12-1950

A Comparison of Enzyme Converted Starches Used in Surface Sizing

Edward E. Stephenson
Western Michigan University

A COMPARISON OF ENZYME CONVERTED STARCHES USED IN SURFACE SIZING

Submitted to Dr. Alfred H. Nadelman as partial fulfillment of the requirements for a Senior project in the Curriculum of Pulp and Paper Technology at Western Michigan College of Education, Kalamazoo, Michigan.

ABSTRACT

A literature survey shows an increasing trend in the direction of using enzyme converted starch tub sizing solutions in paper making. Bacterial alpha amylase seems indicated as the best available enzyme for this type of conversion.

Little or no information concerning the differences in sizing solutions prepared from different varieties of starch was found.

Laboratory work comparing corn and potato starch, both enzyme converted under comparable conditions, indicates a conclusion that the optimum point of starch conversion is obtained by using the minimum concentration of enzyme which is capable of producing the desired sizing solution viscosity.

Potato starch seems to possess the property of reaching sizing viscosities at a lower enzyme conversion concentration than corn starch.

Introduction

This survey of literature concerning surface sizing and enzyme conversion has been undertaken in an effort to compile in one paper those factors important in these two closely related, but separately reported, subjects. In addition to this objective, the literature dealing with species variation in starch has been investigated so that an experimental program may be undertaken to determine any correlation which may exist between the natural source of a starch and its suitability and effectiveness for use as an enzyme converted surface sizing medium.

The Evolution of Surface Sizing

The use of starch in the modification of surface characteristics of a writing medium may actually be older than the art of paper manufacture itself. According to Dard Hunter (7), the first surface sizing of paper with wheat flour was done about 700AD; however, the sizing of papyrus sheets was carried out by the Egyptians and Romans as early as 2000 BC.

This surface sizing process, until relatively recent times, was carried out by preparing a starch bath at whatever viscosity and concentration the natural starch and the whim of the papermaker dictated, dipping the loft dried or wet-pressed handsheets into the bath, pressing out the excess starch sol, and redrying. Quality control, in the sense of making a reproducible product, was practically non-existent, but sheets were produced with the desired property of showing little ink feathering, even with coarse quill pens and the erratic inks of the period.

In modern practice, the utilization of starches modified by acid hydrolysis, oxidation, heat dextrinization, milling, or enzyme conversion has provided a virtually limitless range of starch viscosities, all produced at a purity and standard consistent with the reproducibility demand-

ed by modern industry. For the purposes of this paper, the chemically modified, heat modified, and mechanically modified starches will be dismissed with but one thought: these modified starches are produced to certain rigid standards and each modification is best for one specific set of working conditions. Enzyme conversion, on the other hand, may be carried out by the staff of the using organization to meet a wide range of operating conditions or specifications, thus giving a flexible and highly useful tool to a paper mill making a wide variety of grades of paper.

Advantages of Enzyme Conversion

The flexibility mentioned above makes a study of enzyme conversion particularly valuable to the technical men and the production men of the paper industry. In addition to this factor of flexibility, Casey (3) (4), Kerr (8) and Bingham (1) state that conversion of starch in the mill by enzyme action permits operation at a lower cost than when the more expensive modified starches are used. The additional economic advantage of simplified inventory control with a stock of only one type of starch for several end uses makes this form of modified starch highly interesting from the viewpoint of dollars and cents. Kerr states that there has been a heavy shift in the direction of enzyme conversion for the tub sizing process, particularly in recent years, and Casey (4) states that some mills use enzyme converted starch in the water boxes for calender application.

The Purpose of Surface Sizing with Starch

Surface sizing with starch is limited to the application of a film of starch at the wet calender stack, in the size press, or in a size tub. This excludes laminating adhesives, coating adhesives, and beater starch

from consideration in this paper. Surface sizing, according to Tucker and his associates (18), has as its primary purpose the prevention of feathering in writing inks, the closing of the surface of a sheet, improvement of scuff resistance, and the laying of fuzz.

A survey of the boxboard industry (17) showed that many mills use starch on the calenders for the purpose of reducing the penetration of vehicle in stock for printing with gloss inks. It must be pointed out, however, that this survey showed a great diversity of opinion. Of the 28 mills reporting, only two mills replied that they were using enzyme converted starch for this purpose. Both these mills seemed to feel that they were obtaining satisfactory results, and no mill reported dissatisfaction with enzyme converted starch. When all factors are considered, however, only generalities in this report are of significance. It may be said that the vast majority of the mills reporting felt that starch was the cheapest and most effective sizing agent for this application, but that agreement on how this starch was to be used for maximum effectiveness was completely lacking.

The Trend from Beater to Tub

Although the above mentioned purposes have long been regarded as basic in surface application of starches, the use of low viscosity starches in the tub or size press often brings about highly desirable side effects, usually associated with beater starch. Application at low viscosities permits high concentrations of starch in the bath plus greater penetration of this highly concentrated sol into the sheet with a subsequent improvement of bursting strength, stretch, and tensile strength. Indeed, Casey (4) states that modern papermill practice shows a definite trend toward moving starch from the beaters to the tub or size press where no white water

losses are encountered while physical properties are improved. It is even possible to obtain a slight but measurable increase in strength by calender application.

Enzyme Classification

Following this brief outline of surface sizing with starch, a consideration of the basic classification of enzymes is of importance. Enzymes are, by definition, complex protein molecules which serve as organic catalysts by accelerating specific transformations of material. They are generally classified and named with reference to the reaction catalyzed. The two primary groups of enzymes are the hydrolases, catalysing low energy level hydrolysis reactions, and the desmolases, inducing greater energy change reactions. According to Wallerstein (21), amylases and proteinases are examples of hydrolytic enzymes, and oxidases, reductases, and zymase are examples of desmolases.

Amylases, those enzymes governing the hydrolysis of amylose and amylopectin, the component fractions of starch, have been carefully studied and many excellent reviews are available (13) (14) (16).

Amylases are classified in either of two ways, according to the products of hydrolysis or according to the source of the amylase. The alpha or dextrinogenic amylases bring about liquefaction of starches with the production of relatively high polymeric dextrins as the major reaction. The beta or dextrinogenic amylases influence a hydrolysis to simple sugars with maltose as the predominating type. In addition to the maltose, about 40% of the original starch is not completely hydrolysed and remains as alpha amylodextrin, since beta amylase breaks only the alpha 1,4 glucosidic linkages in starch, stopping action at the anomolous branching points, commonly thought to be 1,6 glucosidic linkages.

This residue probably consists of the remnants of the amylopectin

fraction of starch which Myrbäck (12) has reported on. In addition to a thorough search of the literature on amylopectin, he reported work of the Biokemiska Instituted of Stockholm, Sweden, which seems to substantiate the multiple branching theory of Meyer (9), who states that amylopectin structure is similar to that of a maple tree as opposed to the theories of Haworth with his laminated structure and Staudinger who proposed a side chain hypothesis. (See Figure 1)

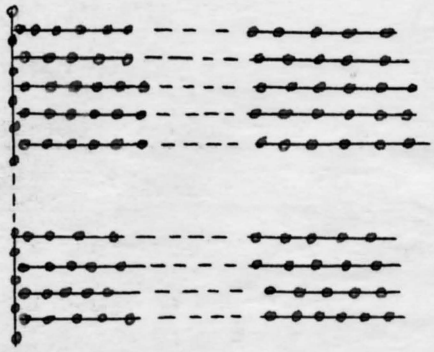
Source Nomenclature for Amylases

Classified according to source, the enzymes are named with reference to the material from which they have been extracted. In this system, we have malt amylase, a mixture of alpha and beta types; fungal amylase, primarily alpha amylase; bacterial amylase, also alpha; and animal amylase, which may be either alpha, beta, or a mixture. Since a low conversion to sugars is desired in surface sizing preparations, the alpha amylases are of major importance to the paper industry and sources high in alpha amylase are to be preferred. Under comparable conditions, amylases from different sources exhibit differing degrees of thermostability, being generally ranked in the order of: bacterial, most stable; malt, intermediate; and fungal, least stable. As a general rule, alpha amylase is more stable with respect to temperature than is beta, causing higher temperatures to favor liquefaction and lower heat levels to favor saccharification when an amylase of mixed alpha and beta type is used.

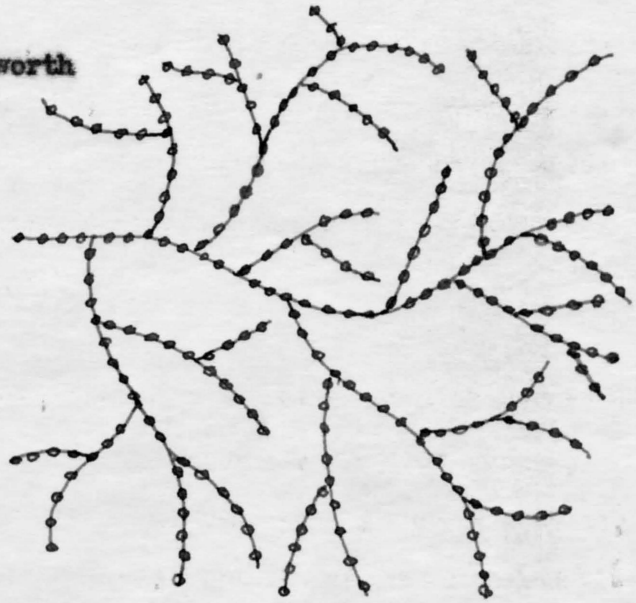
Since the process of extracting high purity enzymes from the natural sources is expensive and difficult, most commercially available enzymes are only partially purified and concentrated, thus making the brand of enzyme selected a major variable in any enzyme conversion. As long as the brand selected comes from a reputable concern and the instructions of the manufacturer are carefully considered, a standardized production is quite possible.

FIGURE 1

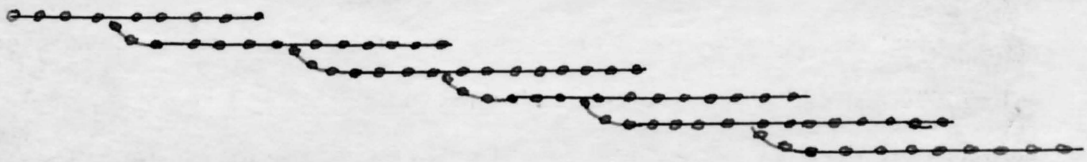
Starch structure according to Haworth



Staudinger formula for starch



Starch formula with multiple branching (Meyer)



"Laminated" formula of Haworth, et al.

From Myrbäck, reference 12.

Species Variation in Starches

Another basic variation in the enzyme conversion process is the source of the starch used. According to Meyer (9), the native source of a starch may govern its end use primarily because of the physical and micellar structure dictated by the biochemical synthesis in the parental plant. These differences may easily be appreciated when viewing the starch granules from different plant sources under the microscope. Sjostrom's excellent work on the microscopy of starches (15) shows the different characteristic forms quite clearly. This study also leads to a measurement of the average granule size of the various starches, which range from 70 microns for potato and sago starch to 5 microns for rice starch. Corn starch, with an average major axis length of about 15 microns, is of intermediate size as is tapioca starch, the other common starch of commerce.

In addition to particle size variation, species differentiation is reported as showing up in average molecular weights. The work of Meyer and Rathgeb (10) as shown in Table I, would show a wide variation in the case of potato and corn starches. The lower molecular weight of the potato amylose fraction might well explain at least a portion of the mystery of the lower gelling tendencies shown by potato starch as compared to corn starch, while the higher average weight and attendant ramification of micellar structure of the amylopectin portion might be a basis for explaining the sinsitivity of potato starch to the action of salts and mechanical shearing forces.

TABLE I — Average Molecular Weights

Subfraction	Corn	Potato
Amylose A_1	13,000	11,500
	24,000	
	33,000	
Amylose A_2	340,000	110,000
Amylopectin	45,000	180,000

From Meyer, reference 10.

Particle Size vs. Ease of Conversion

Since Barnett (1) has stated that certain users of starch in the textile industry prefer potato starch to corn starch for enzyme conversion, an attempt at a laboratory comparison of the two starches in enzyme conversion should be a valuable project. Although the problem of "calling your shot" before actual investigation has taken place may lead to saddening results, the two basic distinctions mentioned above may be applied to the problem in an attempt to predict the probable result of a practical investigation.

The matter of particle size may be tied in with the work of Mullen and Pascu (11) who found a direct correlation between particle size and ease of dispersibility in starches, with the largest particle sizes exhibiting the maximum dispersibility. (See Table II) Kerr (8) in his chapter on conversion of starch, states that corn starch is particularly susceptible to "packing" and "channelling" with the result of an uneven conversion in the acid process.

TABLE II — Order of Dispersibility

Starch	Average Granule Size in microns	Gelatinization Temperature, °C	Heat of Gelatinization, cal/$C_6H_{10}O_5$
Potato	35	61.5	9080
Tapioca	16	63.5	8780
Wheat	16	65.0	7300
Corn	13	68.5	7100
Rice	4	75.0	5700

From Mullen and Pascu, reference 11

Since the action of an enzyme, as a catalyst, must take place at the interface between the water and the starch granule, it would seem that the starch having the maximum dispersibility would require the smallest amount of enzyme for conversion in a limited time period. It would also seem to indicate the possibility of a maximum of effectiveness in the uniformity of conversion. This could easily be one of the basic factors behind the

preference expressed by some textile manufacturers.

Molecular Weight

Consideration of the molecular weight distinctions between the different starches is also of interest with respect to conversion. The previously mentioned lower molecular weight of the amylose fraction and the consequently lower degree of polymerization would indicate the possibility of higher sugar formation or saccharification of this portion of starch when potato starch serves as the hydrolytic base in enzyme conversion. The gelling tendencies should be reduced beyond their normal low point, however, in a very short time.

Action on the larger amylopectin molecules of potato starch would be limited by the more extensive branching since the enzyme is apparently unable to cause the rupture of the 1,6 glucosidic linkage which seems to occur at branching points. This would probably leave as the limit dextrin, amylodextrin, or Schardinger dextrin, a larger molecule of greater adhesive power than in the case of corn starch, but would leave a smaller number of these molecules in the colloidal dispersion.

Another viewpoint of interest which is related to these views is that expressed by Houtz (6), who believes that each starch has a definite state of maximum colloidality. To reach this state, the starch is cooked to a point where it most ideally fulfills the definition of a true colloidal dispersion and is, therefore, most effective as far as its film strength is concerned. His work indicates the point for the common starches he tested and is of interest in any investigation involving the cooking or gelatinization of starches. (See Table III)

TABLE III	Optimum cook for maximum colloidal dispersion	
Starch	Maximum Temperature °C	Time at Temperature Minutes
Tapioca	88	0
Corn	95	0
Potato	96	10
Sweet Potato	96	20

From Houtz, reference 6

Seven Rules for Enzyme Conversion

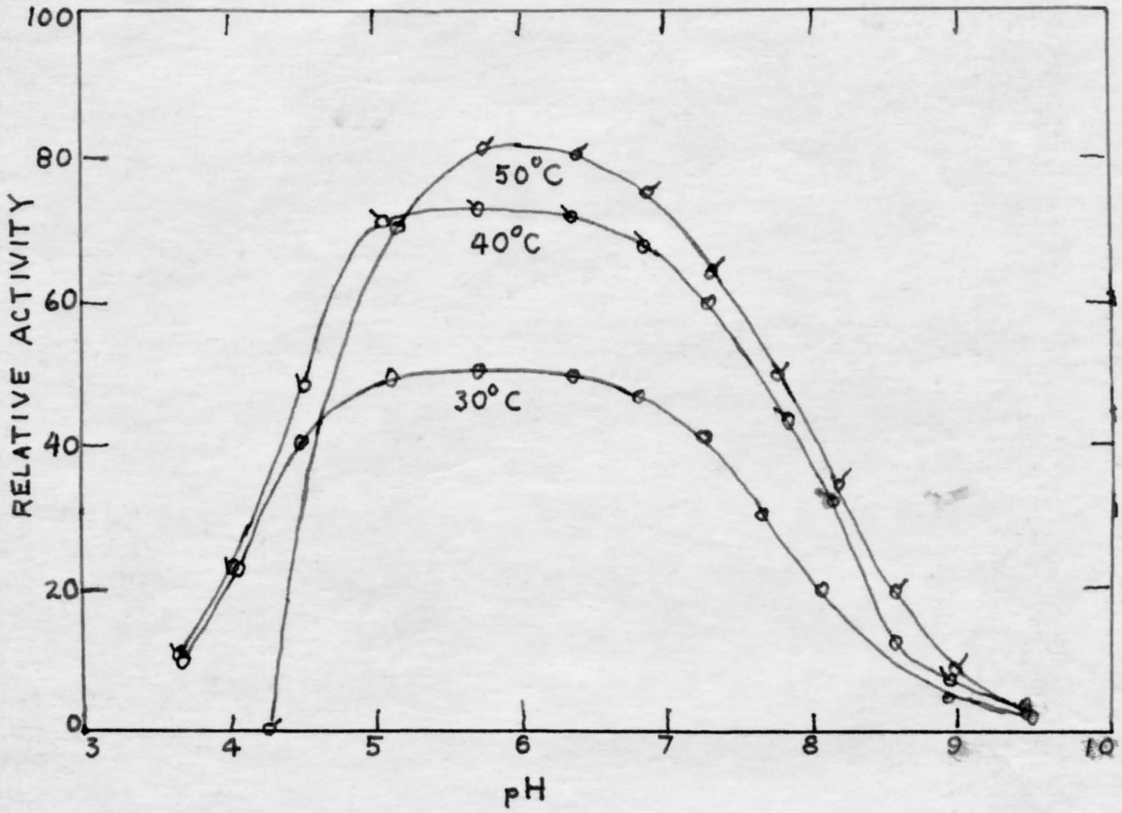
In any enzyme conversion, certain basic factors must be kept in mind. According to Severson (16), there are seven major features of importance. These are summarized and explained as follows:

(1) The rate of enzyme destruction increases with increasing temperature. Enzymes may be readily inactivated by low temperatures, but are destroyed only by the environment of elevated temperatures. From a practical point of view, therefore, each degree of increased temperature is destroying a greater percentage of the enzyme being used until the entire sum of enzyme molecules is destroyed or inactivated by exposure to boiling temperatures. The lower the temperature of conversion, therefore, the lower the rate of destruction of enzyme and the greater the number of molecules of effective enzyme left to perform the conversion.

(2) Increasing temperature increases the activity of the enzyme. This postulate is familiar in chemistry, being given as the temperature coefficient of reaction in chemistry courses, showing as a rule of thumb that the rate of reaction doubles with each rise in temperature of 10°C. This factor, however, is limited by (1) above and holds true only until the rate of destruction of enzyme balances the increase in activity due to temperature. The combination of these two factors governs the most effective temperature of reaction. (See Figure 2)

(3) The higher the pH, up to 7.0, the more stable is alpha amylase

FIGURE 2



Effect of pH and temperature on dextrinizing activity of bacterial alpha amylase

From Redfern, reference 14.

with respect to heat. In other words, the most effective use of the balance point mentioned previously is in an absolutely neutral solution, providing all other factors are carefully eliminated. Increasing either acidity or alkalinity decreases the thermostability of the enzyme and moves the optimum balance point mentioned in (2) to a lower temperature, thus decreasing the efficiency per pound of enzyme purchased. (See Figure 2)

(4) Metal salts affect the stability of enzymes. Although the enzymes are themselves organic catalysts, their degradation or decomposition may be favored or inhibited by certain inorganic catalysts. The calcium ion has a great stabilizing effect on alpha amylase and makes it much more stable in the presence of heat. On the contrary, the presence of the cupric ion is quite detrimental to thermostability in alpha amylase. Knowledge of these factors may be utilized by addition of calcium ion to liquifaction conversions such as are used in surface sizing, and by utilizing either aluminum or stainless steel as the material of construction for starch-enzyme systems.

(5) For complex systems, such as malt enzymes, which contain mixtures of large quantities of beta amylase, the mode of the reaction is affected by the temperature. For instance, beta amylase is inactivated at lower temperatures than alpha amylase and, with the use of malt amylase, high saccharification is obtained at a reaction temperature of 135°F and low saccharification and high liquefaction is obtained at 150°F where the beta amylase is largely inactivated while the alpha amylase is still quite effective, especially in the presence of calcium ions.

(6) Under comparable conditions, the order of thermostability is as follows: Bacterial > Malt > Fungal. Here, from a practical point of view, the current prices of amylases from differing sources must be con-

sidered. Most rapid and most effective conversion should be obtained from bacterial amylase, but a pound for pound effectiveness of enzyme might not be the governing factor if cost per pound of converted starch is considered.

(7) For effective action, starch must be gelatinized. Starch as it occurs naturally, in granules having an outer layer, or husk, of amylopectin, must be gelatinized so that the insoluble amylopectin husk breaks and releases the amylose and inner amylopectin for colloidal dispersion throughout the sol system for action by the enzyme. Here the work of Houtz (6) might be considered if the ultimate in effective utilization of enzyme is to be reached. If gelatinization occurs at a point above the effective balance of thermostability and thermal activity, effectiveness must be sacrificed somewhere along the line.

A Practical Approach

As a compromise between the aforementioned seven points and the dictates of manufacturing expediency, enzyme conversion is often carried out on the following time and temperature schedule:

(1) Slurry the starch in cold water at 10 to 20 percent starch.

(2) Mix in the enzyme. (0.1 to 1.0 percent of the dry starch)

(3) Adjust the pH as recommended by the manufacturer.

(4) Heat the enzyme containing slurry to the gelatinization temperature of the starch being used as quickly as possible, holding it there or increasing it to the maximum temperature consistent with the enzyme being used, until the desired viscosity of starch is obtained.

(5) "Kill" or coagulate the enzyme by inactivating either by temperature or chemical means. Raising the starch to boiling temperature will effectively stop the enzyme action as will the addition of most

phenolic compounds, particularly the chlorinated phenols commonly used in mills for bacterial control. This last action is particularly valuable if food carton stock is being run and a sterile starch application is required. This type of chemical inactivation has a further advantage in that it precludes further liquefaction or saccharification by spore forming bacteria.

The fourth and fifth steps mentioned above may be modified by heating slowly from the cold slurry to inactivation temperature on a strict time and temperature schedule. If starch is being prepared on a three shift schedule, this may be preferable because simple recording instruments can be set up to keep a check on operating personnel in the absence of technically trained supervisors. It is also claimed that greater enzyme economy results from this process.

For maximum enzyme economy, gelatinization of the starch, or raising the starch to the temperature of maximum colloidality and cooling to the optimum conversion temperature before addition of enzyme is often recommended, but seldom used, since additional steam costs apparently come close to balancing the saving in enzyme.

Summary

This survey of literature available shows a need for work to establish two main factors. One of these is the relative ease of conversion of different starches by alpha amylase. The other factor is the determination of any difference in physical properties of the ultimate product which may be traced to the starch source or method of conversion.

A simple check on the ratio of enzyme to starch required for conversion should be a sufficient indication of the relative ease of conversion, and should present no difficult problems.

The logical approach to testing the effectiveness of a surface sizing agent is the application of a surface film to a standard base so that variation in measurable properties may be checked. Although the work of Houtz (6) dealt with beater application of starch, his conclusion that bursting strength is a measure of the effectiveness of a film of starch should be valid for physical properties in surface application as well as beater application. In surface application, determination of the amount of starch added is a simple gravimetric procedure, thus giving a factor lacking in the published work of Houtz.

Application of these tests to starches prepared and selected in accordance with the theories presented herein should provide information of interest to users of starch in surface sizing applications.

Kalamazoo, Michigan
December 14, 1950

Edward E. Stephenson Jr.

Edward E. Stephenson Jr.

LITERATURE CITED

1. Barnett, H. R., Paper Trade J. 128, No. 8:90, 101 (Feb. 24, 1949).

2. Bingham, R. T. (ed), "Starch for Paper Coating", Technical Association of the Pulp and Paper Industry, New York (1947) 120 p.

3. Casey, J. P., Tech. Assoc. Papers 25: 139-147(June 1942).

4. Casey, J. P., Paper Ind. 28, No. 2:268, 270, 272, 274, 276-79 (May 1946).

5. Chapman, S. M., Pulp Paper Mag. Can. 50, No. 3:201-203 (Mar.1947).

6. Houtz, H. H., Tech. Assoc. Papers 24:131-135 (1941).

7. Hunter, Dard, "Papermaking", Alfred A. Knopf, New York, 2 ed. (1947) p. 486.

8. Kerr, R. W., "Chemistry and Industry of Starch", Academic Press, Inc., New York, 2 ed., (1950).

9. Meyer, K. H., "Natural and Synthetic High Polymers", Interscience Publishers Inc., New York (1942).

10. Meyer, K. H., and Rathgeb, P., Helv. Chim. Acta. 31, No. 6:1533-1536 (Oct 15, 1948). B.I.P.C. 19:431.

11. Mullen, J. W., and Pacsu, E., Ind. Eng. Chem. 34:807-812 (Jul. 1942).

12. Myrbäck, Karl, Wallerstein Labs. Commun. 11, No. 34:209-219 (Sep. 1948).

13. Nord, F. F.,"Advances in Enzymology" Vol I--X, Interscience Publishers Inc., New York, (1950).

14. Redfern, S., Wallerstein Labs. Commun. 13, No. 41:89-114 (June 1950).

15. Sjostrom, O., Ind. Eng. Chem. 28, No. 1:63-74 (1936).

16. Severson, G. M., In Kerr, op. cit. p. 443-453.

17. Tappi Special Report 309, "Starch Application to Paperboard for Gloss Ink Printing" (Sept. 6, 1940).

18. Tucker (ed) "The Manufacture of Pulp and Paper, Vol IV", McGraw-Hill Book Co., New York (1938)

19. Vallandigham, V. V., Paper Trade J. 123, No. 17:39-41 (1946).

20. Vallandigham, V. V., Pulp Paper Mag. Canada 46, No. 12:921-925 (1945).

21. Wallerstein, L., Ind. Eng. Chem. 31, No. 10:1218-1224 (Oct. 1939).

LABORATORY EXPERIMENTAL PROGRAM:

As pointed out in the literature survey which precedes this report, scant information has been published concerning the behavior of different starches in enzyme conversion or concerning the effectiveness of the converted sizing solutions.

The two commonest domestic commercial starches were selected for comparison, native potato starch and native corn starch. The various controllable variables in tub sizing were then tabulated. These were as follows: pH of the starch; time of conversion of the starch; temperature of starch conversion; type of enzyme used for conversion; concentration of the converting mixture; and concentration of the enzyme, based on the starch. Conditions were selected to provide evaluation of the two native starches with respect to one basic variable, the concentration of enzyme, while other variables were held constant. Conditions established were as follows:

pH of starch slurry:	6.2--6.6
Time of conversion:	Ten minutes at conversion temperature.
Temperature of conversion:	65°C
Type of enzyme:	Commercial bacterial alpha amylase.
Concentration of starch:	Ten percent.
Concentration of enzyme:	0.125% to 1.0% based on starch.

Experimental Procedure:

Moisture content of the starches to be evaluated was determined by placing the air dry starches in a constant temperature oven for three hours at 135°C. Weights throughout the experimental work were then calculated on this oven dry basis.

Stainless steel beakers and glass stirring rods were tared and starch equivalent to fifty grams oven dry weight added. Distilled water to make up a total starch-water weight of 500 grams completed the weighing. Enzyme, weighed on an analytical balance, was added to the cold slurry with mild agitation to ensure adequate mixing. The mixture, under constant agitation, was placed over a steam bath at atmospheric pressure until conversion temperature was reached. The mixture was held at this temperature for ten minutes. Following this period, the temperature was raised rapidly to 95°C to kill the enzyme.

Beakers containing the starches were cooled promptly to 54°C. Distilled water to make up the weight loss due to evaporation in cooking was added and thoroughly mixed. Viscosities were then determined with a Brookfield viscosimeter, using the number 1 spindle and a speed of 100 rpm.

The various sizing solutions were applied to one side of a commercial 25% rag, 75% sulphite skip-tub sheet. The unsized sheet was 20.5 pound 17x22-500 basis weight and contained 1% rosin size, 3% internal starch sizing, and 1% Titanium Dioxide filler. Canadian Standard Freeness of the beater stock was 410 seconds and freeness after jordaning was 180 seconds.

Sizing solutions were applied to 8½ x 11 sheets of the stock at 54°C. Sizing was accomplished by applying a surplus at the top of a sheet and removing the surplus with a number 18 wire wound doctor. Wet sheets were placed in seven inch drying rings and allowed to dry in a constant humidity room under conditions of 73°F and 50% relative humidity. Following drying, the sheets were tested for the following characteristics:

MIT Folding Endurance

Bursting Strength

Tensile Strength

Gloss (Photovolt)

Brightness (Photovolt)

Elongation

Unsized samples of the base stock were tested for the same characteristics for the purpose of comparison.

Experimental Results:

As shown in the summary of experimental results, Appendix I, brightness and elongation showed no significant variation. Figures for bursting strength, folding endurance and tensile strength, however, showed a definite increase in the sized sheets. As shown in Figure 1, the two starches evaluated brought about comparable or equal increases in strength characteristics over strength of the base stock when converted with 1.0% enzyme.

Decreasing percentages of enzyme, however, showed distinct differences in the performance of the two starches. Under the conditions of this work, potato starch was increasingly effective in supplementing strength properties of the base sheet when the enzyme concentration was reduced to 0.25% based on the dry starch. When the concentration of the enzyme was further reduced, potato starch lost in its effectiveness. Corn starch lost in effectiveness at all the lower enzyme concentrations tested.

A comparison of the data shown on gloss and sizing viscosity in Figure 2, with the strength properties in Figure 1, provides a possible explanation for these results. Viscosities of 30 centipoises and above

were associated with the lower results in physical testing with both varieties of starch. Appreciably higher gloss readings were also associated with the lower physical test results.

A possible explanation for the results shown in these two figures and consistent with the published material dealing with surface sizing is that the potato starch, which was quite fluid when converted with ¼% enzyme, was able to penetrate the sheet to supplement fiber to fiber bonding and consequently improve strength characteristics. The smaller increase in strength brought about by both starches, where low concentrations of enzyme had caused higher viscosities and higher gloss readings, was apparently due to the fact that the sizing solution tended to remain on the surface of the sheet where fiber bonding was not supplemented. The starch which was present in higher viscosity applications seemed to be deposited in the form of a surface film.

The steady increase in physical properties shown by potato starch sized sheets in Figure 1 may be explained by the fact that the final viscosity was less than 25 centipoises at ¼% enzyme, ½% enzyme, and 1% enzyme. The decreasing percentages of enzyme should bring about a proportionally smaller degree of degradation or hydrolysis of the starch molecules. This smaller degree of degradation would leave the maximum of inherent strength within the starch molecules.

Conclusion:

In surface sizing, enzyme conversion with the smallest amount of enzyme which will produce the desired viscosity of sizing solution will produce a sizing solution with maximum ability to supplement the strength of the sheet produced.

Viscosities of less than 25 centipoises, as measured with the Brookfield viscosimeter, seem to provide for maximum penetration and

strength of the finished sheet.

The results of this work, under the conditions and limitations outlined in this report, seem to indicate that potato starch has the property of reaching suitable sizing viscosities with a smaller amount of molecular degradation than does corn starch.

Kalamazoo, Michigan
24 May 1961

Edward E. Stephenson Jr.

Edward E. Stephenson Jr.

APPENDIX I

Average Property Values at Varying Enzyme Concentrations of Potato Starch and Corn Starch

Starch	% Enzyme on Starch	Mullen psi	Fold MD MIT	Elongation MD %	Tensile MD lb/15mm	Brightness %	Gloss %	Viscosi Cp
Base Stock	0	32.5	282	2.9	20.0	83.0	7.0	---
Potato	1	39.7	447	2.7	22.5	82.4	8.7	15
Potato	½	46.0	582	3.3	25.2	82.6	10.4	15
Potato	¼	49.5	611	3.0	25.8	82.8	13.2	25
Potato	1/8	38.2	287	---	20.5	---	17.4	53
Corn	1	39.6	391	2.6	22.5	81.7	10.4	27
Corn	½	37.0	392	---	20.7	---	21.3	30
Corn	¼	37.7	372	---	20.9	---	24.6	71

All MIT folds are expressed as double folds per 15 mm strip with a 1 kg. load.

Brightness and Gloss were recorded on a Photovolt instrument.

Viscosities are Brookfield viscosities, expressed in centipoises at 54°C, number 1 spindle and 100 rpm.

APPENDIX II

The author wishes to express his thanks and appreciation to the following individuals and companies for making this work possible through guidance and donation of materials:

Dr. A. H. Nadelman, Head of the Curriculum of Pulp and Paper Technology, Western Michigan College, Kalamazoo, Michigan.

Mr. D. V. Lunt, Assistant Professor of Pulp and Paper Technology, Western Michigan College, Kalamazoo, Michigan.

American Key Products Company, New York, N. Y.

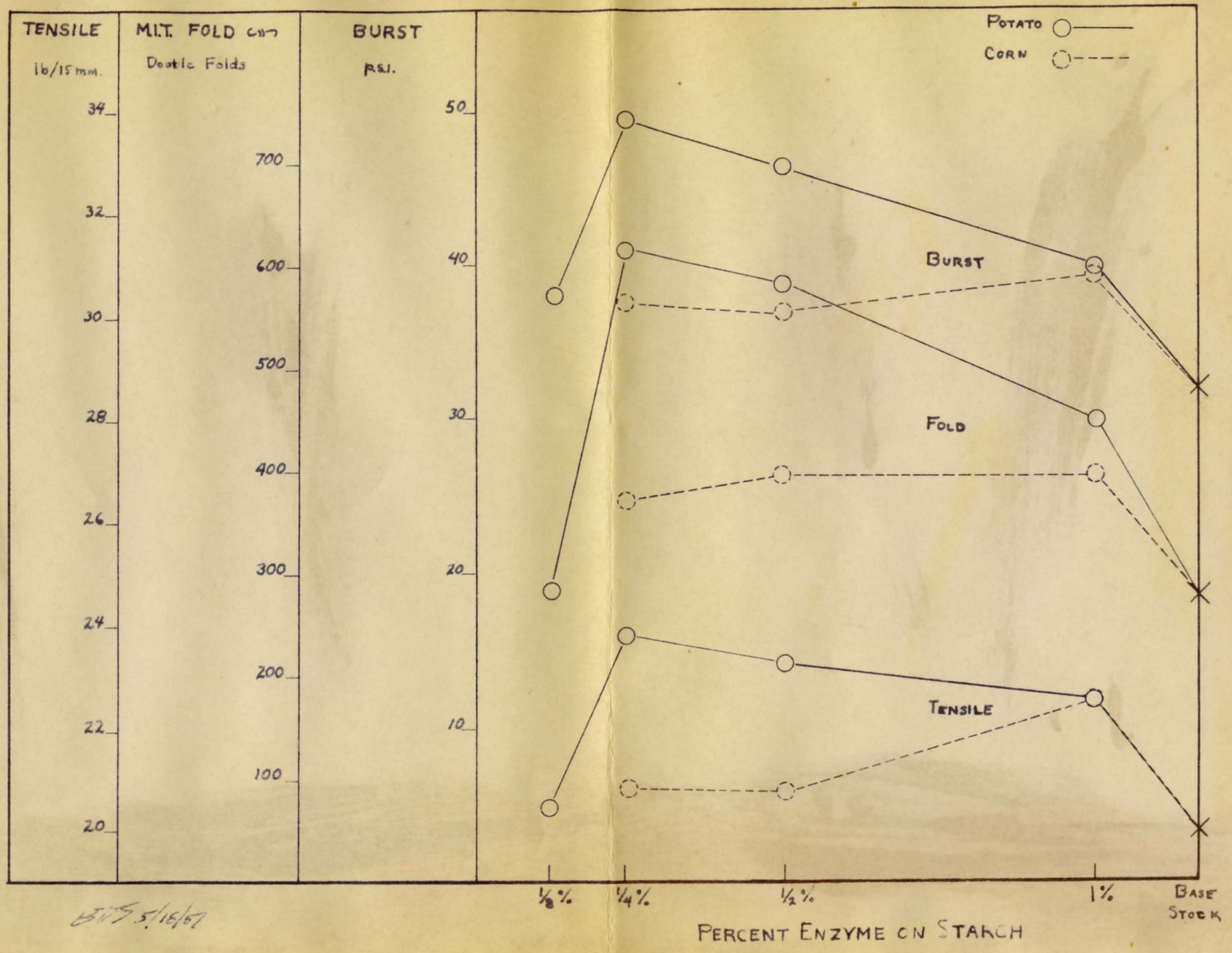
St. Anthony Starch Company, St. Anthony, Idaho.

Lee PaperCompany, Vicksburg, Michigan

St. Regis Paper Company, Kalamazoo, Michigan

Surface Sizing

Effect of Enzyme Concentration on Sheet Strength

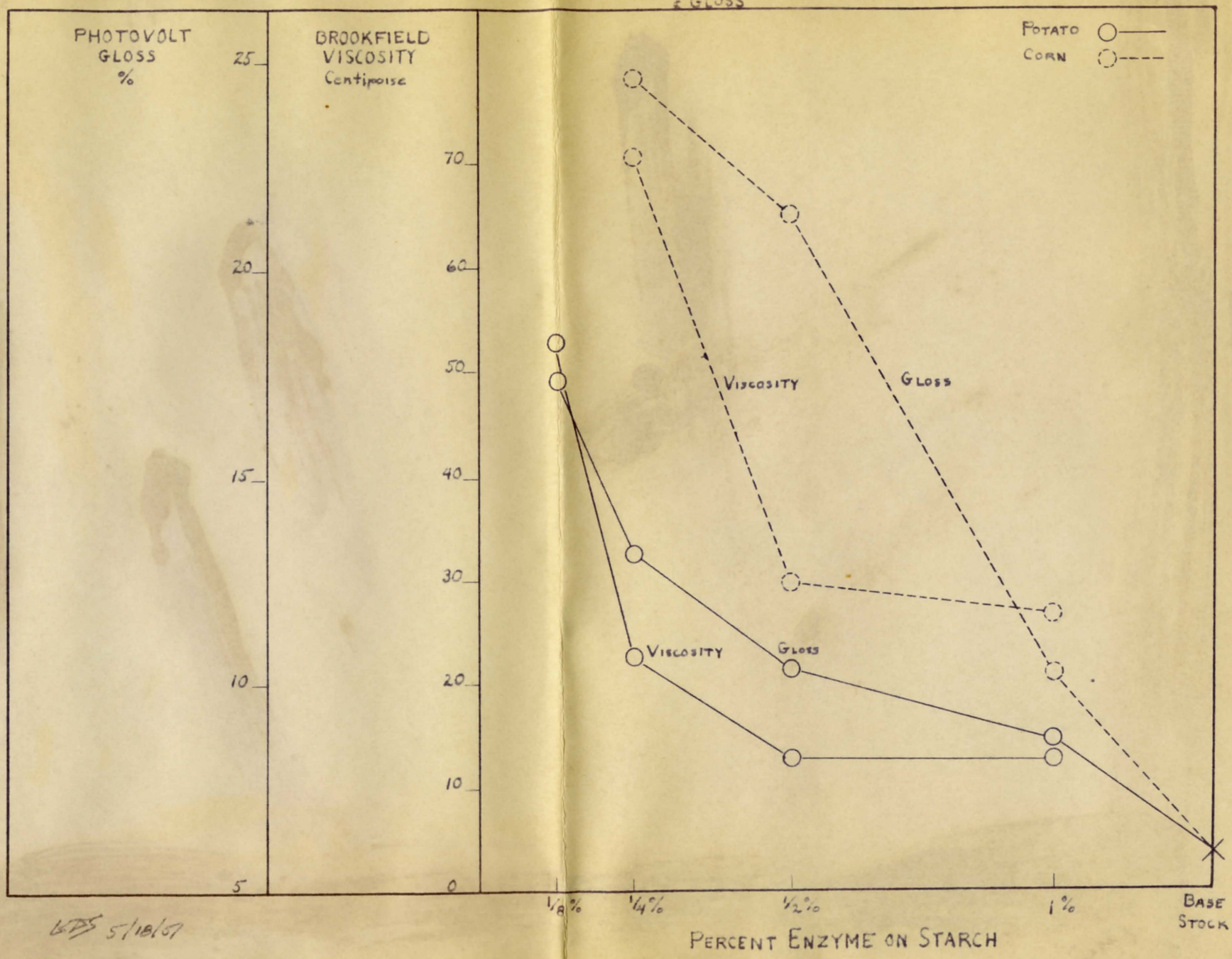


BTS 5/16/67

Figure 1.

Surface Sizing

Effect of Enzyme Concentration on Viscosity & Gloss



GDS 5/18/07

Figure 2