STARCH AS A BEATER ADHESIVE. THE ROLE OF THE STARCH GRANULE

INTRODUCTION

The literature contains a considerable amount of sometimes conflicting evidence on the question of whether cooked corn starch contains relatively effective and ineffective fractions with respect to their function as wet-end adhesives for paper fiber. Starch cooked at or below the boiling point of water normally contains a relatively large portion that can be separated by centrifugation. This insoluble fraction is considered by some (1) to be relatively ineffective as an adhesive. Pearl (2) showed that amylopectin is more effective than amylose.

It was the purpose of this study to determine whether the fractions of cooked corn starch that could be separated by centrifugation followed by precipitation with miscible nonsolvents differ in their effectiveness as wet-end adhesives.

EXPERIMENTAL

A portion of Northwest softwood bleached sulfite pulp was beaten to 700 ml. Schopper-Riegler freeness in a laboratory Valley beater, dewatered, and stored in a cold room maintained at 5°C. This pulp was used for all handsheets. Lots of the pulp were dispersed at 2% consistency in a British disintegrator in deionized water. The indicated amount of starch was added, stirred for 30 minutes, 2% saponified rosin size added, stirred for five minutes, 4% alum added, stirred for 5 minutes, and the stock adjusted to pH 4.5-5.0. The stock was diluted to 0.5% consistency for sheet-making.

Handsheets were formed in a 8 by 8-inch Noble & Wood mold, pressed between blotters at 50 p.s.i., and dried on a steam drum for seven minutes at four p.s.i. steam pressure. The sheets so formed were conditioned at 73°F. and 50 R.H. and tested by TAPPI and IPC standard methods. The starch retention was determined by the method of Browning, Bublitz, and Baker (3).

The starch used throughout this work was a commercial, unmodified pearl cornstarch. One lot of starch was cooked in a Corn Industries Research Foundation viscometer (C.I.V.) for 30 minutes at 95°C. and 5% consistency. To obtain higher yields of dispersible starch, the remaining lots were cooked by passage through a laboratory jet cooker operated at 220 to 230°F. Each lot of starch was centrifuged at 2% solids for 15 minutes at 2500 r.p.m. in an International Centrifuge (Size 2, Model V, Rotor No. 277) to separate the "nondispersibles". These nondispersibles and all subsequent precipitates from nonsolvent addition were redispersed at 2% solids by one-minute treatment in a Waring Blendor prior to addition to the pulp.

In the following fractional precipitations, the proportion of nonsolvent to solvent used was determined by a number of trial and error experiments. It was found that the initial precipitation was sharply defined, and in no case was it possible to secure more than two fractions. The centrifugate from the second precipitation was water-clear and free of dissolved solids.

Ethyl Alcohol Fractionation

Following centrifugal removal of nondispersibles from the jet cooked starch, 400 ml. of 95% ethyl alcohol were added to one liter of the starch dispersion at 2% solids with vigorous stirring. The precipitate obtained was centrifuged out and redispersed in water for sheet-making. To the supernatant, 200 ml. of 95% ethyl alcohol was added. The precipitate was redispersed in water for sheet-making.

Acetone Fractionation

Three hundred milliliters of acetone were added to one liter of the nondispersible supernatant at 2% solids. The precipitate obtained was separated by centrifugation and redispersed in water for sheet-making. To the remaining supernatant 25 ml. of acetone were added and the precipitate was recovered by centrifugation.

Isopropyl Alcohol Fractionation

Three hundred and fifty milliliters of isopropyl alcohol were added to one liter of dispersed starch at 2% solids. The precipitate was removed by centrifugation and redispersed in water for sheet-making. To the

remaining supernatant, 200 ml. of isopropyl alcohol were added, and the precipitate removed and redispersed in water.

Butanol and Ethyl Alcohol Fractionation

One hundred milliliters of butanol and 200 ml. of 95% ethyl alcohol were added in succession to one liter of the dispersed starch at 2% solids. The precipitate was centrifuged out and redispersed in water to use in handsheets. To the remaining supernatant, 400 ml. of ethyl alcohol were added. The precipiate was centrifuged out and redispersed.

Ethyl Alcohol and Butanol Fractionation

Three hundred milliliters of 95% ethyl alcohol and 100 ml. of butanol were added in succession to one liter of dispersed starch at 2% solids. The precipitate was centrifuged out and redispersed in water to form handsheets. To the remaining supernatant, 100 ml. of butanol were added and the precipitate removed by centrifugation.

Butanol and Acetone Fractionation

Two hundred milliliters of acetone and 100 ml. of butanol were added in succession to one liter of dispersed starch at 2% solids. The precipitate was centrifuged out and redispersed in water to form handsheets. To the remaining supernatant, 200 ml. of butanol were added. The precipitate was centrifuged out and redispersed in water.

RESULTS

The results of the several fractionations of cooked starch and the physical tests on papers made with these starches are given in the following paragraphs and tables.

C.I.V. Cooked Starch Frationation, Table I.

The larger portion of the starch was contained in the nondispersed fraction. Somewhat higher retention in the paper was found for the dispersed fraction. There is no significant difference in the strength properties of the papers made with the different fractions.

Ethyl Alcohol Fractionation, Table II

There is no significant difference in the retention or strength properties of the papers made with the several starch fractions.

Acetone Fractionation, Table III

In this case, the sheets made with the nondispersible starch seem to be significantly weaker than those from the other fractions or whole starch.

Isopropyl Alcohol Fractionation, Table IV

There is no significant difference in the retention or strength difference from the fractions of this separation.

Butanol and Ethyl Alcohol Fractionation, Table V

There is no significant difference in the results secured from this fractionation.

Ethyl Alcohol and Butanol Fractionation, Table VI

The nondispersible yield from this cook was very low (5.2%).
Nevertheless, there is no significant difference in performance among
the several fractions.

Acetone and Butanol Fractionation, Table VII

There is no significant difference in retention or paper strength
increments among the several fractions of this separation.

CONCLUSIONS

The methods of fractionation of cooked starch used yielded no
significant difference in paper retention or paper strength increments. It
would be of interest to compare these results with those from other methods
of fractionation.

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(September, 1952).

TABLE I

C.I.V. COOKED STARCH

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	10.1	55	14.4	97
Whole	100	1	40	44.0	10.2	62	15.4	131
		3	23	44.1	10.3	69	16.4	231
		5	28	44.7	10.4	75	18.3	372
Nondispersed	71	1	30	43.7	10.2	61	15.4	160
		3	23	44.6	10.1	68	17.0	299
		5	22	44.7	10.2	73	18.6	295
Dispersed	29	1	60	44.0	10.2	65	16.1	207
		3	50	45.1	10.2	69	17.6	271
		5	46	44.3	10.3	73	17.4	281

TABLE II

ETHYL ALCOHOL PRECIPITATION

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	50	44.7	10.2	63	16.0	131
		3	30	44.7	10.2	73	17.9	270
		5	28	44.9	10.2	81	19.0	324
Nondispersible	18.5	1	40	45.0	10.0	65	16.1	126
		3	27	45.0	10.0	73	17.7	273
		5	24	44.0	9.8	76	17.6	314
First precipitate	38.5	1	40	44.1	9.8	61	14.9	90
		3	30	45.0	9.8	73	17.8	239
		5	26	45.1	9.8	78	18.3	381
Second precipitate	43.0	1	40	44.5	10.1	66	17.0	172
		3	33	44.4	10.1	76	19.2	336
		5	26	44.8	10.2	83	20.3	347

TABLE III

ACETONE PRECIPITATION

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	50	45.2	10.0	68	16.9	151
		3	30	44.4	10.1	76	18.2	259
		5	26	45.3	10.1	83	20.1	377
Nondispersible	23.2	1	40	44.8	10.2	63	16.5	114
		3	27	44.9	10.0	69	17.5	206
		5	24	44.8	10.2	73	18.2	211
First precipitate	47.5	1	30	44.1	10.0	68	16.7	151
		3	27	43.8	10.2	77	17.7	215
		5	28	43.6	9.9	79	19.2	426
Second precipitate	37.5	1	30	44.5	10.1	69	16.7	163
		3	27	44.5	10.1	74	18.6	281
		5	24	43.7	10.2	81	19.3	384

TABLE IV

ISOPROPYL ALCOHOL PRECIPITATION

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	40	44.6	10.1	64	15.7	123
		3	27	45.2	10.3	74	18.2	232
		5	24	44.7	10.2	81	19.1	334
Nondispersible	31.2	1	40	44.6	10.1	66	16.4	126
		3	30	44.5	10.1	70	17.3	218
		5	26	45.3	10.3	75	18.8	290
First precipitate	28.0	1	40	43.9	10.0	63	16.0	125
		3	30	44.9	10.2	68	17.4	182
		5	24	44.8	10.2	76	18.1	296
Second precipitate	41.8	1	40	44.2	10.5	65	16.2	142
		3	27	44.2	10.3	73	18.6	319
		5	24	44.1	10.3	78	19.4	462

TABLE V

BUTANOL AND ETHYL ALCOHOL PRECIPITATION

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	30	44.1	10.0	69	16.1	121
		3	23	44.6	10.1	76	18.2	366
		5	20	44.4	10.3	82	19.1	392
Nondispersible	15.7	1	30	44.4	10.3	69	16.4	139
		3	23	43.9	10.2	72	16.7	227
		5	22	44.0	10.0	76	18.0	360
First precipitate	23.2	1	30	44.9	10.2	65	16.1	120
		3	27	44.1	10.0	73	17.0	252
		5	24	45.1	10.2	78	19.2	335
Second precipitate	61.1	1	20	44.5	10.1	66	16.3	133
		3	20	44.6	10.1	76	17.8	338
		5	20	43.8	10.0	80	18.5	444

TABLE VI

ETHYL ALCOHOL AND BUTANOL PRECIPITATION

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	40	44.9	10.0	61	16.0	145
		3	23	45.4	10.3	75	18.8	265
		5	22	43.5	10.1	77	18.4	423
Nondispersible	5.2	1	40	45.9	10.4	66	16.3	144
		3	30	45.4	10.1	70	17.4	255
		5	22	44.3	10.1	77	18.5	425
First precipitate	60.0	1	40	44.6	10.1	65	16.2	154
		3	30	44.9	10.2	73	18.0	296
		5	26	44.9	10.1	77	18.5	410
Second precipitate	30.0	1	30	44.5	10.1	66	16.4	150
		3	23	44.3	10.1	77	18.1	355
		5	22	44.5	10.1	77	18.3	434

TABLE VII

Starch Fraction	Fraction of Starch, %	Starch Added, %	Starch Retained, %	Basis Wt., lb. (25x40/500)	Apparent Density	Bursting Strength, pt/100 lb.	Tensile, lb./in.	M.I.T. Fold
Control	--	0	--	44.5	9.9	60	15.8	89
Whole	100	1	30	43.9	10.0	67	16.0	150
		3	30	44.9	10.2	74	18.8	305
		5	26	44.1	10.3	79	19.6	413
Nondispersible	29.0	1	30	44.3	10.1	67	16.9	136
		3	27	43.8	10.2	76	17.9	230
		5	24	43.8	10.0	76	18.6	336
First precipitate	62.5	1	40	44.7	10.2	66	16.6	158
		3	30	44.4	10.1	72	17.9	237
		5	26	44.5	9.9	76	18.2	319
Second precipitate	8.8	1	30	44.5	10.1	63	15.8	137
		3	30	44.8	10.2	75	18.6	280
		5	20	43.7	10.2	80	18.1	329

PROJECT REPORT FORM

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LITERATURE REVIEW DISCUSSION

This report is intended to abstract and summarize the literature pertinent to the objective of Project 2615. The objective of the project has been stated: "to isolate and define the factors and interaction of factors affecting the retention and performance of starch as a beater adhesive." In the process, the Abstract Bulletin of The Institute of Paper Chemistry has been searched from 1930 to date. The Institute of Paper Chemistry Bibliographies 12(1936), 112(1941), and 165(1945) [Supplement One (1963)] were checked. The Corn Industries Research Foundation file on starch (1940) was reviewed, and the texts of Kerr (48) and Whistler (73) were consulted. The references are arranged roughly in chronological order.

The primary conclusion of the review is that there is a marked dearth of published material directly pertinent to the objectives of the project. Some of the older references are included simply to show the place of origin of ideas still cited as significant with respect to starch utilization. Although all references are included as having some significance with respect to the objective, the only ones considered at this point to have direct applicability are those of Casey (44), Swanson (56), and Cushing and Schuman (63). The paper of Swanson is of value to this project primarily for its recommendations for future work. The other two papers contain experimental work which might well be reviewed and extended to obtain contributions to the project.

It is hoped that others involved in this project will supplement
_nd _x_..._ _hi_ literature survey. In particular, it is believed that many
valuable papers exist dealing with polymers other than starch (not included
in this survey) which could be adapted to planning the program on starch.

LITERATURE REVIEW

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of beating is proportional to the starch retention, and when rosin size

was precipitated, starch retention increased.

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    of using $CaCl_2$ as a sizing ingredient in combination with resins,

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20. Process for sizing paper. U.S. 1,430,045 (Sept. 26, 1922). The method

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    modified starch and additional silicates of sodium and subsequently

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(June 1934). IPC Bibliography 165:311. A.B.I.P.C 4:89. This is a
preliminary paper in which it is reported that sizing with starch may
be improved by adding 4.5% of cooked starch to pulp, then adding about
2% of alum and finally neutralizing with an alkali, such as ammonia.
By the use of 4% of starch, the pop test was about twice that obtained
with the same amount of starch applied in the usual manner. With higher
additions of starch, the results are proportionally better, the limits
for starch as customarily employed being absent.

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News 59, no. 26:80, 83-4 (June 27, 1936). A.B.I.P.C. 6:482. The
author describes briefly the methods used in purifying corn starch and
the problems involved for obtaining good retention. In the case of
cooked starch best results will be possible when an unconverted starch
is used, cooked just to the swelling point and added to the beater.
The actual retention will depend to some extent upon the weight of
paper produced. Modified starches can be added to the stock in the
headbox in uncooked conditions and retention increases of 50-75% have
been recorded. Uncooked oxidized starches can also be added to the
stock; their use results in better folding endurance of the paper.
When cooked and added to the beater with rosin size, a marked improve-
ment in the sizing very often takes place, probably due to a protective
colloidal action.

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Bolton felt that the soluble portion of starch left with the dilution

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therefore, is to increase contraction or drying or to bind fiber to fiber.

Use of excessive amounts of starch will cause crushing. If starch is

not too degraded, the % required to give maximum strength to the sheet

lies around 0.5%. The fact that strength tests go through a maximum

indicates that starch as a sheet making material is lower in strength

than cellulose fiber. Its reinforcing action is similar to that of

glues which yield a joint stronger than the glue itself in mass.

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A.B.I.P.C. 11:64. The growing importance of starch in paper manufacture

has become more and more apparent.... "An attempt is made to review certain aspects of starch utilization which have become important during recent years, with particular reference to such end application."

36. Rowland, Ben W. Notes on the use of starch in papermaking. Tech. Assoc. Papers 24:525-528 (1941); Paper Trade J. 111, no. 9:71-74 (Aug. 29, 1940); Paper Mill News 63, no. 35:50, 52, 54, 56 (Aug. 31, 1940); Paper Ind. 22, no. 6:594-596 (Sept. 1940). IPC Bibliography 165:311; A.B.I.P.C. 11:64. In the present discussion reference is made only to certain fundamentals which appear particularly essential to the problems of application. An attempt is made to review certain aspects of starch utilization which have become important during recent years, with particular reference to wet-end application. 22 references.

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corn starch cooked at 210° F. for one hour (35% soluble starch and 65% undispersed starch granules); (B) undispersed starch granules removed from a cooked dispersion of unmodified corn starch by settling and washing; (C) soluble starch from a cooked dispersion of unmodified starch, obtained by removing the undispersed granules in a centrifuge; (D) undispersed starch granules homogenized six times in a hand homogenizer to break up the granular structure and give a fine dispersion of starch; (E) oxidized starch cooked one hour at 210° F., to give a highly dispersed starch solution. Tests were made with 2.5% starch on the pulp. The bursting strength was used as a measure of the value of the sheet. The results show that C, D, and E were much more effective in sheets of high density than were A and B. The results indicate that amylopectin has a greater intrinsic adhesive strength than amylose. Another experiment shows the effect of mechanical dispersion by homogenization on a suspension of swollen starch granules (free of soluble starch). The swollen granules are more effective in a sheet of low than one of high density. As these granules are broken down into units of smaller particle size, their effectiveness decreases slightly in a sheet of low density. However, in a sheet of high density, where the area of fiber contact is larger, there is a tremendous increase in effectiveness as the particle size is decreased by the mechanical process of homogenization. Important factors in the use of starch are the selection of the proper type of starch and its use under conditions that ensure proper distribution in the sheet; the latter should be considered in relation to the structural properties of the sheet.

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PROJECT REPORT FORM

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STARCH AS A BEATER ADHESIVE. THE ROLE OF THE STARCH GRANULE

INTERACTIONS OF BLEACHED SOFTWOOD KRAFT FINES,
DEGREE OF DISPERSION OF 2% CORNSTARCH & ALUM

SUMMARY

The effects upon handsheet properties due to adding cornstarch preparations having different degrees of dispersion at the rate of 2% of the fiber weight are compared at pH 4.4, with and without alum, with those due to varying the quantity of fines in the stock suspension over a range of 2 to 9% by weight. The fines component is varied by blending definite proportions of "fines-free" and whole dewatered pulp previously beaten to 700 ml. Schopper-Riegler freeness. This blending procedure produces a series of stock suspensions having the same long fiber characteristics and the fines used are those belonging to the kind of fiber and refining method employed.

The burst, tensile, and fold values of the handsheets increase linearly with increasing amounts of fines in the stock suspension while the logarithm of the Bendtsen air permability rate decreases linearly. These observed trends may be used to deduce the characteristics of a handsheet containing no fines, thus representing the properties due to the longer fibers alone.

At pH 4.4, 0.0002 M alum (1.3% on fiber) decreases the burst and fold resistance of the handsheets without much effect upon the response due to changing the fines concentration. This suggests the detrimental effect of alum is upon the bonding of the long fibers. On the other hand, alum appears to have no effect upon the tensile strength of the handsheets. This may indicate that the effect of alum is upon the flexibility or extensibility of the paper since fold and burst are tensile tests containing a bending stress.

Alum improves the retention of the starch. Its greatest effect is with the most particulate or least dispersed preparation and its least effect is upon the retention of highly dispersed starch. Retention of the least dispersed starch preparation is also improved by increasing the fines level in the pulp suspension. However, the strength performance of the handsheets is either unaffected by the greater starch content or decreased in the case of the folding endurance produced in the alum system.

The characteristics of the starch treatments imply beater starch may be placed in four categories: dispersed and undispersed effective and ineffective starch. It appears effective starch must be dispersed and is likely to be retained by sorption processes. Undispersed ineffective starch, retained mechanically, is more desirable since it would have less effect upon white water viscosity and thus not affect drainage on the wire as much as if dispersed. Other evidence suggests dispersed ineffective starch reduces the tensile strength to about the same degree as alum.

In the absence of alum, the effect of starch and fines is additive, over the range examined, for producing burst and tensile strength. The increment due to starch remains fairly constant as the overall performance improves with increasing amounts of fines. Folding endurance appears to increase with the amount of starch on the fines as well as on the fiber. The fold increment due to starch increases with the fines level. In fact when alum is used, there is almost no fold improvement due to starch if fines are not present since the regression curves for the starch and no-starch systems converge at nearly the same intercept.

An excellent linear fit of the data obtained without starch is found for the logarithm of the Bendsten air permeability as a function of the fines concentration. This is suggested as a means of tentatively assessing the relative amounts of fines, capable of being retained in a single pass, in handsheets prepared under well-defined conditions. Evaluations of the starch performance at equal levels of fines in the paper itself are made on this extended interpretation of the original data.

INTRODUCTION

Institute Project 2615 is directed toward the isolation and definition of the factors, and the interaction of factors, affecting the retention and performance of starch used as a beater adhesive. Extending the present understanding of the role of starch used in this manner is expected to lead to more effective use of starch and other internal adhesives, making the paper industry more adaptable to changing pressures and demands upon its processes and products.

Although a considerable amount of starch is used in the paper industry as a beater adhesive, there is a potential for the use of much larger quantities. "Beater starch" is more effective in some systems than others and almost totally ineffective in some paper products which could use an inexpensive bonding agent. Emperical methods of preparing and adding starch to the papermaking system characterize the present use of this additive.

The degree to which the organized structure of the starch granule persists through the preparation processes preceding introduction of the starch into the papermaking system, is suspected to have some bearing upon its effectiveness as a bonding agent. It is known that cooked starch is more effective than raw starch for this purpose. The resistance of the granule structure to dissolution of the starch polymers by heating in water varies with the botanical source and is probably a major factor leading to differences in the performance of two different starches such as those from corn and potatoes.

Treatments of the hard-to-disperse cornstarch which produce cationic changes on the polymers also produce granular starches which attain high degrees of dispersion, presumably approaching molecular levels when cooked according to current papermaking procedures. Such cornstarch derivatives display improved retention and performance in commercial and laboratory papermaking processes. However, consideration of the characteristics of the fibers in suspension and of the starch itself do not resolve the question whether the improved dispersion or the improved coulombic attraction between fiber and starch, or both, produced the desired changes in the characteristics of the paper product.

Much of the work already completed on this project was directed toward studying the effects of altering the degree of starch dispersion by using families of complexing agents and controlled variations in the cooking procedures. The results of these experiments will be described in separate reports when activities having higher priority are completed. It became apparent in these studies that greater insight would be gained by investigating the effects of changes in the fiber system in conjunction with those due to altering the degree of starch dispersion.

Upon reflection, it was felt our efforts were being hampered by a very limited understanding of the interactions between the starch and the fiber fragments present in the pulp suspension. These fragments are dislodged during refining and other mechanical processing steps involved in converting the pulp suspension into a suitable paper product. The effects of the fiber fragments, or fines, upon the properties of the

of the paper resemble those obtained by adding starch and other internal adhesives. It is thus important to be able to separate the contributions of fines and of starch to paper properties in order to follow changes due to different treatments of the starch.

Earlier attempts to assess the contribution of the fines in our laboratories have been confined to comparing results obtained with whole pulps and "fines-free" pulps obtained by classification procedures. It has not been unusual to find that a starch product will produce a satisfactory strength improvement in paper made from "fines-free" pulp but will show very little improvement with the parent whole pulp. Explanations of such observations have been based upon the proposition that preferential starch sorption occurs on the fines owing to the greater specific surface area of that component. Predictions of performance based on this hypothesis are confusing since two opposing effects must be accounted for. Part of the starch sorbed on the fines will be removed from the system on the fines not retained during sheet formation. On the other hand, starch sorbed on the fines which are retained should improve bonding of the fiber fragments one to another and to the intact fibers.

The cooked cornstarch preparations used in commercial papermaking are not molecular dispersions by intention. Practical results favor preparing the starch in a manner that leaves most of the starch as swollen, intact granules or as large granule fragments. In fact, mechanical entrapment of particulate starch during sheet formation rather than sorption on the fiber has been proposed as the dominant and most desirable starch retention mechanisms.

On the basis of these two mechanisms for starch retention, sorption and entrapment, the fines in the pulp suspension would be expected to affect starch retention in two ways. If the fines concentration increases, sorption on the fines surfaces would be enhanced, and increased plugging of the fiber mat by the fines would hinder the passage of starch particles thereby increasing the retention of particulate starch. If improved retention is accompanied by an improved effectiveness of the starch, then we are faced with the question of which retention mechanism should be enhanced for a specific grade of paper and set of processing conditions. The problem is more complex than this since earlier experience has shown that improved retention does not necessarily produce improved bonding.

If the fines concentration can be altered without affecting the characteristics of the long fibers in a pulp suspension, an examination of the trends in physical characteristics of handsheet could cast some light upon the contribution of the fines and of the degree of dispersion of the starch introduced into the system. This can be done without introducing "artificial" fines by blending different proportions of whole and "fines-free" pulps. For convenience we have chosen to use dewatered pulps which were resuspended in water and analyzed in a Bauer-McNett classifier to determine the weight of the fraction not retained by the 150-mesh screen. It is assumed that the quantity of fines in the stock preparations actually used to prepare handsheets is proportional to the results of such analyses.

The degree of dispersion attained in preparing cornstarch for wet-end addition may be increased merely by increasing the steam jet cooking temperature. We chose 190°F. as being representative of current commercial

practice and 230°F. for attaining greater dispersion. In addition, corn-starch cooked for 30 minutes at 95°C. and then cooled to 50°C. in a Corn Industries Viscometer (C.I.V.) was included in the experiment. The C.I.V. has been a convenient and reproducible way to prepare starch for handsheets in our laboratory, and it was of interest to see how fines affect the performance of starch prepared in this way.

The degree of dispersion obtained by the three cooking procedures was assessed by comparing the ovendry solids of each preparation before and after centrifuging. Dispersed starch thus is that portion of the dilute paste (2%) that is not sedimented during 15 minutes at 2500 r.p.m. (International Size 2, Model V, Rotor no. 277, 250 ml. bottles). Eventually, it may be useful to devise a method of indicating the distribution of particle sizes of the undispersed starch as well as of the fines.

<center>EXPERIMENTAL PROCEDURES</center>

PREPARATION OF PULP

Rayonier bleached western softwood kraft pulp WBS-W (Lot No. W-3398) was beaten in deionized water (1 to 3 megohms resistance) with a laboratory Valley beater to 700 ml. Schopper-Riegler freeness (S.R.F.) One set of eight beater loads (2880 g. O.D.) was dewatered on a Buchner funnel, treated twice in the pulp breaker and placed in a polyethylene bag for refrigerated storage. A second set of eight beater loads was processed in a Bauer-McNett classifier having the 12, 20, 64, and 150-mesh screens in place. The fractions retained on the screen were recombined, dewatered, the filter pad broken up by two passes through the pulp breaker, and then bagged and stored

under refrigeration. Both dewatered pulps were resuspended in water and analyzed in the Bauer-McNett classifier. The results of the tests used to characterize the two pulps are shown in Table I.

PREPARATION OF STARCH DISPERSIONS

Pearl cornstarch (Globe 3001) was cooked at 5% solids in deionized water in the Corn Industries Viscometer (for 30 minutes at 95°C. and then cooled to 50°C. before removal from that instrument), and in the steam jet cooker (190°F. and 230°F., diluted with an equal volume of deionized water immediately after cooking). The concentration of the starch pastes was determined by restoring the C.I.V. paste to the original weight and by determining the dry solids of the jet-cooked pastes by means of the O'Haus moisture balance.

The starch pastes were diluted to 2.0% solids for addition to the fiber suspensions and for the determination of the percentage of dispersed starch. (Percentage dispersed is the ratio of the ovendry solids of the paste remaining in the supernatant liquids after centrifuging the paste at 2500 r.p.m. for 15 minutes in an International Centrifuge (Size 2, Model V, Rotor No. 277).

The pH of the C.I.V. preparations was 4.9 before cooking and 5.1 after cooking. The values for the jet-cooked pastes varied more widely They were pH 5.2, 5.3 before and 6.1, 6.0 after cooking at 190°F. and pH 5.3, 5.3 before and 6.2, 6.3 after cooking at 230°F. The higher pH after jet cooking may be due to organic amines (antiscaling agents) introduced with the steam.

PREPARATION OF FIBER SUSPENSIONS

Portions of the dewatered pulp (3000 g. dry basis) were resuspended in deionized water (2000 ml. total volume) for 300 counts on the British disintegrator. The suspension was then diluted to 1% consistency with deionized water and brought to an alum concentration of 0.0002 $\underline{M}$ by the addition of 3.9 ml. of 10% alum $[Al_2(SO_4)_3 \cdot 18\ H_2O$, 1.3% of fiber weight].

A second series of suspensions was prepared without alum but with the pH adjusted to the same level (pH 4.2-4.5, ave. 4.4) as the alum series with dilute sulfuric acid.

The quantity of fines in each fiber suspension was regulated by blending portions of the whole and "fine-free" pulps in the proportion of 0:30, 1:20, 20:10, and 30:0 grams. On the basis of the analyses shown in Table I, this produced 1.81, 4.12, 6.42, and 8.73% fines by weight in the two series of puop suspensions.

STARCH SORPTION CONDITIONS

The dilute starch paste (30 ml. 2.00%, 2% of the dry weight of the pulp) was blended with the fiber suspension for five minutes at room temperature. (Separate studies show starch sorption is essentially complete at 15 sec.) The alum or sulfuric acid was added before the starch. At the end of the five-minute sorption period, the stock was diluted to 0.5% for handsheet making.

HANDSHEET PREPARATION

Eight 8 by 8-inch, 2.5 g. Noble & Wood handsheets (100-mesh Monel wire) were prepared in deionized water from each fiber suspension. The water in the deckle box was adjusted to pH 4.4 to 4.5 prior to adding the fiber. Each handsheet was transferred to a blotter by pressing with a couch roll, and then pressed between blotters--four sheets at a time, for five minutes at 50 p.s.i. gage pressure. The wet-pressed handsheets were dried on the couch blotters with the blotter against a steam drum (3 p.s.i.g.).

RESULTS

The data describing the raw materials and the performance of the handsheets are given in Tables I and II.

Handsheet Set No. 106:0-A compared with 107:3/0A indicates there are marginal differences between adding the starch before (0-A) or after (3/0A) adding the alum to the stock suspension.

DISCUSSION

Blends of the whole and "fines-free" forms of the same refined pulp produce a range of fines concentrations not readily obtained in other ways. The nature and characteristics of the fines and fibers are those normally produced by the sequence of operations involved in the use of dewatered refined pulps for handsheet evaluations. However, this technique focuses on fines levels equal to or less than that of the whole pulp whereas commercial papermaking is done at fines concentration greater than that of the whole pulp. Recycling of process water reintroduces fines not retained during earlier sheet-forming sequences. On the other hand, the quantity of fiber fragments large enough to be retained in a single pass probably is not much different in the two systems. It is mainly the fiber fragments too small to be efficiently retained that are likely to be recylced in commercial processes.

The fines levels specified in this report are based on the data shown in Table I. Intermediate levels are calculated from the proportions of each pulp used. It is assumed the fines concentrations are predictable and reproducible within the limits of measurement shown in Table I.

EFFECTS OF FINES WITHOUT STARCH

Increasing the quantity of fines in the pulp suspension, without adding starch, increases the apparent density, burst, tensile, and fold values, and decreases the air permeability of the handsheets. In Fig. 1 the apparent density increases linearly with the fines at low pH without alum present. With 0.0002 M alum in the stock suspension, the data are more scattered. These points do show an upward trend with the fines level

probably not greatly different than that found without alum.

Bursting strength appears to increase linearly with the fines level (Fig. 2). The presence of alum lowers the bursting strength of the handsheets in a way suggesting the main effect is upon the bonding of the long fibers. The rate at which burst increases with increasing proportions of fines in the stock is about the same with and without alum.

Folding endurance also appears to increase linearly with the fines fraction (Fig. 3) and the presence of alum harms this property. The slopes of the regression lines seem to be different with and without alum suggesting that perhaps alum is affecting the way both the long fibers and the fines produce folding endurance in the paper structure.

It does not appear that improved fold is due only to the higher apparent densities obtained with increasing fines levels (compare Figures 1 and 3).

The tensile strength of the handsheets also increases in proportion to the fines concentration (Fig. 4), and appears to be independent of the presence or absence of alum at the pH used to produce these handsheets. It is intriguing that alum should affect those tests involving tensile stress plus lateral displacement (burst, fold) but not the pure tensile stress itself. Further examinations should include evaluation of the effect of fines and alum upon elasticity.

In Fig. 5, the logarithm of the Bendtsen air permeability of the handsheets is shown to decrease linearly with increasing quantities of fines in the fiber suspension. The fines should decrease the effective size of the pores in the paper structure and thus decrease the permeation rate. It is therefore surprising that alum in the pulp suspension does not appear to have an effect upon the permeation rate. If alum improves retention of the fines, then the permeability rate present should be decreased. Alternatively, fines flocculated by alum may form larger aggregates which "open up" the paper structure.

The flow rate of fluids through arrays of capillaries or through a porous medium is shown by the Hagen-Poiseuelle and Carman-Kozeny equations to be proportional to the reciprocal of the length of the capillaries or thickness of the medium. If the permabilities of the handsheets are multiplied by the sample thickness, a "permeability factor" is obtained for the conditions of the Bendtsen procedure which compensates for the thickness variation from sample to sample. The permeability factors for the handsheets were computed and subjected to regression analysis by the least squares procedure. In 0.0002 $\underline{M}$ alum, (pH 4.4):

$$\log P = 4.05 - 0.136 \ F \tag{1}$$
$$s_{xy}^2 = 0.0003393$$
$$s_{xy} = 0.0184,$$

and with H_2SO_4 (pH4.4):

$$\log P = 4.00 - 0.133 \ F \tag{2}$$
$$s_{xy}^2 = 0.003387$$
$$s_{xy} = 0.0582,$$

where

P = Bendtsen air permeability factor (mil x ml./min.)

F = Fines fraction in pulp suspension (g./100 g.pulp).

The regression curve for the alum system [Equation (1)] is illustrated in Fig. 6 along with the permeability factors for the systems with and without alum. All of the data, but for one point, fall within the $2s_{xy}$ limits shown in Fig. 6. On this basis and from comparison of the regression coefficients in Equation (1) and Equation (2), it appears highly unlikely that the two systems are different. Thus, it is concluded alum had no effect upon the air permeability rate of the handsheets and probably no effect upon the fines retention.

Equations (1) and (2) may be written in more general form as:

$$\log P = \log P_o - bF_s \tag{3}$$

or: $$bF_s = \log P_o - \log P = \log (P_o/P) \tag{4}$$

where

F_s = fines concentration in pulp suspension, g/100 g. pulp

P = permeability factor, mil x ml./min.

P_o = permeability factor at $F = 0$

B = constant ($d \log P/dF$)

The factor P_o is likely to be a function of the sheet-forming conditions, pressing, and drying procedures as well as of the inherent characteristics of the whole fibers. For a given set of procedures and fiber characteristics, P_o should be a constant.

Thus:

$$bF_s = A - \log P \tag{5}$$

If the single-pass retention of the fines is a constant proportion of the total fines fraction:

$$cF_H = bF_H/e = bF_s \tag{6}$$

where

F_H = fines in handsheet, g./100 g.

e = fines retention efficiency, F_H/F_s,

then the logarithm of the Bendsten air permeability rate is proportional to
the fines content of the paper. This permits an assessment of the effects
of varying levels of fines in the paper which is not readily available by
other means. We shall return to this concept later on in this discussion.

It is of interest that the semilog relationship produces a
straight line whereas the log-log plot (Fig. 7) produces a curved line. On
this basis the semilog form has more practical utility and perhaps funda-
mental significance.

If we accept the premise of a constant retention efficiency for
fines (at least over the range examined in this study), it is possible to
relate the fines content of the paper to the paper structure on a more
fundamental basis. The Hagen-Poiseuille equation for compressible fluids can
be used to gain some insight into this relationship.

$$V = r^4/8\eta\ell \cdot \Delta p \cdot pm/m \tag{7}$$

where

V = volume of fluid flowing through a capillary in a given
time

ℓ = length of the capillary (i.e., thickness of the handsheet)

r = radius of the capillary

η = viscosity of the fluid

Δp = pressure drop

pm = medium pressure of the penetrating gas

p = pressure at which V is measured.

If $P_o = V_o \mathcal{L}$ with no fines in the paper (F_o), a structure having a given

fines component, F_i, will have a different permeability factor, P_i.

Thus, if the pressure factors in Equation (7) are constant,

$$P_o/P_i = r_o^4/r_i^4 \tag{8}$$

and

$$\log P_o/P_i = 4 \log r_o/r_1 \tag{9}$$

Combining Equation (8) with the equalities shown in Equations (5) and

(6) give:

$$cF_H = 4 \log r_o/r_i \tag{10}$$

or

$$c/4 \cdot F_H = B - \log r_1$$

where , B = constant for a given set of long fiber characteristics

and handsheet procedures. Thus, the simplest view of the relationship of the

fines component to the sheet structure is that the logarithm of the average

pore radius decreases linearly with the quantity of fines in the paper

structure.

EFFECTS OF FINES AND 2% CORNSTARCH IN THE PULP SUSPENSION

The three methods of cooking the cornstarch used in this study

produced the three degrees of dispersion shown in Table II. One preparation

was cooked in the C.I.V. which has been used as a reproducible method of

preparing starches for evaluation as internal adhesives in our laboratory.

Another preparation was cooked in our steam jet cooker at 190°F. and is

representative of present commercial papermaking procedures. The similarity

of the degree of dispersion of the jet-cooked starch (av. 19.8%) and the

C.I.V. preparation (av. 29.5%) indicates the C.I.V. produces a reasonable

approximation of the starch dispersion used in commercial papermaking.
The third starch preparation was steam jet cooked at 230°F. to obtain a
high degree of dispersion (av. 98.4%) for comparison with the other two
dispersions.

Introducing two parts of cornstarch per 100 parts of pulp into
the fiber suspension does not appear to affect the way the Bendsten air
permeability of the handsheets changes with the fines concentration in
the pulp suspension (Fig. 8 and 9). The data become more scattered as
more points are plotted but there is no firm basis for changing the
regressive line obtained for the fines alone. It could be expected that
the particles of undispersed starch in the C.I.V. and 190°F. jet
preparations would affect the pore structure of the paper. This appears
to be true only with the least well dispersed starch preparation as
indicated in Fig. 10.

The apparent density of the handsheets (Fig. 10) prepared with
starch changes somewhat erratically with the fines. Because of the
dispersion of points it is not possible to be certain that starch has
altered the effect of the fines on this property. The starch regression
lines shown in Fig.10 do suggest that starch may have some effect upon
sheet density. However, there is no basis for stating one starch preparation
behaves differently than the others.

Bursting strength and folding endurance (Fig. 12 and 13) are
improved by the addition of starch. Without alum (Fig. 12A and 13A) the
effects of starch and fines appear to be additive at pH 4.4. This offers

an explanation for the apparent loss of strength improvement due to starch when whole pulps are compared with "fines-free" pulps. An increment of 8 points burst per 100 lb. is 10% of a "fines-free" control sheet showing 80 pts/100 lb., but only about 7% of a whole pulp control having 110 pts/100 lb. (see Fig. 12A). There does not appear to be any difference in the way the three starch preparations affect burst and fold in the handsheets made without alum.

When alum is used, the burst increment may be additive for starch and fines or the effect of the starch may increase as the fines level increases-- depending upon how one wishes to interpret the small divergence of regression lines in Fig. 12B. However, it is obvious in Fig.13B that the effect of starch upon folding endurance increases rather dramatically as the fines concentration increases. It also appears that starch has little effect upon fold without fines being present in the preparations using alum. It must be pointed out that the data plotted for 1.8% fines are obtained with the unblended, classified pulp which has been referred to as "fines-free" pulp in the earlier work.

The method of preparing the starch has no obvious effect upon the bursting strength in the alum system (Fig. 12B). There is a suggestion in Fig. 13B that the most highly dispersed (starch 230°F. jet) produces greater folding endurance.

The tensile strength imparted the handsheets by starch and fines appears to be additive for both the alum and no alum systems (Fig. 14). The small divergence of lines in Fig. 14A (as well as in Fig. 12B) cannot

be given great significance in view of the available data. Again, the starch cooking method (or degree of starch dispersion) does not appear to affect the tensile strength imparted by 2% starch.

In contrast with these observations, the starch retention efficiency is affected by the degree of dispersion, or cooking method, in both the alum and no-alum systems (Fig. 15). The poorly dispersed starches are retained to a higher degree than the highly dispersed starch and the retention efficiency increases with the fines concentration. Furthermore, starch retention increases as the amount of undispersed starch increases (see Table II). This supports the contention that some "beater starch" is retained mechanically. The filtration efficiency of fiber pad on the wire should increase as void spaces between longer fibers become plugged with more and more fines. On the other hand, the degree of dispersion has no marked effect upon the measured physical properties of the handsheets (Fig. 12-14). This is strong evidence that starch retained mechanically does not improve the physical strength of the paper.

The effective starch fraction must be contained in the dispersed phase. However, the most highly dispersed preparation (230°F. Jet, 98.4% dispersed) was retained to a maximum of about 18% with alum and 16% without alum. Since all three preparations are more highly dispersed than either of these figures, it follows that the effective starch is in the most easily solubilized portion of the starch granule (amylose?) and that the degree of dispersion is not likely to have any effect unless it does not exceed 16 to 18%. These observations lead to the categories of dispersed and undispersed effective and ineffective starch.

As a rule, galactomannan gums are about six times as effective
as starch as an internal adhesive on an equal weight added basis. It is
interesting that the dispersed effective fraction is about 1/6 of the
total starch used to prepare handsheets for this report.

INTERACTION OF FINES AND STARCH IN THE HANDSHEETS

The starch content of the handsheets is measurable by direct
analysis while the fines content is not. Yet interpretation of the combined
effects of starch and fines upon handsheet properties requires some
assessment of the quantity of fines in the paper structure. It is an
unexpected result of blending whole and "fines-free" pulps that the
relative amounts of fines retained in the handsheets can, tentatively, be
given quantitative, though nonspecific, values. However, in order to do
this one must base conclusions upon tentative conclusions. This increases
the risk of obtaining the "wrong answer" but offers new ways of looking
at an old problem.

The Bendtsen air permeability rate of the handsheets prepared
without starch was shown earlier in this report to be a linear, semilogrithmic
function of the fines factor in the pulp suspension (Fig. 5 and 6). The fact
that a physical property affected by the presence of fines in the paper
(rather than the bonding effects of the fines), changes in a regular way
with changes in the composition of the pulp suspension suggests that a
constant proportion of the fines is retained in the handsheet-making process.
That is, the fines retention efficiency at pH 4.4 is at least relatively
constant over the range of fines levels examined and with the particle size

distribution of the fines produced by the kind of pulp and the pulp treat-ments used in this study. If the fines retention efficiency is not relatively constant, one must propose that it is changing in a regular way to account for the good fit of the data to the linear form shown in Fig. 5 and 6. This second proposition is acceptable if fines-flocculation does not occur at pH 4.4. As the voids in the mat of longer fibers become filled with increasing amounts of the larger fines particles, the filtration efficiency of the mat increases to improve the mechanical retention of the smaller, harder-to-filter fiber fragments. However, fines flocculation is believed to occur at lower pH values such as 4.4 Thus, pending further evidence, the proposition of a relatively constant single-pass retention efficiency (in the absence of starch) is the more likely alternative for the system employed in this study.

In either event, fines retention is a regular function of the quantity of fines in the pulp suspension. The simplest interpretation is that the fines retained is linearly related to the fines in the suspension and, hence, is best for an initial evaluation of the interaction of fines and starch.

Comparison of the starch-treated handsheet data with those obtained without starch (Fig. 8-10) does not indicate that the air permeability rate is affected differently by the fines in the pulp suspensions except for some deviation of the lowest dispersions shown in Fig. 10 when starch is present. It will be presumed here that the scatter in Fig. 8 and 9 is due to differences in fines retention in the more complex system which are indicated by the logarithm of the air permeability rate.

The two premises needing verification in the following interpretations are (1) the quantity of fines in the paper is linearly related to the logarithm of the air permeability rate, and (2) beater starch has little or no effect upon that property.

The quantitative concepts relating handsheet permeation rates to the fines content were presented earlier as Equations (5) and (6) which are combined here:

$$cF_H = b\ F_H/e = bF_s = A - \log P \tag{11}$$

where:

F_H = Fines in handsheet, g/100 g.

F_s = Fines in pulp suspension, g/100 g.

e = Fines retention efficiency, $F_H/F_s = 1$

P = Permeability factor, mil x ml/min.

b = proportionality constant for F_s $(-d \log P/dF_s)$

c = " " for F_H $(-d \log P/dF_H)$

A = log permeability factor when F_H or $F_s = 0$ for a given set of longer fiber characteristics and handsheet-making procedures.

The permeability rate, rather than the permeability factor (rate corrected for thickness) will be used since it contains the effects of the sample-to-sample variation of basis weight and thickness also affecting the burst, tensile, and fold data. A comparison of Fig. 5 and 6 will illustrate this substitution has little effect upon the basic relationship. The intercept in Fig. 5, 2300 ml/min., will be used to indicate "no fines" in the paper structure.

In Fig. 16 the quantity of starch in the handsheets is a linear function of the quantity of fines in the handsheet. This parallels the relationships shown in Fig. 15 where the comparison is based on the fines in the pulp suspension. Fig. 16 shows more explicitly than Fig. 15 that alum improves starch retention. The three-dimentional representation in Fig. 16 illustrates low starch retention is improved by decreasing the degree of dispersion (or solubilization) and increasing fines in the paper. Alum appears to have its greatest effect in the most particulate system. That is, with the least dispersed starch preparation with the whole pulp.

The fact that the highly dispersed starch ($230^{o}F$ Jet) does not show greatly improved retention as the fines concentration increases indicates most of the retention is due to the long fibers and not due to the fines. This contradicts the hypothesis that the greater surface area of the fines robs the long fibers of effective starch.

As shown earlier, the improved starch retention due to particulate starch and alum is not reflected in the strength of the handsheets. A comparison of Fig. 17 with Fig. 18 suggests that the improved starch retention in the alum system obtained with the poorly-dispersed starches reduces the folding endurance of the handsheets. The best fold is obtained with the highly dispersed and least well retained starch. This is also shown in the two-dimentional Fig. 18. The curves in that figure converge toward a common intercept suggesting starch has no effect upon the folding endurance of alum-treated long fibers. Fold improvement is a result, apparently, of the combined effects of starch and fiber fines as was concluded earlier on the basis of the trends shown in Fig. 13B. The difference between the dispersed

and particulate starch preparations suggests folding endurance is improved by the starch sorbed by the fines and is harmed by the particulate starch retained mechanically with the fines. However, this explanation does not provide an understanding as to why the folding endurance increases so greatly with only a very small and probably insignificant increase in retention of the 230°F Jet starch.

Without alum, fold appears to be improved by starch on both the fines and on the long fibers in Fig. 20. This is a different interpretation than that derived from Fig. 13A where starch on the fines appears to have no effect.

The fold data for the 230° Jet starch in Fig. 20 suggest an entirely different set of responses when particulate starch is not added to the system. The two points for the two highest fines levels completely alter the trends observed with the other three series of handsheets. If the slopes indicated by the two pairs of data are correct, (i.e., pairs above and below the other starch curves) then there is little difference between slopes of the three starch preparations. On the other hand, if it is assumed that the two suspect points to the right are incorrect and should be disregarded, then the burst and tensile data should also show anomalies which they do not. If the broken line shown in Figure 19 correctly represents the trends with the 230°F. Jet starch, then fold parallels starch retention and increasing amounts of fines in the paper have little effect upon that property. This conclusion is not easily accepted in view of the trends observed with burst and tensile strength. Thus, further evidence is needed to describe the changes in folding endurance produced by highly dispersed starch and fines at pH 4.4 but without alum.

The effect of alum upon tensile strength is examined in Figures 21 and 22. There appears to be no affect due to alum with no starch or with the highly dispersed 230°F Jet starch (Fig. 21). Tensile strength increases linearly with increasing amounts of fines in the paper and the effect of 2% starch is a constant factor added to that of the fines.

In Fig. 22 the effect of starch is also linear and additive to the effect of the fines but alum reduces the tensile strength of the handsheets. The alum effect appears to be related to the bonding of the long fibers as deduced earlier from Fig. 14.

The 230°F. Jet starch curve in Fig. 21 coincides with that for the other two starch dispersions shown for the alum system in Fig. 22. This suggests that something in the dispersed starch is affecting the bonding of the long fibers in the same way as alum. Perhaps dispersed ineffective starch or alum is displacing or competing with dispersed effected starch for sorption sites on the fiber surface. However, whatever mechanism is causing the lower tensile strength, it is not a summation of the effects of both components. The alum treated 230°F. Jet starch handsheets are not different than those prepared without alum. If alum and dispersed ineffective starch are coating the surface of the long fibers, sorption of the effective starch may be inhibited by a reduced number of sites available, or the adhesive bond between effective starch and the fiber surface may be weakened if that component is deposited on the layer of ineffective material.

FURTHER WORK

It is planned to test the linearity of the trends observed in this study over a wider range of fines levels by refining the bleached western softwood kraft pulp to 300 ml. S.-R. freeness. The results of this study and the one reported here will then serve as a comparison for evaluations using other pulp sources.

Other workers may wish to use the pulp blending technique to examine the effects of residual levels of fines upon such parameters as the hydrodynamic specific surface area and swollen volume, drainage rates, optical properties, or other parameters influenced in some degree by fiber fragments.

ACKNOWLEDGEMENTS

The assistance and competence of Donald Gilbert in preparing the pulp and the handsheets is gratefully acknowledged and attested by the quality of the data.

TABLE I

PROPERTIES OF WHOLE AND "FINES-FREE"
SOFTWOOD BLEACHED KRAFT PULPS

	Whole Pulp	"Fines-Free" Pulp
Storage consistency	24.7%	30.2%
Schopper-Riegler Freeness	690 ml.	860 ml.

Bauer-McNett Classification[a]:

	Whole Pulp	"Fines-Free" Pulp
Retained on Screen No. 12	$58.4 \pm 4.9\%$[b]	$63.3 \pm 12.0\%$[b]
" " " " 20	15.8 ± 2.9	17.4 ± 8.0
" " " " 65	15.0 ± 1.8	15.6 ± 3.4
" " " " 150	2.04 ± 0.09	1.88 ± 0.13
Difference through No. 150	8.73 ± 0.19	1.81 ± 0.40

[a]Redispersed 10 g. pulp in 2000 ml. for 600 counts in British Disintegrator

[b]Limits shown are $\pm$ one standard deviation based on the range of duplicate determinations expressed in terms of the pulp sample rather than of the individual fractions

TABLE II

BLENDS OF WHOLE AND "FINES-FREE" PULP TREATED WITH 2% CORNSTARCH

Sample Identification (Number of Tests)	Whole Pulp[a], %	Starch Cooking Method	Dispersed Starch, % (2)	Starch in Handsheets[b], g/100g paper (2)	Starch Retention Efficiency, %	Basis Wt. (25x40/500) lb./ream (1)	Thickness, mils (7)	Apparent Density	Burst pt./100 lb. (5)	Instron Tensile, lb./in. (5)	M.I.T. Fold (10)	Bendtsen Air Permeability[c], ml./min. (5)
H₂SO₄ to pH 4.4:												
105:0/3N	0	Not used		0.06	0	45.6	4.8	9.5	92	17.8	795	1290
105:1/2N	33			0.06	0	43.8	4.5	9.7	96	20.4	1080	534
105:2/1N	67			0.06	0	44.1	4.4	10.0	99	20.3	1220	337
105:3/0N	100			0.06	0	44.3	4.3	10.3	114	22.3	1280	162
106:0/3N	0	C.I.V.	29.2	0.36	18	44.8	4.6	9.7	97	19.2	1170	1170
106:1/2N	33		"	0.55	28	45.4	4.5	10.1	103	22.3	1280	577
107:2/1N	67		29.8	0.56	28	43.6	4.3	10.1	110	22.9	1490	347
107:3/0N	100		"	0.66	33	45.5	4.4	10.3	121	25.3	1760	146
108:0/3N	0	Jet 190°F.	21.0	0.46	23	45.6	4.7	9.7	100	19.8	1190	1200
108:1/2N	33		"	0.54	27	44.6	4.5	9.9	107	22.3	1370	626
109:2/1N	67		18.6	0.60	30	44.9	4.5	10.0	115	23.4	1590	323
109:3/0N	100		"	0.68	34	44.1	4.3	10.3	117	24.6	1880	148
110:0/3N	0	Jet 230°F.	98.6	0.23	12	44.7	4.6	9.7	98	19.4	1330	1180
110:1/2N	33		"	0.28	14	44.6	4.5	9.9	109	22.5	1520	602
111:2/1N	67		98.2	0.31	16	44.3	4.4	9.8	113	22.3	1390	323
111:3/0N	100		"	0.29	14	44.6	4.4	10.1	115	24.0	1620	174
0.0002M Alum, pH 4.4:												
105:0/3A	0	Not Used		0.06	0	45.5	4.7	9.7	81	17.2	731	1340
105:1/2A	33			0.06	0	43.9	4.6	9.5	95	19.0	937	682
105:2/1A	67			0.06	0	44.5	4.4	10.1	95	20.2	954	359
105:3/0A	100			0.06	0	42.3	4.2	10.1	107	21.8	1210	169
106:0/3A	0	C.I.V.	29.2	0.38	19	43.6	4.7	9.3	91	18.4	838	1490
106:1/2A	33		"	0.58	29	44.9	4.5	10.0	103	20.7	1190	599
107:2/1A	67		29.8	0.64	32	44.2	4.5	9.8	112	22.0	1480	276
107:3/0A	100		"	0.70	35	43.1	4.2	10.3	115	22.0	1500	200
(106:0-A)[d]	(100)		(29.2)	(0.68)	(34)	(44.7)	(4.4)	(10.2)	(117)	(23.3)	(1590)	(160)
108:0/3A	0	Jet 190°F.	21.0	0.45	22	42.6	4.5	9.5	87	18.3	834	1580
108:1/2A	33		"	0.58	29	44.9	4.5	10.0	103	21.2	1170	588
109:2/1A	67		18.6	0.68	34	45.2	4.5	10.0	99	21.6	1270	408
109:3/0A	100		"	0.76	39	45.0	4.5	10.0	111	22.9	1670	220
110:0/3A	0	Jet 230°F.	98.6	0.27	14	45.3	4.7	9.6	92	19.2	976	1340
110:1/2A	33		"	0.35	18	44.3	4.6	9.6	98	20.0	1250	771
111:2/1A	67		98.2	0.34	17	43.3	4.4	9.8	112	21.5	1520	356
111:3/0A	100		"	0.36	18	44.9	4.4	10.2	120	23.8	1890	183

a Equivalent to: 1.81, 4.12, 6.42, and 8.73 g. Fines/100 g. Pulp, or: 1.84, 4.42, 7.00, and 9.56 g. Fines/100 g. Long Fiber

b Usually reported to nearest 0.1%

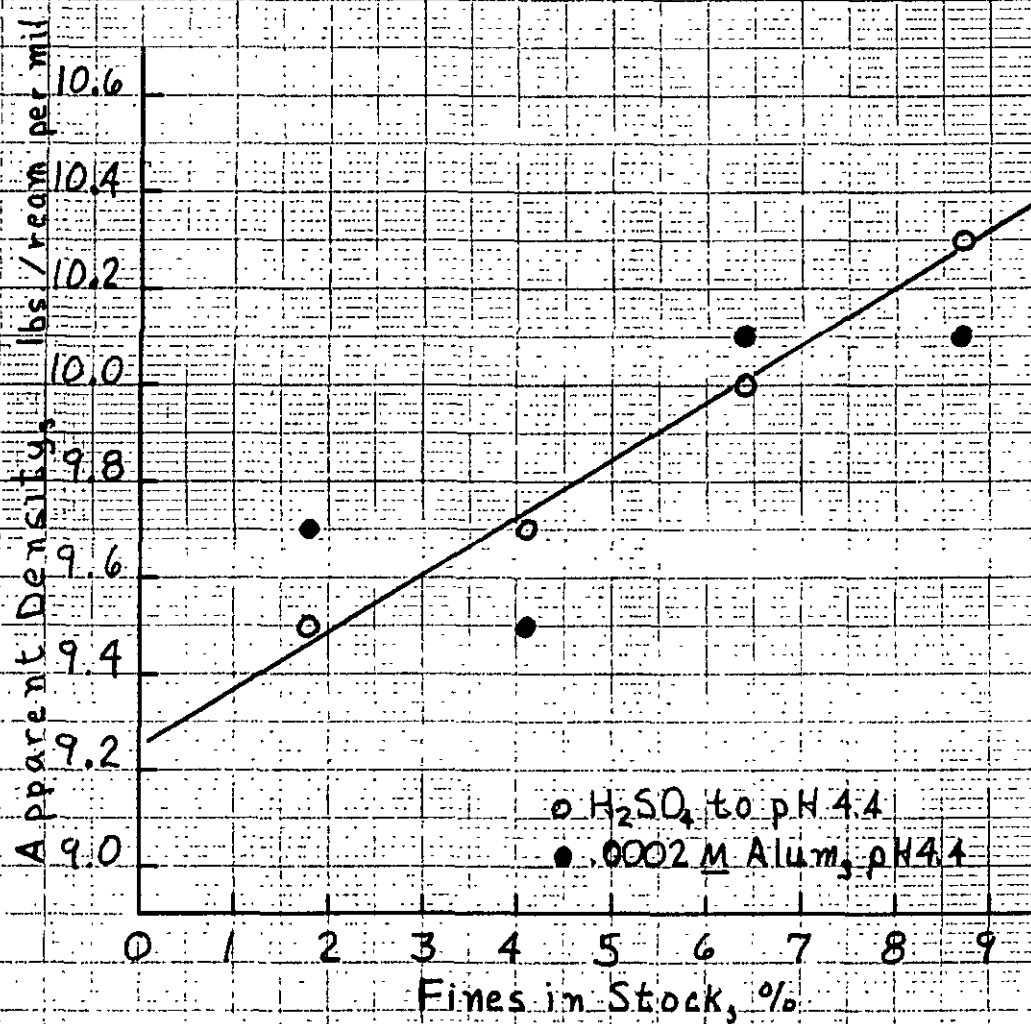c 10.0 cm.² area at 150 mm. (water)

d Starch added before the alum

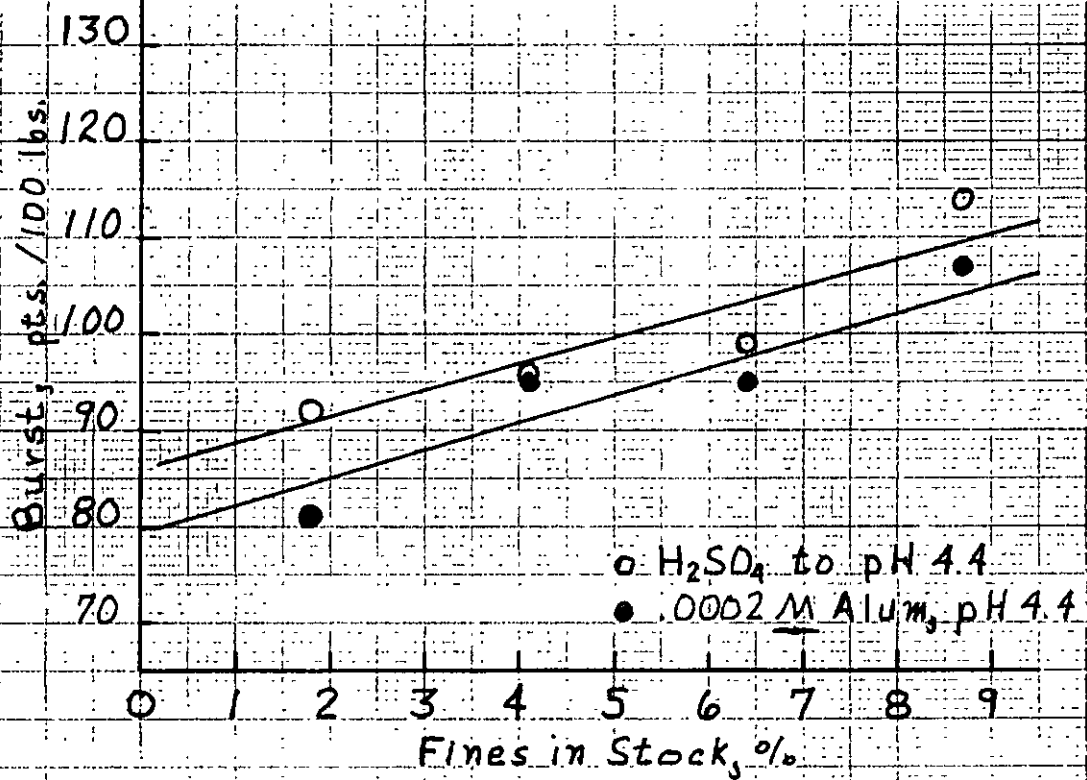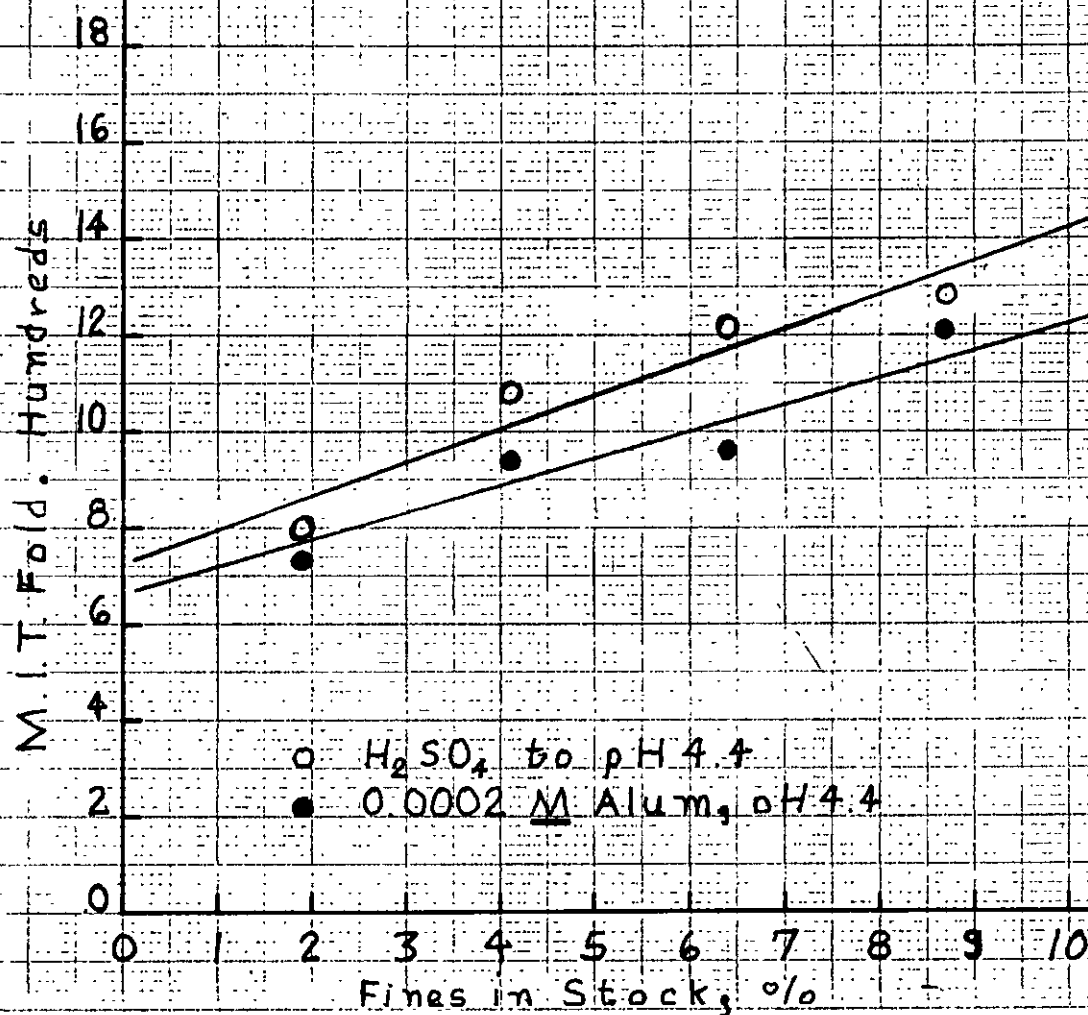FIGURE 1. Apparent Density as a Function of the Fines Concentration

Figure 2. Bursting Strength as a Function of Fines Concentration

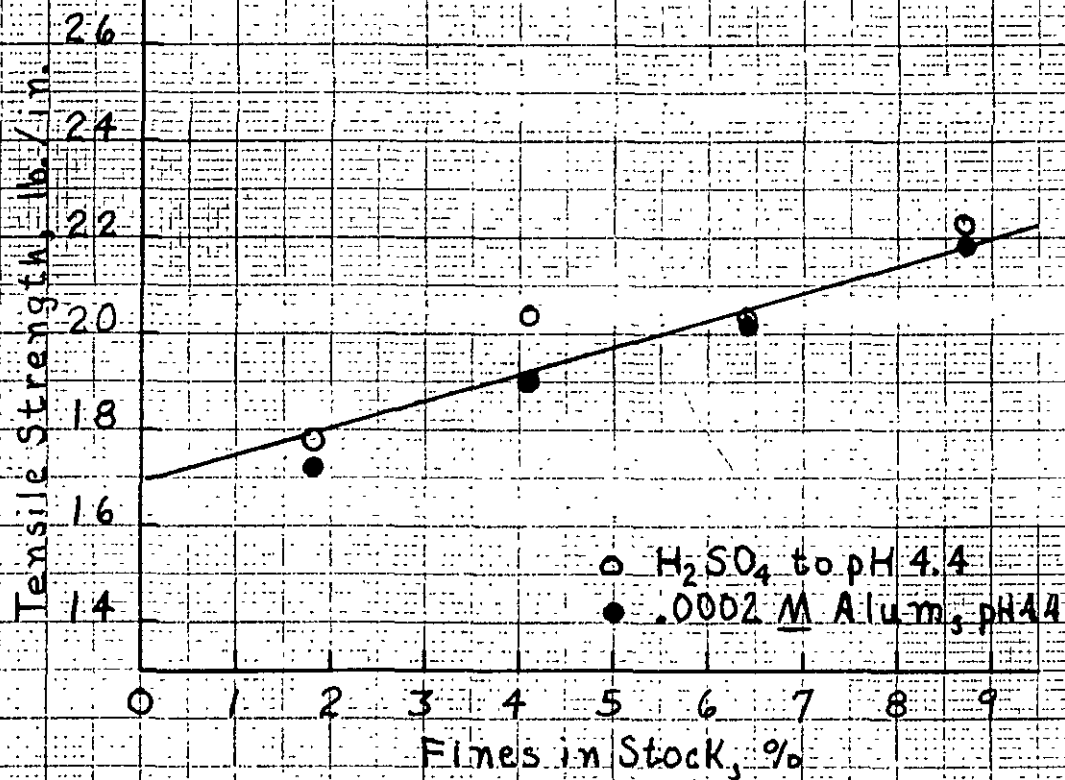Figure 3. Folding Endurance as a Function of Fines Concentration
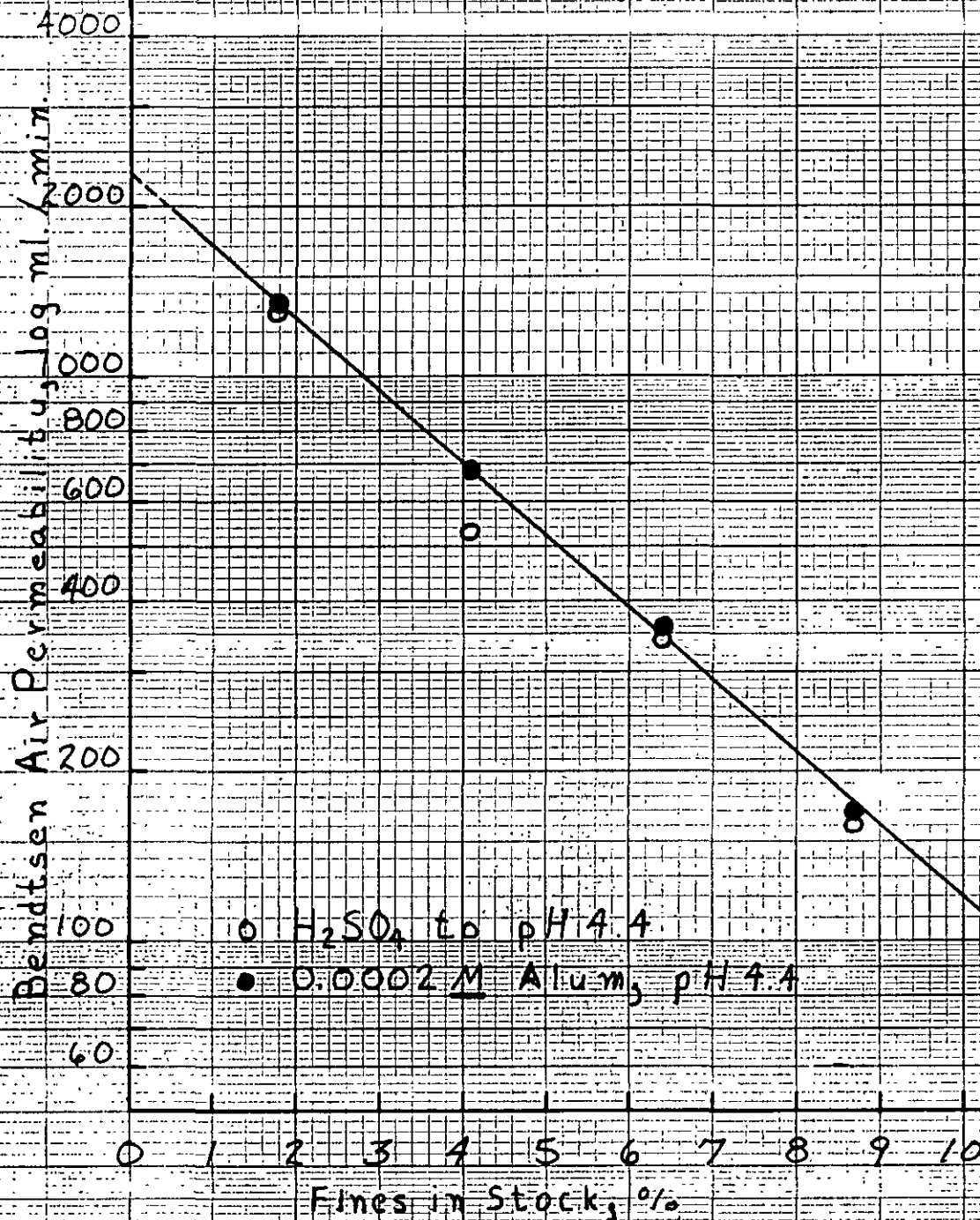
Figure 4. Tensile Strength as a Function of the Fines Concentration

Figure 5. Bendtsen Air Permeability as a Function of the Fines Concentration

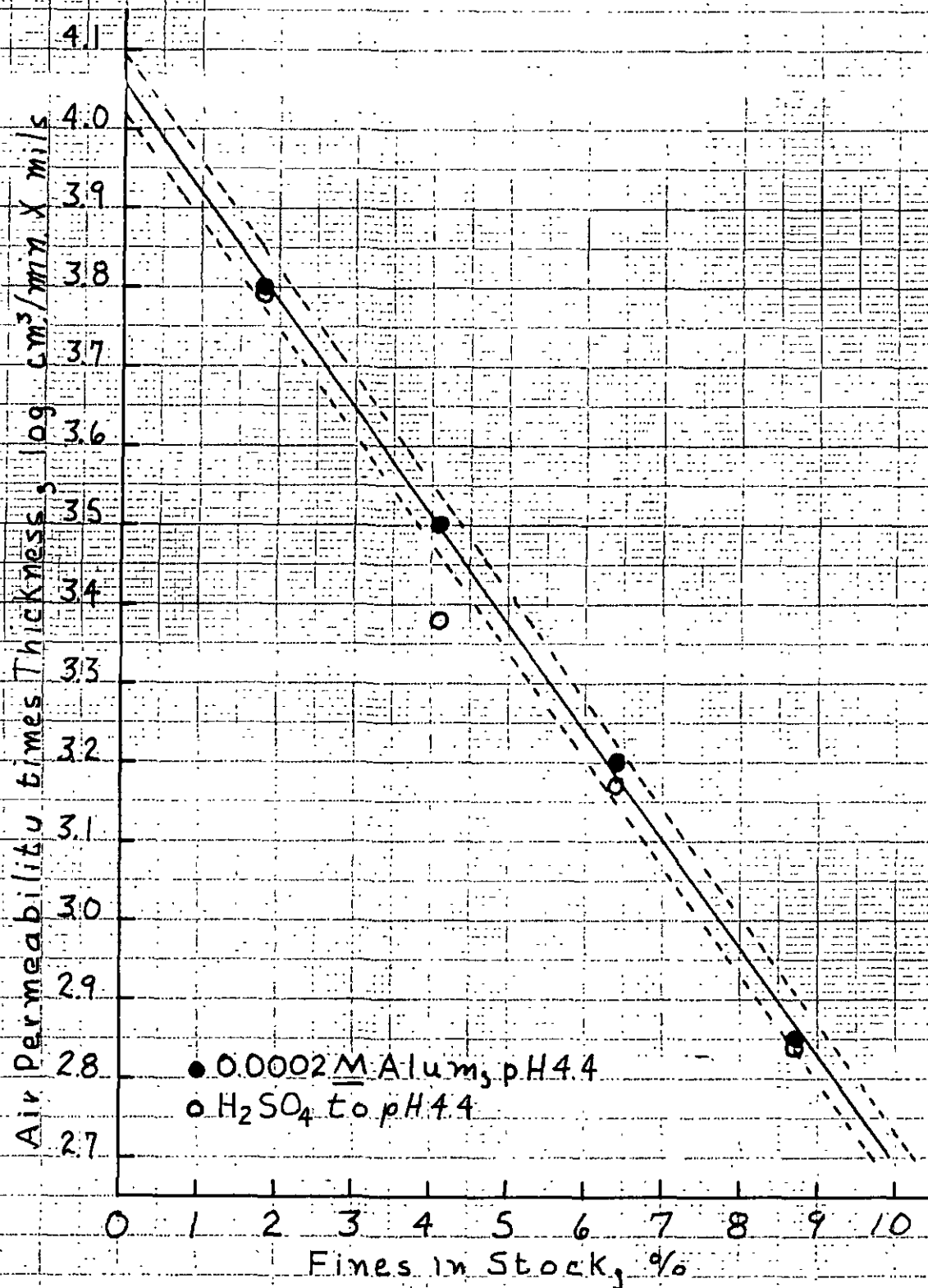Figure 6. Bendtsen Air Permeability Factor as a Function of Fines Concentration. The Solid Line Represents the Regression Line Based on the Data for the Handsheets Made With Alum. The Broken Lines Represent the Limits Defined by $\pm 2s_{xy}$
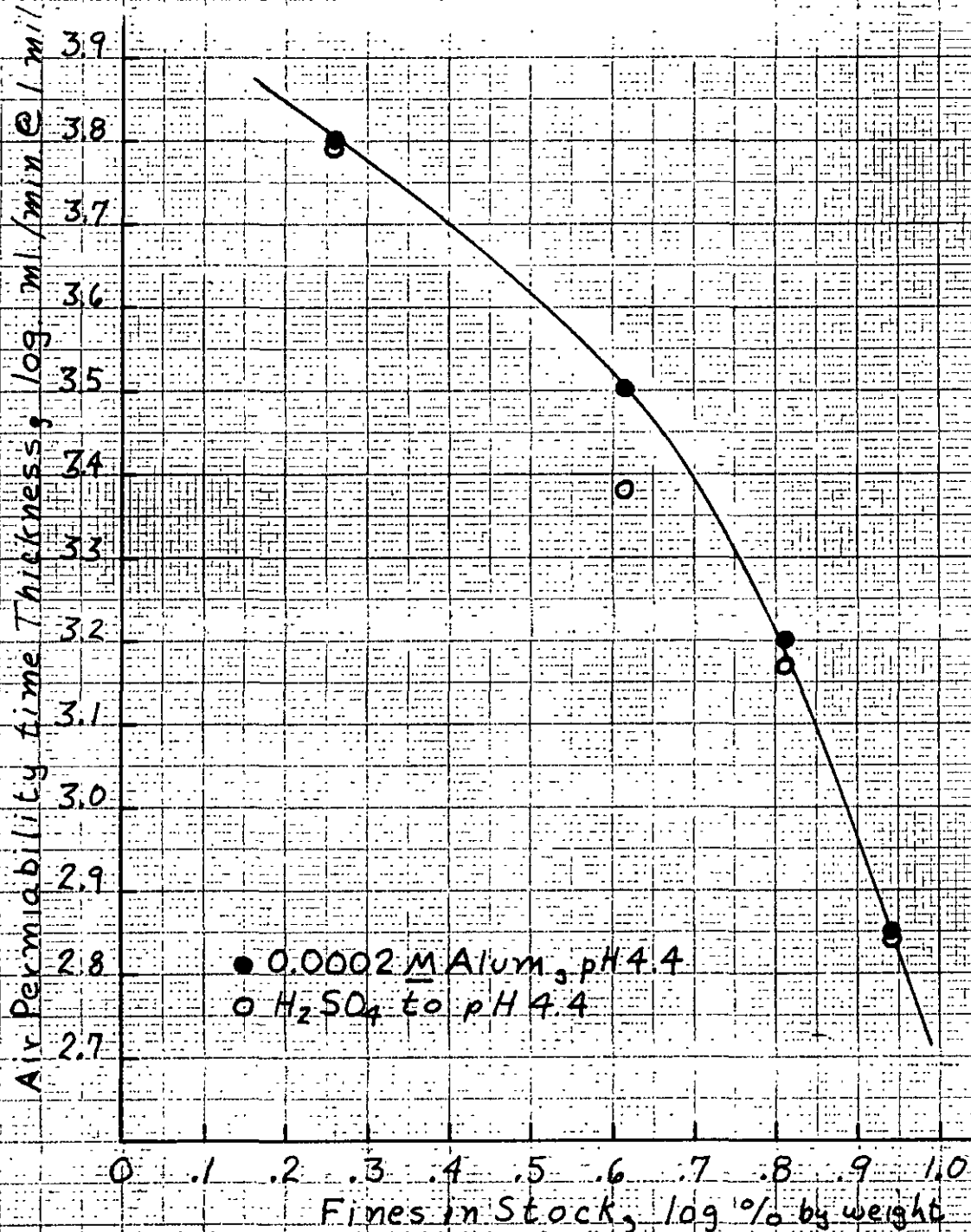
Figure 7. Log-log Plot of Air Permeability Factor as a Function of Concentration of Fines the Stock Used to Make the Handsheets

Legend on plot:
● 0.0002 M Alum, pH 4.4
○ H₂SO₄ to pH 4.4

Y-axis: Air Permeability time Thickness, log ml/min @ 1/m l/
X-axis: Fines in Stock, log % by weight
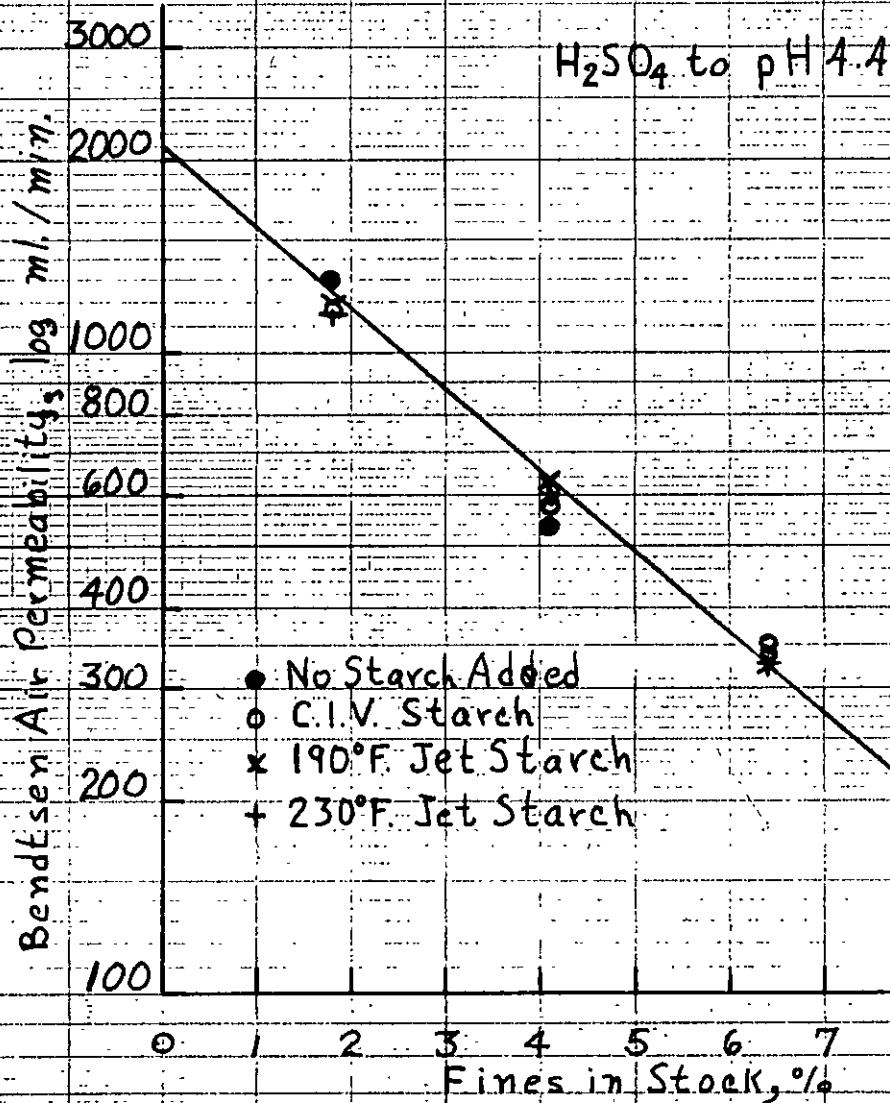
Figure 8. Bendtsen Air Permeability as a Function of the Fines Concentration with 2% Starch, But Without Alum
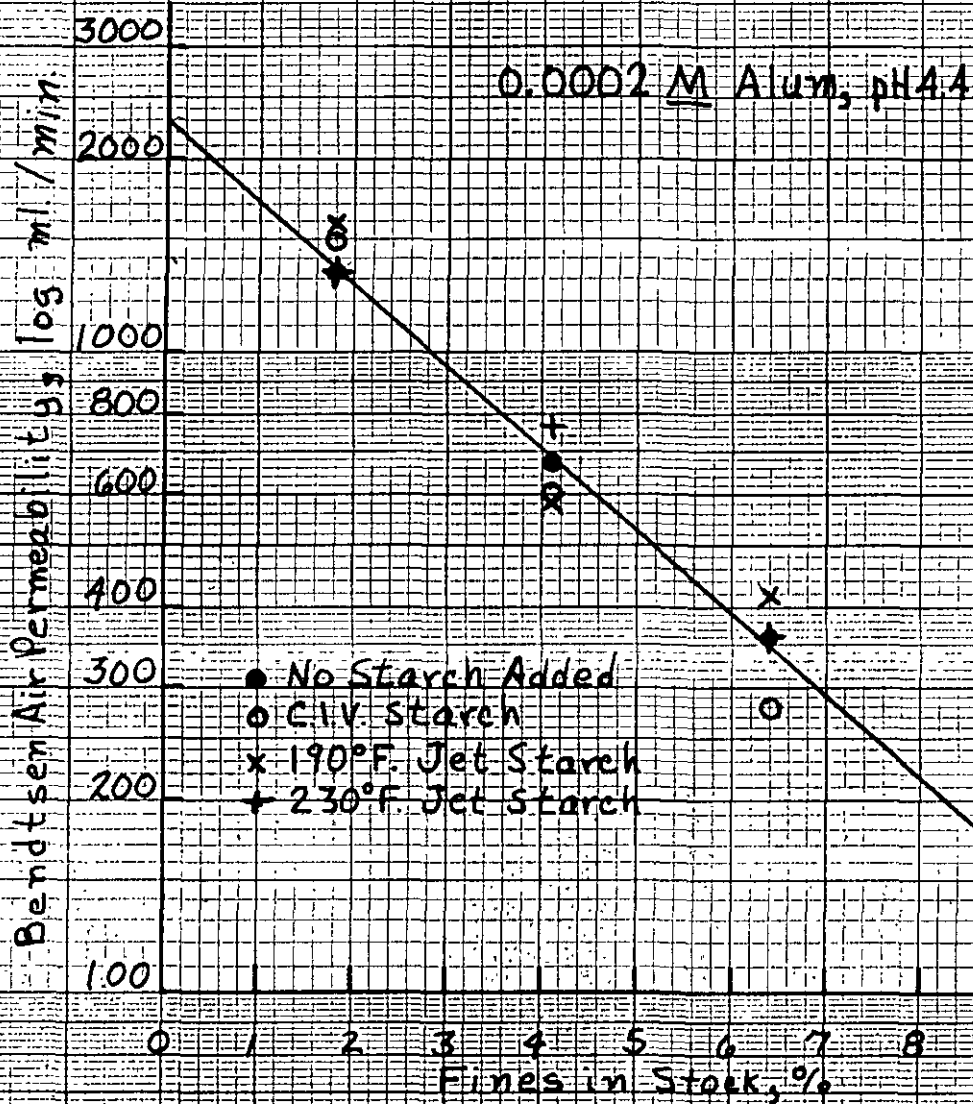
Figure 9. Bendtsen Air Permeability as a Function of the Fines Concentration with 2% Starch and With Alum
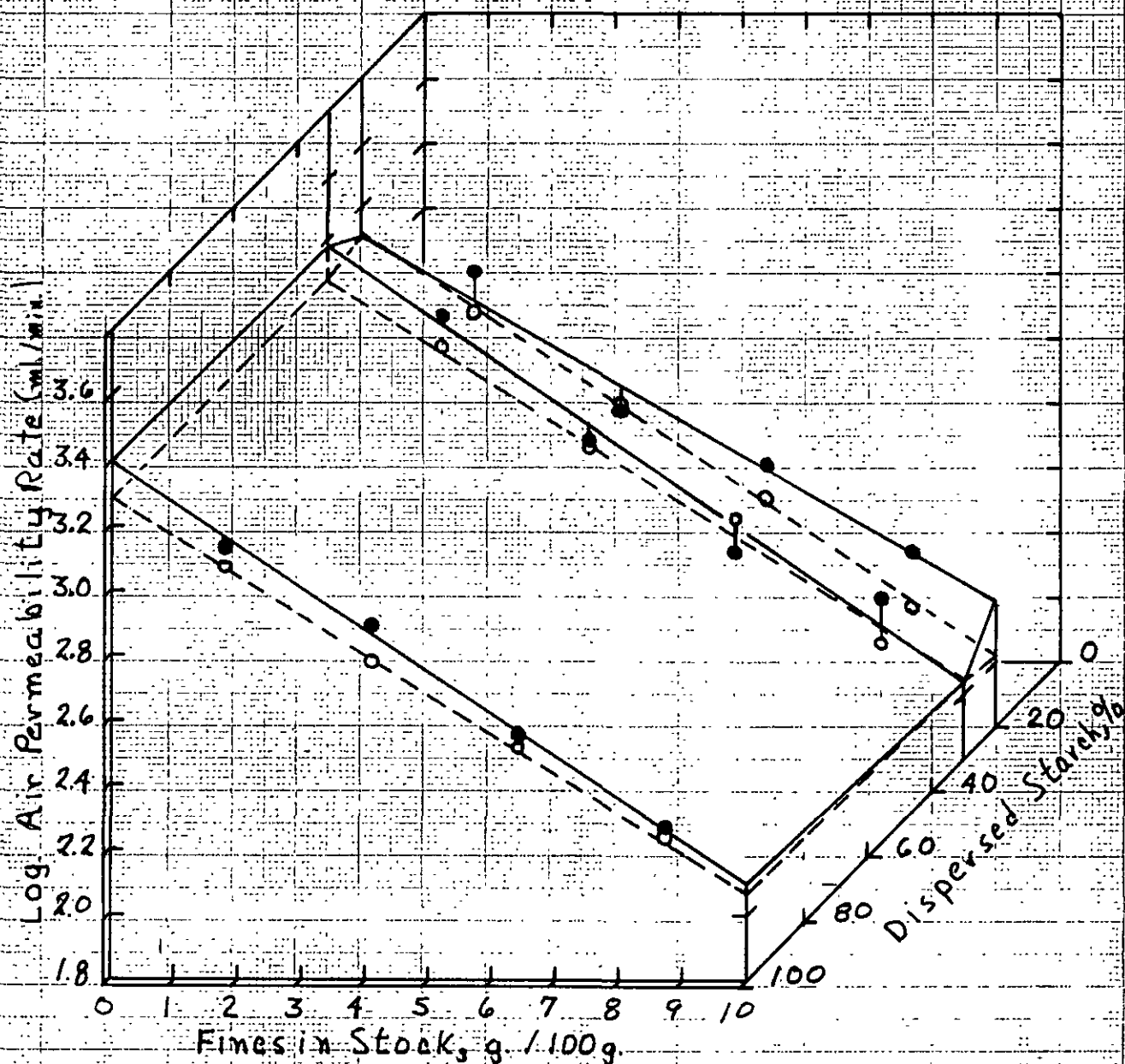
Figure 10. Handsheet Air Permeability Rates as Function of the Fines Concentration in the Pulp Suspension and the Degree of Starch Dispersion
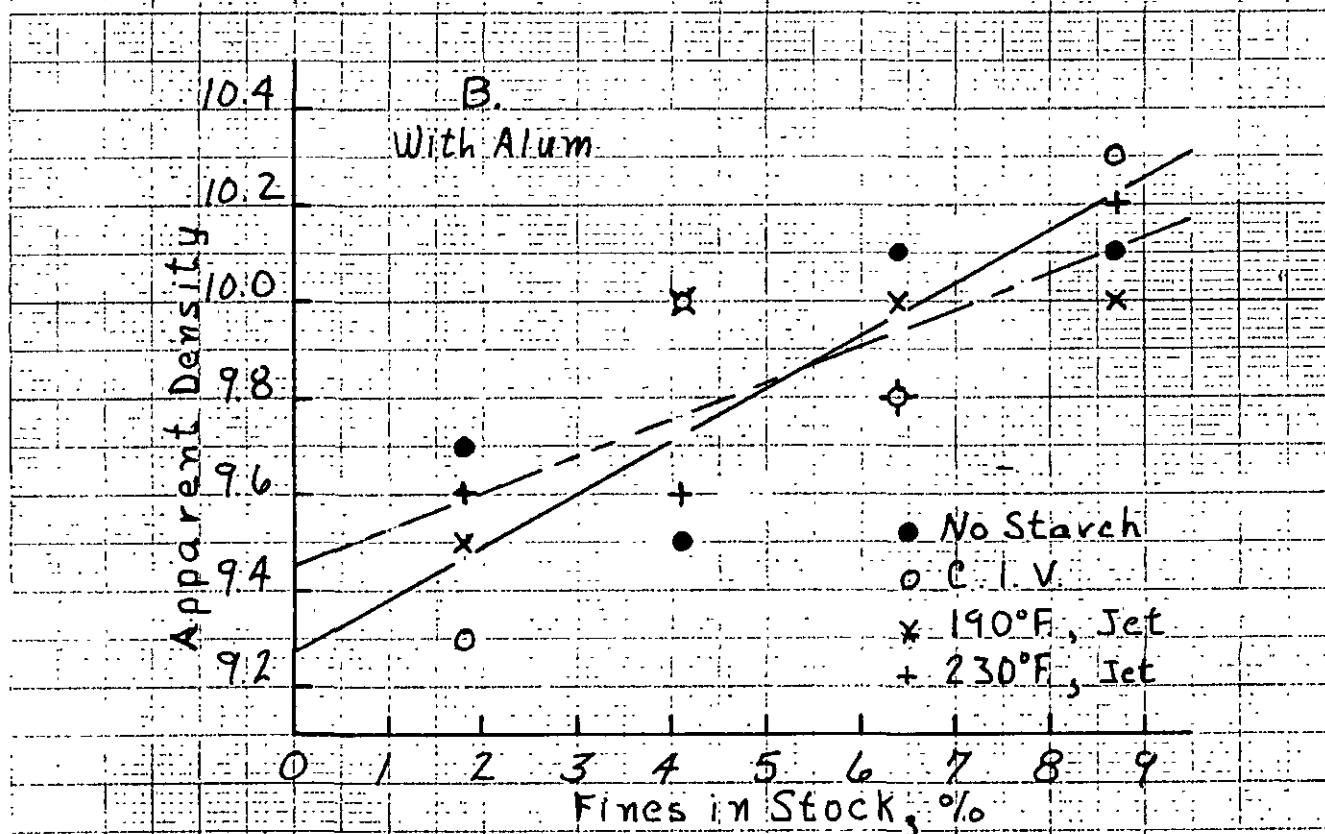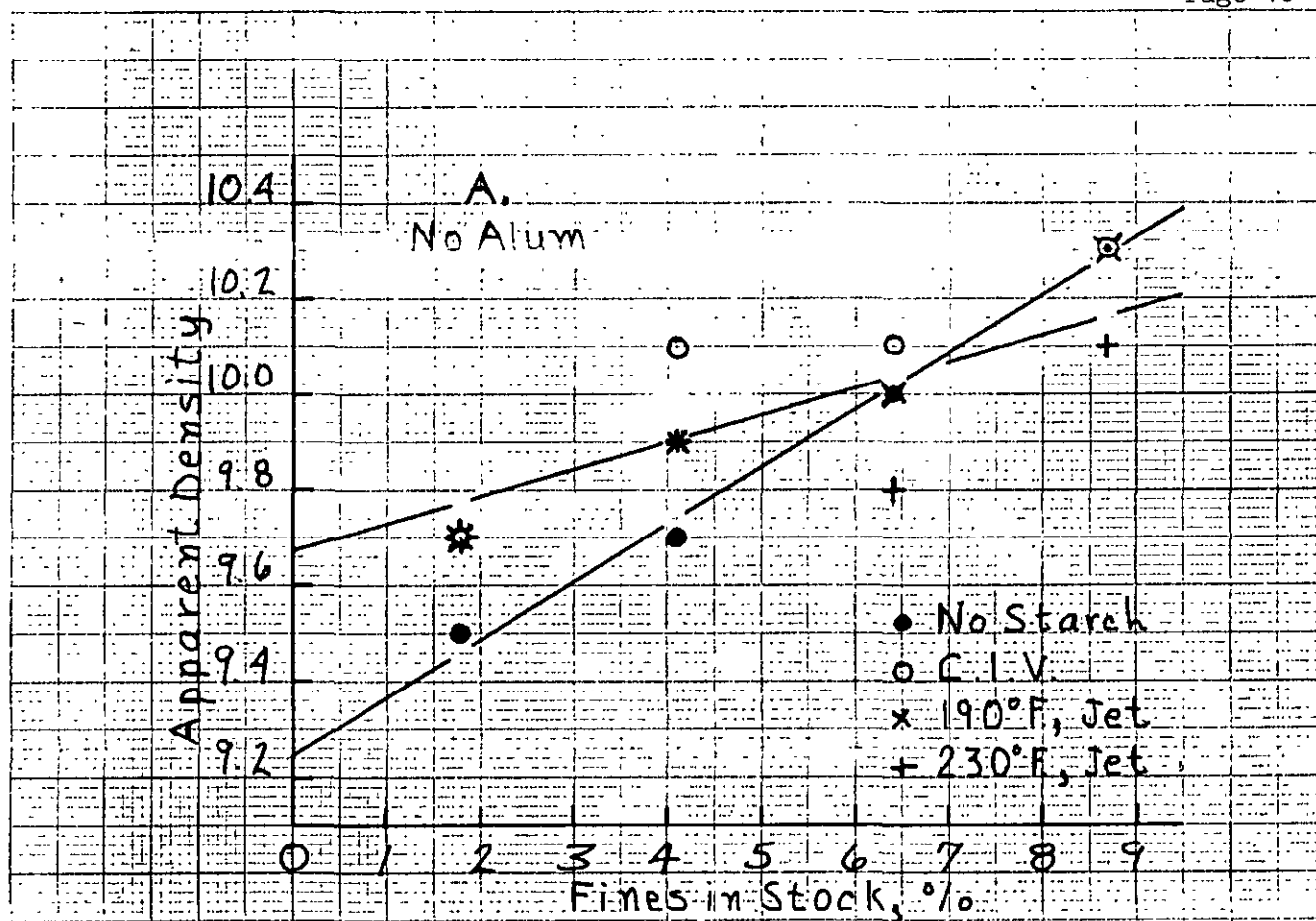
Figure 11. Apparent Density of the Handsheets as a Function of the Fines Concentration with 2% Starch Added
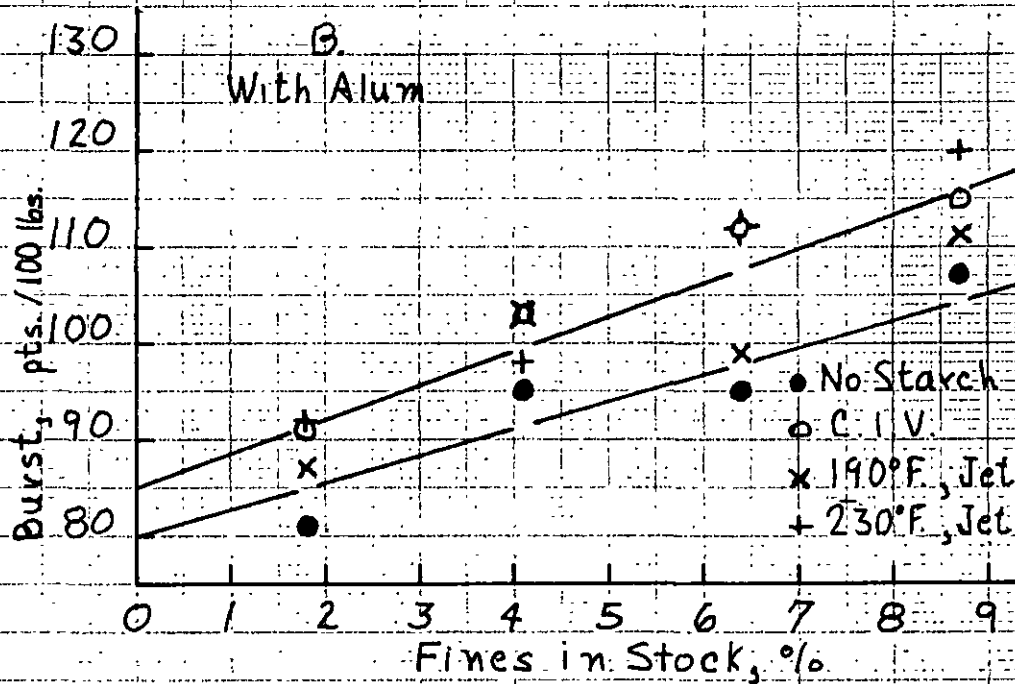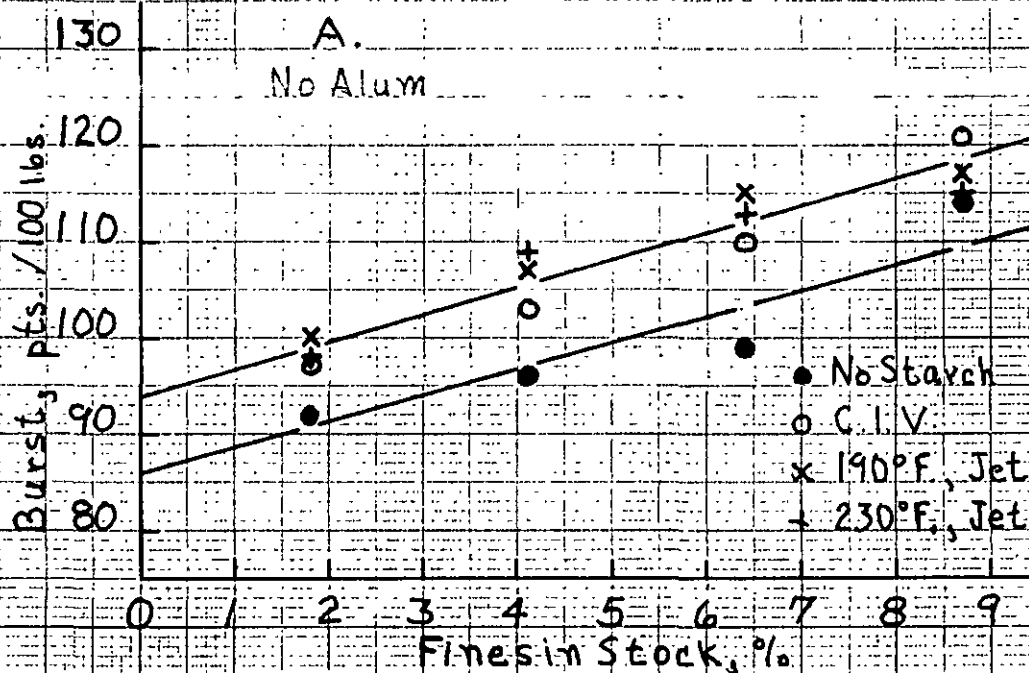
Figure 12. Bursting Strength as a Function of the Fines Concentration with 2% Starch Added

Figure 13. Folding Endurance as a Function of Fines
Concentration with 2% Starch Added
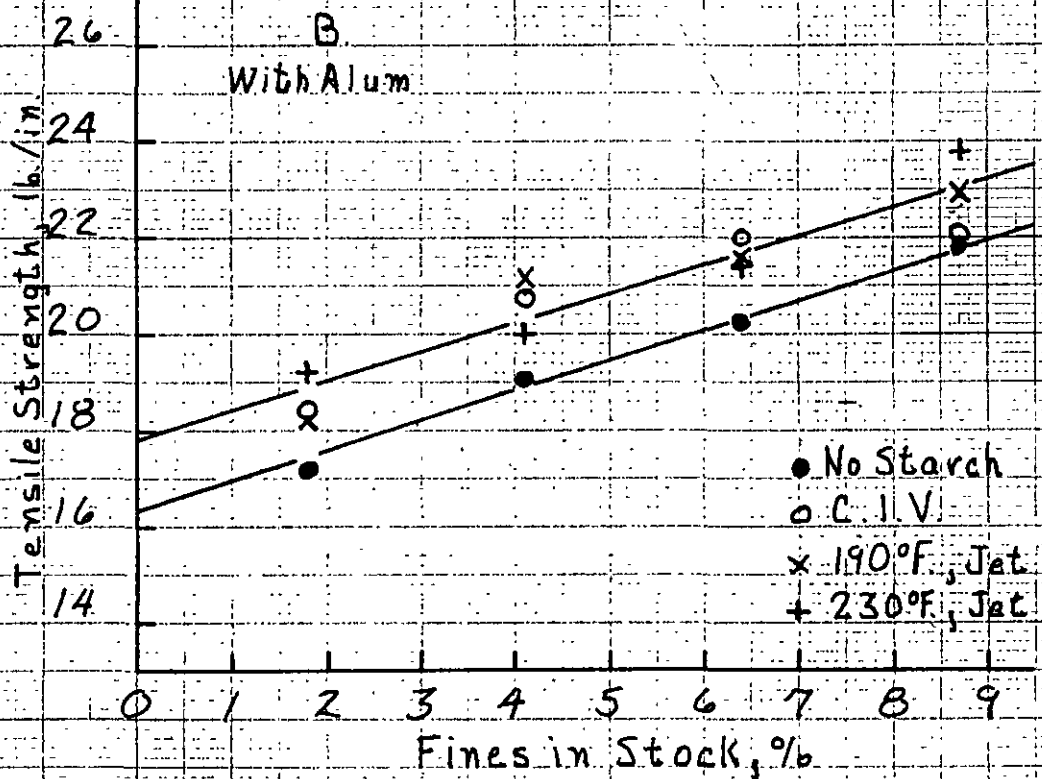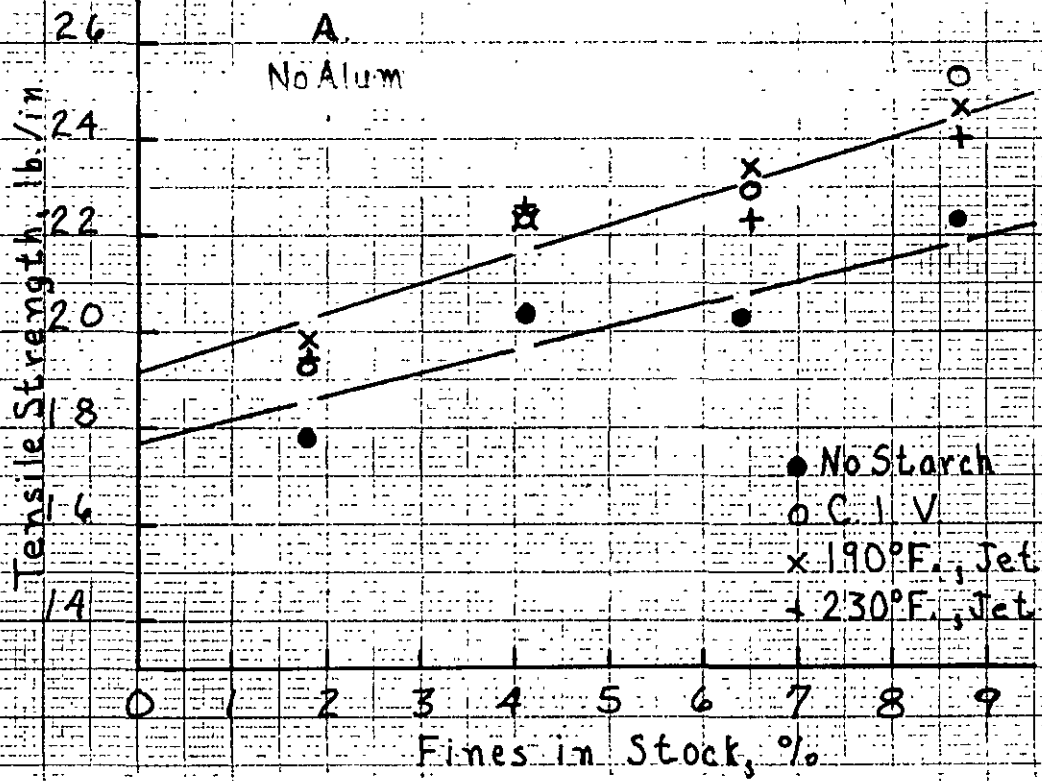
Figure 14. Tensile Strength as a Function of Fines
Concentration with 2% Starch Added

Figure 15. Retention Efficiency of 2% Cornstarch as a Function of Fines Concentration
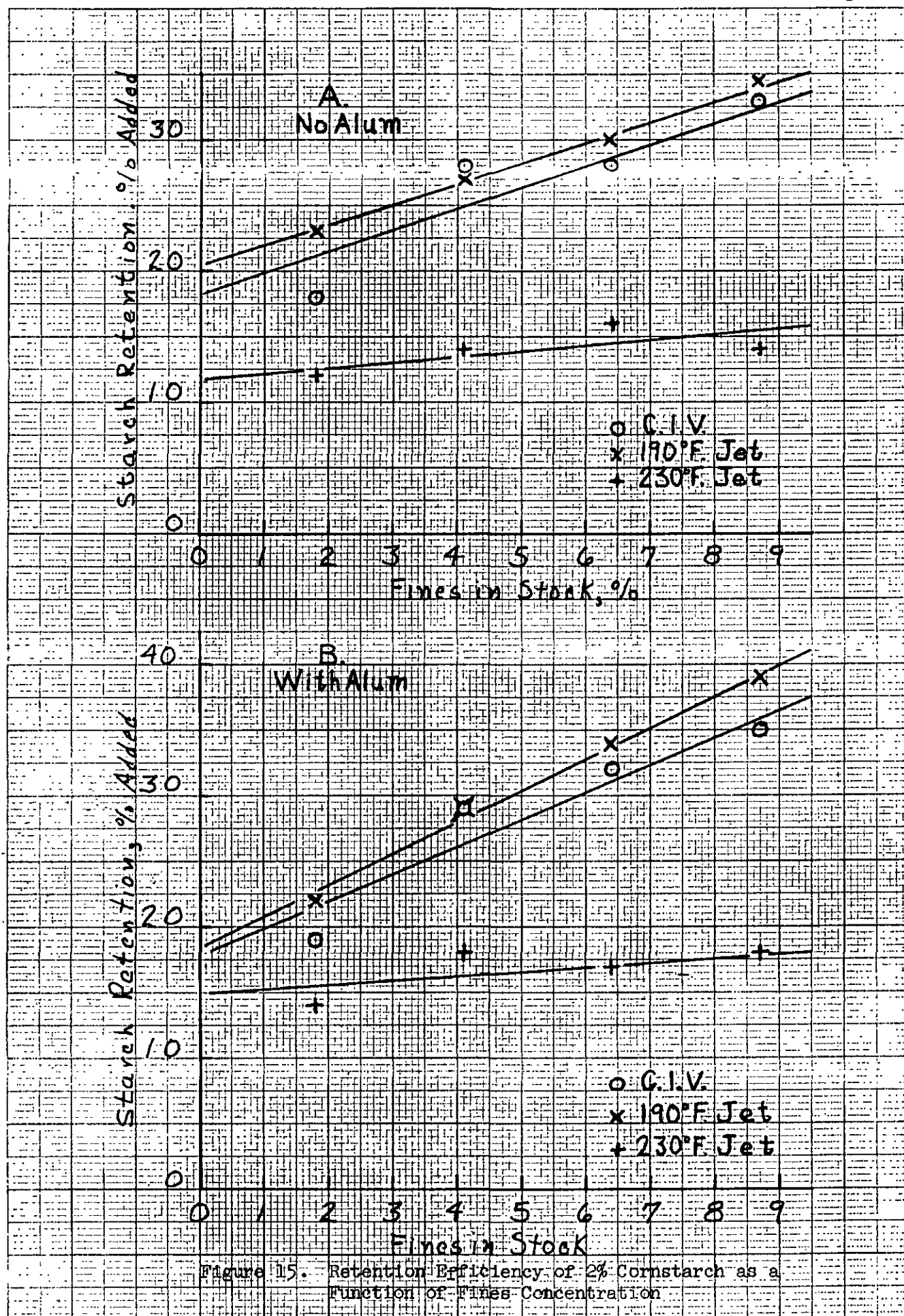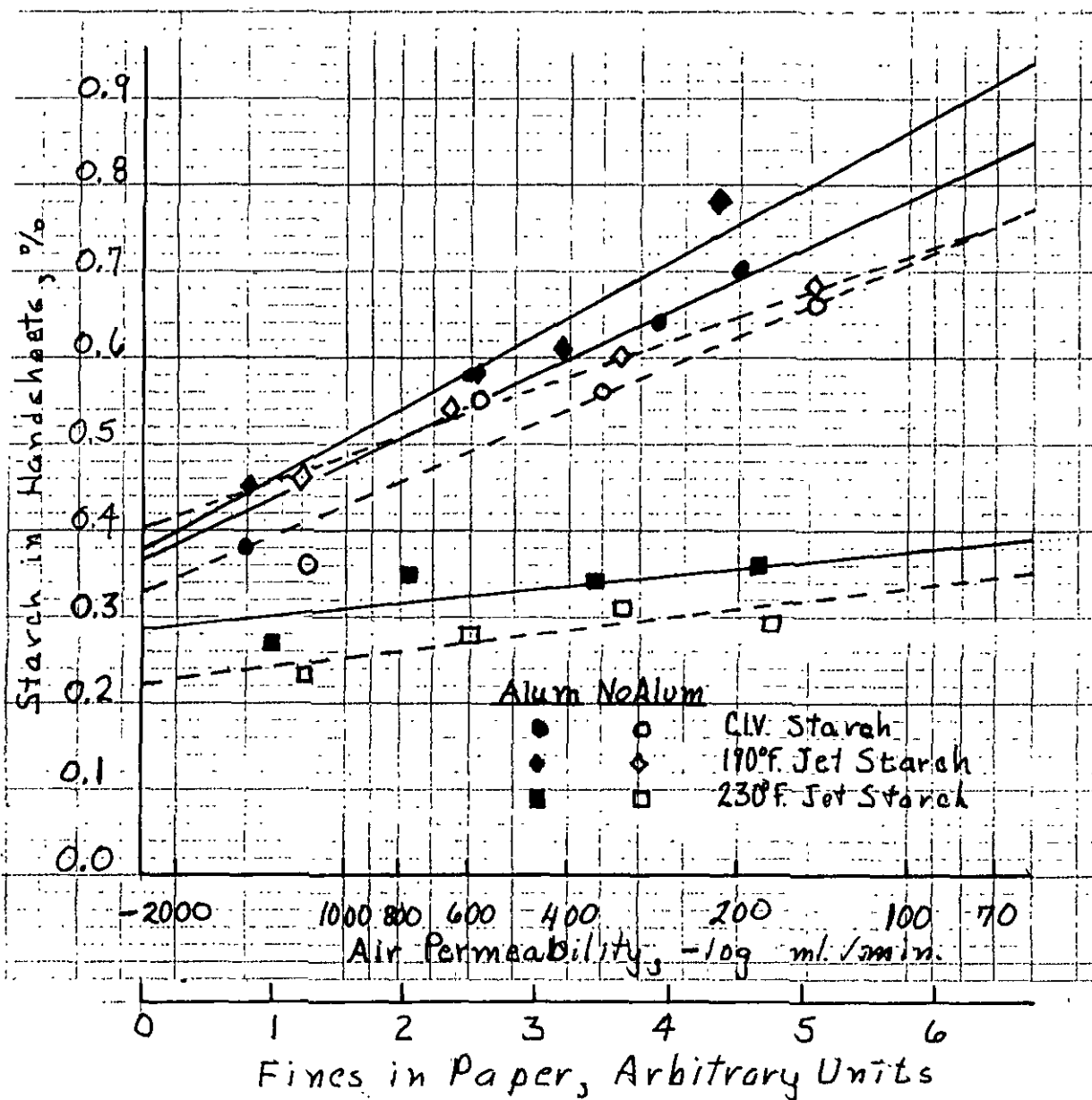
Figure 16.   Starch Retention as a Function of Fines Concentration
             in the Paper
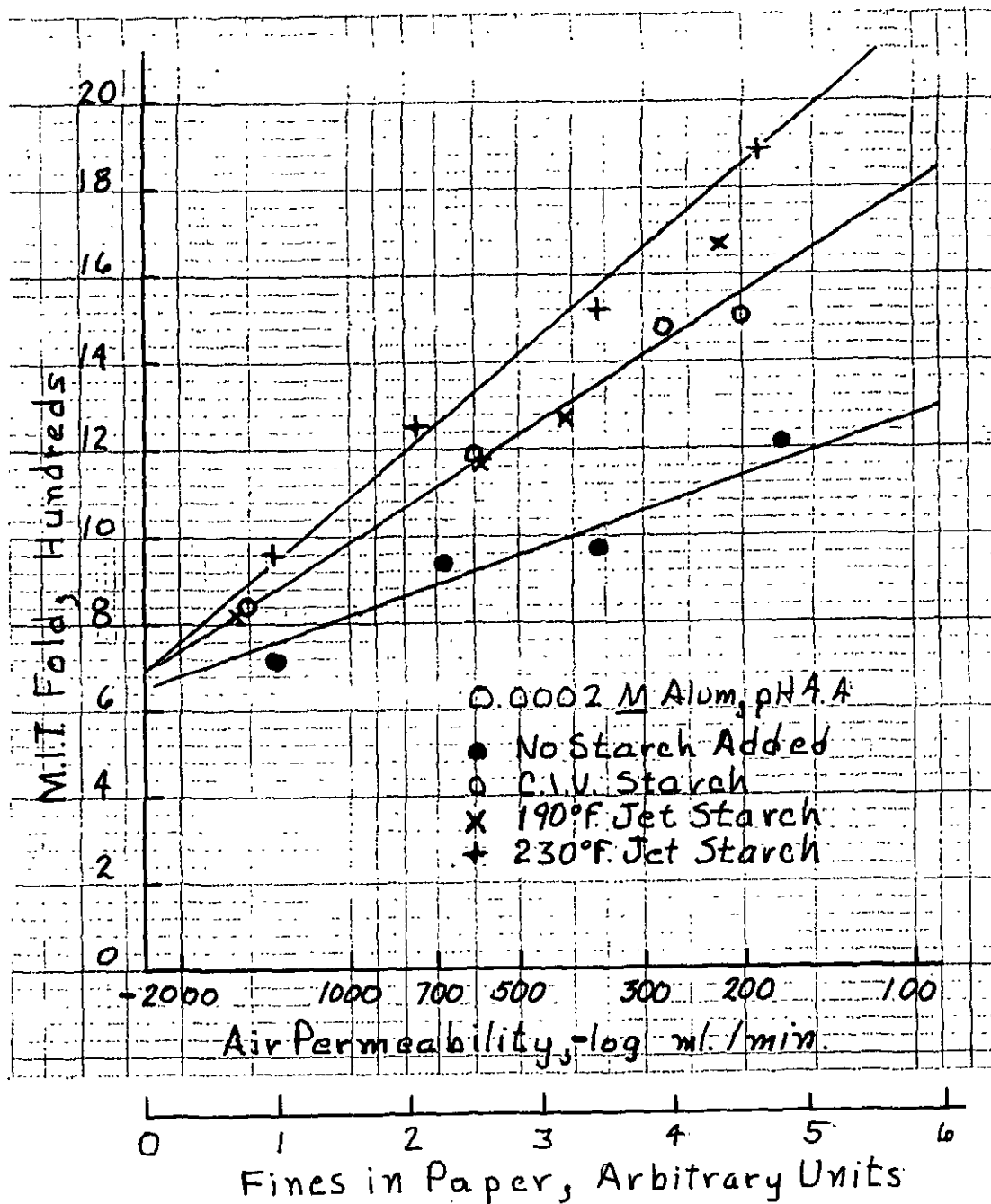
Figure 17. Starch Retention as a Function of Starch Dispersion and Fines in Handsheets Made With 2% Starch

Figure 18. Folding Endurance as a Function of Starch Dispersion and Fines in Handsheets Made in 0.0002M alum (2% starch added). The Broken Lines Indicate the Response Without Starch
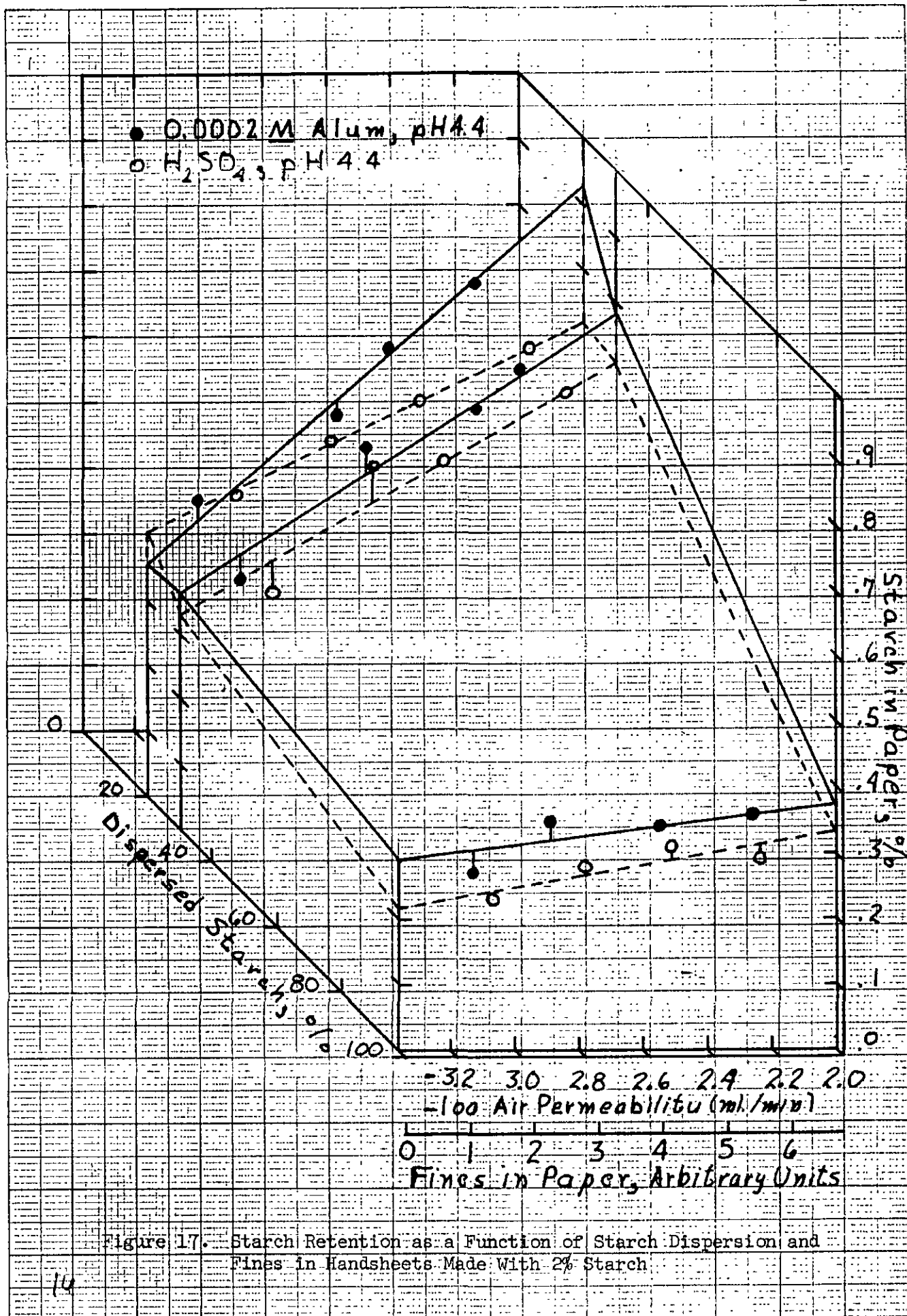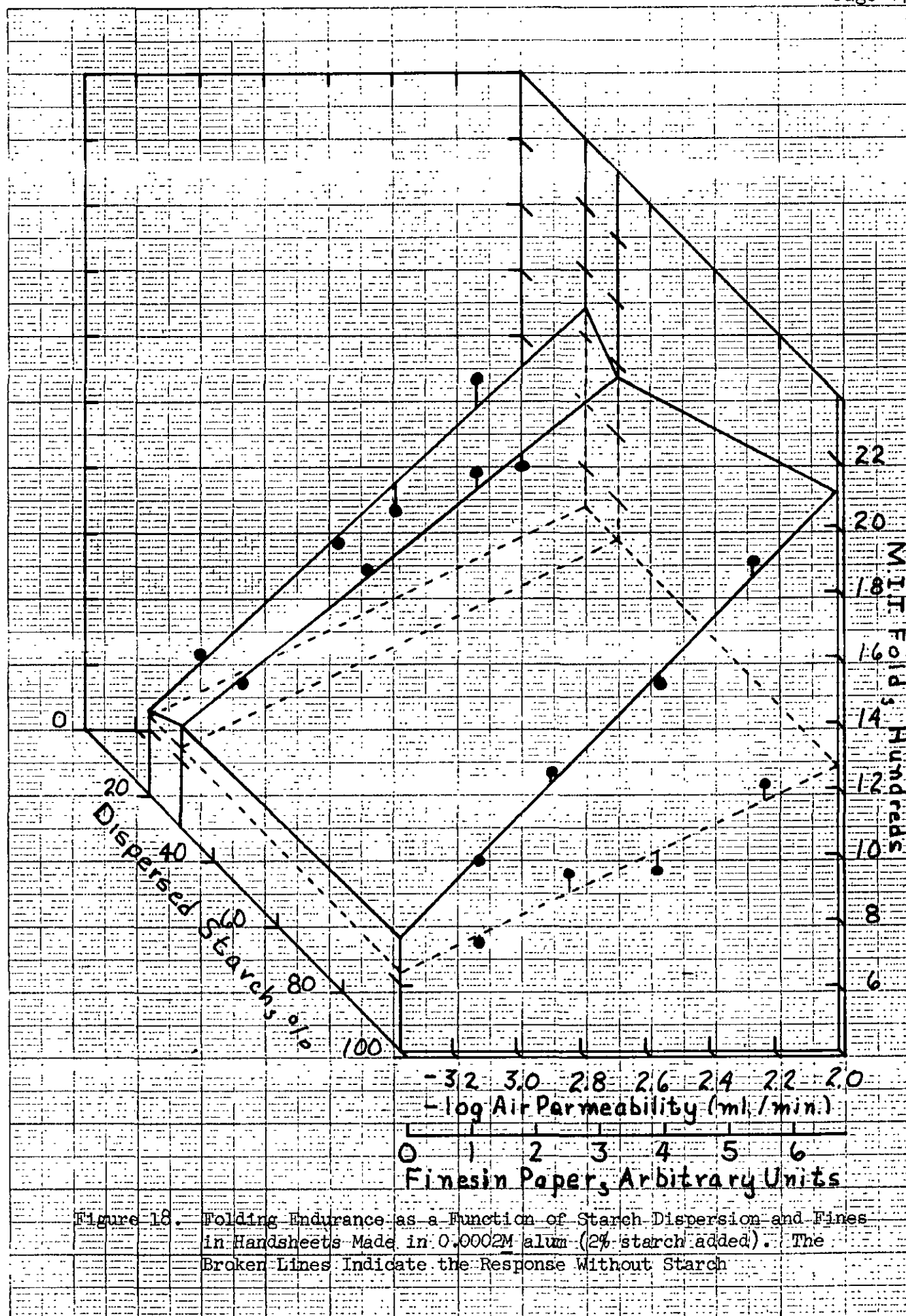
Figure 19.   M.I.T. Fold of Handsheets Made With Alum and 2% Cornstarch
as a Function of Fines in the Paper
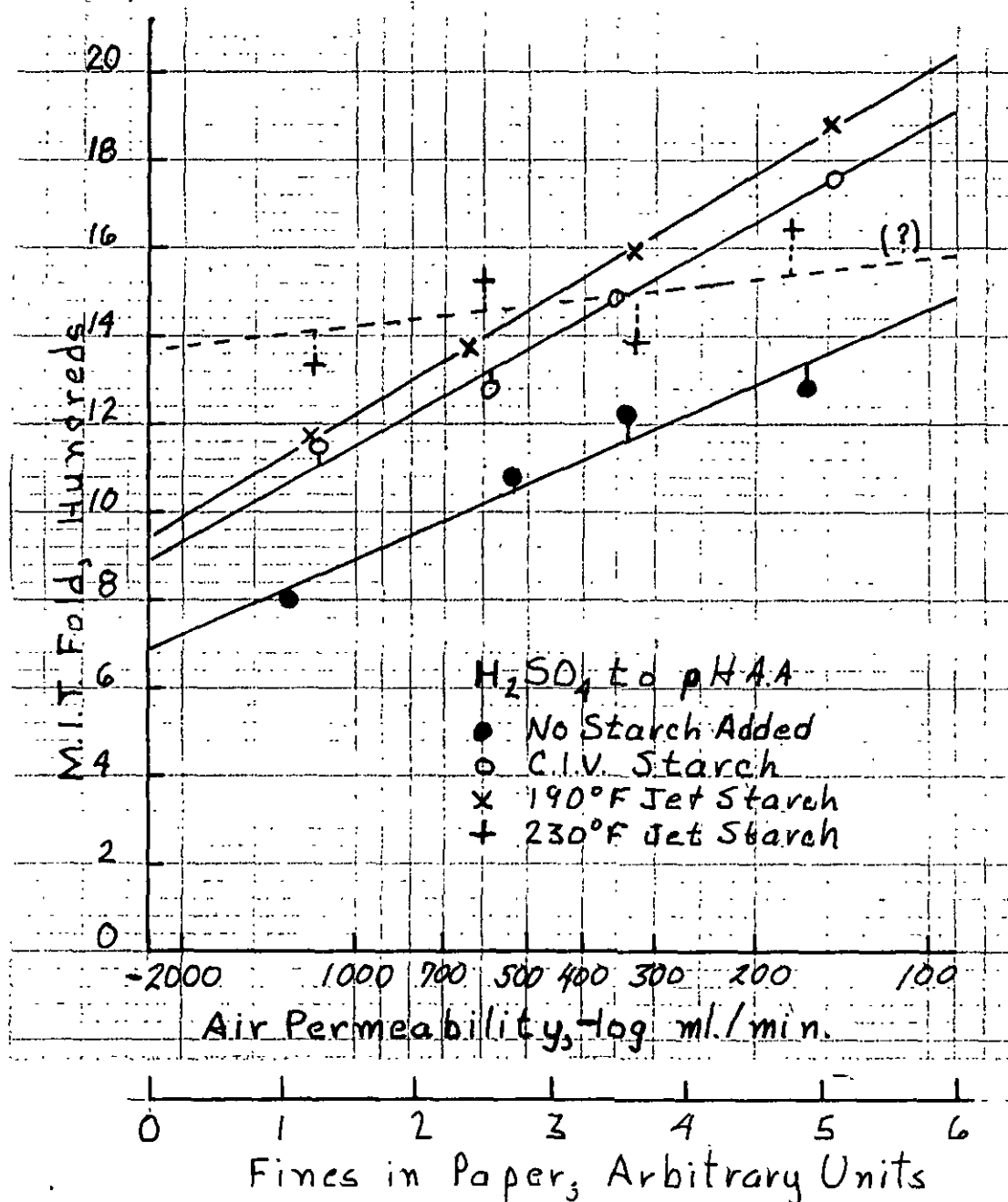
Figure 20. M. I. T. Fold of Handsheets Made With 2% Cornstarch,
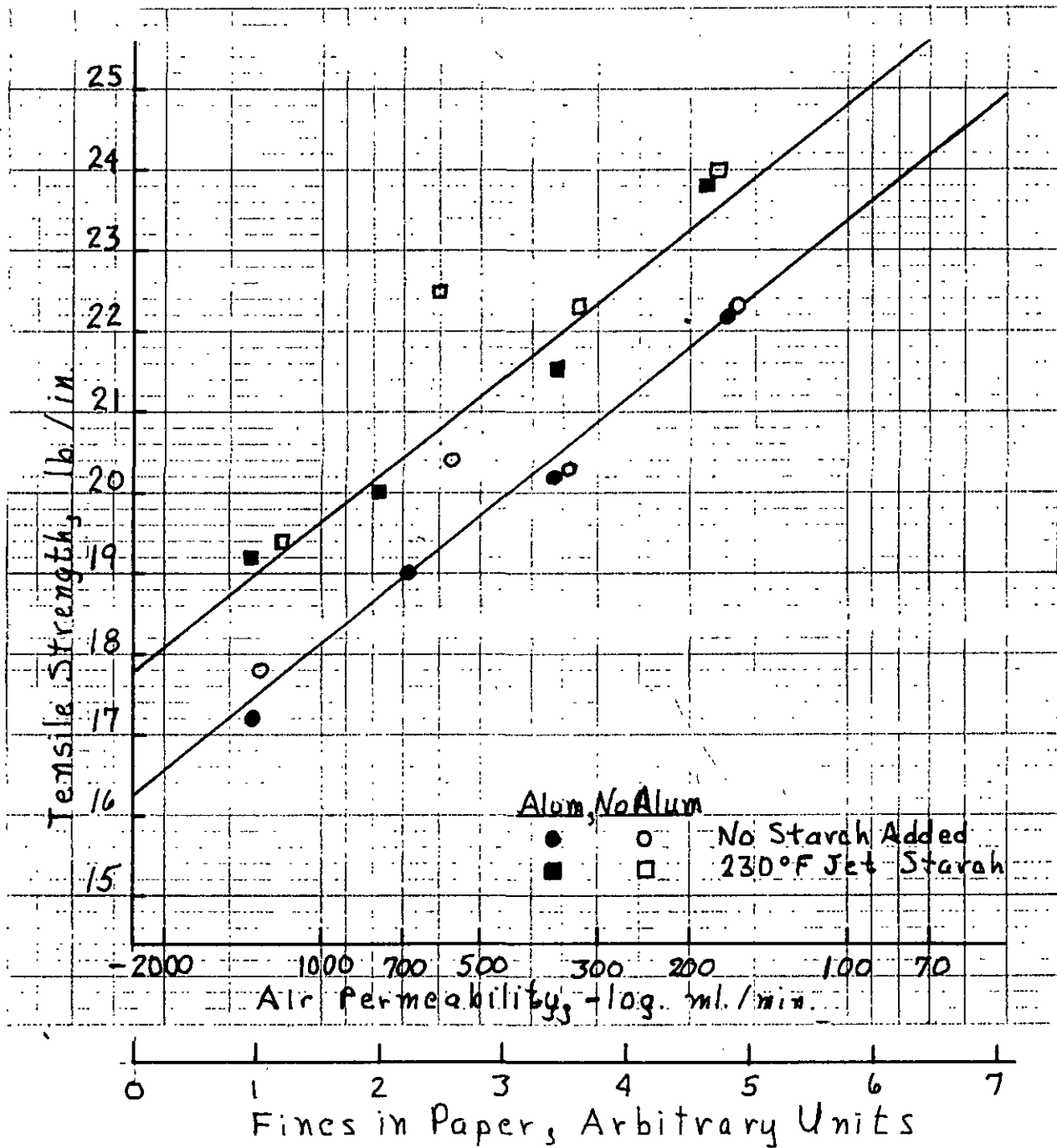Without Alum, as a Function of the Fines in the Paper

Figure 21. Tensile Strength of Control Sheets and 2% Highly Dispersed Starch
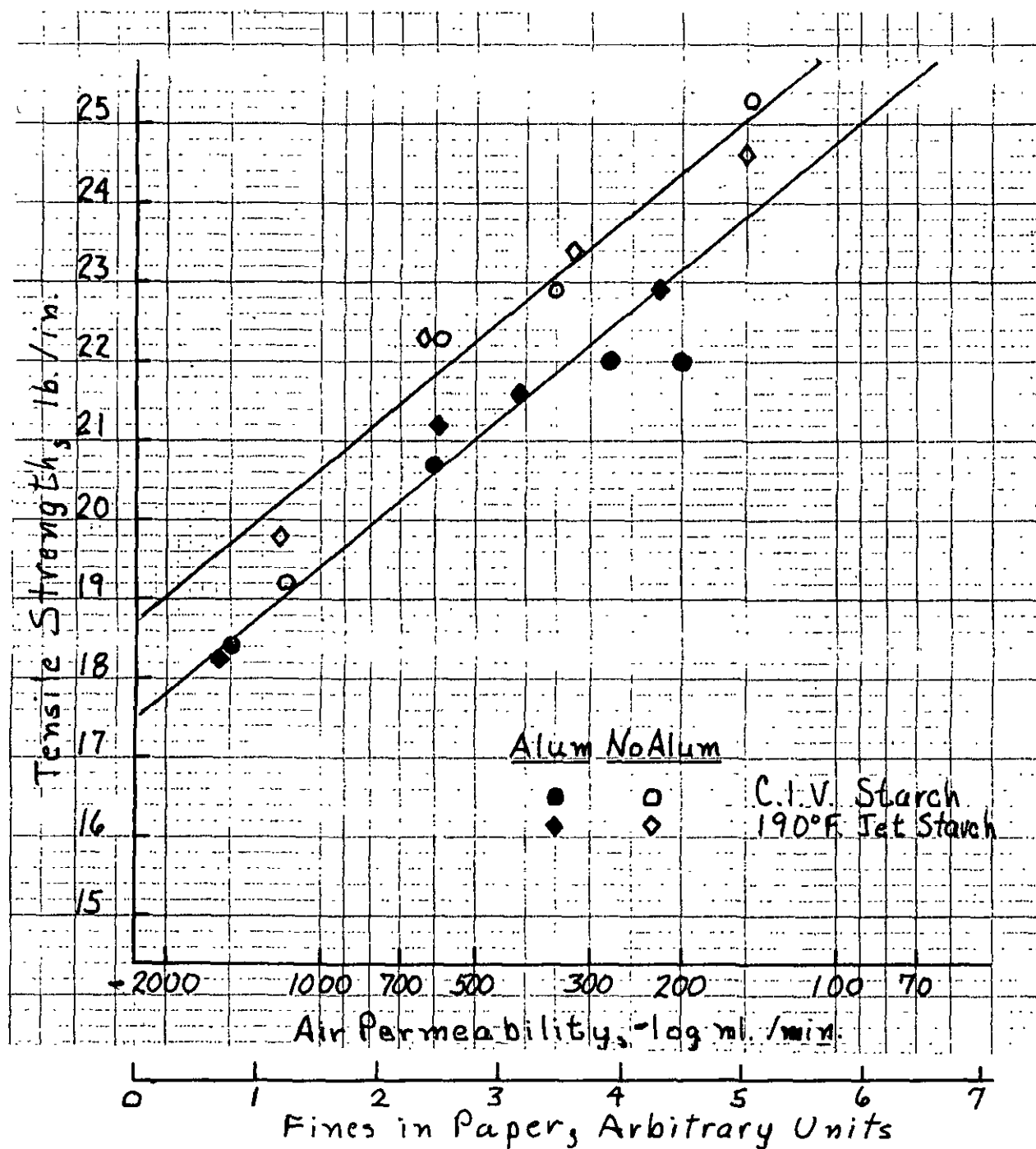Preparation as a Function of Fines in the Paper

Figure 22. Tensile Strength of Control Sheets and 2% Highly Dispersed Starch
Preparation as a Function of Fines in the Paper