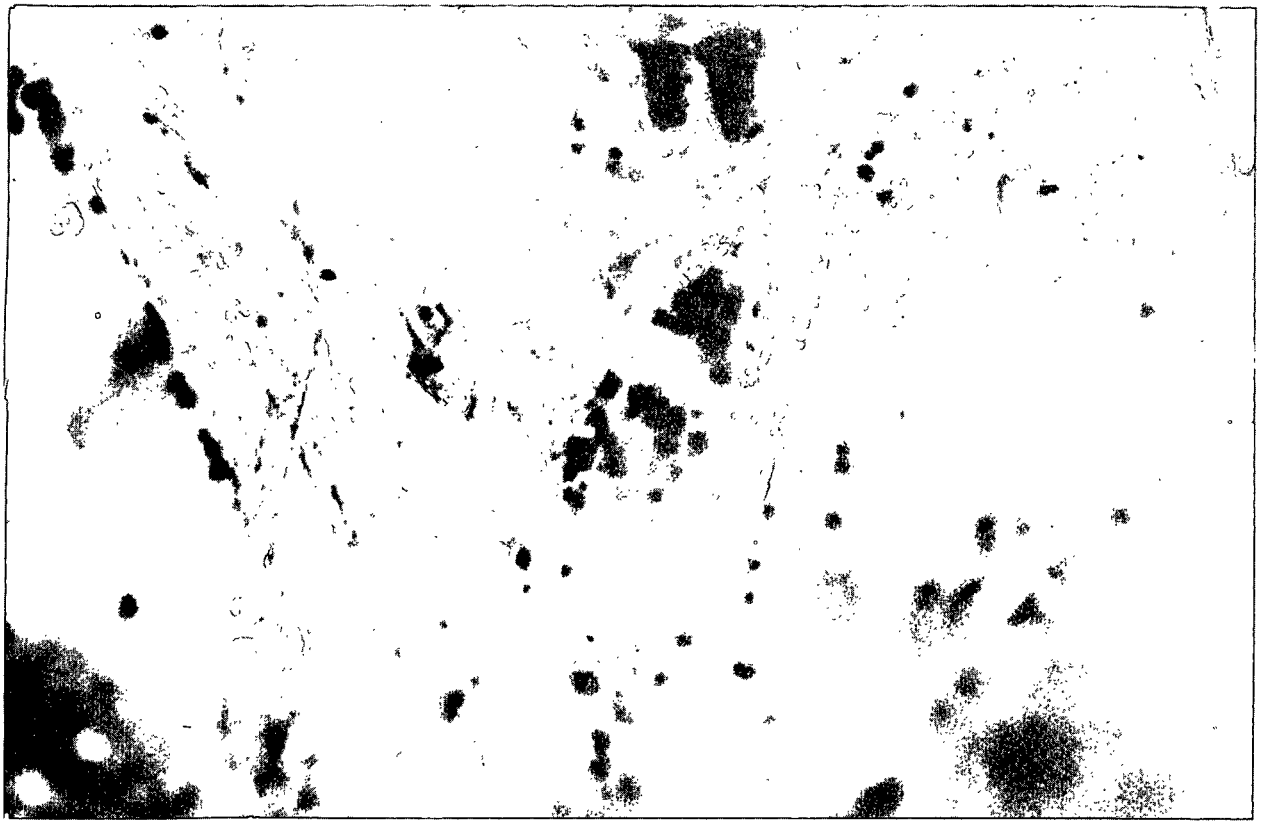


Figure 28. Surface View, Rough Nonreceptive Medium, 1.2-Mil Depth, 230X

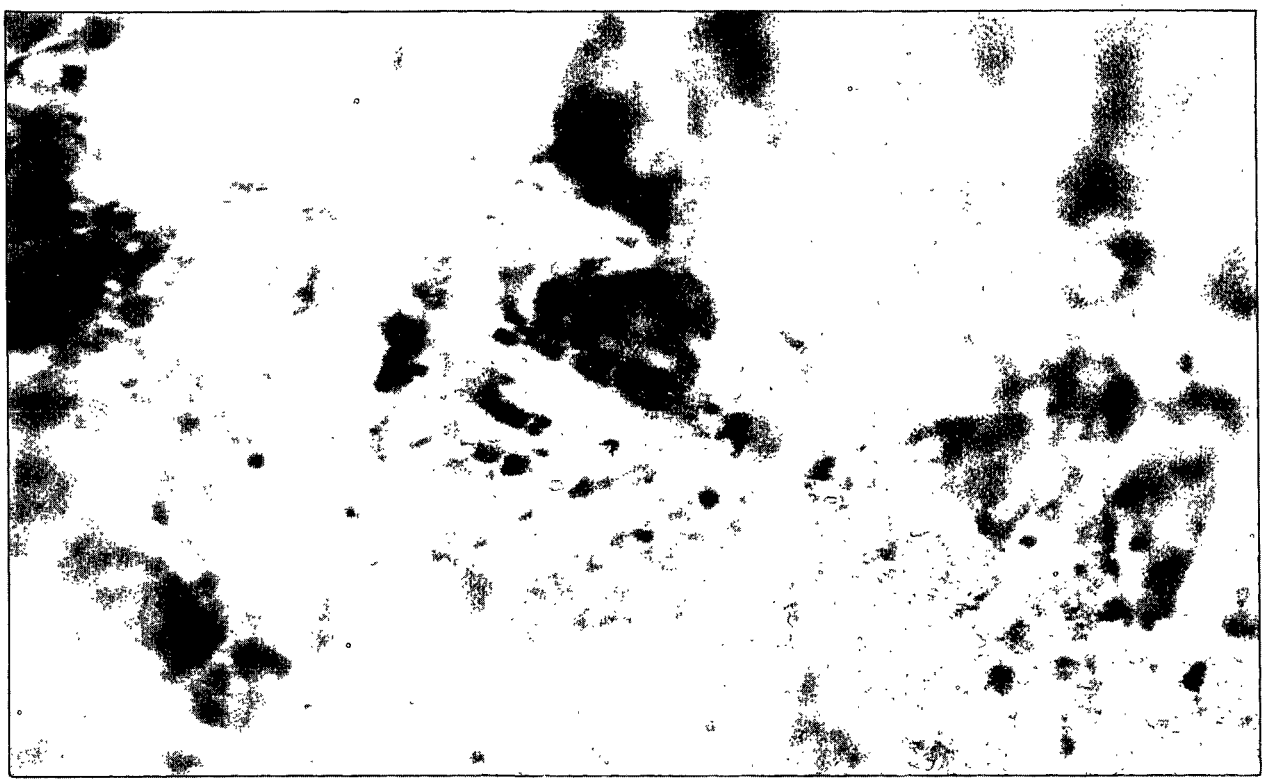


Figure 29. Surface View, Rough Nonreceptive Medium, 1.8-Mil Depth, 230X

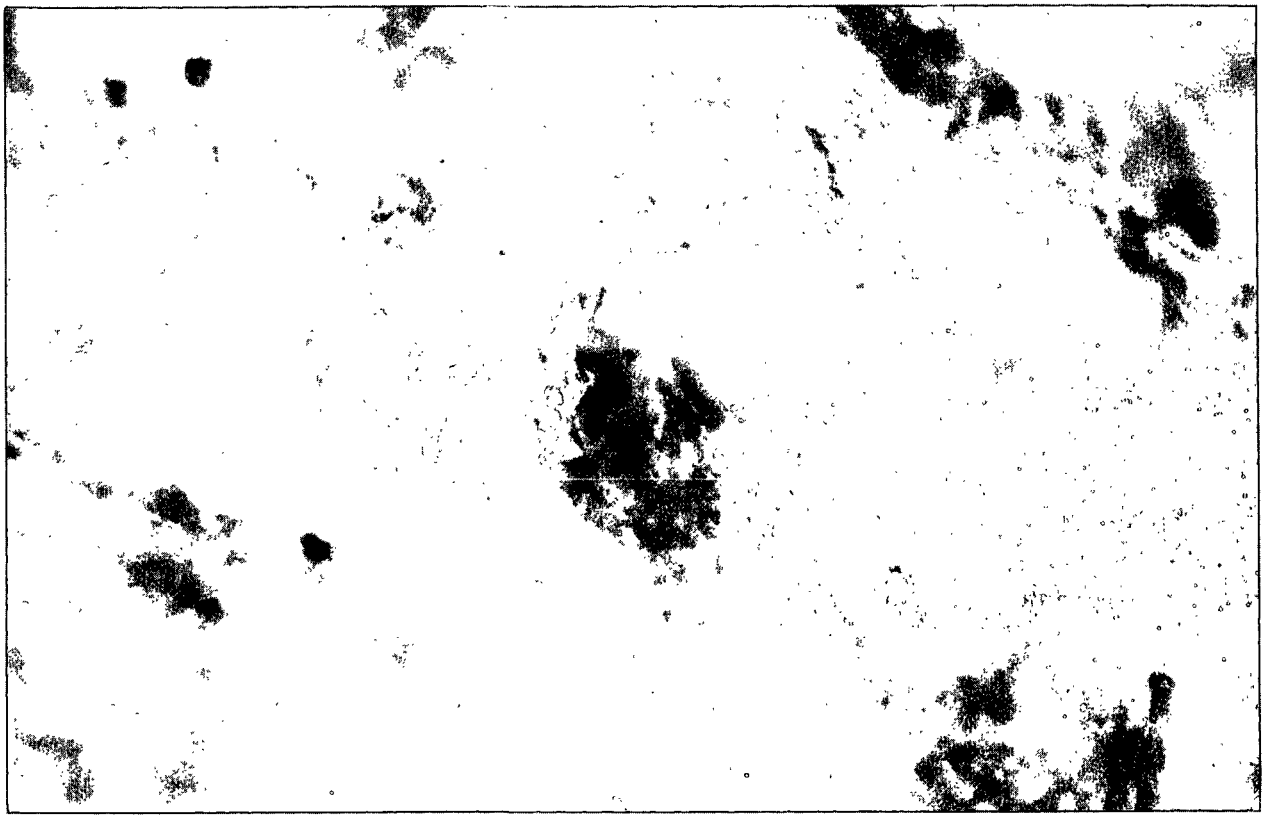


Figure 30. Surface View, Rough Nonreceptive Medium, 2.4-Mil Depth, 230X

DISCUSSION OF RESULTS

Calendering was found to have a roughly equal effect on the two mediums with respect to changes in caliper and density (Table I). Caliper was decreased 32-33% and density was increased 44-47%. The nonreceptive medium (No. 5111) underwent a slightly greater change in both properties. It will be of interest to note that the caliper of the freeze-dried samples from the starch immobilization device was 7.5 mils compared to an original thickness of 9.9-10.3 mils before calendering. Hence, application of the adhesive did not result in a spontaneous swelling to match the original thickness of the uncalendered medium. Conceivably, some localized swelling occurred in the surface region which did not produce a substantial increase in total thickness.

The effect of calendering became more appreciable in air permeability (Bendtsen porosity) wherein the nonreceptive medium showed a 65% reduction compared to 51% for the receptive medium. Hence, the receptive medium maintained a notably higher permeability level after calendering. In so far as mercury intrusion porosity is concerned, the results in Fig. 1 to 4 reveal that calendering effected a marked reduction in cumulative pore volume and a reduction in the frequency of the larger pores. A shift in the number and size of the most frequent pores from the range of 5 to 15 μm. down to 2 to 10 μm. is also indicated. Calendering had little effect on pore sizes smaller than 3 to 4 μm. except for elimination of some pores at 1-2 μm. Hence, as might be expected, calendering appears to have its greatest effect on the larger surface pores.

Wettability tests (water drop and contact angle) again show a marked difference in the receptivity of the two mediums. In general, calendering had little effect on these results with the exception of a slightly higher contact

angle against starch on the rough side of the receptive medium. Some decline in receptivity might be expected as a result of the natural aging of the medium.

Air escape smoothness was greatly increased (Bendtsen smoothness value decreased) as a result of calendering in all cases with the "smooth" surface maintaining its relative position. This would be in agreement with the reduction in the number of large surface pores indicated by the mercury intrusion data. Calendering produced a notable reduction in surface bonding strength particularly for the rough surfaces, possibly suggesting rupture of some surface fibers and fiber bonds which could result in reduced pin adhesion.

The total adhesive volumes recorded in Tables IV and V show marked differences in the amount of adhesive accepted by the two mediums and in the amount measured by the two analytical methods. The lower volumes accepted by Medium No. 5111 is attributed to lower receptivity and, in this respect, the current results parallel those given in Report One for the uncalendered medium. However, calendering reduced differences in roughness to the point where both sides of the receptive medium retained approximately equal volumes of adhesive as measured by the two analytical methods.

The notable difference in the total adhesive volumes based on the two analytical methods indicates a pronounced initial classification of starch and water at the time of application. Presumably, uncooked starch is rejected at the nip in favor of water and possibly some cooked starch. The fact that the difference in adhesive volumes (Table VIII) is nearly constant suggests that this initial classification is probably not a function of some property of the medium but only of the application process. Since the total volume accepted by the nonreceptive medium was lower, the ratio of volumes on this substrate was somewhat

higher than on the other mediums. In effect, the nonreceptive medium accepted more water per unit of starch than the receptive surfaces.

Differences in adhesive volume retained by the calendered mediums at the two contact times were minor compared to that previously reported for the uncalendered mediums.

Results in Tables IV-VII and Fig. 9-12 indicate an additional classification of starch and water as a function of the depth of penetration. Most of the starch (56-82%) was retained within 1.2 mils of the surface regardless of the substrate whereas water (liquid) was found in greatest amounts (65-86%) beyond the 1.2-mil depth. By way of comparison, it is interesting to note that starch was able to penetrate the calendered medium to approximately one-half the depth encountered in the uncalendered medium (refer to Report One).

At the short contact time, the receptive medium retained the greatest concentration of starch within 0.6 mil of the surface whereas liquid (water) was found in greatest amounts at the 1.8-2.4 mil depth. The nonreceptive medium retained less starch at the surface but appears to retain more water in proportion to the starch in these regions. Increasing the contact time to 0.6 second resulted in a decrease in the amount of starch within the first depth interval (0.6 mil) and an increase in the 0.6-1.2 mil depth. The longer contact time did not result in as much of a redistribution of water as starch in the outer surface regions and, contrary to expectations, water appears to have penetrated beyond the 1.8-mil depth in greater amounts at 0.06 second contact than at 0.6 second contact. It appears that some redistribution of water occurred in the middle depth intervals at the longer contact time. Also, contrary to observations made in the capillary rise experiments, water migrated beyond the starch in the receptive medium.

The location of the uncooked portion of the starch adhesive is clearly shown by the dark-colored, spherelike spots in the photomicrographs (Fig. 13-30), however, the location of the cooked starch is not as apparent. This results from the preference of the uncooked starch granules for the iodine-KI stain. The cooked starch appears as a dark gray material frequently associated with the starch granules in the surface regions. A small amount of the dispersed starch was indicated to have penetrated away from the granules to about one-third the thickness of the test specimens. The latter effect is probably most evident in Fig. 13 where the cooked starch appears to flow away from the starch granules at the surface and follow the larger channels into the interior of the medium. The dark gray areas surrounding the uncooked starch granules in several of the surface views is also dispersed starch.

In agreement with the analytical results, the photomicrographs show that most of the starch is held at or near the surface of the medium. It would also appear that much of the starch is contained in large surface irregularities which, in some cases extend deeply into the medium. As a result, some of the starch is unavailable for bonding at the surface. The mercury intrusion data indicated that the most frequent pore size for the mediums fell in the range of 2-10 μm. but a smaller number of larger pores was also indicated. Most of the starch granules shown in the photomicrographs range in size from 5-15 μm. and are, therefore, small enough to enter not only the larger pores but also some of the smaller, more prevalent pores. A more highly swollen starch granule would not be able to enter some of these pores or cavities and should be better retained in the surface regions. It will be noted that the surface irregularities in the smooth reception medium (Fig. 13) appear to be more completely filled with starch than those in the rough surfaces. Hence, the smooth surface should provide for more intimate contact in corrugating provided the remainder of the surface is completely covered. The

coverage of the outer surfaces is shown to be incomplete in all cases although the relative amount available on the nonreceptive surface appears to be less than that on the receptive surfaces. This again is in agreement with the analytical results. It should be borne in mind that less starch was applied in this application than in practical corrugating, hence the amount available at the surface would also tend to be less. Also, examination under the microscope was limited to a few very small areas subject to considerable variation.

In terms of practical corrugating, the current results would tend to suggest that neither a highly sized nor a completely wettable medium would provide optimum adhesion from the reference starch adhesive. The rough nonreceptive medium retained relatively more water with the starch in the surface regions but the total amount of adhesive retained may be insufficient to provide adequate uniform contact for good adhesion. Under the influence of pressure in the corrugator the uncooked starch may tend to be classified to the outside of the flute tips leaving an insufficient supply at the center. The receptive medium, on the other hand, retained more starch at the surface but, because of the pronounced classification, the uncooked starch may be lacking sufficient water for proper gelation to occur within the short time interval. Further, some of the starch is lost in surface irregularities making it unavailable for bonding. The calendering which occurs in corrugating may weaken the surface of the medium, particularly the rough surfaces, which could lead to reduced pin adhesion. This would apply in particular to cases where starch penetration is inadequate to reinforce the weakened areas.

The smooth receptive surface again emerges as the most logical choice of the three examined but the present results indicate that this is probably not the optimum condition for bonding because the starch at the surface probably lacks water for effective gelation. Conceivably, what is needed for optimum pin adhesion

in so far as the medium is concerned is a reasonably smooth surface but one which has some sizing so that it accepts the adhesive uniformly but does not lose water too rapidly in the surface regions. With respect to the adhesive, a starch suspension containing moderately but uniformly gelled granules would not tend to lose water as readily.

FUTURE WORK

As indicated in the foregoing discussions, it would seem likely that neither a highly sized nor a completely wettable medium would provide optimum adhesion due to either poor acceptance of the adhesive and/or excessive loss of water. Smoothness appears to be a desirable property of the medium but smoothness attained by precalendering prior to corrugating may weaken the surface, particularly the rough surfaces. Future work would be directed at establishing the optimum surface physical and surface chemical properties of the medium for adhesion. Medium would be prepared from a reference fiber furnish under conditions which would provide defined requirements with respect to roughness, sizing, and porosity. Corrugating runs would subsequently be made using the reference starch adhesive and correlations drawn relating adhesion to these properties. Consideration would also be given to modification of the starch adhesive to insure bonding over a wider range of surface properties of the medium.

The information derived from this study should lead to optimization of corrugating adhesion with respect to both the properties of the medium and the starch adhesive.

LITERATURE CITED

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

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