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The Influence of Varying Hydrogen Ion and Alumina Concentrations on the Strength Characteristics of Handsheets Made in the Presence of Locust Bean Gum

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THE INFLUENCE OF VARYING HYDROGEN ION AND ALUMINA
CONCENTRATIONS ON THE STRENGTH CHARACTERISTICS OF
HANDSHEETS MADE IN THE PRESENCE OF LOCUST BEAN GUM.)

Submitted to Dr. Alfred H. Nadelman in partial
fulfillment of the requirements for Thesis 436 Pulp
and Paper Technology at Western Michigan College.

by

Ronald L. Hamilton

June 1, 1954

Kalamazoo, Michigan

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Use of Mannogalactans in Industry

Mannogalactans and particularly locust bean gum are used for a wide variety of applications. They serve as thickening agents and emulsifiers for foodstuffs, in sizing as well as finishing yarns and in creaming rubber latex. The papermaking industry is the largest user of mannogalactans. Here they are used in kraft grades, sulphite, book papers, coating raw stock, offset and printing grades, bonds, ledgers and other fine papers and also in newsprint and other groundwood sheets.

Locust bean gum and methylcellulose are effective as deflocculating agents and are said to surpass the performance of deacetylated karaya gum. Both hydration film and electrokinetic potential on the fiber are involved in fiber flocculation and dispersion (1). Locust bean gum responds to a minimum extent when used with hardwoods. However, mixed hardwood-softwood sheets, produced with a relatively high percentage of hardwood, still maintain appreciable strength properties when locust bean gum is used. Gray and Van den Akker (1) found that an addition of one percent locust bean gum greatly reduced the friction of high consistency stock in pipes.

Mannogalactans, when used as beater additives will tend to increase the retention of some types of fillers. Usually the stock is beaten to maximum tear before addition of the gum. An automatic continuous dispenser has been developed (18), that supplies cooked additive to papermachines in quantities up to 20,000 gallons per day.

History, Development and Preparation of Locust Bean Gum

The first known cultivation of the locust bean or carob bean tree (*Ceratonia siliqua*) was in the fourth century, B.C. and Dioscorides in the first century, A.D. mentions its laxative and diuretic properties in his writings. At present, the United States import the processed

gum from Crete, Greece, Portugal, the Balearic Islands, and Cyprus.

The carob tree grows to a height of thirty to thirty-six inches with a cross section six inches in diameter (19). The fruits of this tree are pods approximately twelve inches long containing twelve to fourteen little red beans. The beans are dried. The outer hulls are removed, leaving just the endosperm, which is soaked in hot water. The product of extraction is then dried by evaporation and the resulting powder mostly exported. It is said that thirty-five pounds of powdered gum are obtained from one thousand pounds of beans. A Balearic Island factory produces one hundred and forty pounds per day. In 1949 the total United States imports of this product was 4,750,000 pounds (13).

During the period of World War II, when the supply of locust bean gum was cut off, guar gum was developed in the United States. This gum is used even today as a substitute for locust bean gum, since both gums have similar properties.

Chemical Composition of Locust Bean Gum

As suggested by the general classification "mannogalactans", locust bean gum is composed essentially of mannose and galactose units. Table I shows the complete composition.

COMPOSITION OF LOCUST BEAN GUM	
Galactan	29.18 %
Mannan	58.42 %
Pentosans	2.75%
Nitrogen	0.83 %
Cellular Tissue	3.64 %
Ash	0.82 %

TABLE I

Locust bean gum is a branched polysaccharide consisting of about 84 percent d-mannose and 16 percent d-galactopyranose. The proof of the branch-

ing as suggested by Hirst and Jones (15) was verified by Smith (11) who presented the structure of the molecule shown in Figure I.

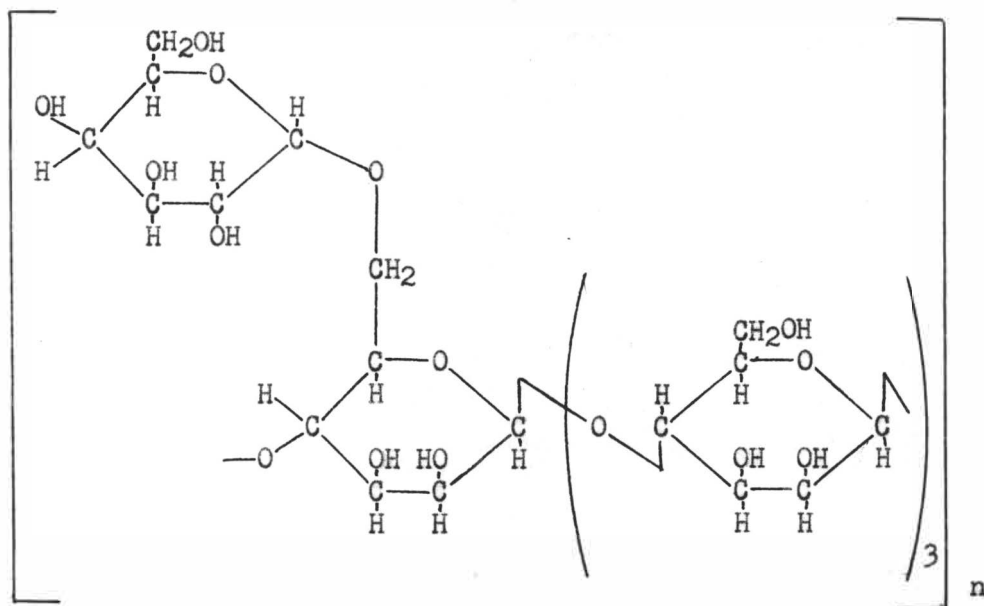


Figure I

Methylation followed by methanolysis at the boiling point with one percent hydrochloric acid, yields one part 2, 3, 4, 6-tetramethyl d-galactoside, two to three parts 2, 3, 6-trimethyl d-mannoside, and one part 2, 3-dimethyl d-mannoside. The gum consists of a chain of d-mannopyranose units joined by 1, 4 glycosidic bonds, believed to be mainly of the beta variety. This assumption explains the low specific rotation of the polysaccharide and its methyl derivative. To the mannopyranose chain are attached side chains of d-galactopyranose units, each one separated from the next by two to three mannose residues.

Hydrolysis with enzymes has been attempted and has proven successful with Taka-diastase and the mixture known as "Pectinol 10M" (15).

Hirst and Jones (15) explain the variation of the ratio of galactose to mannose by the facts that the origin of the gum differs and that the galactose is stored by attaching it randomly to the main chain of

mannose residues. There still is a possibility, however, that the gum is a mixture of several polysaccharides and that the variations in amount of the galactomannan component.

Characteristics of Locust Bean Gum

Locust bean gum exhibits a neutral reaction in water (6, 19). Fermentation causes the solution to become acid. Heavy metal salts cause coagulation and precipitation in concentrated solutions of the gum. This precipitation may be avoided by adding glucose or glycerol to the solution. Alkalies increase the viscosity of a water solution, whereas mineral acids, oxidizing agents and certain enzymes lessen the viscosity. Treatment with alkalies may darken the color of the product.

The molecular weight of the gum is approximately 310,000; the intrinsic viscosity is five; the length of the molecule is 255 Angstrom units and the width of the molecule is 51 Angstroms (5).

As stated above, aqueous solutions of mannogalactans may be precipitated by calcium, magnesium or copper salts. If alkali is added, a gel is formed. On further addition of alkali, syneresis is observed. This method may be used to recover and purify the gum.

Materials similar in chemical composition and structure may be found in *Gleditschia tricanthos* and *Cyamopsis tetragonoloba*. Films of these polysaccharides exhibit excellent pliability, elasticity and tensile strength. Apparently (13) locust bean gum does not contain uronic acid as the exudates do.

Some of the gum's further properties are described as follows: In solution of locust bean gum, the liquid flows freely between the molecules. With increased temperature, the solution becomes rubbery; this is also the case when solutions of the gum are treated with concentrated organic acids (19). Locust bean gum is claimed to give smooth-

ness, elasticity and resilience to paper.

Effects on Cellulose Fiber

The presence of a small amount of locust bean gum tends to decrease flocculation of fibers in beaten pulp, with a resulting improvement of the quality of formation. This is particularly true when long fibered stock is used. This effect of decreasing flocculation is attributed to both a negative electrokinetic potential and a hydrophillic layer which is produced on the cellulose fiber (1). It has been found that although the presence of locust bean gum raises the strength properties of paper, amounts of alum larger than fifteen percent are detrimental to the formation qualities otherwise obtained. The flocculation occurs to a much greater extent in water than in alcohol, benzene or nitrobenzene (1).

Locust bean gum^{is} absorbed by cellulose fiber. This most important desirable characteristic causes the fibers to be coated with a film of highly swollen mucilage which imparts to the pulp many of the same strength characteristics as mechanical treatment in beaters. If the pulp is beaten for fifteen minutes before the addition of the gum, a higher effect is gained due to the roughening of the surface. The above mentioned pulp with the addition of locust bean gum has a bursting strength equivalent to the same pulp without locust bean gum that has been beaten for fifty minutes. Further, pulp with a freeness of eight hundred milliliters in the presence of one percent locust bean gum has strength characteristics equal to pulp beaten to a freeness of four hundred milliliters. In a mill scale trial the presence of one percent locust bean gum accomplished the same results as the use of three percent starch and a jordan (1).

Since pulps and cellulose fibers are hydrophilic, the addition of

several other hydrophilic materials increase the hydrophilic character of the mixture. It is assumed that if the fibers are coated with these materials, they thereby produce a more hydrophilic surface. The more pulp is purified, the less hydrophilic it becomes; therefore, locust bean gum increases in usefulness when applied in presence of highly purified stock.

Table II shows to what extent each area contributes to the improvement in strength characteristics.

STRENGTH INCREASES DUE TO	CONTRIBUTION (%)
Increased bonded area	15
Improved formation	25
Increased bonding strength	60
Increased fiber strength	0

TABLE II

It is thought that locust bean gum makes a more flexible bond between cellulose molecules than do two cellulose molecules alone, which are held in rigid crystalline structure (44). Moreover, the less branched locust bean gum is absorbed more rapidly than the more branched guar gum (17).

Gruenhut (17) points out that the rate of sorption of locust bean gum onto the fiber varies with concentration, temperature, and pH. This rate of sorption under these conditions can be considered as an indication of hydrogen bonding, as water is less associated when hot than cold and because of the exothermic nature of hydrogen bonding. A three dimensional gel-network is formed by di-diol complexes which exist in the form of dynamic equilibrium. The above mentioned complex is shown in Figure II where B is borax.

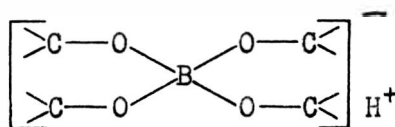


Figure II

When locust bean gum is treated with small amounts of soluble borate, a water insoluble gel is formed that is suitable for use in wet strength paper. The latter is limited to papers that will be wet for only periods of time (transitory wet strength).

Tests for Locust Bean Gum

Several methods are in use for identification of locust bean gum which include the anthrone test and periodate oxidation. Furthermore, the following reagents are used: barium hydroxide and borax, lead acetate, sodium hydroxide, concentrated sulfuric acid as well as, finally, borax solution.

In the anthrone test, a positive result is indicated when a blue green color is produced. It is thought (3) that this color is due to the formation of furfural type compounds in the concentrated sulfuric acid. With this method one can measure concentration changes of 0.0001 grams per one hundred milliliters and 0.0002 grams per one hundred milliliters.

The periodate oxidation is used to measure locust bean gum content. First the gum is hydrolyzed with three to five percent sulfuric acid at 135°C. for eighty minutes; thereupon the sugars are recovered and separated by paper partition chromatography. The galactose is determined by oxidation with sodium periodate (22). One mole of the oxidant is consumed per hexose unit and the cleavage products yield glyoxal upon hydrolysis, which shows the presence of 1, 4 linkages.

Qualitative tests are made by adding saturated barium hydroxide solution to a solution of locust bean gum. This yields a voluminous, opaque, stringy precipitate. A confirmation is obtained by adding four percent borax which results in a gelatinizing (20). Guar gum also reacts in this manner. Lead acetate and tannic acid give a white pre-

cipitate, sodium hydroxide gives a yellow color, concentrated sulfuric acid gives a clear yellow color and addition of a borax solution to a solution of the gum causes a gel. The latter test of this last group is the most sensitive one.

Effect of Alum and Aluminate on Water

Since this thesis deals to a large extent with the effect of alum and aluminate, it was thought that some information on the effect of these substances on water should be included.

Miller and Lanz (7) reported that when a sodium aluminate solution, containing four hundred and ten parts per million of aluminate, is titrated by acid, a formation of a floc begins at a pH of 9.6. This seems to indicate a specific reaction occurring between aluminate solution and magnesia "hardness" which induces floc formation. The composition appears to be; $3\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 14\text{H}_2\text{O}$. In titrating a solution of 410 parts per million of sodium aluminate with a solution of magnesium bicarbonate, and addition of 151 parts per million causes a floc to appear at a pH of 9.3.

Thus the conclusion is drawn that the hardness of the water used in the manufacture of paper may have a decided influence upon aluminate flocculation, particularly where magnesium salts are present in appreciable quantities.

Since gum additives have earned a definite place in paper mills, it was decided to determine if the effect of alum, aluminate and the corresponding range of pH values influence the performance of the gum.

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Experimentation

In previous work, Robert Witters, (*loc. cit.*), attempts were made to determine the influence of alum, sodium aluminate and hydrogen ion concentration in the strength characteristics of handsheets formed in the presence of locust bean gum. The addition of alkaline Kalamazoo water to the proportioning tank and sheet mold of the Noble and Wood sheet machine greatly changed the pH values at which the sheets were formed. It was therefore decided to study the effect of controlled pH condition on the strength characteristics of handsheets adding the same chemicals as used by Witters. It was attempted to maintain uniform pH values throughout the entire sheet forming operation. This was accomplished by the addition of proper quantities of sulphuric acid or sodium hydroxide.

Following Witter's plan, it was decided to make the addition of locust bean gum to the stock at beater consistency, namely, 1.57 percent, in quantities of two, five, ten and twenty pounds per ton of air dry pulp. After an adequate retention period and while still under the stirrer, the alum or sodium aluminate was added in concentrations of 50 and 100 pounds per ton of air dry pulp. In the case of adding acid or alkali, it was further decided to use sulphuric acid and sodium hydroxide. The quantities of acid or base used were sufficient to obtain a pH equivalent to that established by the alum or sodium aluminate. A preliminary titration with sulphuric acid was performed. Five sets of handsheets were made which contained neither alum, sodium aluminate, acid nor base. These sets were used as a control since they contained only pulp and locust bean gum from zero to one percent concentration. A summary of the furnishes for the forty-five sets of handsheets produced may be seen on Table III.

PERCENT ADDITIVE

	pH	0.0	0.1	0.25	0.5	1.0
Per- cent 5.0 Sod.	9.7	1 Set	1 Set	1 Set	1 Set	1 Set
Alum. 2.5	9.4	1 Set	1 Set	1 Set	1 Set	1 Set
Blank 0.0	7.3	1 Set	1 Set	1 Set	1 Set	1 Set
Per- cent 2.5	6.0	1 Set	1 Set	1 Set	1 Set	1 Set
Alum 5.0	4.9	1 Set	1 Set	1 Set	1 Set	1 Set

TABLE III

Experimental Procedure

Canadian unbleached sulphite pulp was beaten in a Valley Laboratory Beater for fifteen minutes to a freeness of approximately 590 milliliters (C.S.F.). The consistency in the beater was 1.57 percent.

The locust bean gum was cooked on a steam bath for 45 minutes at 200°F. in a concentration of one percent. In order to insure rapid cooling after the cook, the gum was diluted to 0.5 percent consistency. The additive at this consistency was blended into the pulp. A fresh cook was made at the start of each run.

All sheets were formed on the Noble and Wood sheet machine. Pulp containing thirty grams of air dry fiber was placed under a stirrer. Whenever required, locust bean gum was added in the desired quantities. A retention period of five minutes followed the addition of the gum. Thereupon, in the sets so designated, the desired amounts of alum or sodium aluminate were added from stock solutions and allowed to mix for five minutes. At the end of this time a pH reading was taken by means of a Beckman pH meter. The pulp mixture was added to the proportioning tank of the sheet machine and, in the case of the use of alum, sufficient sulphuric acid was added to reach the pH measured

previously. Again, when each sheet was made in the sheet mold, sulphuric acid was added in quantities necessary to maintain the desired pH. To match the pH values obtained with sodium aluminate, sodium hydroxide was employed.

The use of alum resulted in pH values of 6.0 and 4.9, while addition of sodium aluminate caused pH values of 9.3 and 9.7. The control sets were made without any pH adjustment, so that the pH under which these sets were produced was that of tap water, namely, 7.3.

The sheets were pressed and dried on the wire in the Noble and Wood drum drier at 250°F. The dried sheets were then stored under controlled conditions of 73°F. and 50 percent relative humidity for several days.

After the conditioning period, the sheets were tested for basis weight, bursting strength, tensile strength, tearing resistance, and ash content. The basis weight was taken so that corrections for the fluctuations in basis weight could be applied to the test results.

From nine sheets comprising a set, six sheets most uniform in basis weight and formation were used for testing purposes. For bursting strength, twenty tests were taken, for tensile strength, twelve tests were made, for tearing resistance, twelve tests were run, and for ash content, two samples were tested from each set. The corrected absolute values of these tests may be seen in graphical form in Figures III through V. Percent locust bean gum is plotted against the value of the test. Figures IIIA, IVA, and VA combine in two groups the results obtained either with 2.5 percent alum, sodium aluminate, equivalent quantities of sulphuric acid and sodium hydroxide, or with 5.0 percent of alum, sodium aluminate, equivalent quantities of acid and alkali. Figures IIIB, IVB, and VB group together either all values

obtained in presence of alum and sodium aluminate or all results obtained with sulphuric acid and sodium hydroxide.

Results of Experimentation

In the sets containing no locust bean gum, the presence of sodium aluminate as well as sodium hydroxide consistently decreased bursting strength. The presence of alum or sulphuric acid with pH values of 6.0 and 4.9 increased the bursting strength. The pattern shown by the control sets prevailed, with a few exceptions, upon addition of 0.10, 0.25, 0.50 and 1.00 percent of locust bean gum. The trend remained the same in all cases despite the fact that the addition of alum to a pH of 4.9 in the presence of the gum resulted in a small loss of bursting strength when more than 0.10 percent of the additive was used.

The tensile strength characteristics followed the pattern outlined under bursting strength. In the absence of locust bean gum the presence of sodium aluminate and sodium hydroxide resulted in decreased tensile strength and the presence of alum and sulphuric acid increased the tensile strength. When sodium aluminate was added under the pH condition of 9.4, there was a different trend in the results of tests. In the presence of 1.00 percent locust bean gum, no loss in tensile strength due to the presence of sodium aluminate was noticed.

The results of the tearing resistance tests followed the general pattern. Increased values in bursting strength and tensile strength corresponded to decreased values in tearing resistance. Thus, the presence of sodium aluminate and sodium hydroxide increased the tearing resistance, whereas, the presence of alum and sulphuric acid decreased the same property. A family of curves was formed by seven out of eight series of experiments. The only irregularities observed were shown when 5.0 percent sodium aluminate was present.

Upon analysis of the results of ash determinations, it was observed that the presence of sodium aluminate and sodium hydroxide in the sets containing no locust bean gum greatly increased the ash content. With increasing quantities of locust bean gum, the ash content in the case of sodium aluminate decreased, while the values remained unchanged in the case of sodium hydroxide. The ash content remained fairly uniform when alum and sulphuric acid were used and the results remained in the range of the values determined for the control sets.

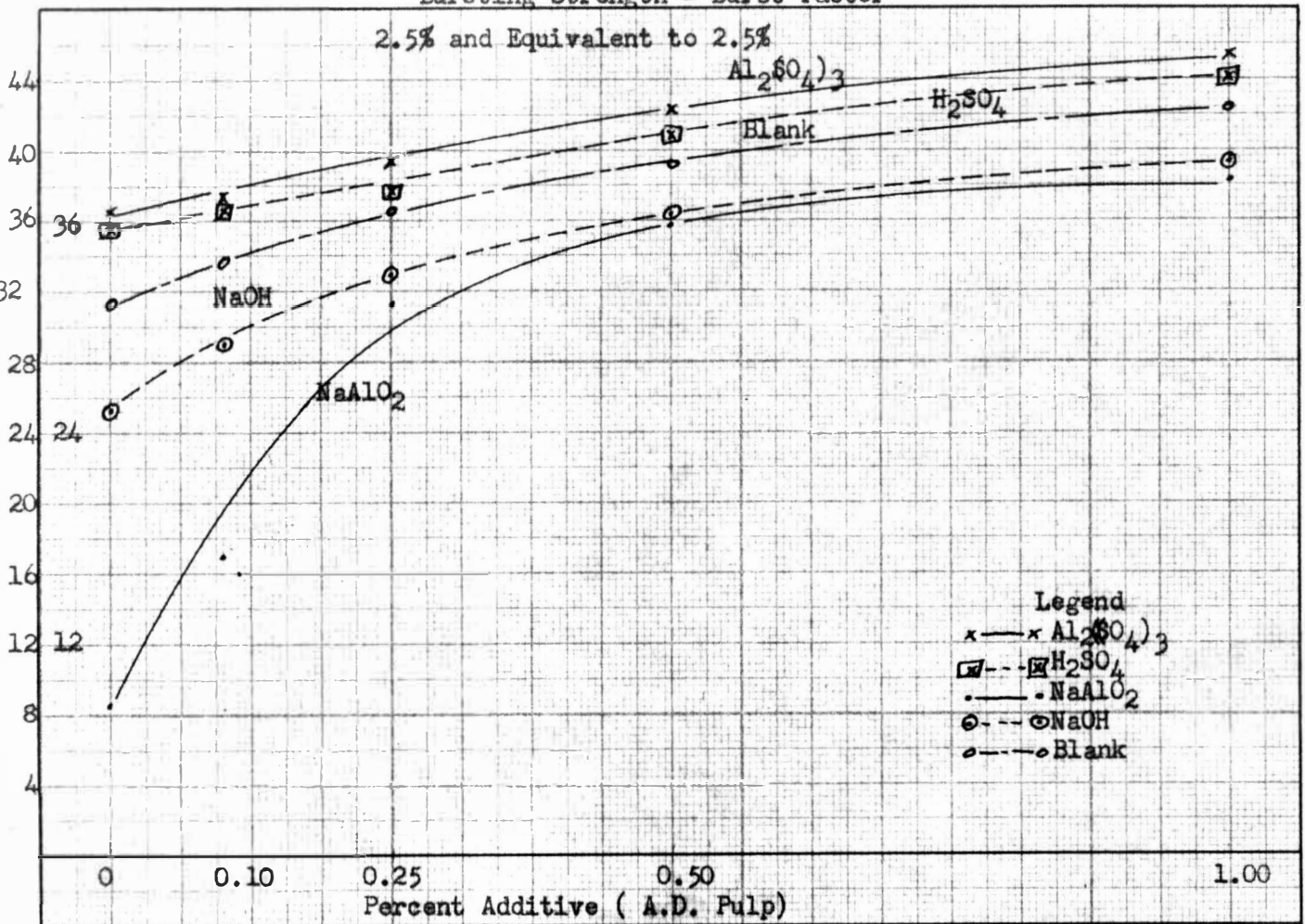
The unexpected increase in basis weight and softness of the sets containing sodium aluminate was explained by determining the ash content. As shown by Figure VI, the degree of softness decreased with decreasing ash content and increased quantities of locust bean gum.

Further noted was the fact that the series of experiments carried out for this thesis showed much more pronounced effects on the strength properties in the presence of alum and sodium aluminate in the low range of locust bean gum addition than those shown in Witter's work. Also, this thesis showed that constant pH conditions greatly increased the ash content in the presence of sodium aluminate and sodium hydroxide. The effects on the strength properties, in general, were less pronounced in the higher range of locust bean gum concentration under conditions of controlled pH.

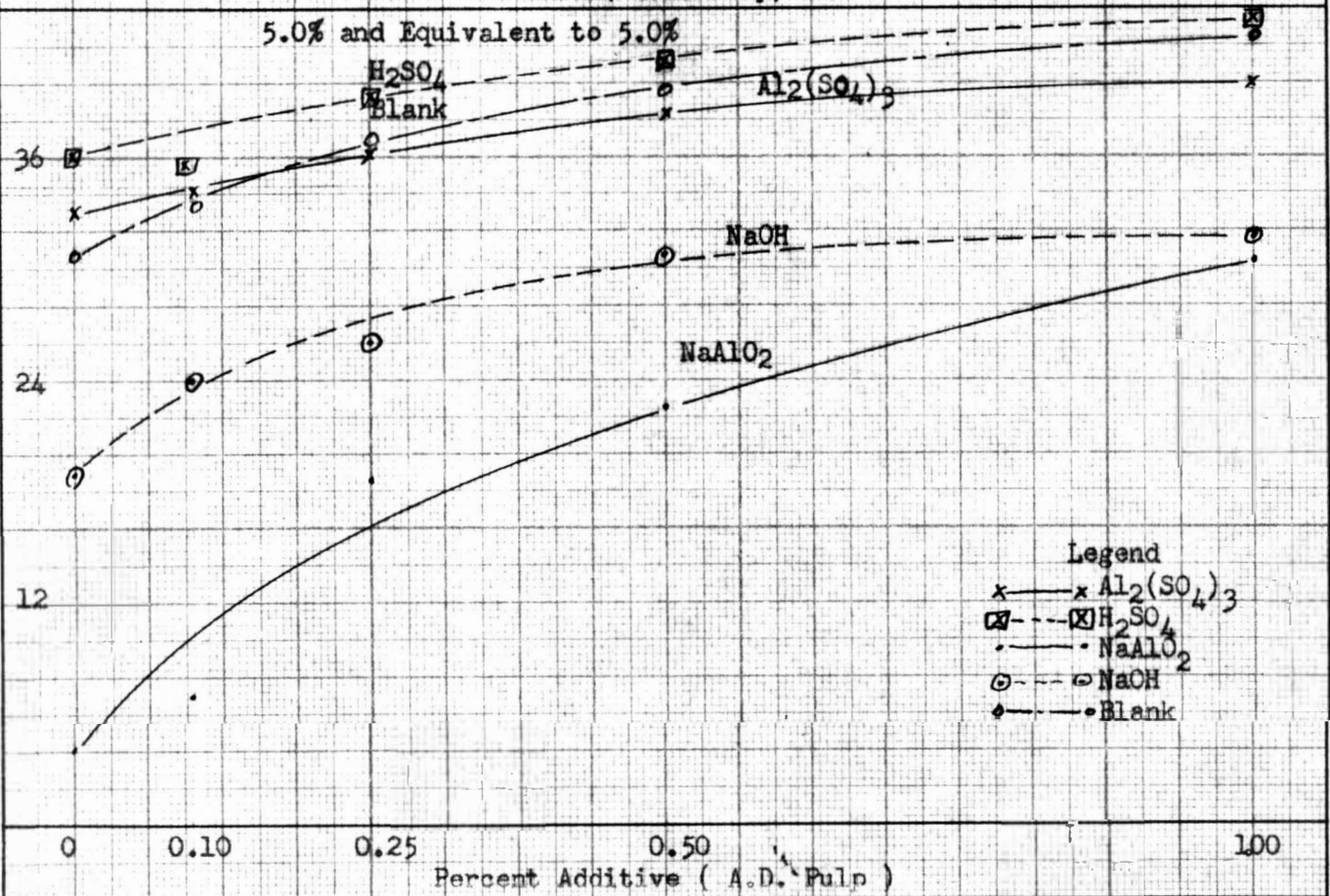
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Bursting Strength - Burst Factor

2.5% and Equivalent to 2.5%



5.0% and Equivalent to 5.0%



Bursting Strength - Burst Factor

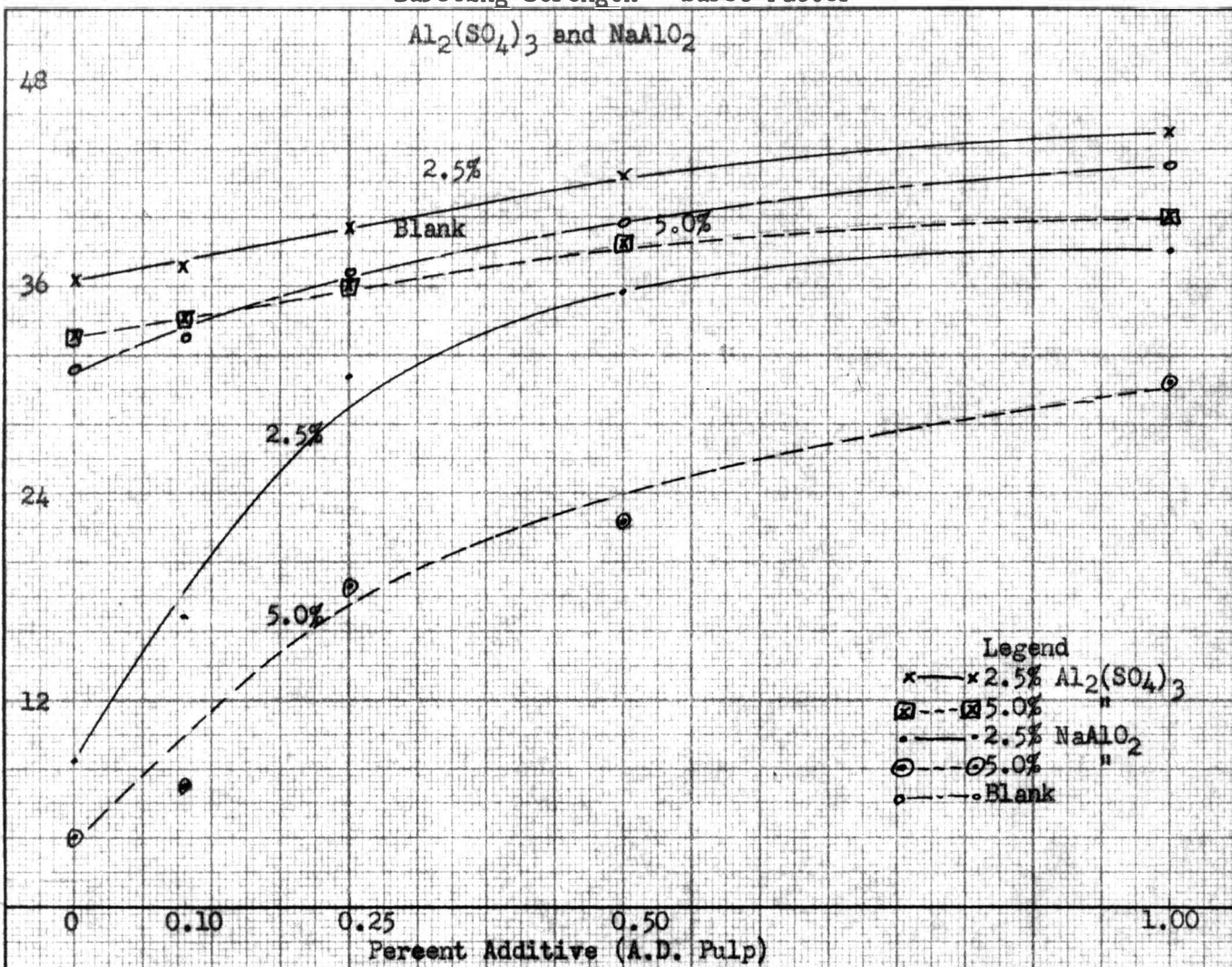
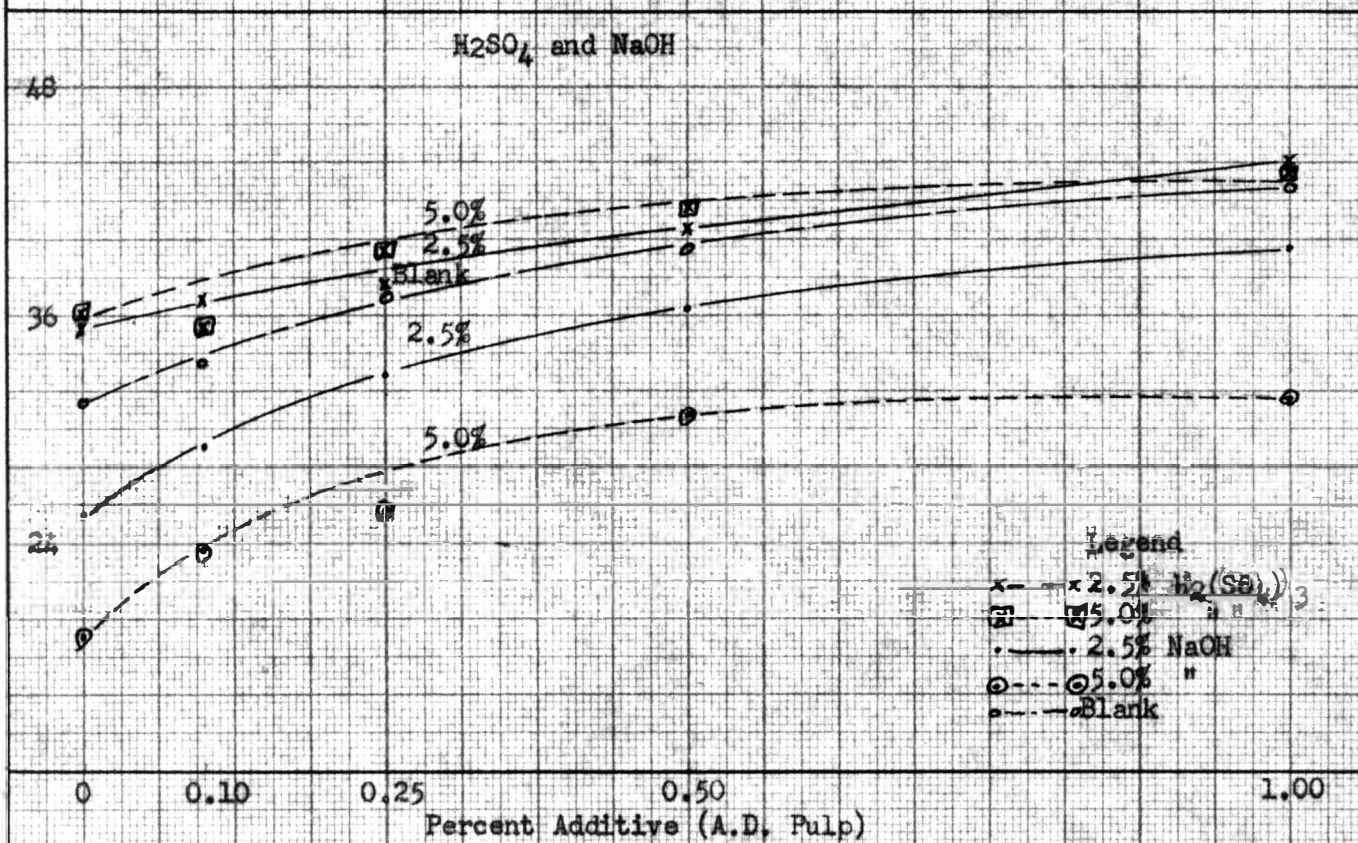
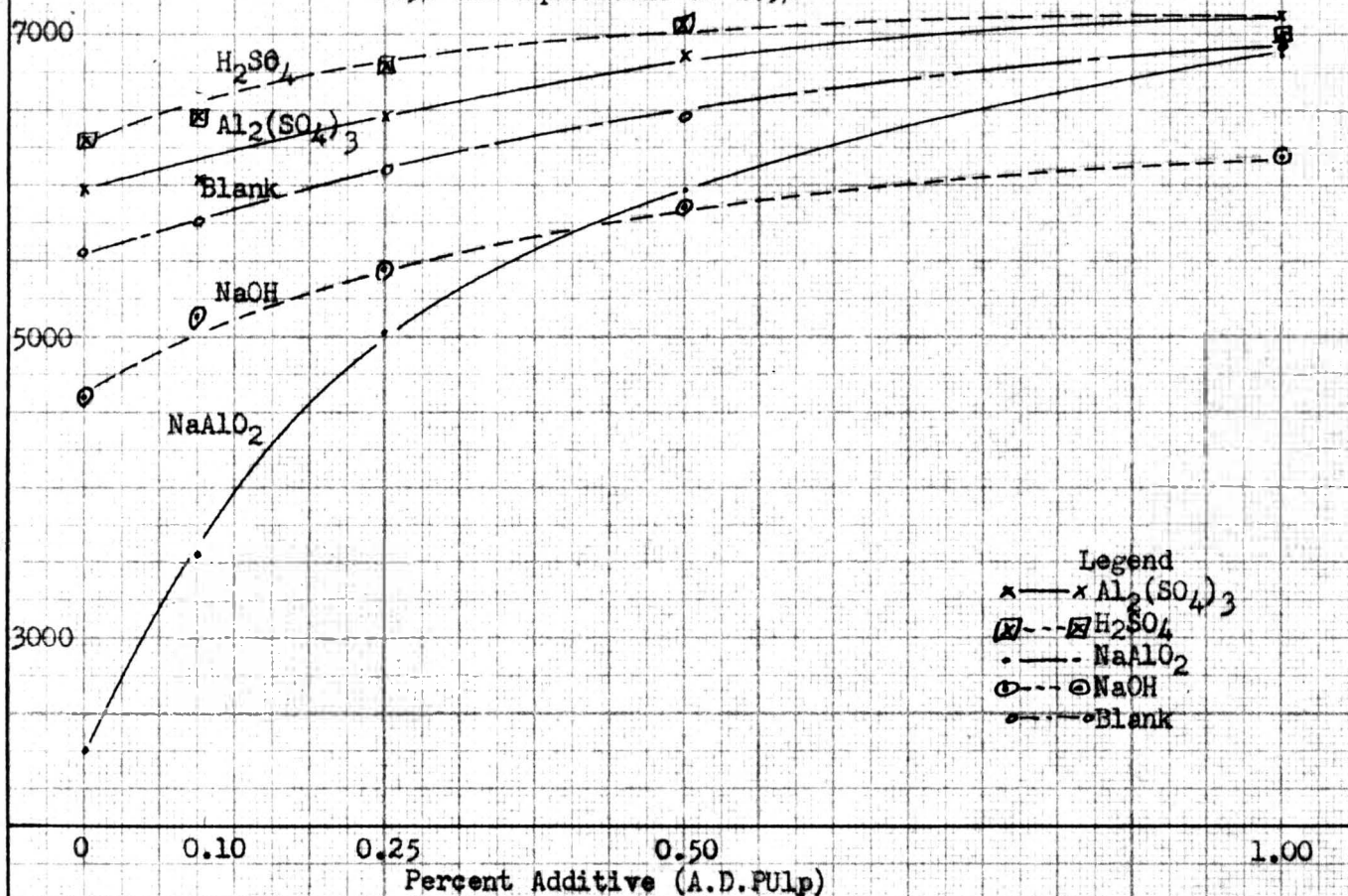
 $\text{Al}_2(\text{SO}_4)_3$ and NaAlO_2  H_2SO_4 and NaOH 

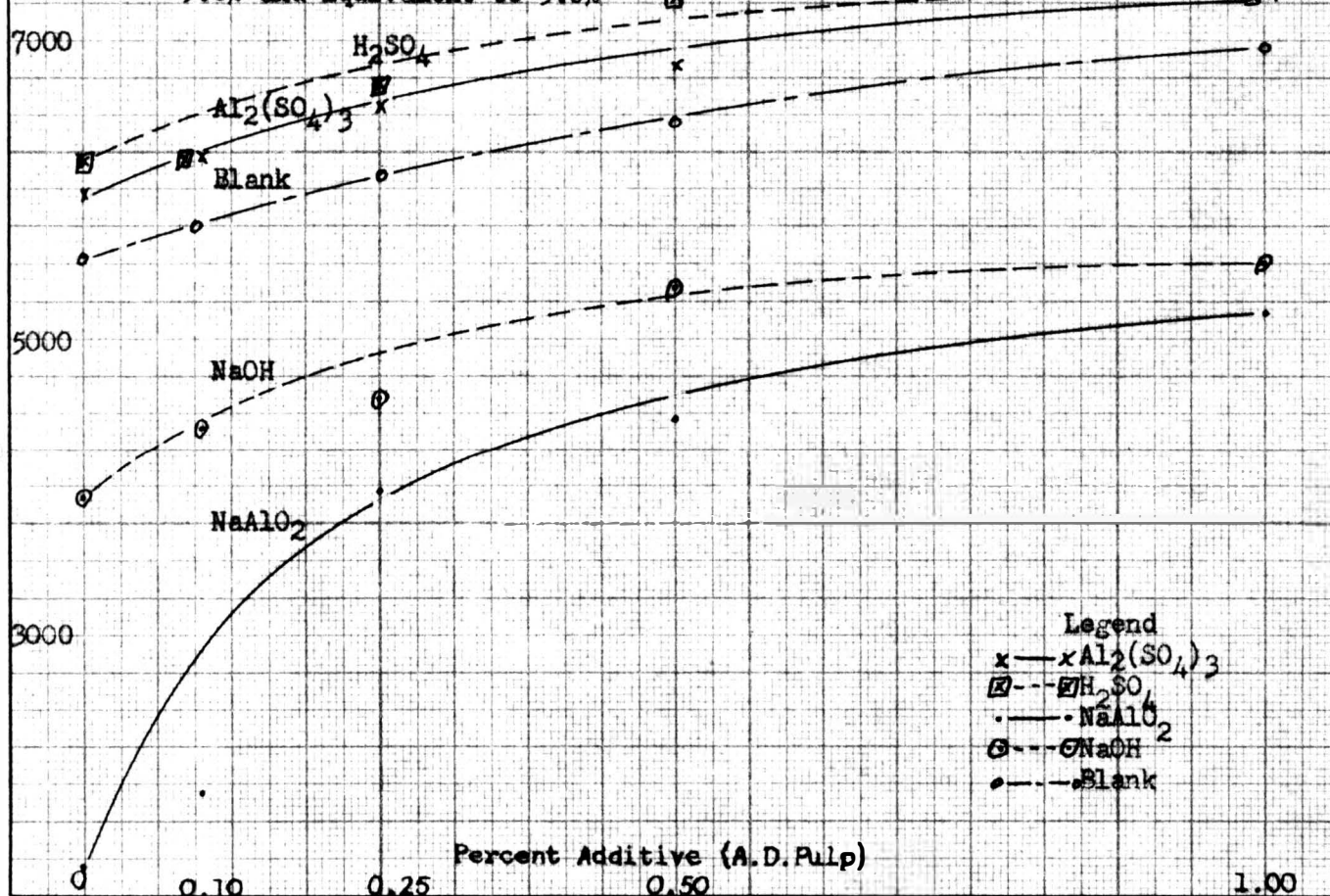
Figure IVA

Tensile Strength - Breaking Length

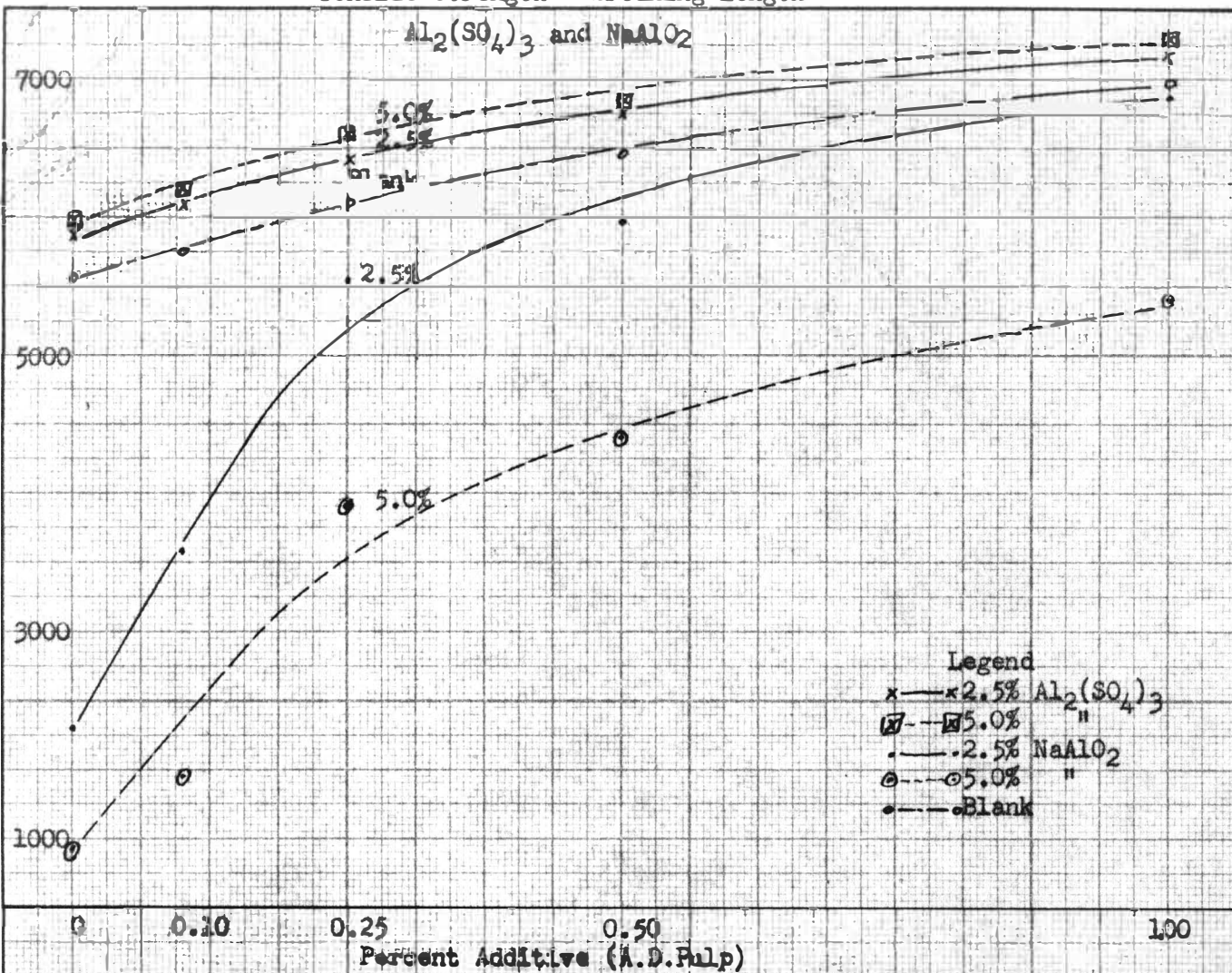
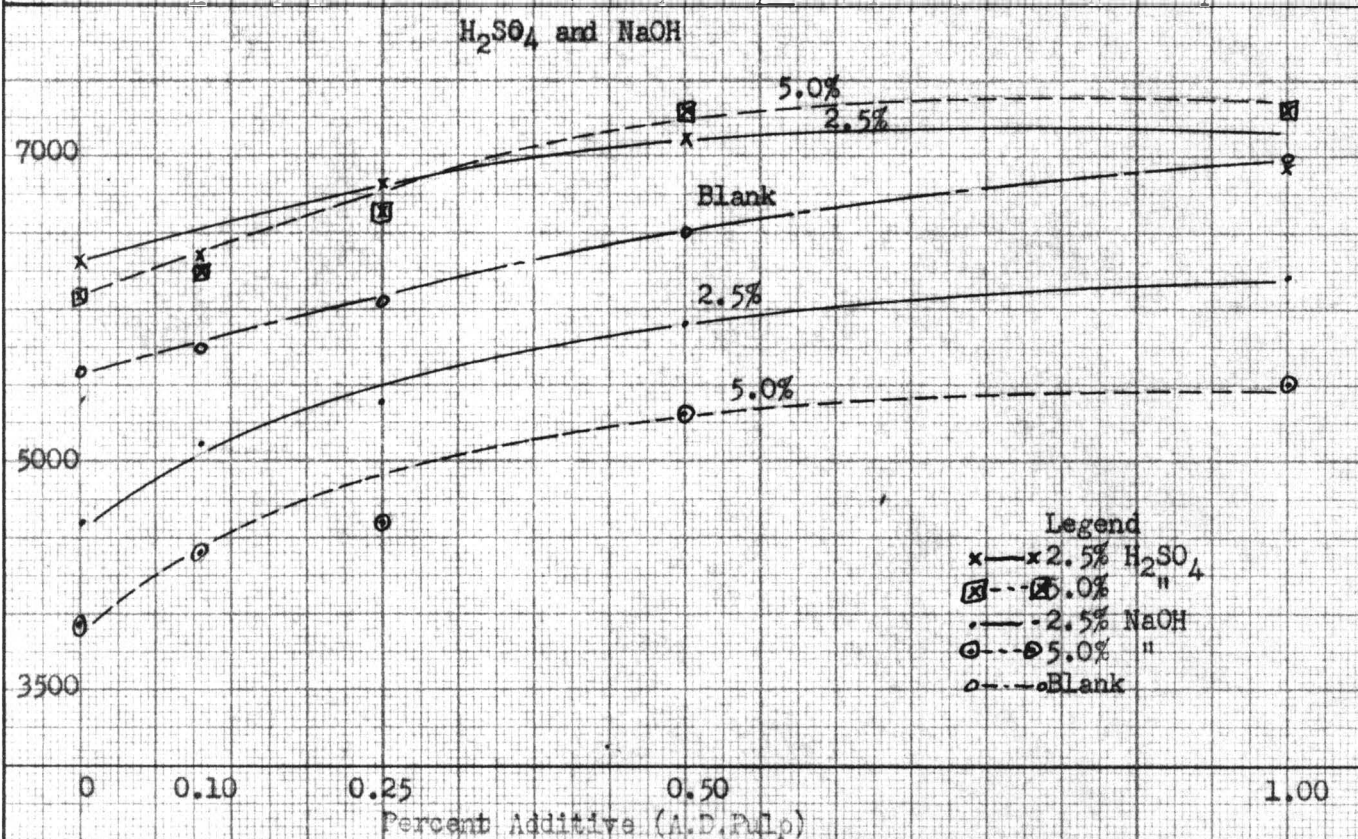
2.5% and Equivalent to 2.5%



5.0% and Equivalent to 5.0%

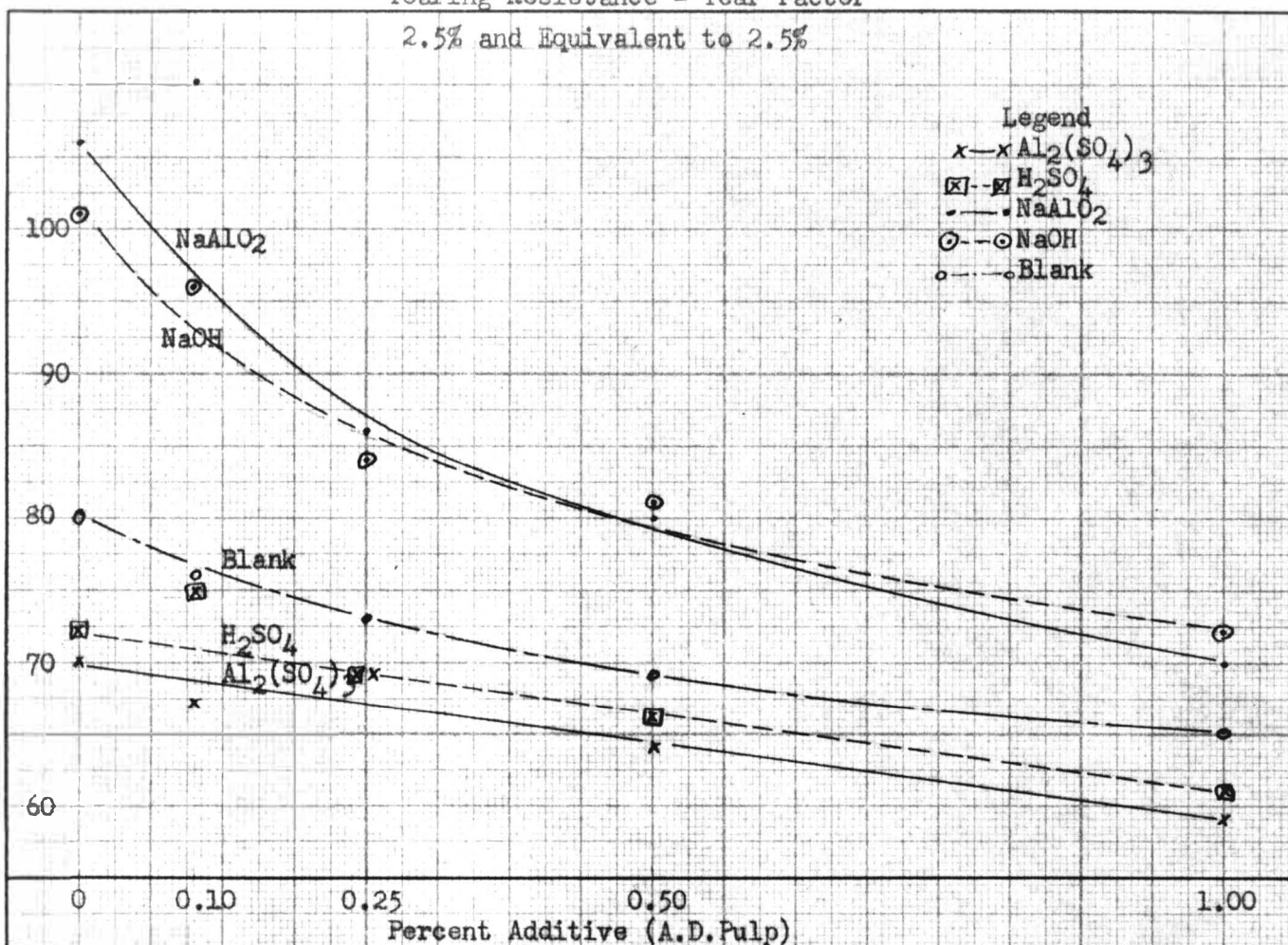


Tensile Strength - Breaking Length

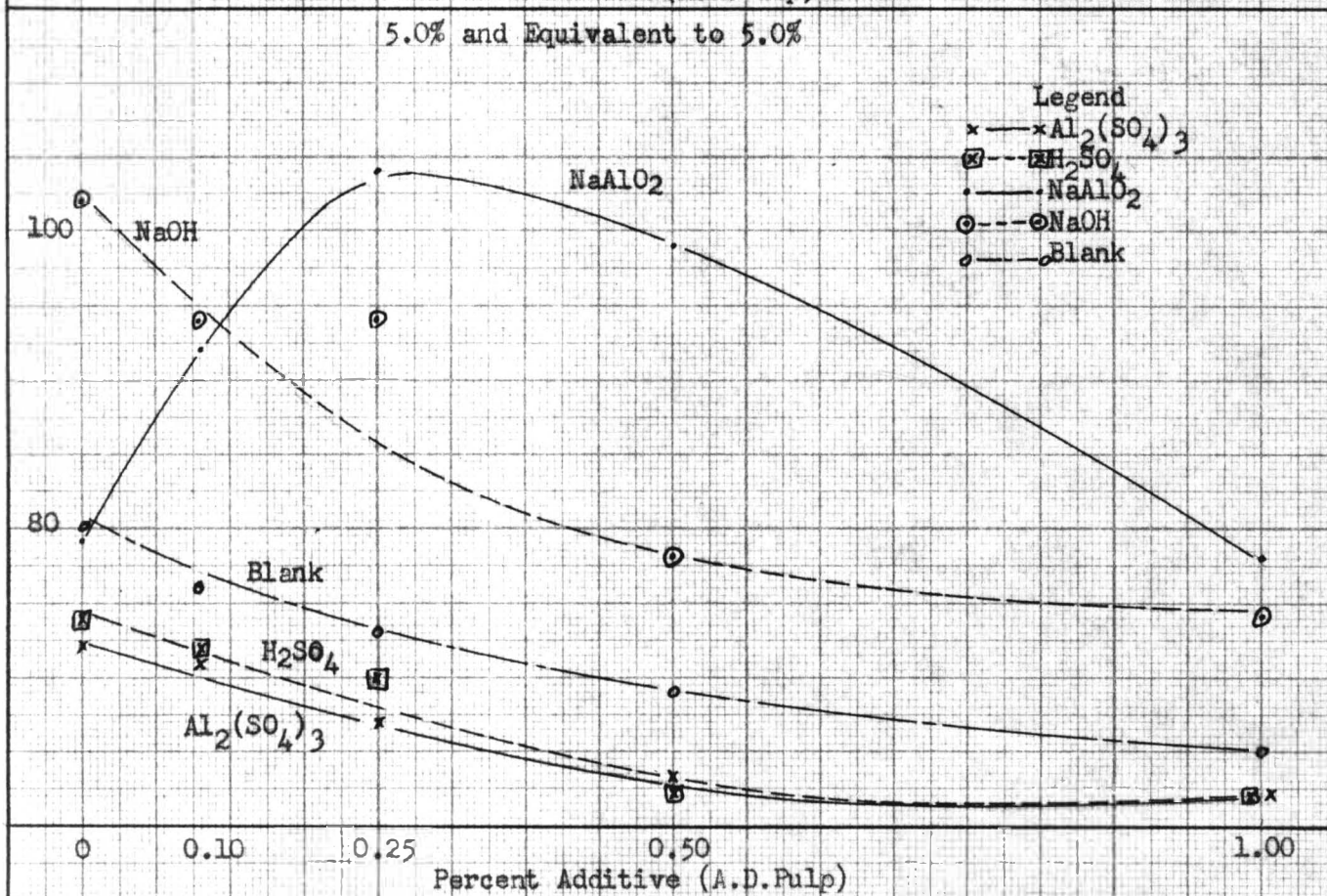
 $\text{Al}_2(\text{SO}_4)_3$ and NaAlO_2  H_2SO_4 and NaOH 

Tearing Resistance - Tear Factor

2.5% and Equivalent to 2.5%

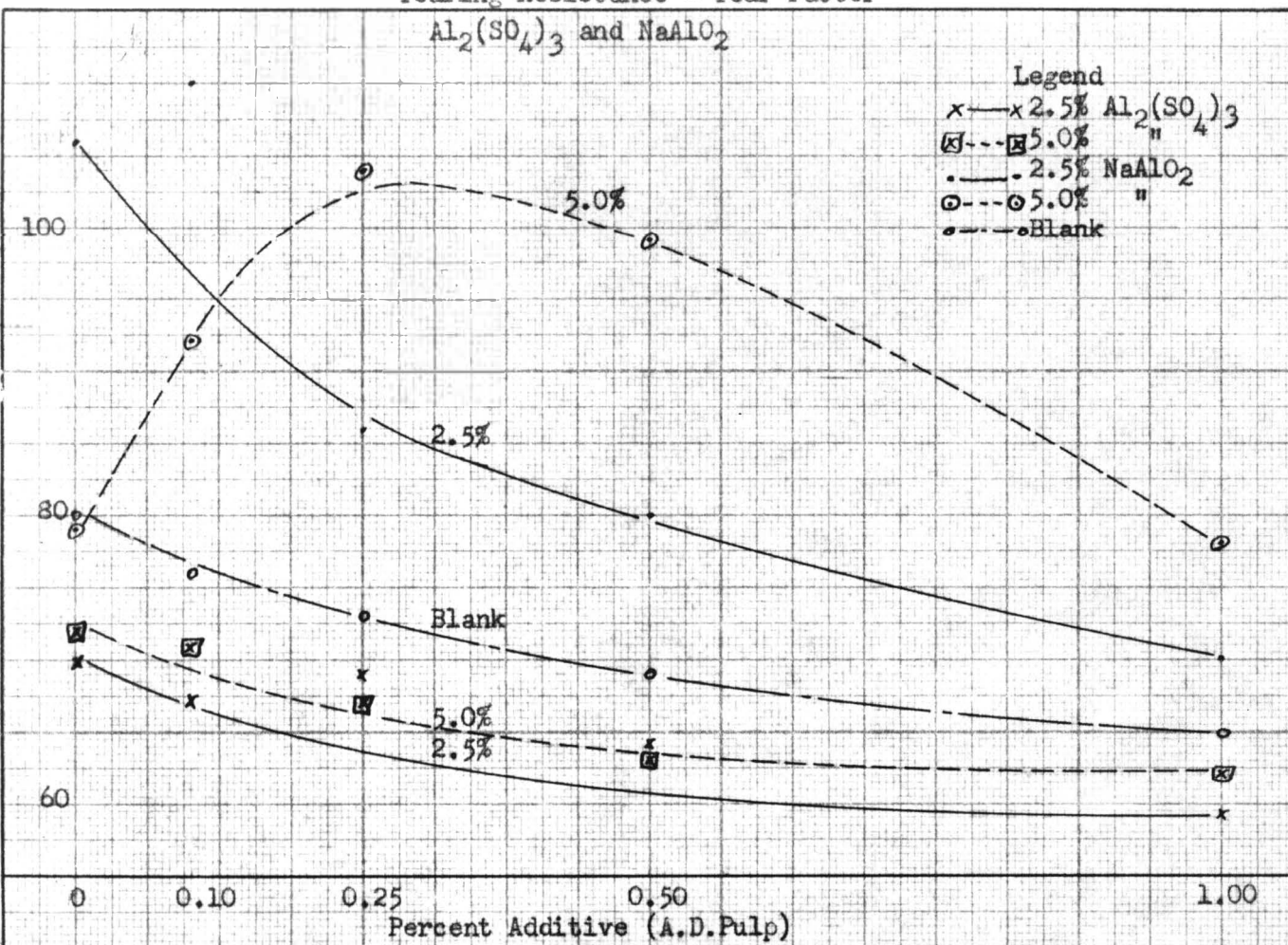


5.0% and Equivalent to 5.0%

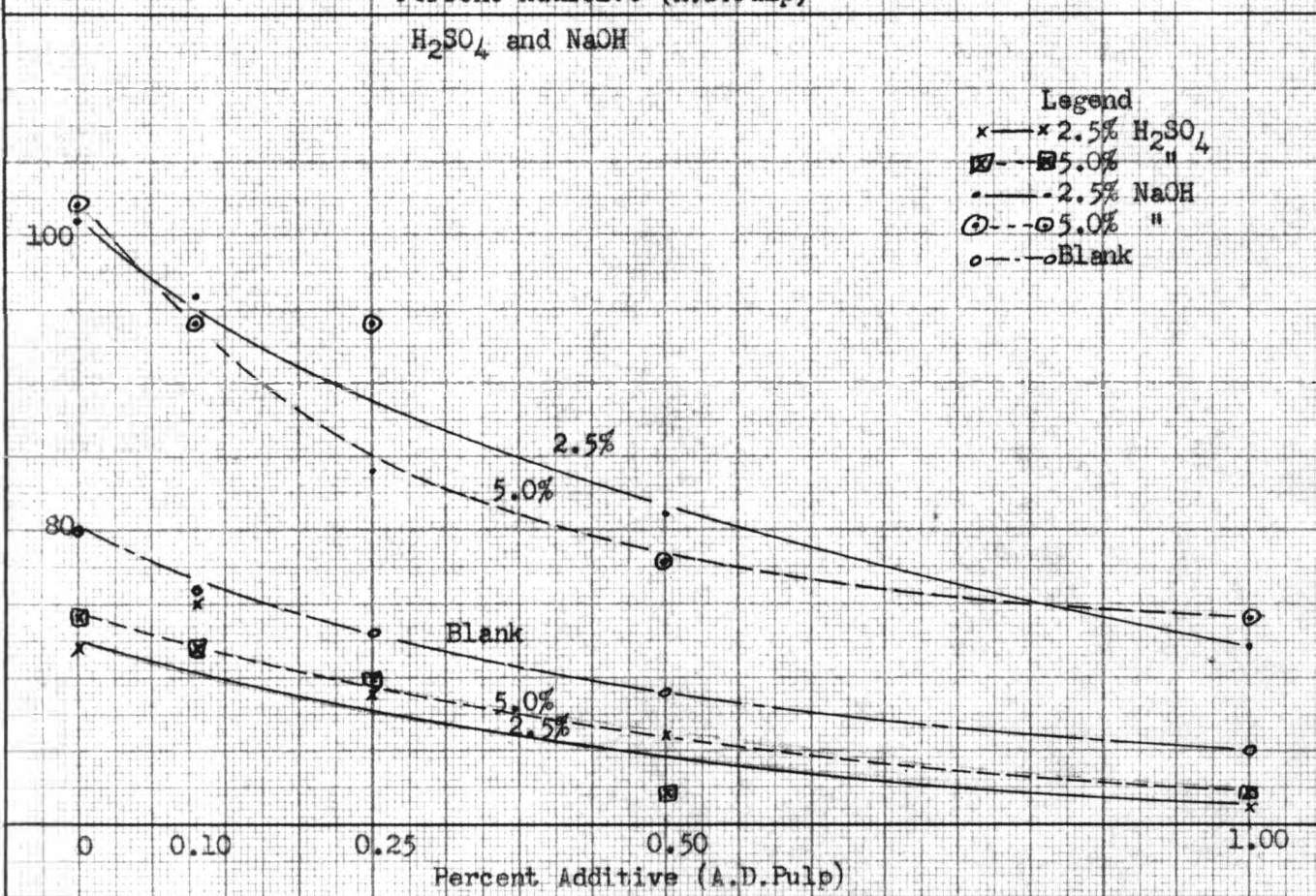


Tearing Resistance - Tear Factor

$Al_2(SO_4)_3$ and $NaAlO_2$

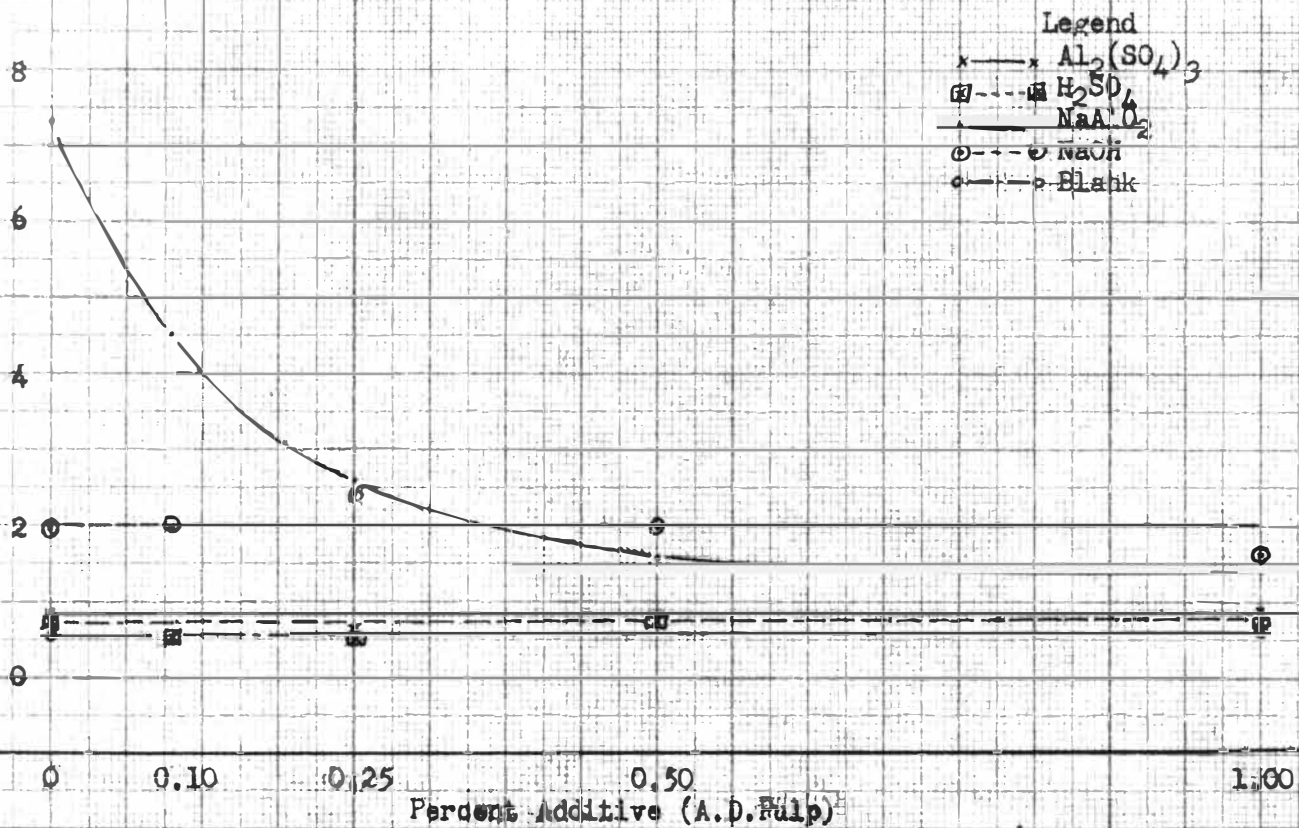


H_2SO_4 and $NaOH$



Ash Content - Percent Ash

2.5% and Equivalent to 2.5%



5.0% and Equivalent to 5.0%

