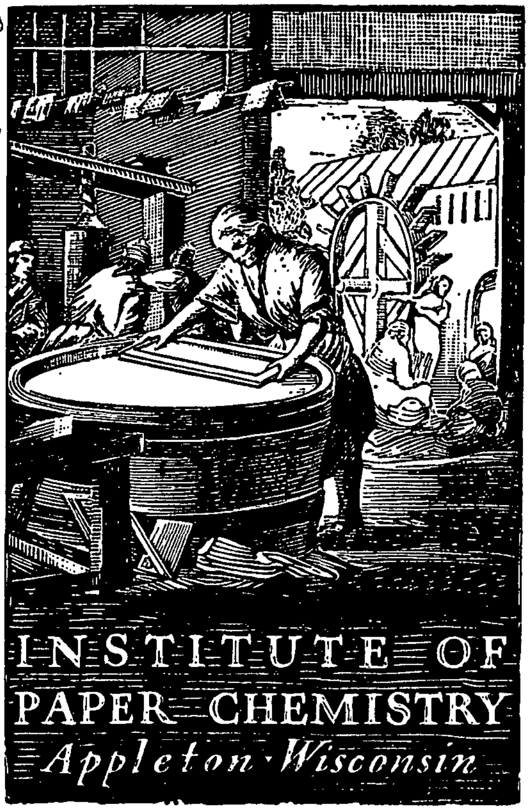

OPTIMIZATION OF COLD-SET ADHESIVE

Project 2696-15

Report One

A Progress Report

to

FOURDRINIER KRAFT BOARD INSTITUTE, INC.

January 15, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

In pursuing work with starch cold-set adhesives for corrugating, a study was made of means to: 1. enhance fiber failure in the pin adhesion test, 2. impart a measure of elasticity in the persulfate-modified starch, and 3. induce cross-linking for purposes of moisture resistance. In conjunction with these studies, an examination was also made of the time and temperature stability of the cold-set adhesive with respect to viscosity and gelation temperature.

Corrugator trials were conducted involving the use of adhesives ($\cong$ 22-23% solids) varying in composition and mediums ranging in water drop number from approximately 20 to 560 sec. Consistent fiber failure in the pin adhesion test was attained when using the most receptive medium whereas failure occurred at the medium-adhesive or liner-adhesive interface in most other cases. Incorporation of additives such as borax and polyvinyl alcohol was restricted to low levels due to their tendency to increase viscosity and, under these conditions, they failed to enhance fiber pull or significantly reduce the tendency for the persulfate-modified starch to fail at the fiber-adhesive interface. Reduction of the persulfate content and/or elimination of sodium sulfite in the adhesive formulation also failed to markedly improve pin adhesion or the failure pattern. High adhesive viscosity was again found to be detrimental to pin adhesion whereas an increase in film clearance from 0.010 to 0.012 mils improved adhesion significantly. Optimum results were obtained with an alkaline (pH 9-10) cold-set adhesive applied to presteamed medium. This combination provided the best pin adhesion values which were maintained at a reasonably high level at corrugating speeds up to 600 fpm.

Acidic cold-set adhesives (pH 3-4) containing 0.2% persulfate provided better moisture insensitivity than the alkaline adhesive but only low levels of cross-linking agent could be tolerated because of viscosity limitations and, as a result, a significant level of water resistance failed to develop in the absence of heat drying. Of the cold-set formulations tested, one containing 3% of glyoxal offered the best dry and moist pin adhesion.

Neutral and alkaline cold-set adhesives were found to be stable with respect to viscosity and gelation temperature for 1-2 hours if held in closed containers at 85-90°C. In contrast, the viscosity of acidic cold-set adhesives decreased as a function of time after jet cooking, presumably due to continued chemical conversion. Adhesives with low-medium initial viscosities tolerated short-term temperature decreases of 16°F without seriously affecting the viscosity measured at the holding temperature. However, repeated temperature cycling produced significant increases in viscosity when the initial level approached 200 Brabender units.

With the information available as a result of this work, the recommendation was made that further work with starch cold-set adhesives take the form of full-scale in-plant machine trials.

INTRODUCTION

This is Progress Report One on Project 2696-15 concerned with optimization of the starch cold-set adhesive for corrugating as outlined under Part A of the experimental program in Proposal No. 2212. In general, the results obtained in the initial investigation of starch cold-set adhesives under Project 2696-11 were very encouraging. In review, pin adhesion values comparable to the standard two-component starch adhesive were attained under essentially neutral conditions at a solids level of 23% and the values increased significantly as the adhesive solids increased to 33%. As the corrugating speed increased to 660 fpm the cold-set adhesive provided rather constant pin adhesion values whereas the adhesion level for the conventional starch heat-set adhesive declined at speeds in excess of 300-400 fpm. However, a number of potential problem areas appeared in this work which suggested the need for further study. One persistent problem was the lack of visual fiber pull in the pin adhesion test in spite of adequate adhesive strength in terms of force. In general, failure occurred at the medium-adhesive interface suggesting a lack of penetration prior to setting of the adhesive. The second and somewhat related problem was a tendency for the cold-set adhesive to be brittle, i.e., the adhesive tended to lack flexibility after setting up. The current program is directed at resolving these problem areas or, in effect, at optimizing the cold-set adhesive. In pursuing the experimental program, consideration was also given to better definition of the limitations of the process with respect to temperature and time variations as they relate to the viscosity and gelation temperature of the adhesive and, ultimately, to adhesive performance.

EXPERIMENTAL

GENERAL PROCEDURES

The procedures utilized in preparing, testing, and applying starch cold-set adhesives were similar to those given in Progress Report One on Project 2696-11. In brief, a commercial pearl cornstarch was dispersed at approximately 24% solids in tap water in the presence of specified amounts of modifiers including sodium sulfite, sodium hydroxide, borax, ammonium persulfate, etc. The persulfate was usually added last in amounts ranging from 0.2 to 0.6% and, after several minutes stirring, the slurry was passed through the steam jet cooker at 230-240°F at a dwell time of 6 or 13 sec. (Note: The maximum dwell time attainable with the existing equipment is 13 sec.) The cooked adhesive was collected in preheated Dewar flasks and then transferred to a holding tank which was stationed in a water bath heated to 185-190°F by steam injection. In some cases, agents were added to the cooked starch at this point in the process. In all cases the amount of agent added was expressed in terms of percentage based on dry weight of starch. Adhesive samples for pH, solids, viscosity, and gelation temperature measurements were taken either directly from the Dewar flask or from the holding tanks. Solids determinations were made by taking weighed samples to dryness at 105°C. Viscosity and gelation temperature were again measured with the Brabender Amylograph Viscograph according to procedures described previously (1).

The cold-set adhesive was applied on a hot-melt corrugator at 77-91°C (171-196°F) at speeds up to 600 fpm utilizing 26-lb medium and a standard 42-lb liner. The film clearance was either 10 or 12 mils and the pressure roll temperature was ambient. For purposes of control, a conventional two-component adhesive was utilized under normal operating conditions.

As a means of comparing the apparent brittleness of the experimental adhesives, films of hot adhesive were cast on teflon sheeting using a coarse (40-mil) fixed clearance bar. These films were allowed to air dry at 73°F and 50% RH during which time they released from the teflon. The apparent flexibility was judged subjectively by flexing the film until it fractured. Actually, all adhesive films prepared from the persulfate-modified starch tended to be brittle regardless of the adhesive formulation. The most flexible films were provided by the alkaline adhesives but these were only moderately better than other formulations.

SPECIFIC STUDIES

The Effect of Component Receptivity and Adhesive Composition

The effect of the receptivity of the medium on adhesive performance was explored in several series of corrugator trials in which the chemical composition of the adhesive was varied. The purpose of this work was to promote penetration of the adhesive into the board components so as to enhance fiber failure in the pin adhesion test. The first series of trials utilized a "standard" cold-set starch adhesive containing 0.5% of persulfate, 0.5% of sodium sulfite, and 0.3% of NaOH (based on starch). Two adhesive samples with this composition were prepared. The first of these incorporated the use of an ammonium persulfate sample which had aged for some time in the laboratory. The viscosity and gelation temperature of this adhesive were higher than expected on the basis of earlier work whereas the second adhesive utilized a fresh sample of persulfate and was of lower viscosity. The adhesives were applied to mediums known to vary in water drop value from approximately 20-560 sec. The results of these trials along with porosity and smoothness data for the mediums are recorded in Table I. Pin adhesion as a function of corrugating speed is presented in Fig. 1.

TABLE I

THE EFFECT OF MEDIUM PROPERTIES AND ADHESIVE VISCOSITY ON PIN ADHESION

Corrugator Run No.	Code No. of Medium	Receptivity of Medium, water drop, sec	Bendtsen Air Permeability of Medium, ml/min	Bendtsen Smoothness of Medium, ml/min	Adhesive No.	Adhesive Solids Content, %	Final pH	Brabender Viscosity at 95°C	Gelation Temp., °C	Operating Temperature, °F Pan	Operating Temperature, °F Glue Roll	Corrugating Speed, fpm	Pin Adhesion, lb	Major Locus of Failure
1	5476	19-27	1005	2140	1	22.9	7.5	270	67(153°F)	194	205	100	71.6	Within medium
												200	66.2	" "
												300	59.2	Within medium and at medium-adhesive interface
												400	56.6	" " " " " "
												500	52.2	" " " " " "
												600	Medium fractured	
2	16442	412-564	938	3000+	1	22.9	7.5	270	67(153°F)	190	205	100	65.8	At liner-adhesive interface
												200	64.0	" " " "
												300	65.6	" " " "
												400	61.2	" " " "
												500	Medium fractured	
3	16029	90	1362	3000+	1	22.9	7.5	270	67(153°F)	190	205	100	62.0	At medium-adhesive interface
												200	65.8	" " " "
												300	51.6	" " " "
												400	49.0	" " " "
												500	51.6	" " " "
												600	43.2	" " " "
4	16334	115-165	482	2804	1	22.9	7.5	270	67(153°F)	190	205	100	70.6	At medium-adhesive interface
												200	75.4	" " " "
												300	68.6	" " " "
												400	68.8	" " " "
												500	69.4	At medium-adhesive interface and at liner-adhesive interface
												600	59.8	" " " " " " " " "
5	5476	19-27	1005	2140	2	22.2	7.1	165	64(147°F)	192	208	100	77.4	Within medium and at medium-adhesive interface
												200	77.4	" " " " " "
												300	70.6	Within medium
												400	63.4	" "
												500	Medium fractured	
6	16442	412-564	938	3000+	2	22.2	7.1	165	64(147°F)	192	210	100	83.6	At liner-adhesive interface
												200	75.6	" " " "
												300	66.6	At liner-adhesive interface and at medium-adhesive interface
												400	Medium fractured	
7	16029	90	1362	3000+	2	22.2	7.1	165	64(147°F)	192	205	100	70.6	At medium-adhesive interface and within medium
												200	69.4	" " " " " " "
												300	59.0	At medium-adhesive interface
												400	54.6	" " " "
												500	55.0	" " " "
												600	56.8	" " " "
8	16334	115-165	482	2804	2	22.2	7.1	165	64(147°F)	190	205	100	87.0	At medium-adhesive interface and at liner-adhesive interface
												200	87.2	At medium-adhesive interface
												300	69.4	" " " "
												400	68.6	At medium-adhesive interface and at liner-adhesive interface
												500	69.8	" " " " " " " " "
												600	63.2	" " " " " " " " "

NOTES: All adhesives contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, and 0.3% of NaOH.
The persulfate used in corrugator Runs 1-4 had aged for 1-2 years.
The jet cooking temperature was 230-240°F in all cases: the Bendtsen air permeability and smoothness values for the liner were 727 and 3000+ ml/min, respectively.
The water drop value of liner was 600+ sec.

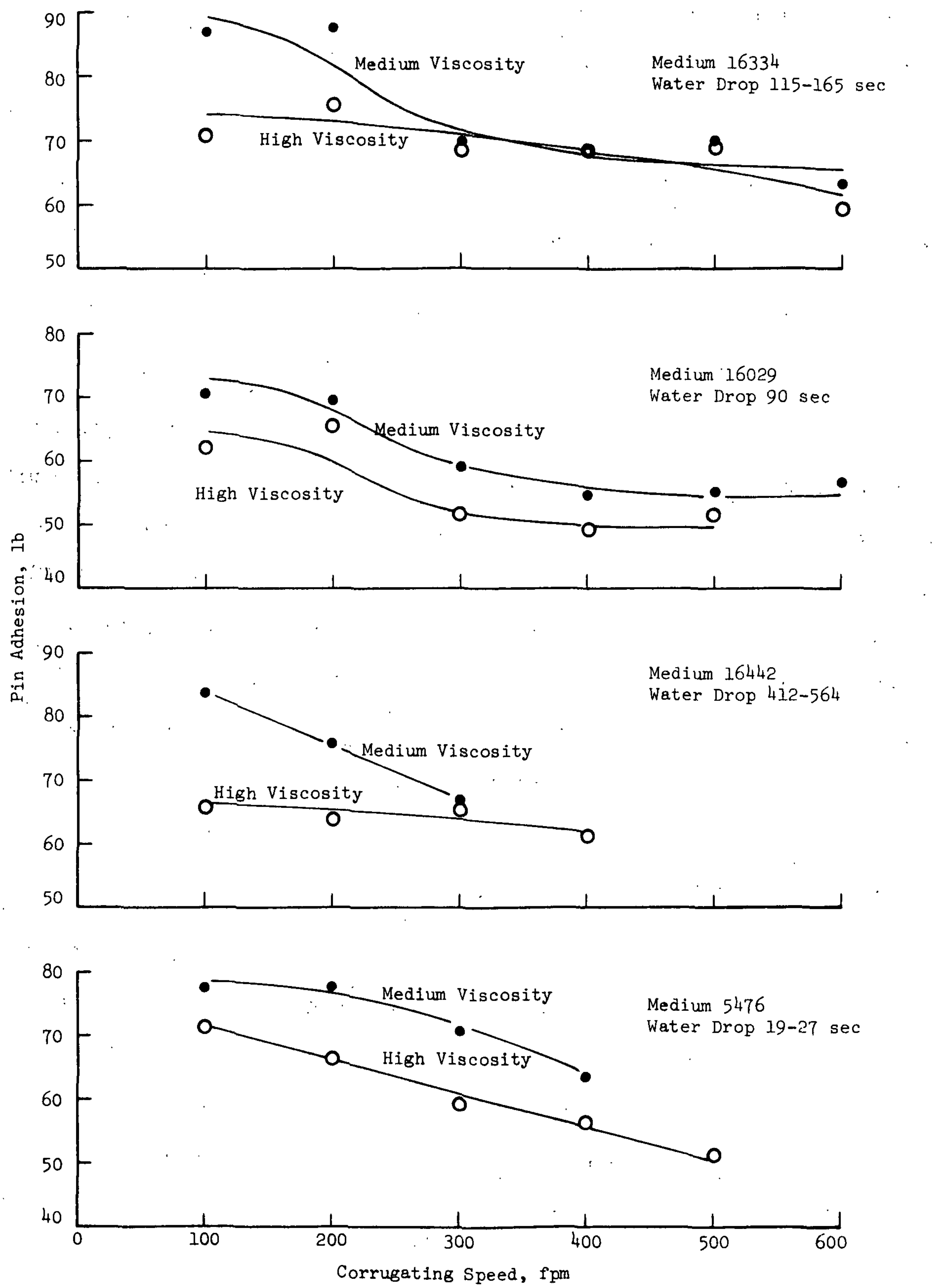

Figure 1. The Effect of Adhesive Viscosity and Corrugating Speed on Pin Adhesion for Mediums Differing in Receptivity

For purposes of reference, a conventional two-component starch adhesive was applied to the same mediums on the hot-melt corrugator. Results are given in Table II.

A subsequent series of corrugator trials utilized cold-set adhesives containing 0.5% of persulfate and 0.5% of sulfite with the following modifications.

1. Addition of 0.7% of borax (based on starch), and
2. incorporation of alkali to provide a pH of approximately 10.

Application of alkaline adhesives was considered a means of improving penetration into sized components whereas borax was selected for its complexing ability with carbohydrates. The conditions employed in these trials were selected on the basis of preliminary tests with small batches of adhesive (Tables III and IV). The effect of adding borax before and after jet cooking is shown in Fig. 2. A borax addition level of 0.7% prior to jet cooking was selected on the basis of the viscosity-concentration relationship in Fig. 2 since this level is indicated to produce some complexing but the resulting viscosity was less than 200 Brabender units. Results of corrugator trials utilizing alkaline and borax-modified adhesives are presented in Tables V and VI.

The next series of trials examined the effects of presteaming the medium as a means of enhancing adhesive wetting and penetration. Since increasing the adhesive pH appeared to have had an advantage in the previous series (Table VI), an alkaline adhesive was utilized in conjunction with the steam pretreatment. Results are recorded in Table VII. The effect of the various modifications on pin adhesion are summarized in Fig. 3-6.

TABLE II

CONTROLS — CONVENTIONAL HEAT-SET CORRUGATING ADHESIVE

Corrugator Run No.	Code No. of Medium	Receptivity of Medium, water drop, sec	Bendtsen Air Permeability of Medium, ml/min	Bendtsen Smoothness of Medium, ml/min	Corrugating Speed, fpm	Pin Adhesion, lb	Major Locus of Failure
9	5476	19-27	1005	2140	100	80.6	Within medium
					200	72.8	Within liner
					300	69.4	Within medium
					400	40.4	At liner-adhesive interface
					500	25.6	Within adhesive
					600	Medium fractured	
10	16442	412-564	938	3000+	100	89.4	Within medium
					200	82.6	Within liner
					300	Medium fractured	
11	16029	90	1362	3000+	100	77.4	Within adhesive
					200	73.6	Within medium
					300	64.2	Within medium
					400	55.4	At medium-adhesive interface
					500	36.4	Within adhesive
					600	14.0	Within adhesive
12	16334	115-165	482	2804	100	99.8	Within liner
					200	91.0	Within liner
					300	87.2	At liner-adhesive interface
					400	57.6	At liner-adhesive interface
					500	31.2	At liner-adhesive interface
					600	24.6	Within adhesive

NOTES: The adhesive (No. 3) was applied on the hot-melt corrugator.
Solids content approximately 20%.

TABLE III

THE EFFECT OF BORAX ON ADHESIVE PROPERTIES

Adhesive No.	Borax Added Before Cooking, % based on starch solids	Borax Added After Cooking, % based on starch solids	Final pH	Solids Content, %	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
4	0.5	--	8.3	--	180	61(142°F)
5	0.7	--	8.4	21.7	190	62(144°F)
6	0.8	--	8.3	--	195	62(144°F)
7	1.2	--	8.3	22.8	240	70(158°F)
8	--	0.5	7.8	22.3	165	63(145°F)
9	--	0.8	8.0	--	170	63(145°F)
10	--	1.2	8.0	22.2	200	64(147°F)
11	--	1.5	8.1	22.3	285	71(160°F)
12	--	2.0	8.2	23.0	295	71(160°F)
2 (Control)	None	None	7.1	22.2	165	64(147°F)

NOTES: The adhesive formulation contained 0.5% ammonium persulfate, 0.5% of sodium sulfite, and 0.3% NaOH. The jet cooking temperature was 230-240°F and the dwell time in the cooker was six seconds.

TABLE IV

THE EFFECT OF ALKALI ON ADHESIVE PROPERTIES

Adhesive No.	NaOH Added Before Cooking, % based on starch solids	NaOH Added After Cooking, % based on starch solids	Total NaOH Added, % based on starch solids	Final pH	Solids Content, %	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
13	0.3	0.55	0.85	10.0	22.6	165	62(144°F)
14	0.3	0.37	0.67	10.0	21.3	160	60(140°F)
15	0.3	5.00	5.30	11.0	23.7	320	60(140°F)
16	0.55	--	0.55	9.2	22.9	220	68(154°F)
17	1.00	--	1.00	10.0	22.0	290	67(153°F)
2 (Control)	0.3	--	0.3	7.1	22.2	165	64(147°F)

NOTES: The adhesive formulations contained 0.5% of ammonium persulfate and 0.5% of sodium sulfite (based on starch).
The jet cooking temperature was 230-240°F and the dwell time in the jet cooker was six seconds.

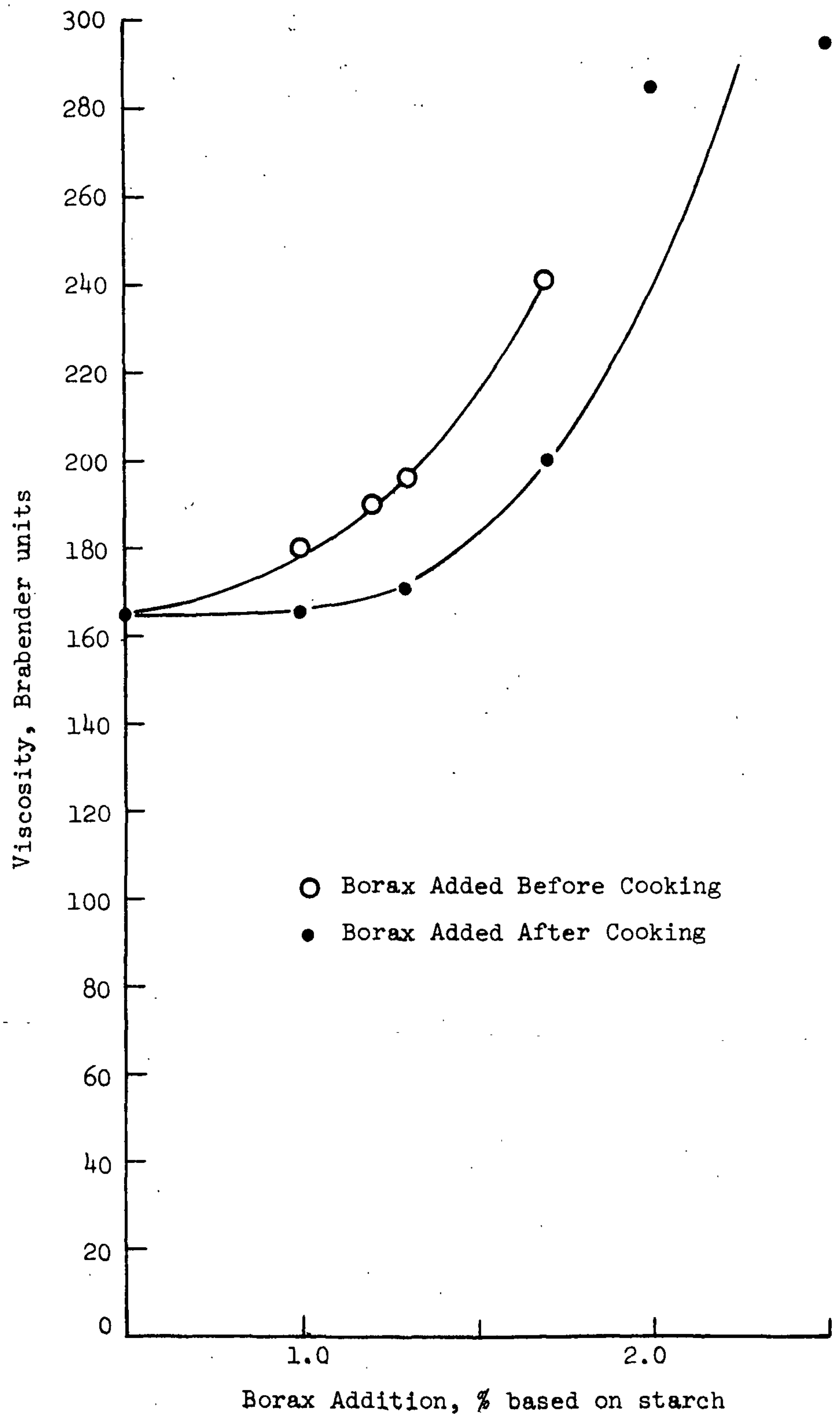

Figure 2. The Effect of Borax on Adhesive Viscosity

TABLE V

THE EFFECT OF BORAX ON ADHESIVE PERFORMANCE

Corrugator Run No.	Code No. of Medium	Receptivity of Medium, water drop, sec	Bendtsen Air Permeability of Medium, ml/min	Bendtsen Smoothness of Medium, ml/min	Adhesive No.	Adhesive Solids Content, %	Final pH	Brabender Viscosity at 95°C	Gelation Temp., °C	Operating Temperature Pan, °F	Operating Temperature Glue Roll, °F	Corrugating Speed, fpm	Pin Adhesion, lb	Major Locus of Failure
13	5476	19-27	1005	2140	18	21.7	8.4	190	62(144°F)	187	205	100	72.8	Within medium
												200	63.0	" "
												300	61.2	" "
												400	57.2	" "
												500	Medium fractured	
14	16442	412-564	938	3000+	18	21.7	8.4	190	62(144°F)	189	205	100	76.8	At medium-adhesive interface
												200	64.6	At liner-adhesive interface
												300	66.4	At medium-adhesive interface
												400	55.8	" " " "
												500	Medium fractured	
15	16029	90	1362	3000+	18	21.7	8.4	190	62(144°F)	190	205	100	75.0	At medium-adhesive interface
												200	65.0	At medium-adhesive interface & within medium
												300	59.4	At medium-adhesive interface
												400	56.0	" " " "
												500	49.6	" " " "
												600	42.0	" " " "
16	16334	115-165	482	2804	18	21.7	8.4	190	62(144°F)	196	210	100	83.0	At medium-adhesive interface
												200	71.6	" " " "
												300	75.2	" " " "
												400	73.4	" " " "
												500	71.2	" " " "
												600	72.0	At liner-adhesive interface
17[a]	16334	115-165	482	2804	18	21.7	8.4	190	62(144°F)	196	210	100	92.0	At medium-adhesive interface
												200	79.8	At medium-adhesive interface & at liner-adhesive interface
												300	80.4	At liner-adhesive interface
												400	84.0	At medium-adhesive interface
												500	81.6	" " " "
												600	78.4	" " " "

[a] Steam was applied to medium in this run.

NOTE: The adhesive contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, 0.3% of NaOH, and 0.7% of borax (based on starch) prior to jet cooking.

TABLE VI

THE EFFECT OF ALKALI ON ADHESIVE PERFORMANCE (pH 10)

Corrugator Run No.	Code No. of Medium	Receptivity of Medium, water drop, sec	Bendtsen Air Permeability of Medium, ml/min	Bendtsen Smoothness of Medium, ml/min	Adhesive No.	Adhesive Solids Content, %	Brabender Viscosity at 95°C	Gelation Temp., °C	Operating Temperature Pan, °F	Operating Temperature Glue Roll, °F	Corrugating Speed, fpm	Pin Adhesion, lb	Major Locus of Failure
18	5476	19-27	1005	2140	19	22.5	190	65(149°F)	192	205	100	76.6	Within medium
											200	70.8	" "
											300	66.6	" "
											400	65.6	" "
											500	Medium fractured	
19	16442	412-564	938	3000+	19	22.5	190	65(149°F)	190	205	100	76.0	At liner-adhesive interface
											200	69.0	" " " "
											300	73.0	" " " "
											400	62.8	" " " "
											500	Medium fractured	
20	16029	90	1362	3000+	19	22.5	190	65(149°F)	190	208	100	70.4	At medium-adhesive interface
											200	65.4	" " " "
											300	57.6	" " " "
											400	53.2	" " " "
											500	56.0	" " " "
											600	49.2	" " " "
21	16334	115-165	482	2804	19	22.5	190	65(149°F)	190	205	100	87.6	At medium-adhesive interface
											200	73.0	" " " "
											300	75.6	" " " "
											400	72.0	" " " "
											500	74.8	" " " "
											600	76.6	At liner-adhesive interface

NOTE: The adhesive contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, and 0.3% NaOH prior to jet cooking. Approximately 0.55% of NaOH added after jet cooking to adjust pH to 10.

TABLE VII

THE EFFECT OF STEAM ON MEDIUM USING ALKALINE COLD-SET ADHESIVE (pH 9-10)

Corrugator Run No.	Code No. of Medium	Receptivity of Medium, water drop, sec	Bendtsen Air Permeability of Medium, ml/min	Bendtsen Smoothness of Medium, ml/min	Adhesive No.	Adhesive Solids Content, %	Brabender Viscosity at 95°C	Gelation Temp., °C	Operating Temperature Pan, °F	Operating Temperature Glue Roll, °F	Corrugating Speed, fpm	Pin Adhesion, lb	Major Locus of Failure
22	5476	19-27	1005	2140	20	21.3	165	62(144°F)	192	210	100	87.2	Within medium and at medium-adhesive interface
											200	80.0	" " " " " " "
											300	77.2	Within medium
											400	Medium fractured	
23	16442	412-564	938	3000+	20	21.3	165	62(144°F)	190	215	100	86.6	At medium-adhesive interface
											200	75.2	" " " "
											300	Medium fractured	
24	16029	90	1362	3000+	20	21.3	165	62(144°F)	189	210	100	73.0	At medium-adhesive interface
											200	66.0	" " " "
											300	65.4	" " " "
											400	67.4	" " " "
											500	64.0	" " " "
											600	66.0	" " " "
25	16334	115-165	482	2804	20	21.3	165	62(144°F)	192	210	100	82.4	At medium-adhesive interface
											200	85.8	" " " "
											300	87.6	" " " "
											400	82.2	At medium-adhesive interface & within liner
											500	77.0	At medium-adhesive interface
											600	78.2	At liner-adhesive interface

NOTE: The adhesive contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, and 0.3% of NaOH prior to jet cooking. Approximately 0.55% of NaOH was added after jet cooking.

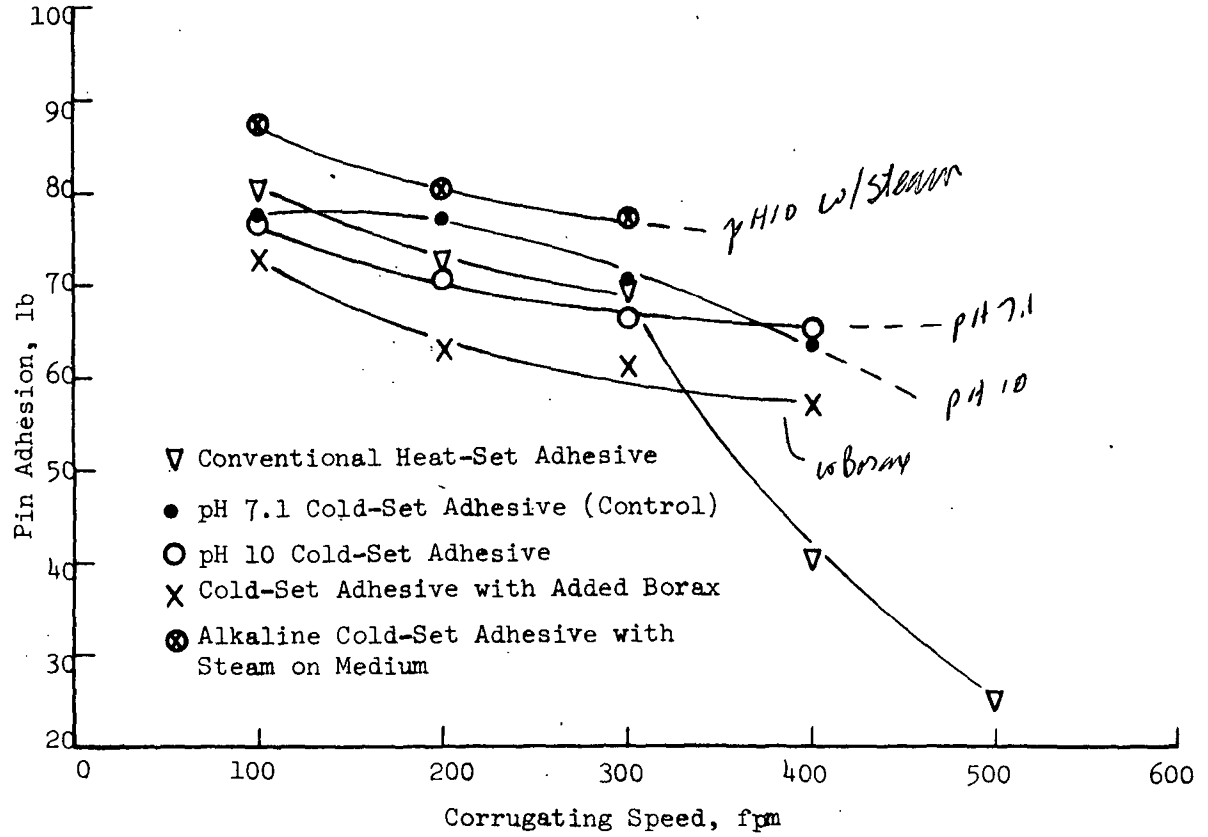

Figure 3. The Effect of Various Modifications on Pin Adhesion Using a Medium of 19-27 sec Water Drop

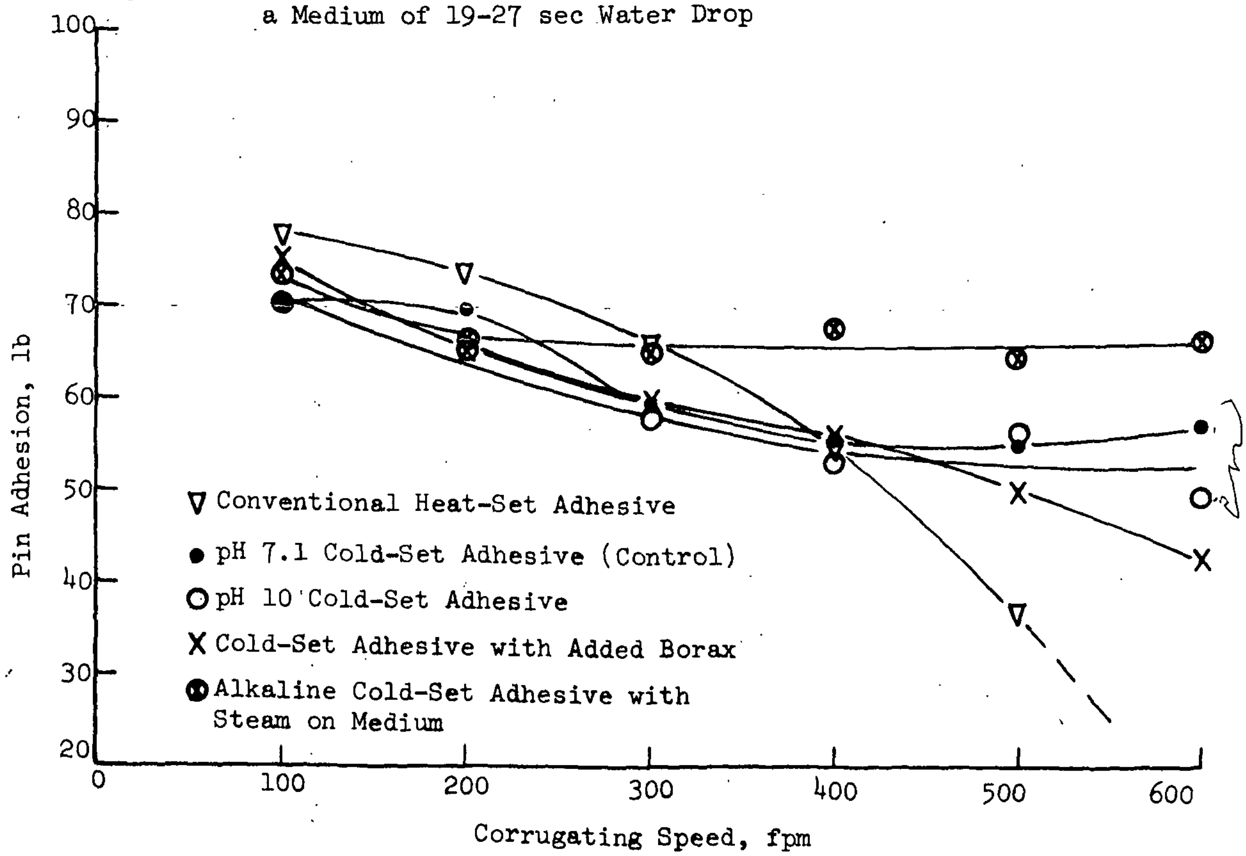

Figure 4. The Effect of Various Modifications on Pin Adhesion Using a Medium of 90 sec Water Drop

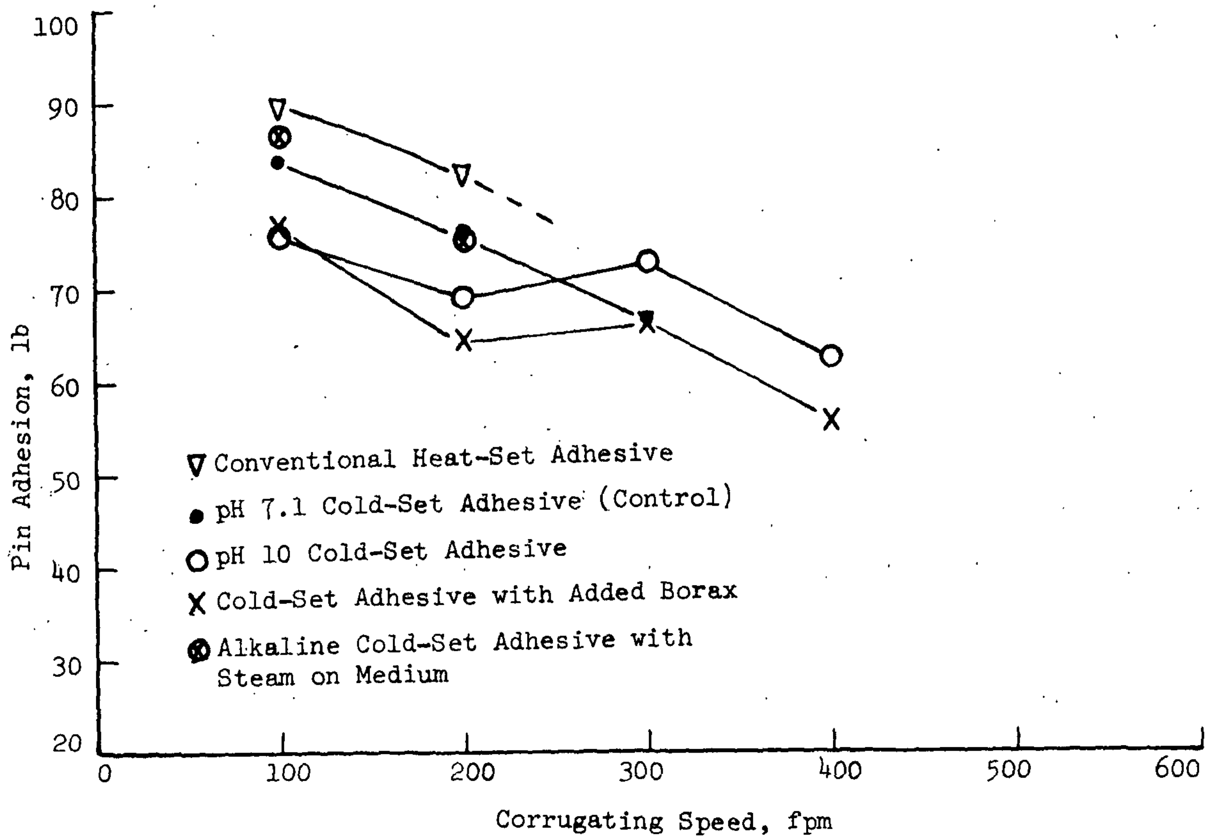

Figure 5. The Effect of Various Modifications on Pin Adhesion Using a Medium of 412-564 sec Water Drop

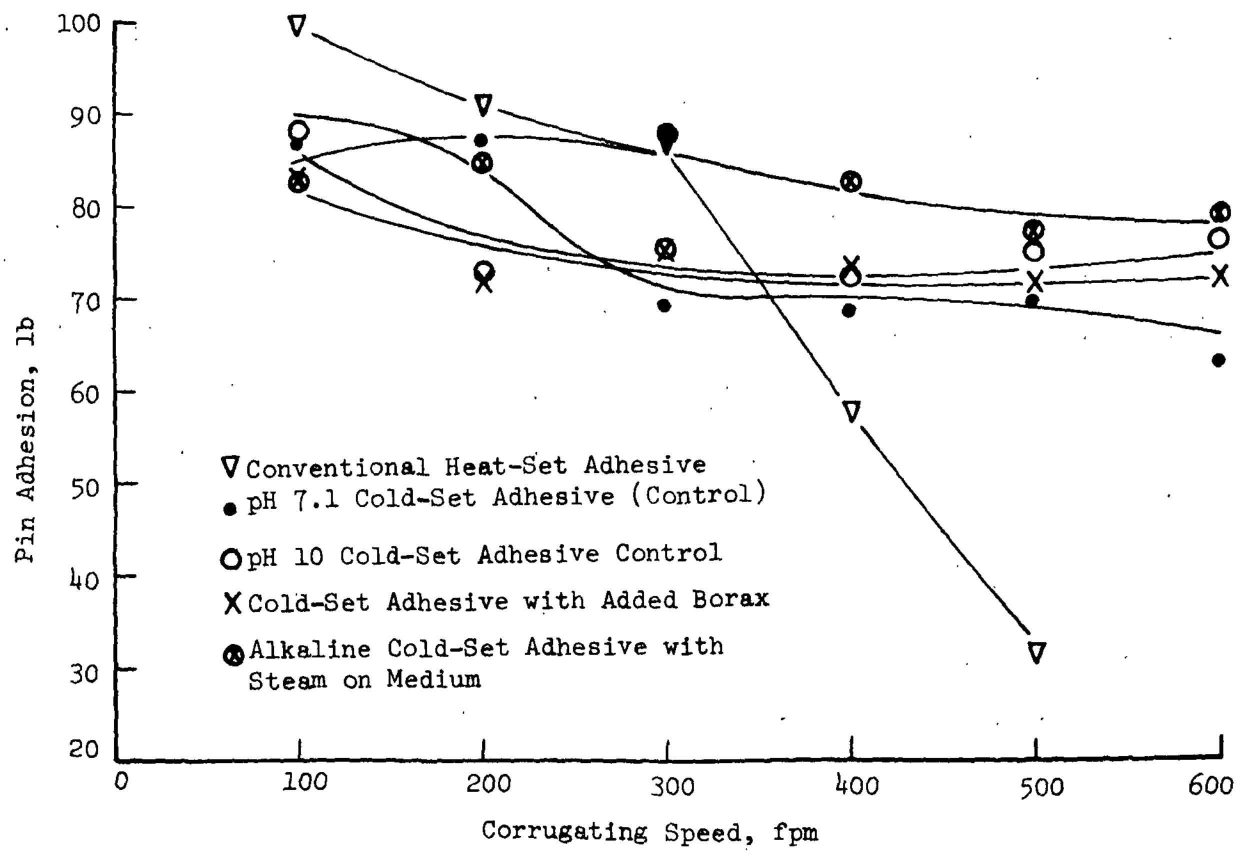

Figure 6. The Effect of Various Modifications on Pin Adhesion Using a Medium of 115-165 sec Water Drop

Consideration was then given to (1) incorporation of wood fiber in the cold-set adhesive, (2) addition of polyvinyl alcohol, and (3) reduced chemical modifier. All of these modifications were examined in preliminary work with small batches of adhesive.

Addition of kraft fiber was considered a potential means of reinforcing the adhesive in the bonded area. For this purpose unbleached softwood kraft pulp at 660 ml CF was incorporated directly into the adhesive slurry prior to jet cooking. Two adhesive formulations were examined in preliminary work. The first was the "standard" cold-set formulation; the second was a modified formulation prepared under more alkaline conditions without sodium sulfite. Results are given in Table VIII.

The effect of polyvinyl alcohol on adhesive properties was tested in a similar series of experiments. Elvanol 72-60 (E. I. du Pont) was dusted into the adhesive slurry in amounts ranging from 1-5% based on starch. The PVA was subsequently cooked with the starch in the jet-processing step. Results of the exploratory tests are given in Table IX.

The effect of reduced chemical modifier was examined over a wide range of conditions with respect to persulfate and alkali levels. Sodium sulfite was eliminated from all formulations since it was reasoned that the inherent brittleness of the cold-set adhesive was possibly due to the relatively high level of modifiers employed in the formulations. When the adhesive became acidic through reduction or elimination of alkali, the resulting viscosities and gelation temperatures increased dramatically. However, as the cooked adhesive aged at the holding temperature of 85-90°C, the viscosity and gelation temperature declined as indicated in Table X and Fig. 7.

TABLE VIII

THE EFFECT OF KRAFT FIBER ON ADHESIVE PROPERTIES

Adhesive No.	Ammonium Persulfate Added, % based on starch	Sodium Sulfite Added, % based on starch	NaOH Added, % based on starch	Kraft Fiber Added, % based on starch	Final pH	Adhesive Solids Content, %	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
21	0.5	0.5	0.3	0.33	8.0	23.1	190	64(147°F)
22	0.5	0.5	0.3	0.50	7.9	22.6	210	65(149°F)
23	0.5	0.5	0.3	1.00	8.1	23.2	245	65(149°F)
24	0.5	0.5	0.3	3.00	8.1	22.3	430	66(151°F)
25	0.5	None	0.5	0.5	8.3	22.8	165	64(147°F)
26	0.5	None	0.5	1.0	8.5	23.1	250	67(153°F)
27	0.6	None	0.5	1.0	8.0	22.8	155	63(145°F)
28	0.6	None	0.7	1.0	9.3	23.0	195	65(149°F)
2 (Control)	0.5	0.5	0.3	None	7.1	22.2	165	64(147°F)

TABLE IX

THE EFFECT OF POLYVINYL ALCOHOL (PVA) ON ADHESIVE PROPERTIES

Adhesive No.	Ammonium Persulfate Added, % based on starch	Sodium Sulfite Added, % based on starch	NaOH Added, % based on starch	PVA Added, % based on starch	Final pH	Adhesive Solids Content, %	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
29	0.5	0.5	0.3	1.0	7.4	22.8	185	64(147°F)
30	0.5	0.5	0.3	1.5	7.8	22.6	185	64(147°F)
31	0.5	0.5	0.3	2.0	7.7	22.8	205	64(147°F)
32	0.5	0.5	0.3	5.0	8.0	23.8	325	70(158°F)
33	0.5	None	0.5	1.0	9.1	22.8	150	63(145°F)
34	0.5	None	0.5	2.0	9.0	23.0	165	65(149°F)
35	0.5	None	0.5	4.0	8.9	23.3	200	66(151°F)
2 (Control)	0.5	0.5	0.3	None	7.1	22.2	165	64(147°F)

TABLE X

THE EFFECT OF REDUCED MODIFIER AND pH ON ADHESIVE PROPERTIES

Adhesive No.	Ammonium Persulfate Added, % based on starch	Sodium Sulfite Added, % based on starch	NaOH Added, % based on starch	Jet Cooking Temp., °F	Dwell Time in Jet Cooker, sec	Final pH	Adhesive Solids Content, %	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
36	0.5	None	0.5	230-240	6	8.4	22.7	125	61 (142°F)
37	0.5	None	0.7	230-240	6	9.2	22.8	180	65 (149°F)
38	0.5	None	1.0	230-240	6	10.0	23.2	240	70 (158°F)
39	0.4	None	0.5	230-240	6	8.6	22.6	190	67 (153°F)
40	0.4	None	0.5	230-240	6	8.8	21.7	175	64 (147°F)
41	0.3	None	0.5	230-240	6	9.1	22.5	290	71 (160°F)
42	0.3	None	0.5	230-240	6	8.8	18.5	170	61 (142°F)
43	0.3	None	0.5	230-240	13	9.4	22.7	280	71 (160°F)
44	0.3	None	0.5	230-240	13	9.0	19.8	200	63 (145°F)
45	0.3	None	0.1	230-240	6	4.9	22.9	410 340[b]	72 (162°F) 69[b] (156°F)
46	0.3	None	None	230-240	6	2.8	22.3	380 120[b]	66 (151°F) 56[b] (133°F)
47	0.25	None	None	230-240	6	2.8	22.2	170[b]	60[b] (140°F)
48	0.20	None	0.1	230-240	6	4.1	22.3	1060	73 (163°F)
49	0.20	None	None	230-240	6	3.0	22.7	720 340[a] 225[b] 140[c]	73 (163°F) 67[a] (153°F) 64[b] (147°F) 60[c] (140°F)
2 (Control)	0.5	0.5	0.3	230-240	6	7.1	22.2	165	64 (147°F)

[a]Measured after adhesive had aged 1 hour at 85-90°C.
[b]Measured after adhesive had aged 1 1/2 hours at 85-90°C.
[c]Measured after adhesive had aged 3 hours at 85-90°C.

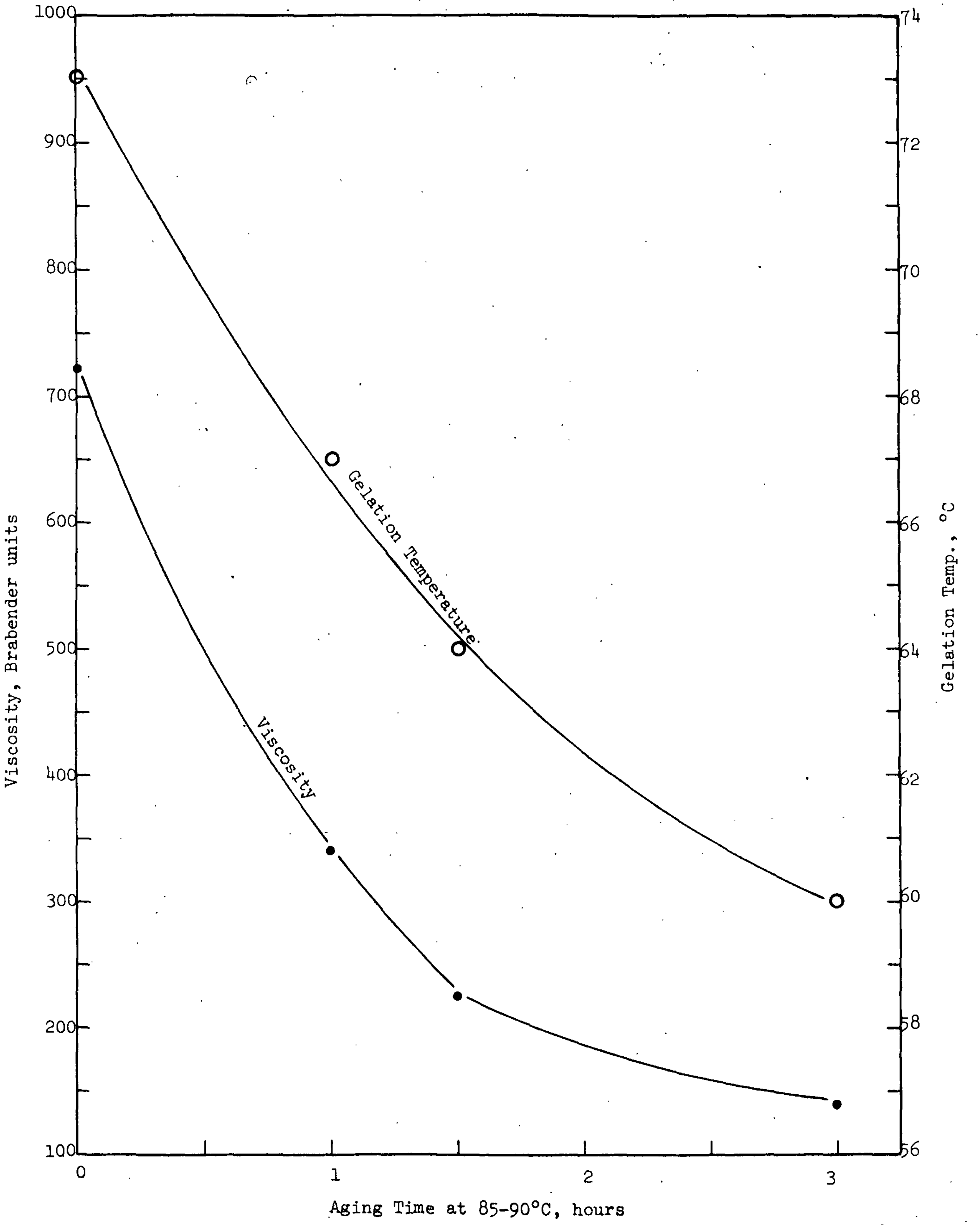

Figure 7. The Effect of Aging an Acidic Adhesive on Viscosity and Gelation Temperature

Selection of adhesives from Tables VIII-X was necessarily based on viscosity and gelation temperature since these govern the practical runnability of the adhesive. In general, adhesives having viscosities of 160-200 and gelation temperature of 62-65°C were considered acceptable. Adhesive formulations selected on this basis were utilized in corrugating at film clearances of 0.012 and 0.010 in. In this and all subsequent corrugator trials, applications were limited to a "standard" medium (Code No. 16334) and liner. Application of adhesives containing kraft fiber did not prove satisfactory due to the type of metering system on the "hot-melt" corrugator wherein the fibers tended to accumulate under the metering bar thereby greatly reducing the effective adhesive film thickness. Accordingly, the amount of fiber carried with the adhesive into the bonded area was not representative of the original formulation. However, in spite of this limitation, results obtained with kraft fiber are included in the summarized corrugating results given in Table XI. The effect of adhesive viscosity and film thickness on pin adhesion are shown graphically in Fig. 8-12.

A final series of corrugator trials was conducted with acidic cold-set adhesive formulations to test the possibility of forming water-resistant bonds. As a preliminary to this series, adhesives containing 0.2% persulfate were allowed to age 1-1/2 to 3 hours at 85-90°C (185-194°F) followed by the addition of low levels of cross-linking agent or resin. The aging procedure was necessary to provide a sufficiently low initial viscosity for corrugating. (Addition of cross-linking agent prior to jet cooking generally produced gelation in the jet-processing step.) Glyoxal, urea-formaldehyde (UF) and melamine-formaldehyde (MF) resin as well as polyvinyl acetate (PVAc) were added in amounts ranging from 1-10% based on starch. The effect of these agents on adhesive properties is recorded in Table XII. As indicated in the results, only low levels of cross-linking agents could be tolerated without excessive increases in viscosity.

TABLE XI

THE EFFECT OF REDUCED CHEMICAL MODIFIER AND OTHER VARIATIONS ON ADHESIVE PERFORMANCE

Corrugator Run No.	Adhesive No.	Adhesive Modifiers & Additives, % based on starch	Adhesive Solids Content, %	Final pH	Clearance, inch	Brabender Viscosity at 95°C	Gelation Temp., °C	Operating Temperature Pan, °F	Operating Temperature Glue Roll, °F	Corrugating Speed, fpm	Pin Adhesion lb	Major Locus of Failure
26	50	Ammonium persulfate, 0.5; sodium hydroxide, 0.7	22.2	9.4	0.012	280	69(156°F)	189	200	100	79.0	At medium-adhesive interface
										200	71.8	At liner-adhesive interface
										300	64.8	Within liner
										400	57.4	Within liner and at liner-adhesive interface
										500	60.2	Within liner
										600	57.6	Within liner and at medium-adhesive interface
27	50	Ammonium persulfate, 0.5; sodium hydroxide, 0.7	22.2	9.4	0.010	280	69(156°F)	187	200	100	52.4	At liner-adhesive interface
										200	47.8	" " " "
										300	47.6	At liner-adhesive interface and within liner
										400	47.4	" " " " " " "
										500	42.6	At liner-adhesive interface
										600	40.0	At medium-adhesive interface
28	51	Ammonium persulfate, 0.5; sodium hydroxide, 0.6	22.0	8.8	0.012	180	65.5(150°F)	190	210	100	85.4	At medium-adhesive interface
										200	80.6	" " " "
										300	84.0	" " " "
										400	81.0	" " " "
										500	78.4	" " " "
										600	72.8	At liner-adhesive interface
29	51	Ammonium persulfate, 0.5; sodium hydroxide, 0.6	22.0	8.8	0.010	180	65.5(150°F)	192	210	100	80.6	At liner-adhesive and medium-adhesive interface
										200	77.8	At medium-adhesive interface
										300	70.4	" " " "
										400	68.0	Within liner and at liner-adhesive interface
										500	67.4	At medium-adhesive interface
										600	66.2	Within liner
30	52	Ammonium persulfate, 0.6; sodium hydroxide, 0.5; kraft fiber, 1.0	22.2	7.3	0.012	180	60(140°F)	181	200	100	79.8	At medium-adhesive interface
										200	76.8	" " " "
										300	71.0	Within liner and at medium-adhesive interface
										400	75.8	Within liner and at liner-adhesive interface
										500	71.2	At medium-adhesive interface
										600	73.6	At liner-adhesive interface
31	53	Ammonium persulfate, 0.55; sodium hydroxide, 0.5; PVA, 3.0	22.2	7.5	0.012	180	62(144°F)	185	205	100	84.8	At liner-adhesive interface
										200	77.0	At medium-adhesive interface
										300	78.8	" " " "
										400	75.6	At liner-adhesive and medium-adhesive interface
										500	79.8	At liner-adhesive interface
										600	78.6	" " " "
32	53	Ammonium persulfate, 0.55; sodium hydroxide, 0.5; PVA, 3.0	22.2	7.5	0.010	180	62(144°F)	187	200	100	72.2	At medium-adhesive interface
										200	69.4	" " " "
										300	64.0	" " " "
										400	60.0	At liner-adhesive interface
										500	61.8	" " " "
										600	60.2	" " " "

NOTE: These corrugator trials utilized a standard medium having a water drop no. of 115-165 sec. Steam was applied to the medium in all cases.

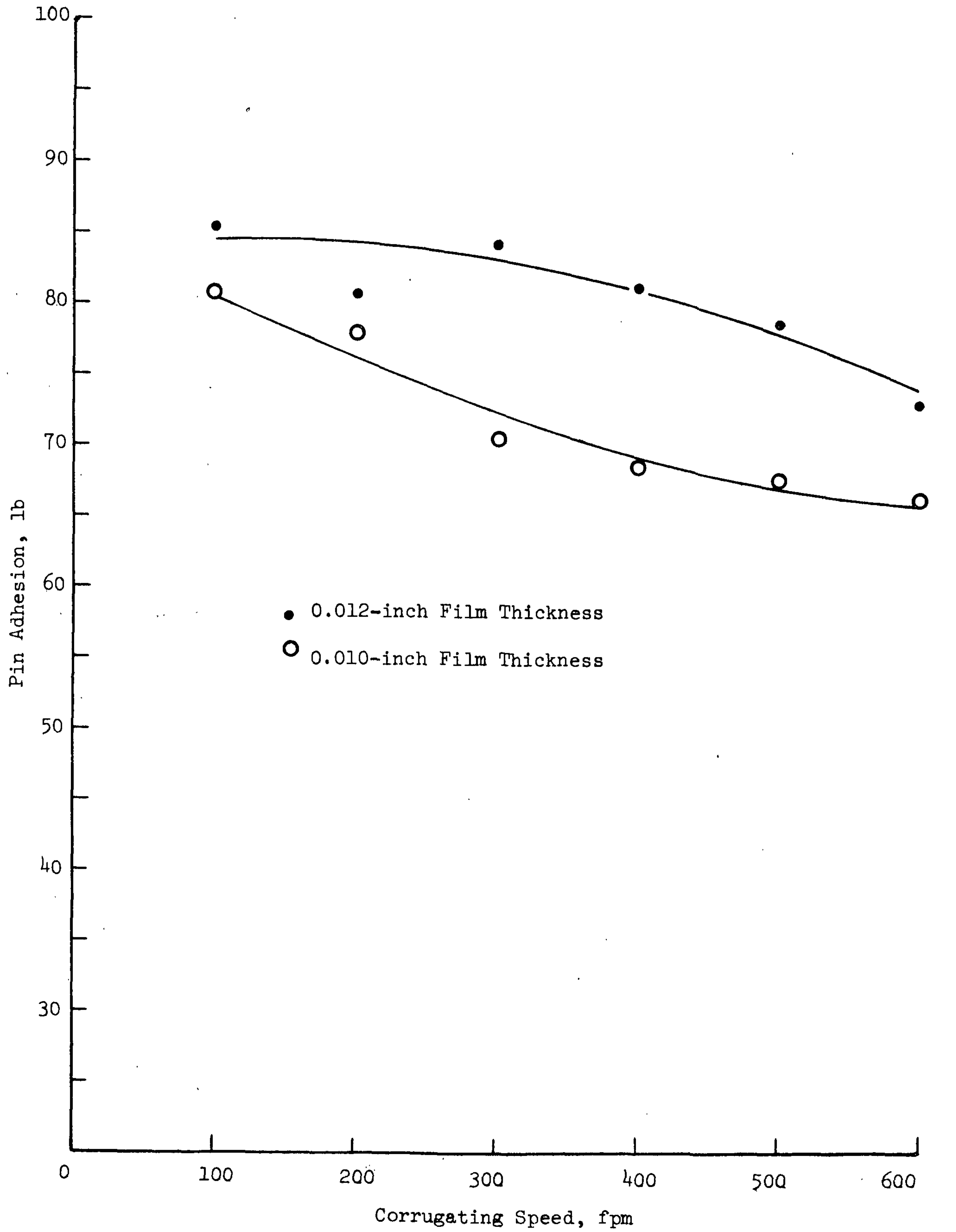

Figure 8. The Effect of Adhesive Film Thickness and Corrugating Speed on Pin Adhesion — Medium Viscosity Adhesive — pH 8.8 (Reduced Chemical Modifier)

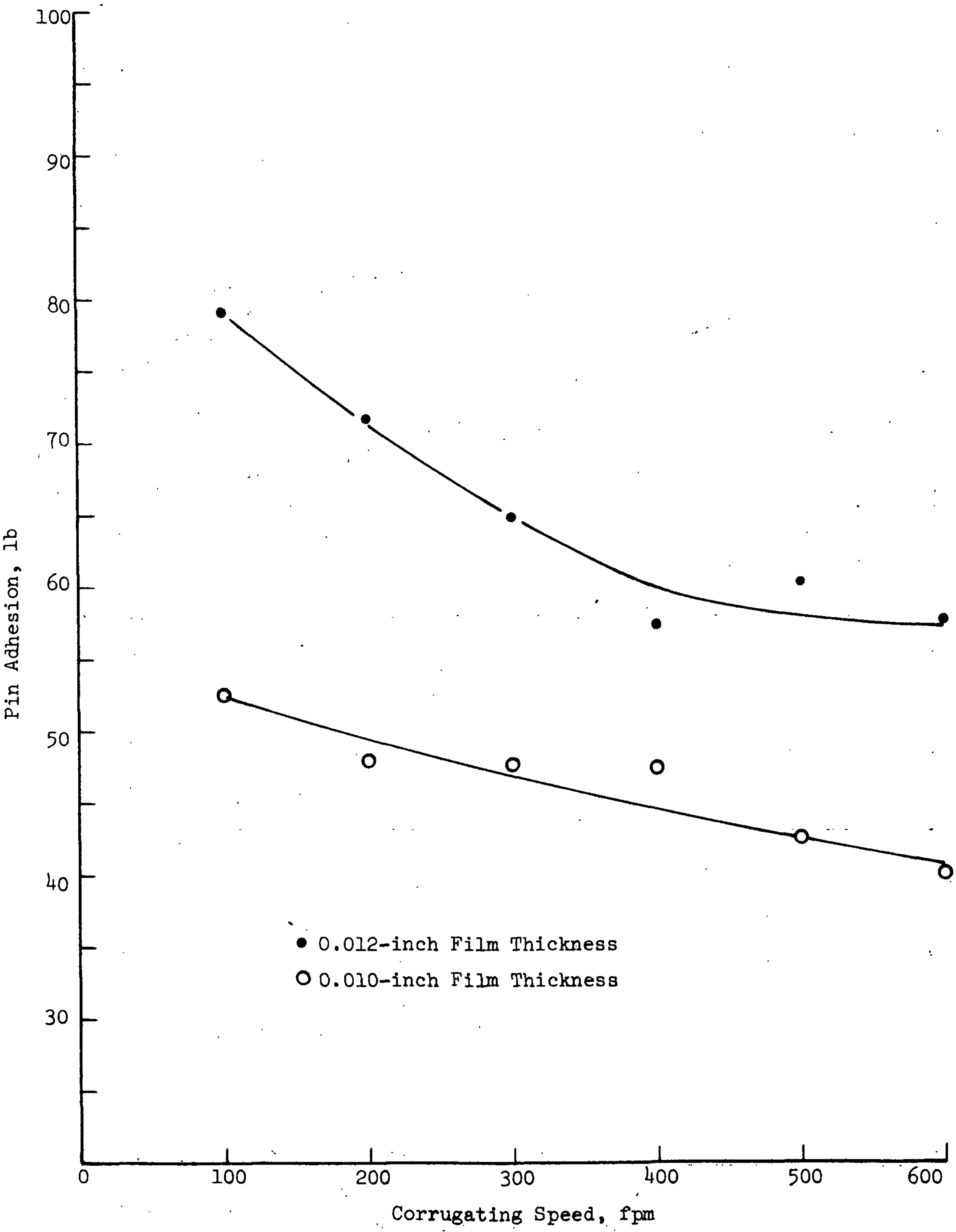

Figure 9. The Effect of Adhesive Film Thickness and Corrugating Speed on Pin Adhesion — High Viscosity Adhesive — pH 9.4 (Reduced Chemical Modifier)

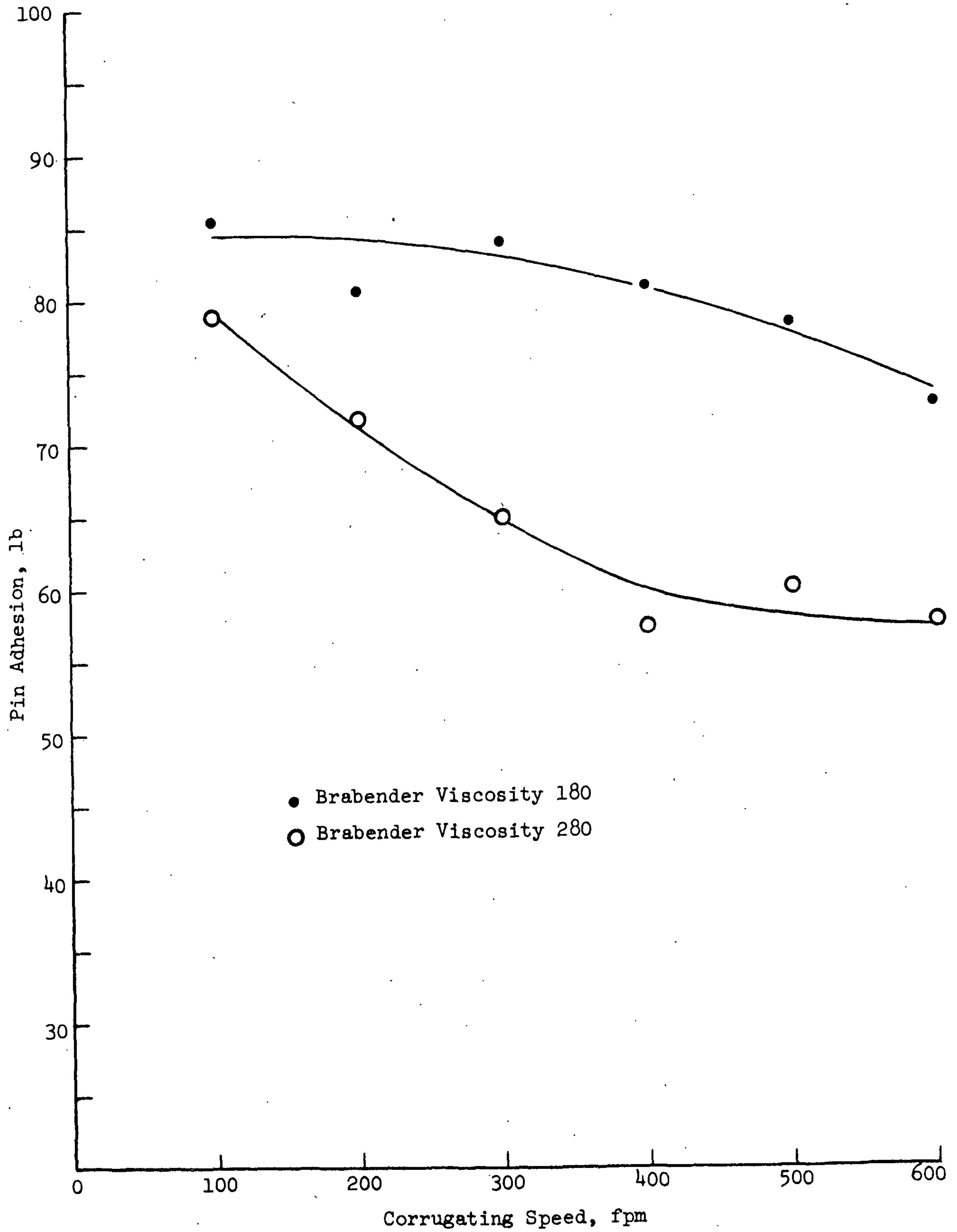

Figure 10. The Effect of Adhesive Viscosity and Corrugating Speed on Pin Adhesion — Reduced Chemical Modifier — 0.012 Inch Film Thickness

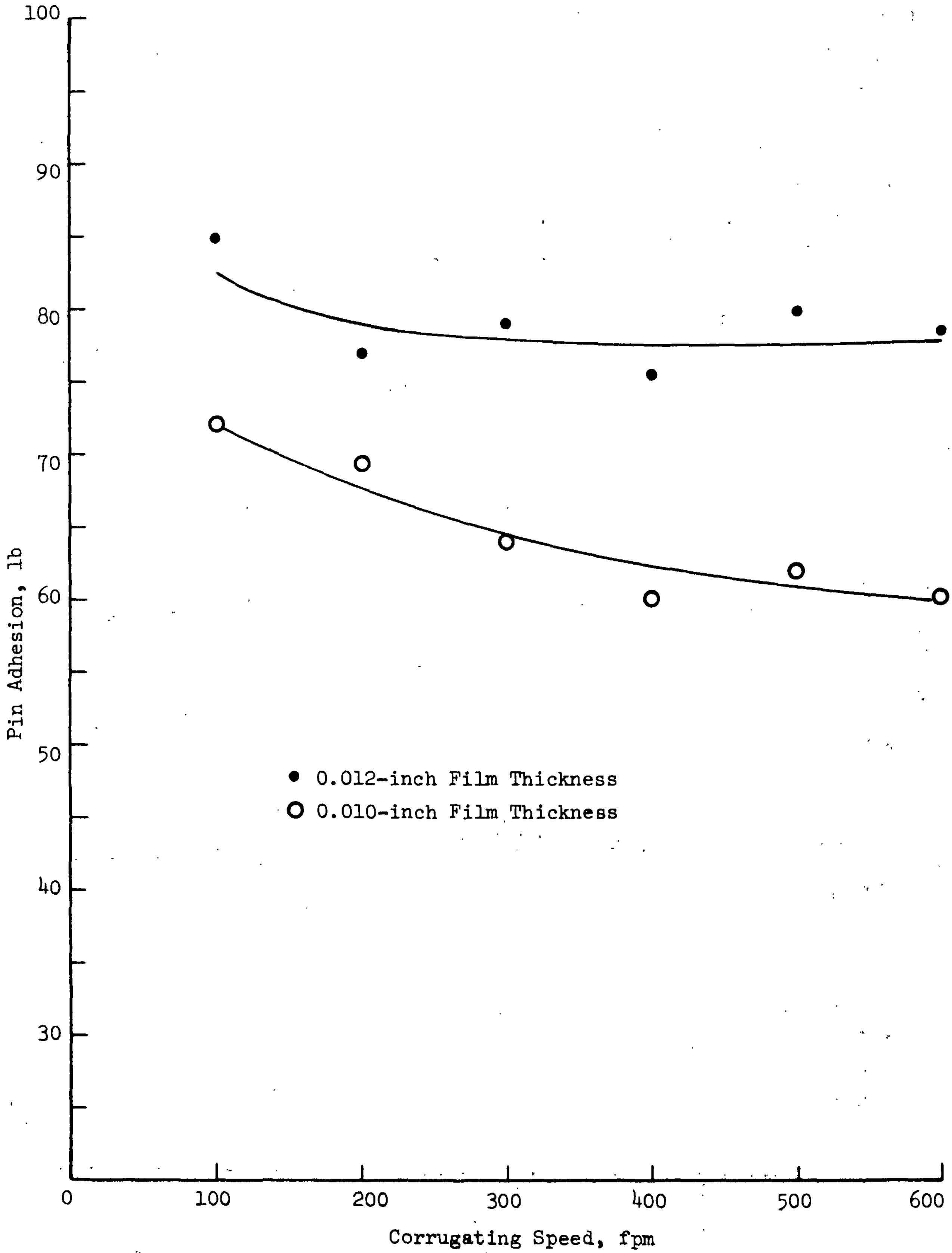

Figure 11. The Effect of Adhesive Film Thickness and Corrugating Speed on Pin Adhesion — PVA Added, pH 7.5

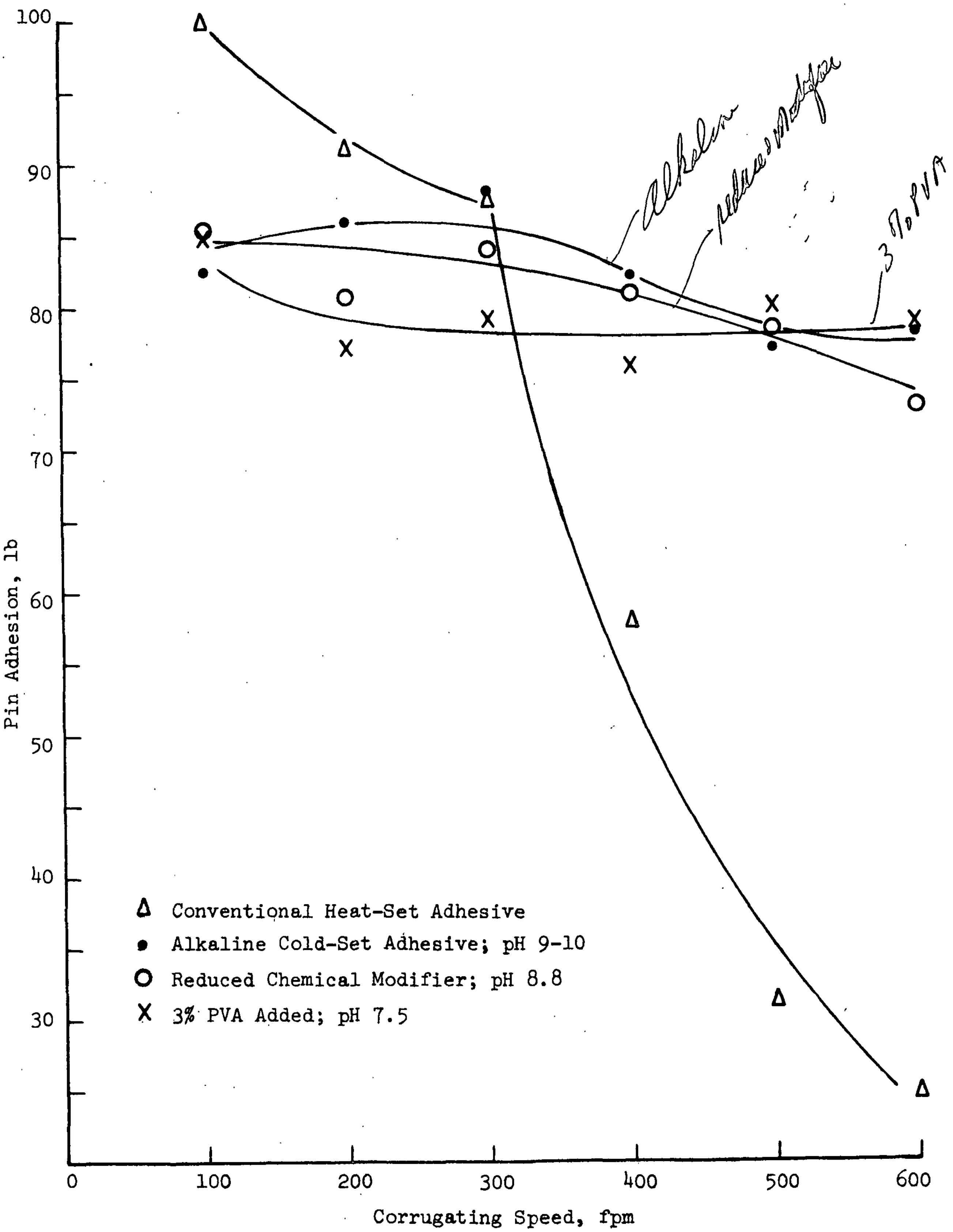

Figure 12. A Comparison of Cold-Set Adhesives (Steam on Medium, 0.012 Inch Clearance)

TABLE XII

THE EFFECT OF CROSS-LINKING AGENTS AND OTHER ADDITIVES ON ADHESIVE PROPERTIES

Adhesive No.	Additive, % (based on starch)	Final pH	Adhesive Solids Content, %	Holding Time at 85-90°C, hours	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C
49	Ammonium persulfate, 0.2	3.0	22.7	1.5	225	64 (147°F)
				3.0	140	60 (140°F)
54	Ammonium persulfate, 0.2; glyoxal, 1.0	3.1	22.6	3.0	120	59 (138°F)
55	Ammonium persulfate, 0.2; glyoxal, 2.0	3.1	22.8	2.0	200	60 (140°F)
56	Ammonium persulfate, 0.2; glyoxal, 3.0	3.1	22.5	2.0	215	60 (140°F)
57	Ammonium persulfate, 0.2; glyoxal, 5.0	--	22.5	2.0	Adhesive set up	
58	Ammonium persulfate, 0.2; Parez 608, 1.0	3.0	22.8	2.5	170	60 (140°F)
59	Ammonium persulfate, 0.2; Parez 608, 2.0	3.0	22.8	2.5	Adhesive set up	
60	Ammonium persulfate, 0.2; Parez 611, 2.0	4.7	22.9	2.0	190	58 (136°F)
61	Ammonium persulfate, 0.2; Parez 611, 10.0	--	22.9	2.0	Adhesive set up	
62	Ammonium persulfate, 0.2; Resyn 25-1103, 5.0	3.0	22.8	1.5	255	65 (149°F)
63	Ammonium persulfate, 0.2; Resyn 25-1103, 10.0	3.7	23.4	2.0	210	63 (145°F)
64	Ammonium persulfate, 0.2; Resyn 25-1103, 10.0	3.7	22.6	3.0	120	59 (138°F)

NOTES: Glyoxal LV PM5554 — Union Carbide.
Parez 608 — urea-formaldehyde resin — American Cyanamid.
Parez 611 — melamine-formaldehyde resin — American Cyanamid.
Resyn 25-1103 — polyvinyl acetate emulsion — National Starch & Chemical Corp.

All of the aforementioned agents were added after the indicated holding time.

Corrugator trials were subsequently carried out utilizing adhesives containing 3% of glyoxal, 1% of UF resin, and 10% of PVAc. A control adhesive prepared without cross-linking agent was included in this series. Since previous experience (1) indicated that wet strength medium could not be satisfactorily processed on the "hot melt" corrugator without fracturing, it was necessary to use standard components. The corrugated board was subsequently tested for pin adhesion after conditioning at 50 and 85% RH and the results are recorded in Table XIII. Results obtained with an alkaline cold-set adhesive are included in the table for purposes of comparison. Also included are results obtained with a reference two-component heat-set starch adhesive applied on the hot melt corrugator. Pin adhesion as a function of corrugating speed is presented graphically in Fig. 13 and 14 for selected formulations.

Adhesive Stability

Conceptually, the preparation and utilization of the cold-set adhesive in practical corrugating would be a continuous process with no provision or requirement for extended adhesive storage. However, relatively short holding periods may be incurred during unexpected downtime or loss of proper temperature control. Under these conditions, knowledge of adhesive stability with respect to time and temperature would be essential. In response to this potential problem area, several series of tests were conducted in the current program. A number of the cold-set adhesives utilized in the previously described corrugating trials were tested for viscosity, gelation temperature, solids content, and pH as a function of holding time at 185-190°F. The adhesive holding tank was covered but not sealed during the course of these tests. Results are recorded in Table XIV.

TABLE XIII

THE EFFECT OF CROSS-LINKING AGENTS ON MOISTURE SENSITIVITY

Corrugator Run No.	Adhesive No.	Adhesive Modifiers & Additives, %, based on starch	Adhesive Solids Content, %	Final pH	Brabender Viscosity at 95°C & 190 rpm, units	Gelation Temp., °C	Operating Temperature Pan, °F	Operating Temperature Glue Roll, °F	Corrugating Speed, fpm	Pin Adhesion at 50% RH, lb	Pin Adhesion at 85% RH, lb	Moist/Dry Pin Adhesion, %
25	20	Ammonium persulfate, 0.5; sodium sulfite, 0.5; sodium hydroxide (total), 0.85%	21.3	9-10	165	62(144°F)	192	210	100	82.4	35.4	43.0
									200	85.8	32.4	37.8
									300	87.6	33.8	38.6
									400	82.2	27.4	33.3
									500	77.0	24.8	32.2
									600	78.2	23.2	29.7
33	65	Ammonium persulfate, 0.2 (control)	22.4	3.0	190	64(147°F)	185	205	100	68.0	33.2	48.8
									200	66.8	38.4	57.5
									300	67.8	37.8	55.8
									400	70.8	38.0	55.4
									500	68.6	39.6	57.7
									600	66.6	35.6	53.4
34	66	Ammonium persulfate, 0.2; glyoxal, 3.0	23.2	3.0	200	62(144°F)	181	205	100	79.0	41.4	52.4
									200	76.4	39.0	51.0
									300	74.0	43.4	58.6
									400	72.4	42.6	58.8
									500	76.2	44.8	58.8
									600	71.6	41.2	57.5
35	67	Ammonium persulfate, 0.2; polyvinyl acetate[a], 10.0	23.6	3.7	220	65(149°F)	171	200	100	65.2	--	--
									200	59.6	--	--
									300	57.4	--	--
									400	50.6	27.0	53.3
									500	47.4	--	--
									600	54.6	30.4	55.7
36	68	Ammonium persulfate, 0.2; UF resin[b], 1.0	22.3	3.0	220	63(145°F)	181	205	100	79.4	44.8	56.4
									200	77.4	43.2	56.1
									300	63.0	30.0	47.6
									400	68.2	36.0	52.8
									500	62.2	29.8	47.9
									600	63.8	32.2	50.4
--	--	Standard two-component starch adhesive applied on hot-melt corrugator	20.0	12.6	--	--	--	--	300	87.2	53.6	61.5
									400	57.6	35.0	60.8
									500	31.2	16.8	53.8

[a]Resyn 25-1103 — National Starch & Chemical Corp.
[b]Parez 608 — American Cyanamid Co.

NOTE: Steam shower on medium, adhesive film clearance 12-mil.

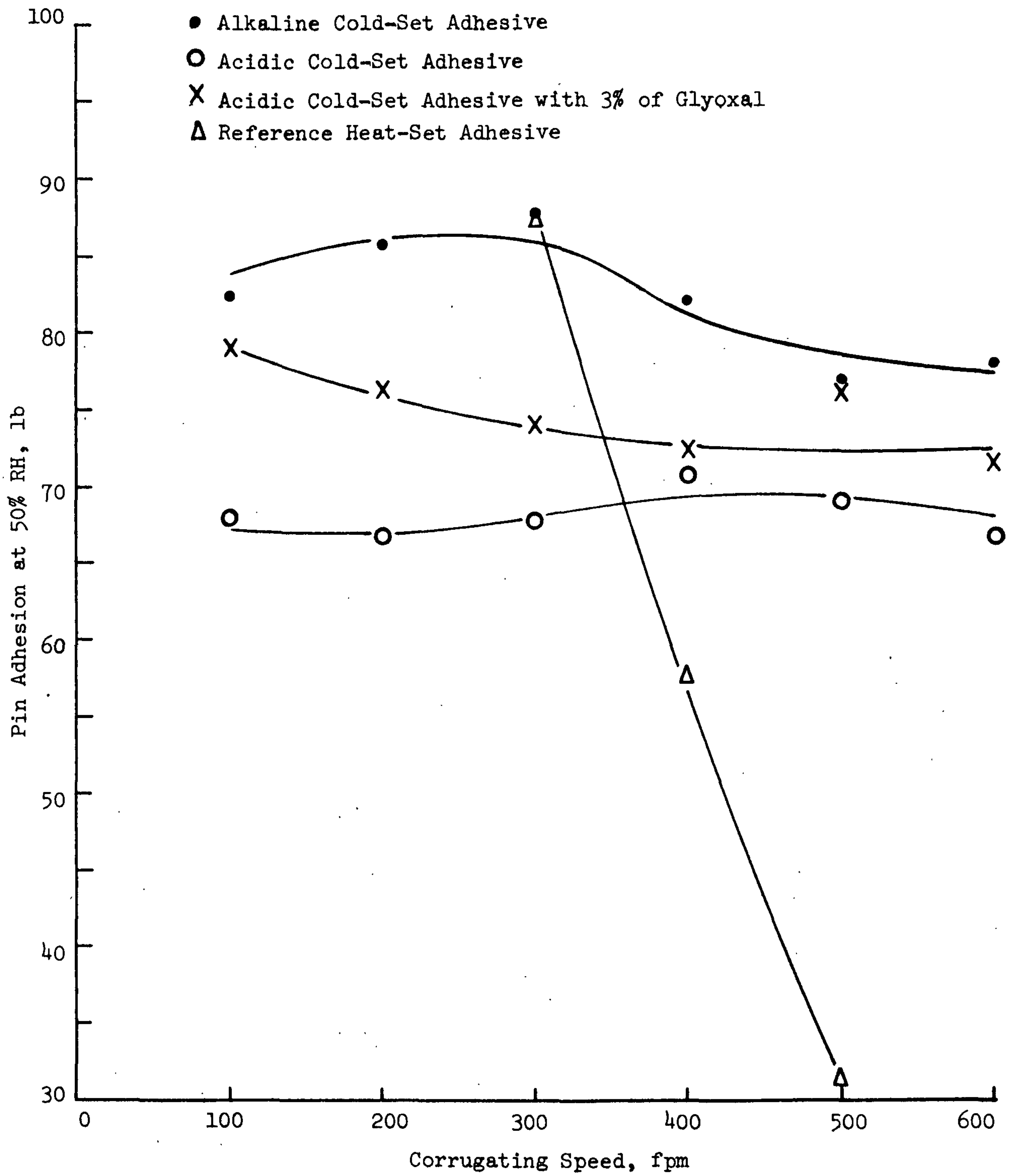

Figure 13. The Effect of Adhesive Formulation on Pin Adhesion Measured at 50% RH

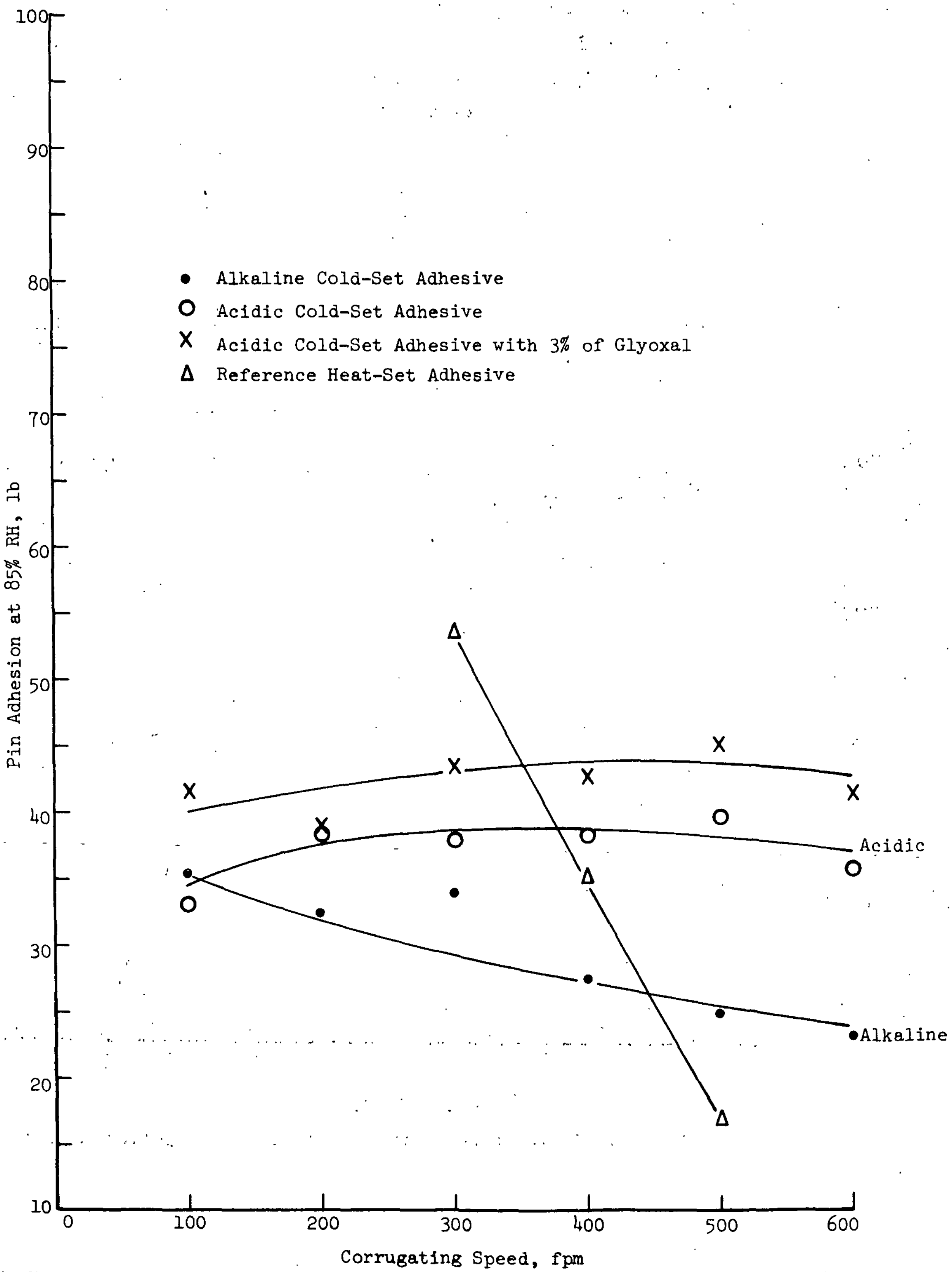

Figure 14. The Effect of Adhesive Formulation on Pin Adhesion Measured at 85% RH

TABLE XIV

THE EFFECT OF HOLDING TIME ON ADHESIVE PROPERTIES

Adhesive No.	Adhesive Modifiers, % (based on starch)	Holding Time at 185-190°F, hours	Final pH	Adhesive Solids Content, %	Brabender Viscosity at 95°C (203°F)	Brabender Viscosity at 185°F	Gelation Temp., °C
1	Ammonium persulfate, 0.5;	Initially	7.5	22.9	270	290	67(153°F)
	sodium sulfite, 0.5;	1.25	--	23.5	270	300	67(153°F)
	total NaOH, 0.3	3.5	--	24.3	350	390	68(154°F)
		4.5	--	24.9	550	560	68(154°F)
		6.0	--	25.4	920	1000	73(163°F)
2	Ammonium persulfate, 0.5;	Initially	7.1	22.2	165	185	64(147°F)
	sodium sulfite, 0.5;	1.5	--	22.6	160	185	64(147°F)
	total NaOH, 0.3	3.0	--	23.1	170	185	63(145°F)
		4.5	--	23.5	180	200	63(145°F)
		6.0	--	23.8	200	215	64(147°F)
19	Ammonium persulfate, 0.5;	Initially	10.1	22.5	190	250	65(149°F)
	sodium sulfite, 0.5;	1.25	--	22.9	200	250	65(149°F)
	total NaOH, 0.85[a]	2.5	9.2	23.3	240	260	65(149°F)
		3.8	8.2	23.7	260	270	64(147°F)
		5.2	7.2	24.2	285	310	65(149°F)
18	Ammonium persulfate, 0.5;	Initially	8.4	21.7	190	230	62(144°F)
	sodium sulfite, 0.5;	1.25	8.4	21.8	190	220	62(144°F)
	total NaOH, 0.3	2.5	8.2	22.4	190	230	63(145°F)
	borax, 0.7	3.75	8.3	22.7	230	250	63(145°F)
20	Ammonium persulfate, 0.5;	Initially	10.0	21.3	165	200	62(144°F)
	sodium sulfite, 0.5;	1.5	8.9	21.5	170	200	60(140°F)
	total NaOH, 0.85[a]	3.25	8.8	21.5	165	185	60(140°F)
		4.5	8.2	--	--	--	--
49[b]	Ammonium persulfate, 0.2	Initially	3.0	22.7	720	--	73(163°F)
		1.0	--	--	340	--	67(153°F)
		1.5	--	--	225	--	64(147°F)
		3.0	--	--	140	--	60(140°F)

[a] 0.3% Added before cooking, 0.55% added after cooking.
[b] This adhesive sample was not used in corrugating.

The effect of temperature cycling was examined with additional adhesives prepared according to the standard formulation (0.5% persulfate, 0.5% sulfite, 0.3% alkali, pH 7-8). In these tests, separate adhesive samples were allowed to cool to a specified temperature then held at that temperature for five minutes followed by reheating to a holding temperature of 185-190°F. The temperatures selected were 160, 169, 178, and 185°F. The effects of this type of cycling on adhesive viscosity are recorded in Table XV.

Finally, the effect of repeated temperature cycling on a single adhesive sample was examined over the same temperature range, i.e., 185-160°F. In this case, the adhesive was allowed to cool to 160°F and, after holding at that temperature for five minutes, the sample was reheated to 185°F. The same sample was then allowed to cool to 169°F followed after five minutes by reheating to 185°F. This process was repeated with the temperature difference reduced by 8-9 degrees in each cycle. The effect of repeated temperature cycling on adhesive viscosity is shown in Table XVI.

TABLE XV

THE EFFECT OF TEMPERATURE CYCLING ON ADHESIVE PROPERTIES

Adhesive No.	Brabender Viscosity at 190 rpm at Indicated Temperature: At 95°C (203°F)	At 185°F	After Cooling to 160°F	After 5 min at 160°F	After Cooling to 169°F	After 5 min at 169°F	After Cooling to 178°F	After 5 min at 178°F	After Holding at 185°F	After Reheating to 185°F	After Reheating to 203°F	Total Elapsed Time, min	Adhesive Solids, %	Adhesive pH
69	160	170	230	240	--	--	--	--	--	190	190	36.9	22.3	7.1
70	150	160	--	--	195	200	--	--	--	175	160	30.2	22.4	7.1
71	155	170	--	--	--	--	185	180	--	170	150	23.6	22.8	7.1
72	175	195	--	--	--	--	--	--	185	--	165	37.2	22.6	7.1

NOTES: In all cases, the adhesive formulation contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, and 0.3% of NaOH based on dry weight of starch. The cooking temperature was 230-240°F, the dwell time in the cooker was six seconds. In the case of adhesive No. 69 the temperature was held at 185°F for 24 minutes.

TABLE XVI

THE EFFECT OF REPEATED TEMPERATURE CYCLING ON A SINGLE ADHESIVE SAMPLE
(Solids 23%; pH 7.2)

Adhesive No.	Temperature Sequence, °F	Initial Brabender Viscosity at 190 rpm at Indicated Temp., units	Brabender Viscosity at 190 rpm After Holding 5 Min at Indicated Temp.
73	203	195	--
	185	235	--
	160	345	370
	185	290	250
	169	300	335
	185	285	275
	178	305	310
	185	290	285
	203	230	--

NOTES: The adhesive utilized in this experiment contained 0.5% of ammonium persulfate, 0.5% of sodium sulfite, and 0.3% of NaOH based on dry weight of starch. The cooking temperature was 230-240°F and the dwell time was six seconds.

DISCUSSION

The current results confirm earlier evidence (1) that the effectiveness of the cold-set starch adhesive, in so far as pin adhesion is concerned, depends upon the viscosity of the adhesive. As indicated in Table I, Fig. 1, and again in Table XI, Fig. 8-10 adhesives with viscosities well in excess of 200 Brabender units tend to provide low pin adhesion values compared to those in the range of 160-200 Brabender units. The evidence further indicates that this applies to mediums varying over a wide range in water drop number. Receptivity would also be expected to be an important property since both viscosity and receptivity relate to the penetration of a liquid adhesive in short time intervals. Indeed fiber pull was achieved only in the case of the most receptive medium (No. 5476, Table I). In all cases of reduced receptivity (increased water drop), failure occurred primarily at the medium-adhesive or liner-adhesive interface. Hence, in some respects, component receptivity may be of equal or greater importance than adhesive viscosity, particularly in the case of the cold-set adhesive. Of course, fiber failure in the most receptive medium could also reflect a low level of surface bonding strength although this is probably not the case since the pin adhesion values for that medium were roughly equivalent to those of other mediums having higher water drop numbers.

Fiber failure was also obtained in a subsequent series of tests when a high-viscosity alkaline adhesive was applied to medium of intermediate receptivity (Corrugator Run No. 26 in Table XI). In that case, however, the pin-adhesion values were notably lower than those obtained with a similar adhesive of lower viscosity applied to the same components (Corrugator Run No. 28 in Table XI). Failure occurred primarily at the medium-adhesive interface in the latter case.

Hence, while fiber pull may be a desirable characteristic in a failure pattern, it does not necessarily reflect a high level of adhesive strength. The most desirable results up to this point in the program with respect to both pin-adhesion value and failure pattern were achieved with adhesives of intermediate viscosity (160-210 Brabender units) and a medium of high receptivity.

A rather disturbing trend is indicated in the results in Table I and Fig. 1 in that pin adhesion shows a tendency to decline as a function of corrugating speed, particularly in the case of the lower viscosity adhesive. This was not found in the earlier work (1) which utilized a reference medium similar to No. 16334 in Table I. Efforts to improve upon the results in Table I examined the effects of several additives and adhesive modifications. In comparing the various modifications covered in Tables III-VII and Fig. 2-6, it becomes apparent that the most effective conditions for utilizing the cold-set adhesive consisted of applying an alkaline adhesive to steamed medium (Table VII). Under these conditions, the pin adhesion values tended to remain at a relatively high level as a function of corrugating speed in three of four cases. Results for the fourth medium are rather inconclusive because of the tendency for this medium to fracture at higher corrugating speeds. Since utilization of an alkaline adhesive without steamed medium (Table VI) did not match the performance of the combination of alkalinity plus steam, it is assumed that the steam treatment assists wetting and/or penetration of the adhesive although it did not enhance fiber failure in the less receptive mediums. Borax was found to be of benefit in one case (Medium No. 16334 in Table V) but proved detrimental when utilized on the other three mediums. As was found in the initial series of experiments, a consistent fibr failure pattern was obtained only in the case of the most receptive medium, thereby confirming the importance of receptivity to the cold-set adhesive.

In line with earlier results (1), the cold-set adhesives provided an advantage over the reference heat-set adhesive (Table II, Fig. 3-6) at higher corrugating speeds although the difference was probably magnified by a lack of preheater capacity on the hot melt corrugator. In spite of the favorable results obtained with the alkaline adhesives and the highly receptive medium, examination of air-dried films indicated a persistent tendency for the cold-set adhesive to be brittle although the alkaline films showed some improvement in this respect.

Further efforts to improve the properties of the cold-set adhesive incorporated the use of kraft fiber, polyvinyl alcohol, and reduced chemical modifier (Tables VIII-XI; Fig. 8-11). The potential advantage of adding kraft fiber to the cold-set adhesive could not be established due to the fiber classification problem resulting from the type of metering system on the hot-melt corrugator. The other two adhesives were applied at two film clearances and, additionally, the adhesive with reduced modifier was applied at two viscosity levels. The effect of viscosity was discussed previously and will not be repeated at this time. A difference in film clearance of 0.002 in. is shown to have a pronounced effect on the pin adhesion resulting from the use of an adhesive formulated without sodium sulfite. Conceivably increasing the film clearance to in excess of 0.012 in. would have further improved pin adhesion although this was not necessarily indicated in earlier work (1). Heavy adhesive films would tend to cool more slowly thereby delaying gelation and posing a potential problem in green bond formation. Further, heavy films would require dissipation of additional water into the board components. While fiber pull was not found to be the dominant type of failure in any series in Table XI, it is interesting to note that some liner failure occurred in Runs 26, 27, and 29 and this, in spite of relatively low pin-adhesion values in Runs 27 and 29. The adhesives utilized in these runs were known to have somewhat higher-than-normal gelation temperatures and, while it is rather difficult to produce the combination of low viscosity and high gelation temperature in persulfate-modified starches, it appears that slightly higher gelation temperature (66-69°C; 151-156°F) may be of benefit from the standpoint of failure pattern.

Results obtained with the modified formulations in Table XI are compared to the alkaline cold-set adhesive and to the conventional heat-set adhesive in Fig. 12. On this basis, elimination of sodium sulfite or addition of polyvinyl alcohol does not appear to provide a consistent advantage in pin adhesion. The cast film containing PVA showed slightly improved flexibility but not materially better than the previously tested alkaline adhesives.

The final series of corrugator trials explored the potential of adding cross-linking agents to cold-set starch formulations for purposes of developing water resistance (Table XIII; Fig. 13 and 14). It is evident in these results that a significant level of water resistance was not attained under any conditions due probably to at least two factors: (1) the inability to add 5-10% of cross-linking agent (glyoxal or UF resin) as is normally done in insolubilizing starch, and (2) the lack of heat required for adequate curing of the resin. However, in spite of these limitations, there is an indication in Table XIII that some water insensitivity develops among the acidic starch formulations. The alkaline adhesive (No. 20) shows the most drastic decline in pin adhesion at the higher humidity and, hence, the lowest percentage of moist/dry adhesion. While the acidic adhesives did not match the dry pin adhesion values of the alkaline product, several provided a better strength level under the higher humidity condition. This applies to the acidic adhesive without cross-linking agent (No. 65) as well as those containing glyoxal and the urea-formaldehyde resin.

While the polyvinyl acetate resin provided roughly equivalent percentage moist/dry adhesion, the actual pin values were low. The best overall results for the cold-set adhesive were produced by glyoxal (No. 66) which improved dry adhesion as well as moist adhesion. Apparently, the acidic conditions were sufficient to induce a very low level of cross-linking which might be further enhanced at higher glyoxal levels. Hence, reformulating to accommodate higher level of cross-linking agent would appear to be worthy of further consideration.

Results of the adhesive aging experiments (Table XIV) indicate that neutral and alkaline cold-set adhesives will remain reasonably stable with respect to viscosity and gelation temperature for at least 1-2 hours if the temperature is maintained at 185-190°F. The increase in viscosity which may be related to an increase in solids content becomes more pronounced as the initial viscosity exceeds 200 Brabender units. In contrast, strongly acidic adhesives were unstable presumably due to continued chemical modification which occurs after the short cooking time under pressure. It is assumed that this problem would be greatly reduced or eliminated in a jet cooker designed for persulfate modification, i.e., one providing a longer dwell time.

The temperature cycling experiments (Table XV and XVI) indicate that the starch cold-set adhesive can tolerate moderate temperature fluctuations over short time intervals without incurring serious increases in viscosity. Most of the adhesives utilized in these tests had initial viscosities in the range of 150-175 Brabender units and, under these conditions, a temperature drop 16°F below the holding temperature followed by reheating resulted in a viscosity increase of only 15 Brabender units which would leave the viscosity at an acceptable level for corrugating. However, adhesives with initial viscosities approaching 200 Brabender units, as in Table XVI, cannot tolerate significant temperature cycling and certainly not repeated cycling without excessive increases in viscosity. Hence, a reasonable level of stability is indicated for neutral and alkaline adhesives with low-medium viscosities. As the initial viscosity increases, the tolerance for temperature fluctuations diminishes because of the limiting viscosity for effective corrugating.

In review, optimum pin adhesion results in this study were obtained with an alkaline cold-set adhesive when utilizing presteamed medium. This applied to mediums varying widely in water receptivity. Under the optimum conditions, pin adhesion was maintained at a relatively high level as a function of corrugating speed although the adhesive bond tended to be brittle and fiber failure consistently occurred only in the case of the most receptive medium. Once again adhesives with viscosities well in excess of 200 Brabender units provided lower pin numbers than similar formulations of lower viscosity. Modified adhesive formulations incorporating the use of borax, polyvinyl alcohol, reduced chemical modifier, etc., were not found to provide consistent advantages under the conditions of these experiments.

While none of the formulations provided a high level of water resistance, the acidic cold-set adhesives were found to provide better resistance than the alkaline adhesives and a low level of insolubilization was indicated in the presence of glyoxal.

Neutral and alkaline cold-set adhesives were found to be reasonably stable with respect to viscosity for at least 1-2 hours if held at 85-90°C in covered containers. Likewise adhesives of low-intermediate viscosity were found to be tolerant to moderate decreases in temperature if reheated to the holding temperature within a short time. However, repeated temperature cycling of an adhesive with an initial viscosity approaching 200 Brabender units was found to produce viscosity increases which are known to reduce efficiency in corrugating.

FUTURE WORK

With the results obtained in this study serving as background, it now appears that the most fruitful area for future work would consist of practical in-plant corrugating trials. The direction of this work would logically follow the outline given in Part B of the experimental program in Proposal No. 2212.

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