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ACID TREATMENT OF PULP AT DIFFERENT TEMPERATURES AND THE RESULTANT CHANGE IN PULP CHARACTERISTICS

PART I

by

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PULP AND PAPER CURRICULUM
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LITERATURE SURVEY

The aim of this thesis is to investigate the acid treatment of pulp at different temperatures. In the experimental work, enough sulfuric acid is used to neutralize the mixture of pulp and water and thereafter reach in the pH range of one and eight tenths to two at atmospheric pressure. Temperatures during experimentation range from room temperature to 100° Centigrade.

Prehydrolysis (Effect of Acids on Wood)

The effect of dilute acids is used in prehydrolysis of wood; prehydrolysis is applied in sulphate pulping with the goal of reducing hemicelluloses in wood, as much as possible, before treating with the cooking liquors. Prehydrolysis is defined as subjecting wood chips to a hydrolytic treatment with dilute mineral acids at or below boiling temperatures (1).

Prehydrolysis of wood with water at high temperatures and pressures results in furthering the hydrolysis and solution of some components, softening wood, and making wood more pliable(2). Hawley and Wise (3) state that the dilute acid hydrolysis of wood under pressure results in the formation of acetic acid from acetyl groups; the formation of methanol from methoxy groups, the hydrolysis of starches to sugars, of pentosans to pentoses, of hemicelluloses to sugars, decomposition of pentoses to furfural as formic acid, and of hexoses to acetic as well as formic acids. Hagglund(4) finds that the effect of prehydrolysis of wood in alkaline pulping produced a favorable effect with hardwood, straw, and other raw materials rich in pentosans. A high yield in alpha cellulose and easier bleaching of the pulps was obtained.

Lautsch(5) made a study on the influence of prehydrolysis of beechwood on delignification by the sulphite process. His best results were with wood heated with a one and a half percent solution of sulphur dioxide (wood to liquor ratio of one to twenty) for three hours at 105° Centigrade. He extracted 30 percent of the original wood weight. The residue was pulped at 135° Centigrade with five-tenths molar sodium sulphite for eight hours at a pH of six. Lautsch then pulped the residue with five percent sulphur dioxide and nine-tenths percent sodium hydroxide for six hours. His resulting pulp yield was 41.7 percent.

In Germany there are two methods of prehydrolysis in use in making high alpha pulps. In the Waldhof procedure(6) the prehydrolysis is carried out in ordinary sulphate pulping steel digesters at 140° Centigrade, with a pressure of four to five atmospheres, for a half an hour to two hours. The extraction removes six to eight percent hemicellulosic material. The resulting bleached pulp yield is 38 percent of wood, while the alpha cellulose content is 94 percent. In the Phrix procedure the prehydrolysis is carried out in stone-lined digesters at 125° Centigrade, four atmospheres for two to three hours. Three-tenths percent sulphuric acid was used with a liquor to wood ratio of four and a half to one. The extraction removed nineteen percent of the wood. The resulting bleached pulp yield was 32 percent of wood while the alpha cellulose content was 92 to 94 percent.

One study on the specific action of acid anions in the partial hydrolysis of wood was made by Ploetz(7). His treatment was the following: 600 milliliters of aqueous sulphuric acid was allowed to react for four hours with 40 grams of beechwood. As the result of this treatment 0.76 milligrams of reducing sugars per milliliter of solution were obtained. After heating six hours longer, the yield was raised to one and seven-tenths milligrams per milliliter. In all cases this second hydrolysis was effected with eight percent sulphuric acid. In every prehydrolysis (even the mildest), cellulose as well as the hemicelluloses were affected.

Another study on the effect of acids upon the hydrolysis of wood was made by Sherrard and Gauget(8), with a mixture of 100 grams of white spruce sawdust, 200 grams of water and two and a half grams (100 percent) of sulphuric acid. This mixture was subjected to a steam pressure of 115 pounds at 175° Centigrade in an autoclave for fifteen minutes. The experiment gave a yield of 21.14 percent of reducing sugar, of which 66 percent was fermentable.

Results of an experiment by Sherrard and Gauget on the effect of different percentages of sulphuric acid may be seen from Table 1.

Grams of sulphuric acid per 100 grams of dry wood	Total reducing sugars	Fermentable sugars	Cellulose unchanged	Cellulose removed
	(in percent of original dry wood)			
5	21.98	16.29	31.70	26.50
10	21.54	18.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

Table 1

The Effect of Varying Percentages of Sulphuric Acid.

Effect of Acid on Cellulose

Because acid treatment of pulp is a pertinent subject in this thesis, the effect of acids on cellulose must be studied. Many theories on the hydrolysis of cellulose have been given. One theory was presented by Hiller, Lijaren, and Pacsu(9). The authors claim that weak acids do not hydrolyze one, four glucosidic bonds, but rather hydrolyze semiacetal bonds which connect the primary chain molecules together to give rise to secondary chain molecules. This process results in a leaching out of the smaller molecules leaving a residue of larger primary chain molecules. The loss of physical strength is caused by breaking of a number of hydrogen bonds and by the loss of small molecules.

Stamm and Harris(10) indicated the stepwise action of hydrolysis of cellulose in the following manner: Wood $\xrightarrow{(a)}$ Insoluble, stable cellulose depolymerization product plus simple sugars from hemicellulose plus lignin $\xrightarrow{(b)}$ Insoluble hydrocellulose plus lignin $\xrightarrow{(c)}$ Soluble polysaccharides plus lignin $\xrightarrow{(d)}$ Glucose plus lignin. Phillipp, Nelson, and Ziifle(11) concluded from their data, based on an interpretation in the study of the kinetics of the heterogenous hydrolysis of cellulose, that there were two distinct rates of cellulose hydrolysis: (a) that the rates were attributed to the rapid hydrolysis of the loose amorphous regions and (b) that the rates were attributed to the slow hydrolysis of the dense crystalline portions of the fiber.

On the degradation by acids on cellulose, Ott(12) noted that there was a shortening of the cellulosic chain to fragments having lower average molecular weights than that of the untreated cellulose, a decrease in pulp strength, an increase in reducing properties arising from the production of hemiacetal end groups, and that while the solution of the lignin (in sulphite process) is in progress, an acid hydrolysis of the hemicelluloses is also taking place, resulting in the formation of units whose chain lengths are sufficiently reduced to permit solution.

When cellulose is treated with dilute mineral acids, either for a long time in the cold, or for a shorter period with warming, the mechanical strength of the fibers disappears, and they disintegrate into a powder called hydrocellulose. Hydrocelluloses are water-insoluble mixtures resulting from the degradation of cellulose caused by the hydrolysis of glucosidic linkages in the macromolecule. This involves a shortening of the chains, that is the production of fragments having lower molecular weight than that of the untreated cellulose. Acid treatment also serves to decrease lateral cohesion between these fragmented chains with resulting slippage and a great decrease in tensile strength(13).

The following table II represents an analysis of white spruce hydrolysis with dilute sulphuric acid under steam pressure, by Sherrard and Blanco.

Parts of Wood	Unhydrolyzed(80-100 mesh)	Hydrolyzed(80-100 mesh)
(All figures are in percent of weight of O.D. wood before hydrolysis)		
Moisture	6.21	4.73
Pentosan	10.76	1.79
Cellulose	58.33	33.67
Lignin	29.19	29.63
Ash	0.26	0.06
Cellulose Analysis:		
Alpha	54.79	54.82
Beta	21.67	40.69
Gamma	23.54	4.49

Table II

Analysis of White Spruce Hydrolysis

As was shown here, 18.66 percent of cellulose has disappeared during hydrolysis of the wood from which 19.35 percent of reducing sugars were produced. The pentosan and methyl pentosan (not shown) content of the cellulose from the original wood has been reduced 79 percent and 11.47 percent, respectively.

Table III shows the hydrolysis and crystallization of cellulose with variations in temperatures.

Controls °C.	15 min.	30 min.	1 hr.	2 hr.	4 hr.	6 hr.	8 hr.	24 hr.
			--Raw Cotton--					
5-3200	2100	1780	1620	1615	1590	1560	1485	1060
18-3200	1680	1590	1440	1320	1249	1150	1065	723
40-3200	1131	918	728	546	484	450	40	-
Boil-3200	240	-	-	-	-	-	-	-
			--Wood Pulp--					
5-1030	1015	1002	990	970	940	930	912	858
18-1030	946	940	924	848	755	718	690	475
40-1030	742	663	585	514	440	398	352	-
Boil-1030	297	-	-	-	-	-	-	-

Table III

Average Basis D.P. in 5N HCl acid.

Table IV shows the quantitative weight loss data with time of hydrolysis of purified cotton.

Hydrolysis-Time (Min.)	%Hydrocellulose Residue	Basis D.P.
Control	-	3200
5	92.01	257
10	91.42	244
15	91.03	242
20	90.05	233
30	89.79	230

Table IV

Effect of Acids on Hemicelluloses

Holocellulose or 67-80 percent of wood constituents contains twelve to twenty-five percent hemicellulose. Hemicellulose may be dissolved from the holocellulose by using a cold aqueous alkali. Hemicelluloses can be distinguished from cellulose by their solubility in alkali and their hydrolysis with hot mineral acids.

A study was made by Ploetz(14) on the specific action of several acids in the hydrolytic removal of hemicelluloses from beechwood. Acids used were (a) 0.36 percent hydrochloric (pH 1.07), (b) 0.81 percent hydrobromic (pH 1.08), (c) 1.69 percent oxalic (pH 1.16), (d) 0.82 percent sulphuric (pH 1.04), and (e) 4.8 percent phosphoric (pH 1.13). In each case 800 milliliters of acid was heated with 50 grams extracted beechwood meal for four hours on a boiling water bath. Pentosan determinations were made on an aliquot portion after one hour and a half and on the washed wood residues after four hours. Of the acids used, hydrochloric had the most marked action on the hemicelluloses while phosphoric had the least action. Hydrobromic was an exception and had somewhat less action on the hemicelluloses than had oxalic, although its molecular volume is lower. Of the sulphuric and phosphoric, which had identical volumes, the latter was considerably less active than the former. Sulphate pulps prepared from the beechwood residues in each case gave yields which fell into the same order as did the respective wood residues. Thus prehydrolysis with hydrochloric acid gave the lowest and phosphoric acid the highest pulp yield.

Two Theories on Protection by Lignin

Cundy and Beck(15) found higher alpha cellulose content in unbleached pulp than in the same pulp after treatment with sodium chlorite bleach. They explained that in unbleached pulp, some part of the hemicelluloses is protected by the lignin.

Correns(16) wrote that in the isolated fibers which have been freed of lignin, the acid acts on the cellulose and damages it, but in the intact wood the cellulose is protected by the lignin, and only the wood polysaccharides are attacked.

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EXPERIMENTAL WORK

Purpose

The experimental work was done to find indication of changes in pulp characteristics after acid hydrolysis. Also, because of the differing amounts of hemicelluloses in bleached and unbleached Mitscherlich pulps, it was decided to investigate the effects of post-hydrolysis on the strength of both types of pulps.

Apparatus

For the acid hydrolysis, a drill press was used as agitator employing a disk type blade $4\frac{5}{8}$ inches in diameter in every case. Since the stock would not circulate at 600 r.p.m., the press had to be run at 1500 r.p.m. In the beater run, a Valley Beater was used. The sheets were made with the TAPPI Standard British Sheet Mold, Sheet Press, and Rings and Plates. After drying in the standard humidity room, the sheets were tested for burst, tear, tensile, and fold. The Perkins Mullen Tester, the Elmendorf Tear Tester, the Schopper Tensile Tester, and the M. I. T. Fold Tester were used. A record of freeness development was kept during the beater run.

Stock Preparation and Acid Hydrolysis

Before acid treatment, each pulp was soaked for twenty-four hours. The pulp was then broken up and disintegrated. Following disintegration, the pulp was heated by steam to a temperature of 90 degrees Centigrade. Then the pulp , at a consistency of 2.5 percent, was cooked for an hour and a half at 90 degrees Centigrade in a solution of water and sulfuric acid adjusted to approximately a pH of 2.0. At the end of the cook, two normal sodium hydroxide was added and the pulp was washed with water.

Pulp Beating and Sheet Formation

All pulp testing was done according to TAPPI Standards. For beating the pulp T 200 m-45 was followed. In sheet formation, the TAPPI Standard T 205 m-53 was used.

Sheet Testing

The TAPPI Standards used for sheet testing were the following: Freeness (T 227 m-50), mullen (T 403 m-53), tear (T 414 m-49), tensile (T 404 m-50), and fold (T 423 m-50).

Experimental Results

The results of the four sets of evaluations by the beater method may be seen from the following tabulation. The values for bursting strength, tearing resistance, and breaking length represent factors established to eliminate the effect of variations in basis weight. The values for folding endurance are the number of double folds required to break the specimen under a load of one kilogram. No correction for variation in basis weight were applied in the case of folding endurance.

All values represent averages of a number of tests thought to be sufficient for normal statistical accuracy.

Results of Evaluations by the Beater Method

Beating Time	0'	5'	10'	15'	20'	25'	30'	35'	40'	50'
					Freeness					
Bleached	653	589	493	380	261	175	110	63	—	—
Bl. Acid	684	584	431	291	177	98	45	26	—	—
Unbl.	673	—	468	—	200	—	79	—	28	—
Unbl.Acid	642	—	426	—	201	—	75	—	—	—
					Tearing Resistance Factor					
Bleached	145.9	95.3	102.7	78.8	71.7	72.8	64.2	65.4	—	—
Bl. Acid	149	82.5	68.6	59.7	55.8	57.2	49.7	44.7	—	—
Unbl.	89.4	—	69.4	—	52.8	—	44.2	—	38.9	36.2
Unbl.Acid	79.2	—	56.4	—	49.0	—	45.4	—	41.4	36.3
					Burst Factor					
Bleached	26.7	44.7	54.5	60.8	65.8	66.6	66.6	61.6	—	—
Bl. Acid	17.3	38	52.2	59.1	61.2	61.0	62.1	59.3	—	—
Unbl.	31.5	—	50.8	—	57.9	—	58.5	—	56.6	56.8
Unbl.Acid	26.3	—	50.2	—	53.6	—	55.6	—	54.2	49.4
					Breaking Length					
Bleached	11400	15690	19460	22300	23400	22800	24800	23900	—	—
Bl. Acid	7250	14630	19130	20600	22500	22900	22400	22600	—	—
Unbl.	12450	—	21400	—	22300	—	22600	—	20700	23500
Unbl.Acid	9220	—	18840	—	20000	—	20400	—	20800	19360
					Folding Endurance					
Bleached	163.3	442.4	1042	1370	1360	1656	1765	2772	—	—
Bl. Acid	13	173	550	407	419	866	1611	1991	—	—
Unbl.	283	—	845	—	937	—	1404	—	1418	3109
Unbl.Acid	30	—	368	—	550	—	780	—	1279	1662

Conclusions

The acid treatment resulted in the following characteristics:

1. Freeness: The drop in Canadian Standard freeness as a result of beating was conspicuously accelerated in the case of the acid treated, bleached pulp. This condition was not observed to such a drastic extent in the case of the unbleached pulp.

2. Tearing Resistance: The progressive decrease of tearing resistance as result of beating was substantially accelerated in the

case of the acid treated bleached pulp. This condition was found to be true for acid treated unbleached pulp only at the early part of the beating cycle.

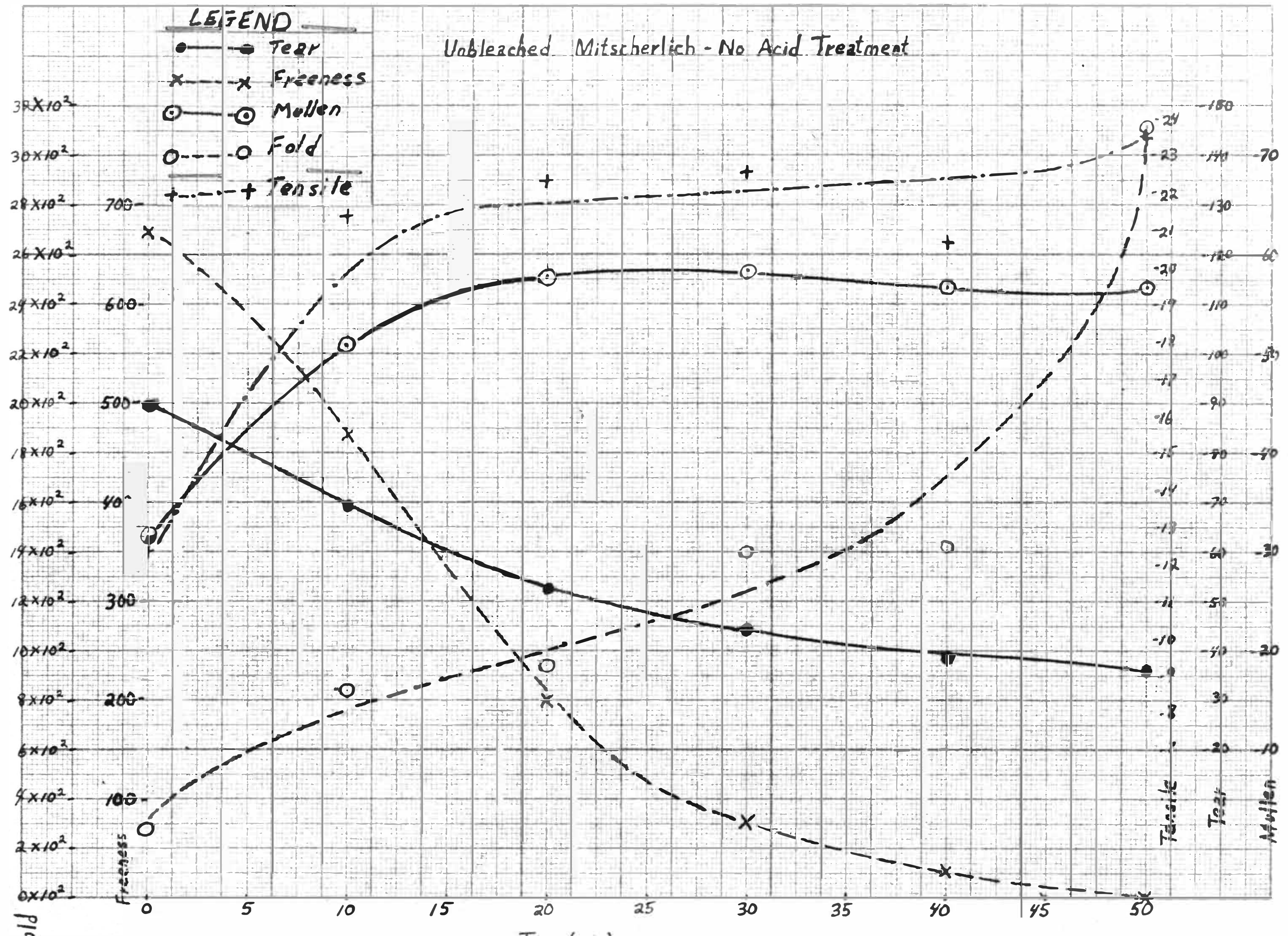
3. Bursting Strength: This property was decreased over the total beating cycle in both cases of acid treated bleached and unbleached pulps. The change was in a larger order of magnitude in the case of the bleached pulp.

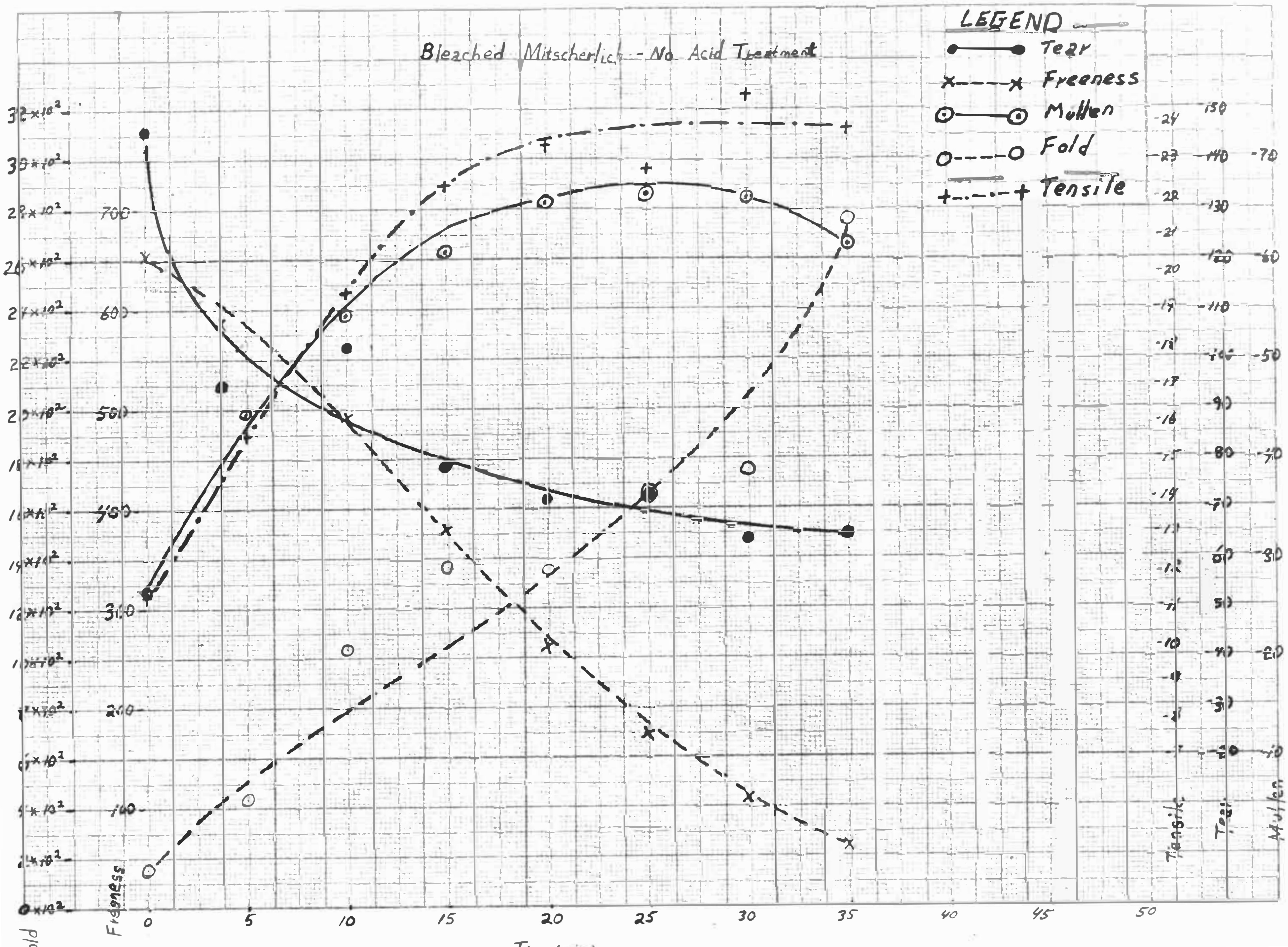
4. Breaking Length (Tensile strength): Both acid treated pulps, bleached and unbleached, showed decrease in tensile strength over the total range of the beating cycle. The extent of change was similar in both cases.

5. Folding Endurance: This very sensitive characteristic showed conspicuous decrease in the case of both acid treated pulps.

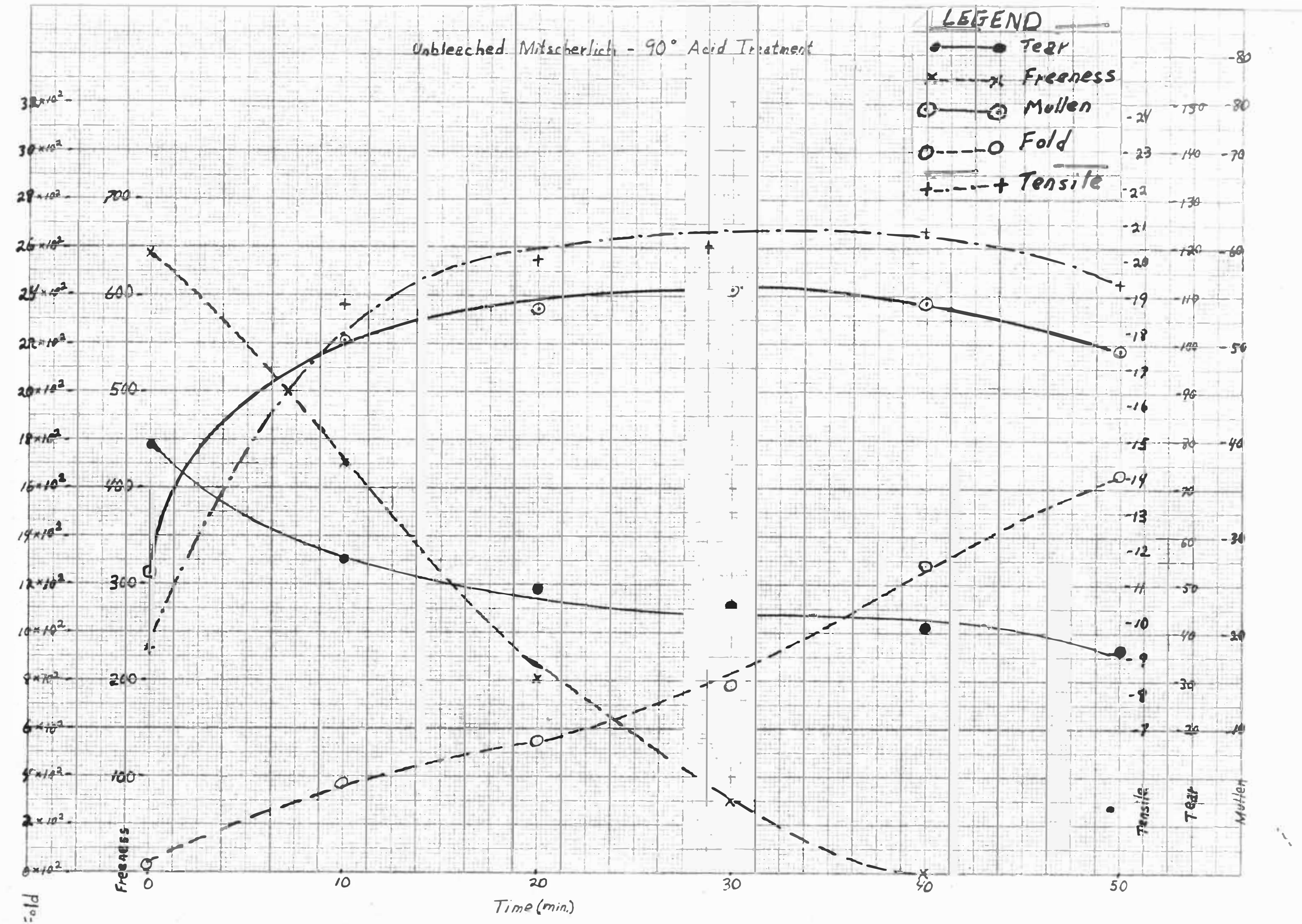
To summarize: The strength characteristics of both bleached and unbleached pulps decreased after acid treatment. The effect was most pronounced in the case of the bleached pulp.

Kent Dickerman
6/1/54

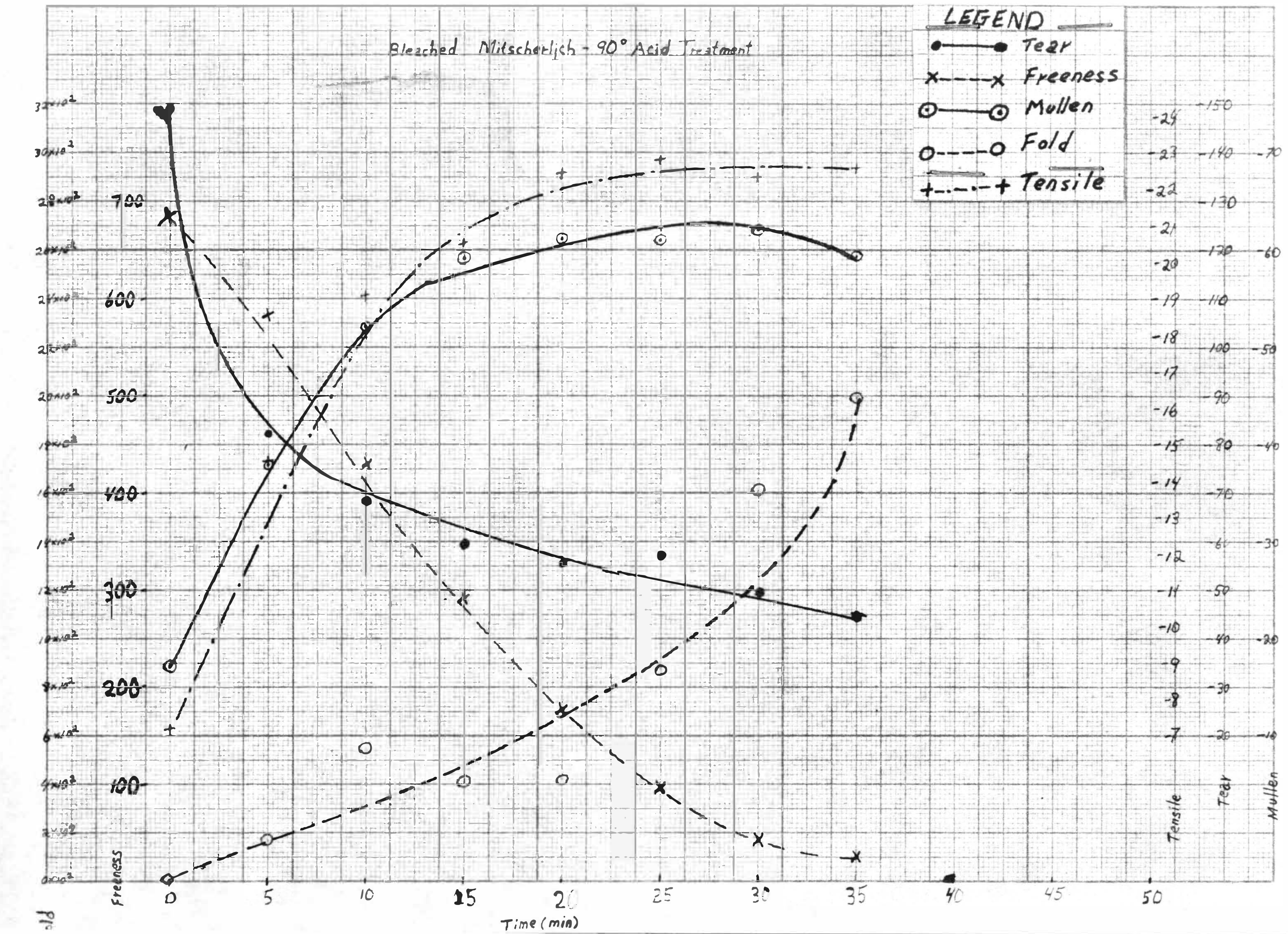

Unbleached Mitscherlich - No Acid Treatment
LEGEND
Tear
Freeness
Mullen
Fold
Tensile
Freeness
Tensile
Tear
Mullen
0
5
10
15
20
25
30
35
40
45
50



Bleached Mitscherlich - No Acid Treatment
LEGEND
Tear
Freeness
Mullen
Fold
Tensile
700
600
500
400
300
200
100
0
5
10
15
20
25
30
35
40
45
50
Freeness
Tensile
Tear
Mullen



Unbleached Mitscherlich - 90° Acid Treatment
LEGEND
Tear
Freeness
Mullen
Fold
Tensile
Time (min.)
Freeness
Fold
Tensile
Tear
Mullen
0
10
20
30
40
50
100
200
300
400
500
600
700



Bleached Mitscherlich - 90° Acid Treatment
LEGEND
Tear
Freeness
Mullen
Fold
Tensile
Time (min)
Freeness
Fold
Tensile
Tear
Mullen
0
5
10
15
20
25
30
35
40
45
50
100
200
300
400
500
600
700