



4-1966

A Study of the Efficiency of Certain Starch-Cationic Resin Complexes

William E. Hellman
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>

 Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Hellman, William E., "A Study of the Efficiency of Certain Starch-Cationic Resin Complexes" (1966). *Paper Engineering Senior Theses*. 257.

<https://scholarworks.wmich.edu/engineer-senior-theses/257>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



A STUDY OF THE EFFICIENCY OF CERTAIN
STARCH-CATIONIC RESIN COMPLEXES

A THESIS SUBMITTED TO THE DEPARTMENT OF
PAPER TECHNOLOGY AS A PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR A B.S. DEGREE.

WILLIAM E. HELLMAN
KALAMAZOO, MICHIGAN
APRIL 13, 1966

TABLE OF CONTENTS

Page 1	Literature Search
Page 5	Experimental Procedure
Page 9A	Data and Results
Page 11	Conclusions
Page 13	Literature Cited

An attempt is made herein to compare the efficiency of commercially available cationic starches and those prepared in the laboratory using a pearl corn starch and different cationic resins. The efficiency of each is determined through evaluation of the resulting wet-web strength and dry strength tests. Results show that cationic starches can be prepared in the mill and comparable strengths are obtained with their use.

It has long been known that cellulose develops a negative charge from the carboxyl groups when dispersed in water. The same effect is found when starch is diluted in water. Wet end addition of starch has been proven to improve the strength of the resulting mat of fibers. This strength improvement results mainly from the entanglement of the fibers and starch molecules. The retention of starch in this type of system is very poor.¹

This phenomena of cellulose having a negative charge, often called the electrokinetic potential, has been exploited with the result that starches which possess a cationic (positive) charge in water have been developed. Thus, when the cationic starch is added to the negative fiber system, the starch is quickly attached to the fiber and increased retention results. Because of the increased retention and the increased entanglement of the fibers drawn together by the cationic starch, an increase in sheet strength follows.

Since cationic starch efficiency is related to this electrokinetic potential, a clear understanding and a study of their measurement were undertaken. Riddick² describes this electrokinetic or zeta potential as a measurement of the electrokinetic charge that surrounds suspended

particulate matter and recommends the use of a Zeta Meter for its measurement. It is believed that at zero zeta-potential the fibers will not only not repel each other, but when mechanical agitation brings them into contact, dispersion and Van der Waals' secondary forces come into effect and an attraction is exerted. Other descriptions and discussions of zeta-potential are offered in the literature^{3,4}, along with various ways of measurement.

A method of measuring the amount of cationic material to produce a zero zeta potential which yields complete saturation of fibers with the cationic material, is outlined in a U.S. Patent, No. 2,694,633⁵. This is a method of electrometric titration. In this method the cellulose suspension is titrated with a solution of the cationic starch of known concentration. The change in the hydrogen-ion concentration due to the hydrogen displacement at the point of contact of fiber-cationic starch is measured with a sensitive potentiometer so that the optimum amounts of starch solution attached can be determined.

The above electrometric titration method was tried on two complexes; a fiber-starch complex and a resin-carboxymethyl cellulose complex. Because of the lack of sensitive enough equipment, this method had to be abandoned in the proposed project of measuring cationic efficiency.

A method for determining cationic efficiency of pulp-cationic starch complexes is fully discussed by Mehlretter.⁶ This article describes a simple color absorption procedure which can be applied routinely to determine cationic efficiency of nitrogen-substituted starches after retention on cellulose pulps. The method depends on the indirect determination of the amount of electronegatively charged pigment absorbed by a standard pulp after the treatment of known quantities of cationic starches.

This method of spectrophotometric analysis as outlined above was exhausted to the object of this project. However, the above method does not take into account the low concentrations of starch used in this project. It was decided that the efficiency of the cationic starch could best be determined through measurement of the resulting sheet strength.

Much work has been done on the study and measurement of wet-web strength. Especially interesting is the work of Lyne and Gallay^{7,8} who discuss the fiber properties and other relations of wet-web strength and also describes an instrument for the measurement of wet-web strength. R. de Montigny⁹ and Langins¹⁰ also studied the properties, importance, and measurement of wet-web strength. Brecht and Eurfurt¹¹ also studied wet-web and a method of preparing handsheets in strip form to alleviate the tedious task of preparing strips for wet-web strength tests.

All of the literature discussing wet-web strength points to the need for better fiber-fiber bonding in the initial state of web formation to increase wet-web strength. It is hoped that the proper use of cationic starches as used in this paper will improve this bonding and therefore the wet-web strength.

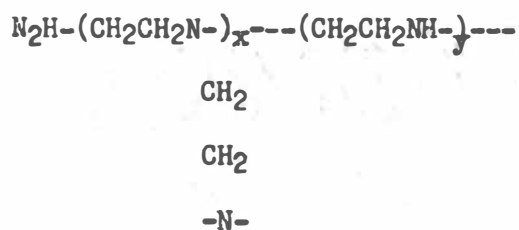
The Brecht Initial Wet Strength Tester was finally adopted for the wet-web testing done on this project.

Many types of cationic resins have been developed, most of which will combine with all the common starches to yield a positive electrokinetic charge in solution. Because of the comparative newness of the subject of cationic starches and resins, and because of the high competitiveness of the paper chemicals industry, very little has been published publicly. It is not possible at this time to give exact structures or formulas of any of the resins because they have not been made public.

Several patents do, however, give basis or general formulas and cover the range of possible applications to the industry. A U.S. Patent of 1952¹² summarizes the preparation of cationic resins which are basically alkylenepolyamines having the general formula of $H_2N(C_nH_{2n}HN)_xH$. Typical polyamines of this type are ethylenediamine, diethylenetriamine, and 1-3 propylenediamine. When reacted with halchydin derivatives of glycerol the products contain quaternary ammonium groups which is the probable reason for their substantivity for cellulose fibers.

The preparation of quaternary ammonium salts having a general formula of $R-CO-NH-CH_2-N(tert.)$ is well covered in U.S. Patent¹³ 2,146,392. These salts impart permanent water-repellant characteristics to cellulose material. They further exhibit the unusual property of fixing starch upon cellulosic materials.

Another cationic material that may be used to impart a positive charge on starch in Polyethyleneimine (PEI). A possible structure for this polymer might be:



Analysis has shown the primary to secondary to tertiary nitrogen ratio to be approximately 1:2:1. PEI, then, is a polymer having a variety of amine nitrogens which makes possible the broad spectrum of applications and reactions which are found in the literature¹⁴. The preparation and examples of the use of these types of resins are well covered in a Canadian Patent¹⁵ of 1958.

The preparation of stabilized cationic starch compositions or cyanimic-starch reaction products is covered in U.S. Patent 3,136,646.¹⁶

EXPERIMENTAL PROCEDURE

The following outlines the procedures used in preparing the starch-resin complexes, the cationic starches, and the fibers in preparation for making Noble and Wood handsheets.

A pearl corn starch was cooked in the following way:

14.0 gms. of starch dispersed in 500ml. of distilled water. The solution was then cooked for 30 minutes @ 185.5 F. The cooked starch was cooled to room temperature. A solids determination was run on three samples (over dried at 105°C. for 24 hours) and an average of 2.51% solids was found.

25.0 gms. of this starch solution was weighed into 17 bottles. (25.0gms. solu. x 2.51gms. solid/100 gms. solu. = .626gm. solid) Each bottle therefore contains .626 gms. solid starch which is exactly 5 percent starch on 12.5 gms. of fibers.

The cationic resinous materials were obtained as samples from the prospective manufacturers and diluted as follows:

1.0gms. of Polyethyleneimine was dissolved in warm water and diluted to 100ml. in a volumetric. The diluted sample therefore contains 0.01gms. of solid resin/ml.

5.0gms. of Polyamide resin which was obtained at 10 percent solids was diluted to 100ml. This solution therefore contains 0.025gms. of solid resin per ml.

Since the resin was to be added on a percent basis of the weight of starch, the volumes needed to obtain the exact volume of resin necessary was calculated and these volumes added to small bottles and kept for addition to the fiber-starch suspension.

The following table shows the percent resin desired and the volume of resin solution added to the fiber-starch solution. Percent of resin desired is based on the weight of the starch.

Percent resin desired on 0.625 gms. of starch	Volume Polyethylenimine resin solution added	Volume resin added
2	1.25ml.	2.5ml.
4	2.5	5.0
6	3.75	7.5
8	5.0	10.0
10	6.25	12.5
15	9.4	18.75
20	12.5	25.0

The commercial cationic starches were prepared in the following way:

Approximately 12.0gms. of the cationic potato and the cationic corn starch were dispersed in separate beakers in approximately 550ml. of distilled water. The starches were then cooked in a water bath for 30-40 minutes at 195 F. according to manufacturers specifications. Three samples of each were then taken for percent solids determinations (oven dried for 24 hours @ 105°C). Cationic corn percent solids were determined at 2.28 percent and the cationic potato percent solids determined at 2.80 percent.

440gms. of the cationic corn starch solution was diluted to 1000 ml., giving a concentration of 0.01 gms. solid starch per ml. 328gms. of the cationic potato starch solution was diluted to 2000ml., giving a concentration of 0.0046gms. of solid starch per ml.

The following table shows the volume of starch solutions added to the fibers to give the desired percent starch on the weight of the fibers.

Table II

Percent starch desired on 12.5 gms. of fibers	Vol. of 0.0046g/ml. cationic potato solution added	Vol. of 0.01 g/ml. cationic corn solution added
2 percent	54.4ml.	25ml.
4	108.8	50
6	162.2	75
8	217.0	100
10	272.0	125
15	408.0	187.5
20	544.0	250

The above volumes of cationic starch solutions were put into bottles and kept for addition to the fiber suspension during sheet making.

Bleached sulfite soft-wood lap pulp was used as the fiber in this project. Approximately 540gms. A.D. pulp was torn into small pieces and soaked 24 hours before addition to the Valley experimental Beater. The pulp was added and diluted to a consistency of 1.5 .2 percent. The pulp was beaten approximately 30 minutes to a Canadian Standard Freeness of 500 25.

The Noble and Wood mixing tank was charged with enough pulp to make eight(8) 2.5gm. handsheets. A 2 liter sample was drawn off, a handsheet made and the sheet weighed. The stock in the mixing tank was then proportioned to five a 2.5 lgm. handsheet. The stock suspension was then drawn off to a predetermined mark where only 10 liters of suspension remained.

In the case of the commercial cationic starches, the prepared samples were added to the fibers. Suspensions (fibers plus starch) were agitated for 10 minutes.

For the starch-resin-fiber sheets, the starch samples were added to the fibers and agitated 5 minutes. The resin samples were then added and the total suspension, (fivers-starch-resin) was agitated for an additional 10 minutes.

Following the prescribed mixing and agitation, 5 handsheets were prepared. One handsheet was prepared with the Brecht wet-web strip maker

and wet-web test immediately run. Four additional handsheets were run for the dry strength tests.

In all cases the sheet was formed on the wire, with care being taken to cut off the vacuum as soon as the water was drained off. This was done because pulling air through the sheet has an effect on the wet-web strength. The sheet was then pressed intact with the wire using the weight of the roll only. One sheet was tested for wet-web strength at this point. The additional four sheets were dried intact with the wire on the Nobel and Wood Drum drier and the sheet removed from the wire. The sheets were all conditioned in the constant humidity room before testing.

In running the wet-web test the Brecht Initial Wet Strength Tester was used. The strips for testing were prepared on the wire as previously noted and placed in a humidity chamber (a desiccator in which the desiccant was replaced by potassium dichromate). The three strips were tested, the breaking force recorded, and the broken strips immediately placed in a small preweighed bottle. The bottle and wet strips were weighed; the bottles and strips were then dried for 36 hours at 105°C and the bottle and dry strips weighed again. The percent moisture and basis weight were then calculated. The breaking force as recorded above was then corrected to a basis weight of .48gms. and recorded as Corrected Breaking Force.

The dry sheets were then tested for Basis Weight, mullen, and dry tensile. Both strength tests were then corrected for basis weight and recorded.

As expected, there was an immediate increase in wet web strength with increasing additions of either the cationic starch-resin complexes (see Fig. I). This increase seems prominent to approximately 10 percent

addition. Beyond this point there is a gradual leveling off but no real drop offs were observed in wet-web breaking strength.

The commercial cationic corn starch gives the largest increase in wet web strength, i.e., 43.50gms. The cationic corn starch used in this project is prepared so as to have a starch-epoxy-anine⁺ structure. This type of structure appears to cause the unusual strength increases observed. The starch-polyethyleneimine resin complex showed an increase of 38 gms., the starch polyamide resin complex 32.5 gms. and the cationic potato starch 21gms.

Of particular interest is the showing of the two starch-resin complexes. The two show an average increase of 35.2gms. of breaking strength. These two prepared cationic starches can be prepared in the mill at a much lower cost. The following table, using the closest approximate prices available show the economies of using a pearl corn starch and a commercial resin. The cost comparisons are done on a ton of fiber basis and at the 10 percent addition level.

Table IV

Lbs. Fibers Used	2000	2000	2000	2000
Lbs. Starch Used	1000	1000	200	200
Cost of Starch Per Pound	\$.06	\$.06	\$.16	\$.24
Total Cost for Starch	\$ 6.00	\$ 6.00	\$32	\$48
Lbs. of Resin Used at 10% of Starch	10	10	-	-
Cost of resin Per Lb.	\$.85	\$.75	-	-
Total Cost of Resin	\$ 8.50	\$ 7.50	-	-
Total	\$14.50	\$13.50	\$32.00	\$48.00

Table III - Data and Results

Sheet Composition	Uncorr. Wet-Web	St. of dry strips	Corr'td. Wet-Web	Uncorr. Mullen	Basis Wt.	Corr'td. Mullen
Pulp I	73.3	.486	77.3	11.7	.614	9.2
Pulp I-A	100.1	.546	83.2	17.9	.583	14.6
Pulp I-2% K	89.9	.479	90.2	19.1	.660	13.9
" 4% K	111.1	.592	90.1	17.3	.584	14.6
" 6% K	103.0	.530	93.4	19.0	.606	15.0
" 8% K	105.0	.537	93.9	13.7	.446	15.1
" 10% K	103.9	.517	96.3	20.8	.621	16.1
" 15% K	93.2	.446	105.4	23.0	.642	17.2
" 20% K	96.5	.421	109.9	20.3	.591	16.5
Pulp I-B	112.2	.603	89.7	13.9	.614	14.3
Pulp I-2% P	107.7	.560	33.3	17.6	.619	13.7
" 4% P	104.4	.526	95.1	13.3	.613	14.3
" 6% P	100.1	.464	103.5	16.4	.594	13.3
" 8% P	33.3	.380	111.1	15.3	.430	12.9
" 10% P	116.1	.482	115.7	20.1	.635	15.2
" 15% P	81.6	.333	117.8	17.5	.441	19.0
" 20% P	96.9	.403	115.3	13.3	.593	15.3
Pulp 2	81.1	.436	80.1	10.6	.572	10.6
Pulp 2-2% S	91.9	.466	94.6	14.6	.573	12.3
" 4% S	102.1	.513	95.5	21.9	.612	17.2
" 6% S	96.3	.461	100.3	22.3	.569	19.2
" 8% S	115.4	.546	101.7	21.8	.622	16.8
" 10% S	112.4	.516	104.6	23.1	.588	13.9
" 15% S	93.1	.448	99.6	25.6	.609	20.2
" 20% S	97.9	.456	102.9	23.7	.563	20.2
Pulp 3	73.7	.475	79.6	10.7	.525	9.3
Pulp 3-2% Q	92.5	.402	110.3	14.4	.572	12.1
" 4% Q	89.7	.389	110.7	29.1	.623	22.4
" 6% Q	94.1	.402	112.1	27.1	.601	21.6
" 8% Q	99.6	.394	121.4	28.8	.618	22.4
" 10% Q	103.3	.431	120.4	21.6	.626	16.6
" 15% Q	104.4	.422	118.7	-	-	-
" 20% Q	111.2	.434	123.1	-	-	-

Notes:

Strengths corrected to 0.43gm. basis.

Pulp I-A is pulp I and free pearl corn starch.

Pulp I-% K is pulp I, free pearl corn starch, and % polyamide.

Pulp I-B is pulp I and free pearl corn starch.

Pulp I-% P is pulp I, free pearl corn starch, and % polyethyleneimine.

Pulp 2-% S is pulp 2, and % cationic potato starch.

Pulp 3-% Q is pulp 3, and % cationic corn starch.

Handsheets at 15 and 20 percent Q could not be removed from the wire in dry form.

WET-WEB BREAKING FORCE (CORRECTED)

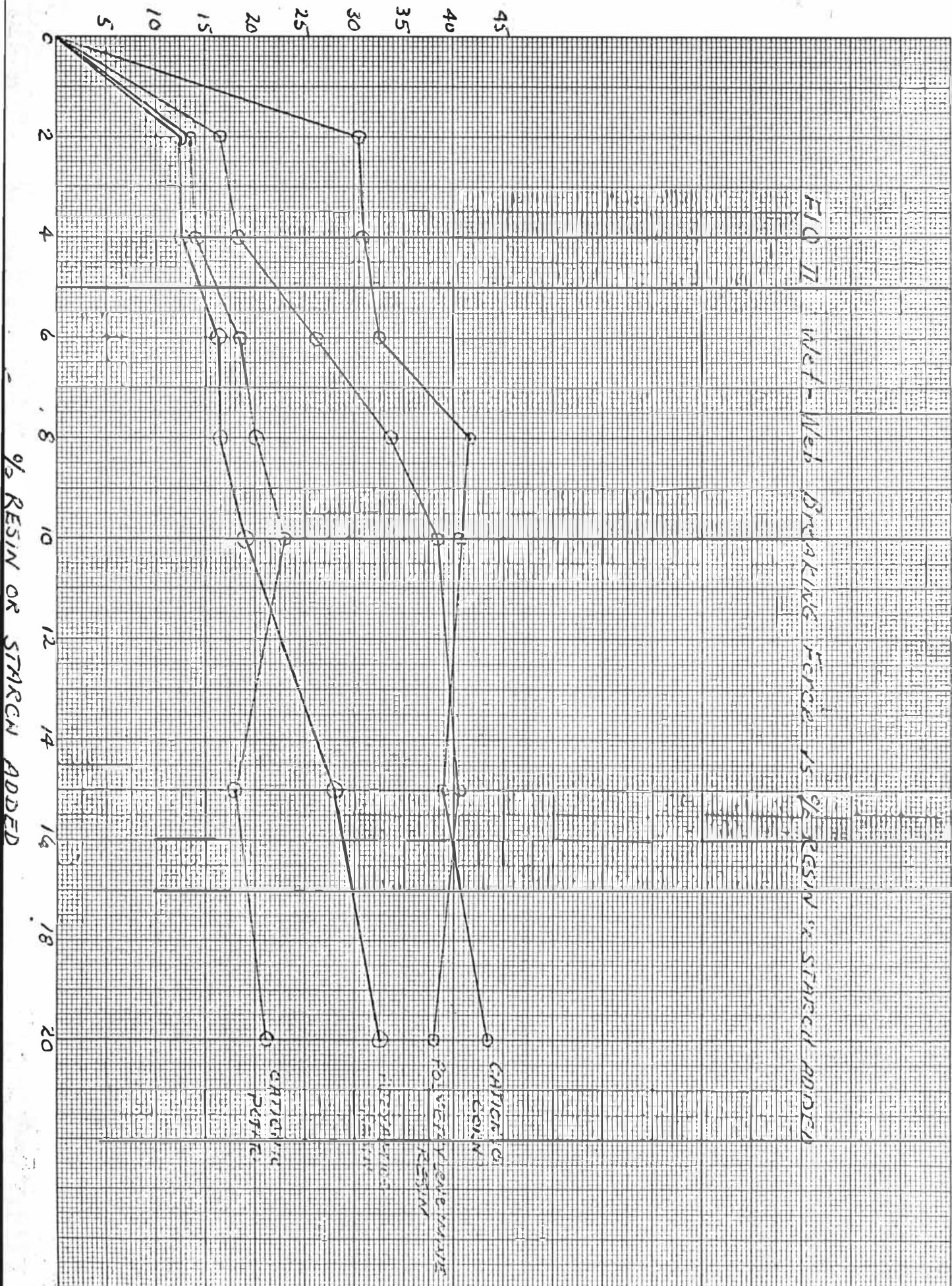
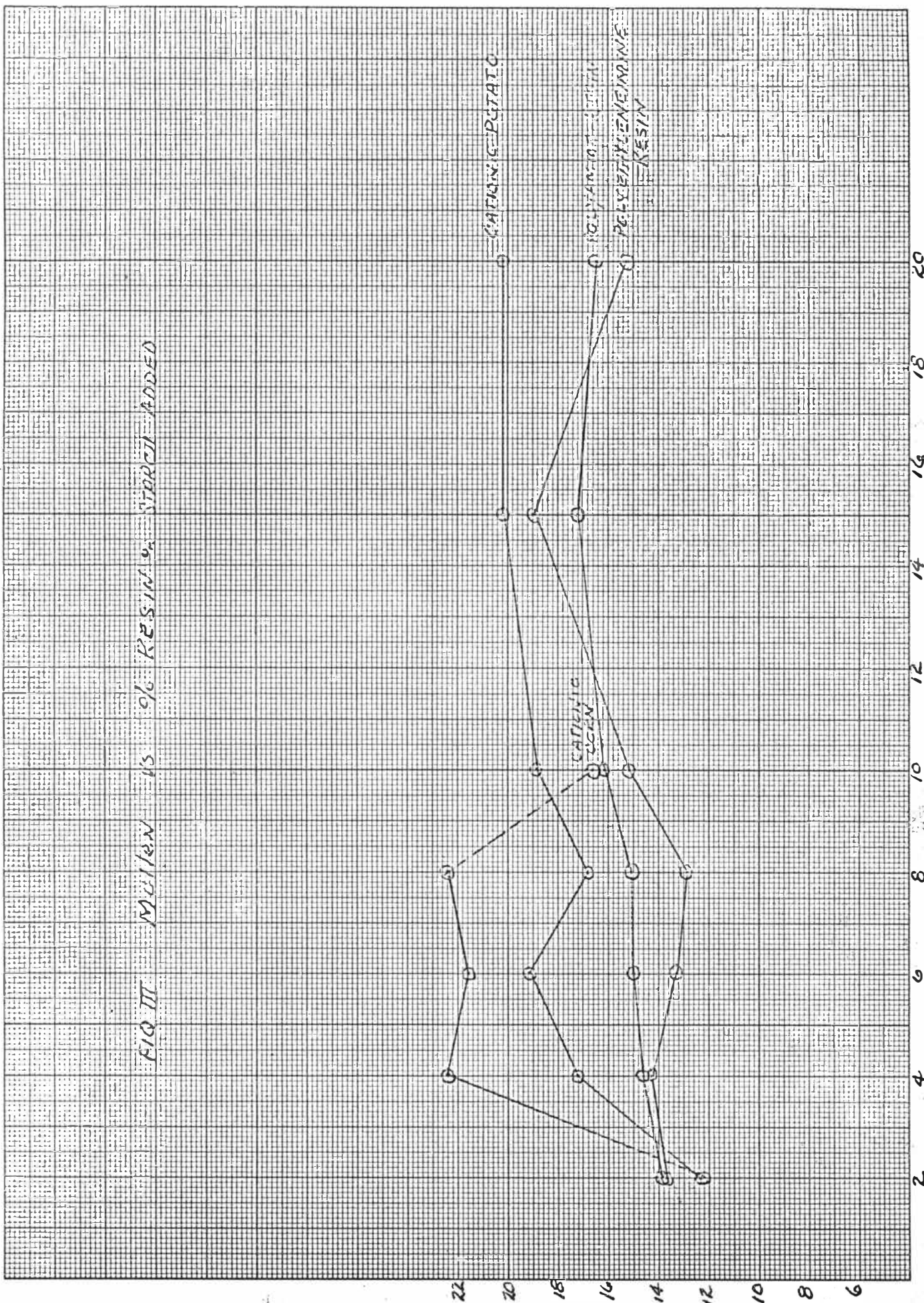


FIG. 71 Wet-Web Breaking Force vs. % Resin or Starch Added

FIG. III Mullen vs. % Resin & Starch Added

MULLEN - (CORRECTED)



% RESIN & STARCH ADDED

There is also an immediate increase in the mullen as shown in Fig. II. The dry strength however tends to level off at about 4 percent addition. The commercial cationic starches show a greater increase in mullen than do the prepared starch-resin complexes. The dotted line or sharp decreases in mullen from 8 to 10 percent addition of the cationic corn starch can be traced to the fact that the sheet began sticking to the wire at this point. The sheets at 15 and 20 percent addition stuck to the wire after drying and could not be removed. It appears that the physical strength in the sheet at 10 percent addition was broken down as it was removed dried from the wire. This caused the sharp decrease in Mullen. It can be assumed that the dry strength of these sheets might continue at about the 22pt. level. Although the dry strength of the sheets prepared are not as high as the sheets prepared with the commercial cationic starches, they are comparable. It is characteristic of wet strength resins that they do not greatly increase dry strengths.

CONCLUSIONS

It may be concluded, within the scope of this paper, that cationic starches will give a sharp increase in wet-web strength which levels off at about 10 percent addition. Cationic starches, furthermore, may be prepared in the mill at a much lower cost, and will give comparable strength to the commercial grades. Although this paper covers only two cationic resins and two commercial cationic starches, the results obtained point out advantages in the use of cationic resins. It is felt that further research be done to study other variables such as the pH of the system, points of addition, and rates of reaction.

Very special thanks are extended to Dr. Stephen Kukulich, thesis advisor, without whose understanding and help this paper would not be possible. Special thanks are also extended to Dow Chemical Company, Hercules Powder Company, Corn Products Co., and National Starch for their supplying sample materials used in this research.

BIBLIOGRAPHY

1. Libby; Pulp and Paper Science and Technology, Vol. II, Pg. 116; Copyright 1962, McGraw Hill, New York.
2. Riddick, Chem. Eng., 68 No. 13, 121-126, June 26, 1961.
3. Mysels, Intro. to Chem. Colloids.
4. Thede, "Too, "Surface Properties of Rosin Size Precipitates", Tappi, Vol. 38 No. 12, 707-09 Dec., 1955.
5. U.S. Patent No. 2,694,633, Issued Nov. 16, 1954.
6. Mehltreter, Tappi, Vol. 46, No. 8, 506-8, Aug. 1965.
7. Lyne, L.M., Gallay, W., Tappi, Vol. 37, No. 12, 581-96, Dec. 1954.
8. Lyne, L.M., Gallay, W., Tappi, Vol. 37, No. 12, 964-704, Dec. 1954.
9. Montigny, R. de, Pulp Paper Mag. Can., 42:410 (1941).
10. Langines, E., Pulp Paper Mag. Can., 53:163 (1952).
11. Brecht, W., Erfurt, N., Tappi, Vol. 42, No. 12, Dec. (1959).
12. U.S. Patent, No. 2,616,874, Issued Nov. 4, 1952.
13. U.S. Patent, No. 2,146,392, Issued Feb. 7, 1939.
14. "Polyethylene Imine", Chemical Corp. Brochure, March, 1956.
15. Canadian Patent No. 566,653, Issued Nov. 25, 1963.
16. U.S. Patent No. 3,136,646, Issued June 7, 1964.