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A Study of the Relationship between the Sugar Content of Enzyme Converted Starch and Pick Values of a Coated Sheet

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A STUDY OF THE RELATIONSHIP
BETWEEN THE SUGAR CONTENT OF
ENZYME CONVERTED STARCH AND
PICK VALUES OF A COATED SHEET

BY

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A Thesis submitted to the Faculty
of the Paper Technology Department
in partial fulfillment of the
Degree of Bachelor of Science

Western Michigan University

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HISTORICAL BACKGROUND

"By far the most commonly used adhesive in paper coating is cornstarch, representing about 74% (140,000 tons yearly) of all binders used, according to a survey made by the 'Paper Trade Journal' (1). Because of the wide use of this product all that is possible should be known about it.

In the case of this research the most critical phase will be the conversion and reducing sugars control. It is basic to understand the characteristics of starch if its behavior is to be controlled.

A granule of starch is an association of amylose and amylopectin. This association is crystalline in nature and makes the granule insoluble in water and resistant to other materials. In order to use starch for coating purposes, it is necessary to disperse this granule. Once dissociation is accomplished, re-association must be prevented.

Dissociation of starch can be carried out in several ways; the most common is enzyme conversion. Enzyme conversion has two advantages over other conversion methods; it is economical and, with enzyme it is somewhat easy to control the degree of conversion (2).

A common procedure is to first slurry the starch at the desired solids level. Then the appropriate amount of enzyme is

added to be followed by a suitable heat converting cycle. "... a typical cycle is as follows:

Heat to 170 degrees F. in 20 minutes
Hold at 170 degrees F. for 30 minutes
Heat to 205 degrees F. in 12 minutes
Hold at 205 degrees F. for 30 minutes" (3)

The principle purpose of slurring the starch is to disperse it in a medium and to obtain the required solids level. Upon heating the starch begins to swell. In a water suspension the non-linear portion of the starch granule becomes quite susceptible to water penetration. This results in swelling. As the temperature of the system is raised the granules continue to swell and soon become very large with indistinct boundaries. This is known as the gelatinization state. Less vulnerable to this state are the micelle regions where linear molecules and linear fractions of the amylopectin are drawn together in crystal-like forms. These regions resist fluid penetration and are generally accredited with rendering rigidity and strength to the starch molecule and therefore stability. The non-linear fraction is amylopectin, a highly branched network. Together the two portions make up a granule which is able to dissociate yet retain a degree of strength.

It is at the gelatinous state that the enzyme, α -amylase, acts the best. It acts at random, through hydrolysis, on the 1,4-a-glucoside linkages of the starch system. Some believe that

two stages exist in the enzyme conversion. "The first stage of the liquefaction with enzyme is similar to the effect which can be obtained by vigorous mechanical shearing of a starch paste". "Relatively little dextrinization or formation of reducing sugars can be detected by common procedures. During the second stage of enzyme action, large fission products are formed and the amylose chains are broken up at random into fragments of high molecular weights." Maryanski (4) says "It is thought the action of amylase on the amylose fraction of the starch is random, so that long chains are attacked indiscriminately with the production of shorter chains. These, in turn, are broken down until the action of the amylase is stopped. The action of alpha amylase on the amylopectin starch fraction is also a random cleavage with the enzyme being able to cleave branch substrate molecules between the branch points " (5).

Enzymes, as biocatalysts, could be classified into the general stages of liquefying, dextrinizing, and saccharifying. "Liquefaction of starch is considered to be a reduction of the starch granule to units of higher dispersability without the production of degradation products such as dextrans or sugars. Dextrinization involves a splitting of the individual starch molecules into molecules of smaller size, without the production of sugars. Saccharification is a splitting of the starch molecule resulting in the production of sugars " (6). Enzyme conversions will always contain all three of these factors with saccharification being held to a minimum.

If there is a lack of control and a relatively large amount of maltose and other low molecular weight polysaccharides, "reducing sugars", are produced, the starch product will suffer a loss in viscosity and a decrease in the binding power as an adhesive.

"It is generally felt that reducing sugars should be kept below 3 percent in any converted paste" (7). The amount and purity of the enzyme are primary factors. Alpha amylase is the desired catalyst while beta amylase is believed to be a contaminant producing principally reducing sugars.

Enzyme is not used up but must be stopped. If allowed to continue functioning the whole system will be reduced to sugars. The two most common methods employed to "kill" the enzyme are by temperature increases and through use of certain chemical additions. The kill temperature usually ranges between 200 - 220 degrees F. with a hold period. "A good rule of thumb is 15 minutes plus one additional minute for each percent solids over 15 percent." (8) Chemical deactivation is also used extensively to stop enzyme conversions. Commonly used are cupric sulfate, cupric nitrate, and mercuric or stannous chloride which lower the pH of the system enough below the stable value of 7.0 pH to be fatal to the enzyme.

Before proceeding to the coating itself, something should be said concerning other factors affecting enzyme conversions. Of the two factions of starch, amylose and amylopectin, the amylopectin is believed to be of the greater value. Its bushy structure enables

it to provide a greater degree of binding power and it is much more resistant to retrogradation tendencies. The amylose fractions are more likely to associate and revert to an insoluble state. This results in a loss of binding power and a great increase in viscosity.

Aside from the starch and enzyme it appears that the most important variable is pH. If allowed to vary too much above or below 7.0, the effect of the enzyme falls off rapidly. Temperature control and sufficient agitation are also important variables.

Starch, as a coating additive, is primarily an adhesive. Two of the main requirements in coating are; good water-binding capacity and pigment binding power. The former insures good coverage of the base sheet while the latter insures good coating to sheet adhesion plus good binding between pigment particles. Starches have these qualities although normally conversion is needed to reduce the viscosity to suitable values. "The conversion of starches with enzymes has the objective of maintaining as much of the water and pigment-binding power of native starches as possible and at the same time reducing the viscosity so that the coating mixture will have the proper rheological properties " (9).

For starch-clay coating mixtures it is generally accepted that the starch addition should be made while the starch is still at relatively high temperatures. This insures better pigment dispersion, a lower final viscosity of the coating, and faster equilibrium conditions. Viscosity, pH, and solids content are three important

factors in a finished starch coating. Lower viscosities result in a binding power loss. pH affects binding power, penetration of adhesive into the paper, and flow. Solids contents are usually at a maximum for a given viscosity to obtain optimum color and retention qualities.

The basics of the coating mixture to be considered here are starch and clay. Starch has already been discussed -- it is the most prominent binder in the industry. Likewise for clay -- it is the most prominent pigment in use. Its color control and coating viscosity characteristics have been highly refined to suit industrial needs. It is relatively cheap, easy to obtain, and is easily augmented to satisfy specific demands. Only the cost of application is disadvantageous.

The theme of this research is to determine as near as possible the effect of the sugar content in the starch binder of a coating. The coating make-up will not be at all concerned with brightness, opacity, etc., but primarily with pick effects. This test will reflect printing qualities of the paper. Time necessitates the neglect of other factors which may be of critical value; e.g., the paper and its finish.

Some work done, previous to this paper but relative to its topic, has yielded the following results:

Table A

Reducing Sugars
Found in a Typical Enzyme Conversion
of Corn Starch at 25% Solids

	% Composition By Weight (D.B.)	Dextrose Equivalent Contributed by Each Polysaccharide
Monosaccharides	---	---
Disaccharides	0.2	0.12
Trisaccharides	0.2	0.08
Tetrasaccharides	0.2	0.06
Pentasaccharides	0.2	0.05
Hexasaccharides	0.6	0.12
Heptasaccharides	0.6	0.10
Octasaccharides	0.3	0.04
Nonasaccharides & higher	97.7	0.13
Total Dextrose Equivalent (Reducing Sugars Dry Basis)		0.7

Conversion Viscosity of 50 Brookfield Centipoises at 20 rpm and 200 degrees immediately after conversion. (10).

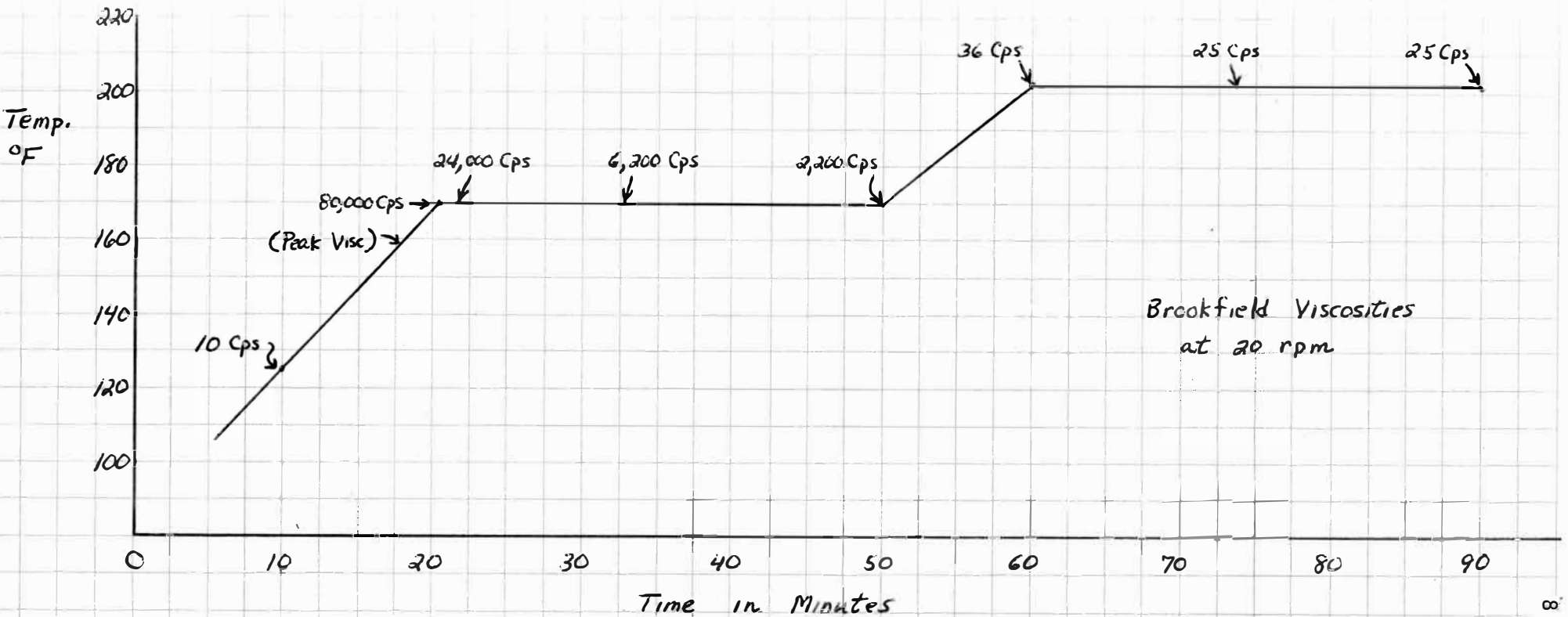
* * *

Most data makes it obvious that as the percent of enzyme on starch increases the viscosity of the paste decreases at a very fast rate.

e.g., % of enzyme on starch	.2	.3	.4	.5	.6	.8	1.0
Brookfield viscosity at 80 deg. F. & 100 rpm (cp.)	25,000	7,000	2,500	950	700	250	95

for corn starch @ 25% conc. with a holding
period of 30 min. @ 170 deg. F. (11)

Fig. 1 - Enzyme Conversion at 25% solids, 0.15% Amylase Enzyme (12)



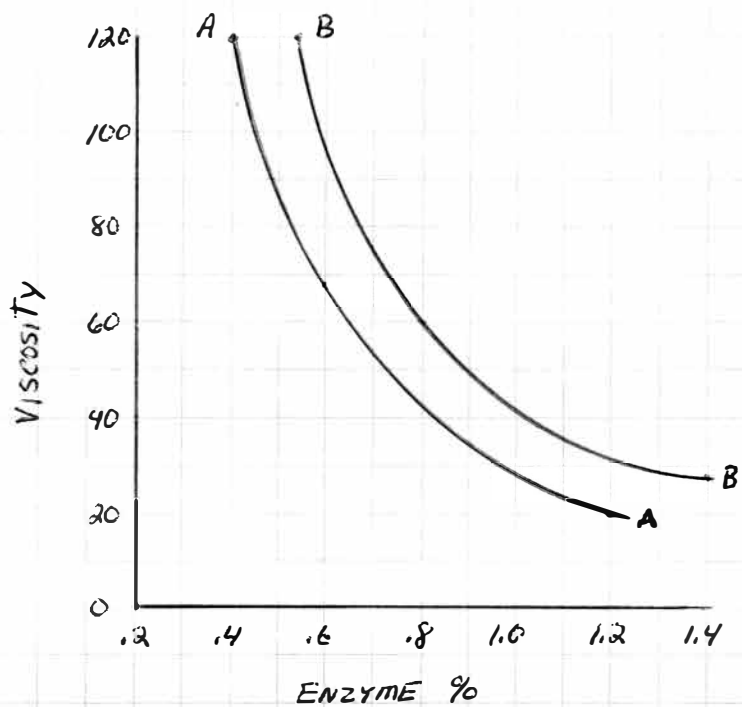


Fig. 2 (LEFT)

Effect on viscosity when starch is converted with enzymes

(A) Predominantly alpha amylase used, (B) Predominantly beta amylase used.

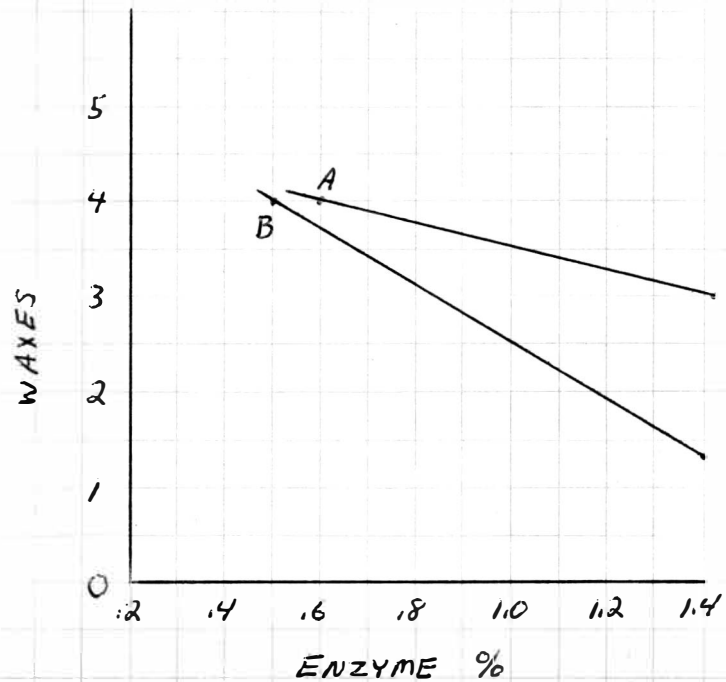


Fig. 3 (RIGHT)

Effect on wax test when starch is converted with enzyme

(A) Predominantly alpha amylase used, (B) Predominantly beta amylase used. (13)

EXPERIMENTAL RESEARCH

ABSTRACT

The purpose of this experiment was to convert starch by the use of enzyme. The conversions were carried out in a way to produce variations in the reducing sugar contents of the cooked starch. These starches were then applied as the adhesive in a coating mixture. Draw downs were made using the variety of coatings and then the sheets were tested for surface strength. The IGT Pick Tester was used. It was hoped that a definite relationship between sugar contents and pick values could be obtained. This, however, was not the case and the experiment would have to be considered inconclusive. Nevertheless, it was observed that at the greater enzyme additions and therefore the higher sugar contents the cooked starch was much less viscous. This was just an observation, though, and immaterial to the initial objective. It could possibly be an area for further research.

OBJECTIVE

The object of this experiment was to enzymatically convert starch to a variety of reducing sugar contents. These starches would then become the adhesive components of a simple coating make-up. Draw downs will be made using these coatings and the

sheets tested for surface strength with the IGT Pick Tester. A relationship will be looked for between the sugar content of the adhesive and the pick value of the coated sheet.

DISCUSSION

Enzymatic conversion of starch requires a relatively effective temperature control and a good system for agitation. The first attempt at the starch cook was made using the oil bath mechanism. This system enables excellent temperature control and allows the possibility of producing a number of cooks simultaneously. The method, however, proved to be a very cumbersome, slow and gave insufficient agitation. Problems were encountered with the starch setting-up inside the bombs. Therefore, it became necessary to use the common lab procedure of gas burner, double-pan cooker, and propeller mixing. All starch batches were made up with 113 grams starch and 1017 grams water -- or 10 percent solids. Taking into account the moisture in the starch these batches were actually made up at 7.15 percent solids. The starch was added to the water slowly while mixing. After allowing time for sufficient dispersion the enzyme was added and heat applied. The cooking temperature of 150 - 170 degrees F. was achieved in about 10 minutes and held for one hour. The enzyme kill included both heat and chemical (mercuric chloride). All batches were run using the same cycle.

Heat to 150 - 170 degrees F. in 10 minutes
 Hold at 150 - 170 degrees F. for 60 minutes
 Heat to 200 degrees F. in 10 minutes
 Add Mercuric Chloride
 Hold at 200 degrees F. for 20 minutes

There are several disadvantages in using this method of starch preparation. Scumming would invariably occur on the surface of the mixture where the cooler air could react with the hot starch. Temperature control required constant attention. The mixer apparatus also proved insufficient especially during the gel period of the starch cook. It was observed that with the higher enzyme additions viscosities were lower, mixing was more efficient, and less scumming occurred.

Sugar content variations were achieved by the amount of enzyme added. Since the enzyme used was in concentrated form and liquid it was necessary to dilute it. The dilution factor was 1000:1, water to enzyme. Enzyme additions and finished cook solids contents and sugar contents are summarized in the following table (Table I).

TABLE I

<u>Cook No.</u>	<u>Enzyme (ml)</u>	<u>Solids (%)</u>	<u>Sugars % (as dextrose)</u>
1.	1.00	13.8	1.4
2.	2.02	10.7	2.9
3.	2.20	12.0	2.8
4.	4.60	11.9	4.9
5.	5.00	11.6	5.8
6.	7.00	10.8	7.4
7.	7.80	10.9	7.7
8.	9.80	10.5	8.3

The relationship between enzyme additions and sugar contents is illustrated in GRAPH I (See p. 17). It represents the expected type of curve.

The sugar contents were found using "Schoorl's Determination of Reducing Sugars in Enzyme Converted Starch." The test involves obtaining a 2.0 gram sample of the converted paste. This is put into a 250 ml Erlenmeyer flask followed by 10 ml additions of Fehling's Solutions numbers 1 and 2. Thirty ml of distilled water is then added. A blank is also prepared in the same way excluding the paste sample. The flasks are covered and brought to a boil in three minutes. A gentle boil is maintained for two minutes followed by quick cooling to room temperature. Then, in order, add 20 ml of 15 percent KI and 10 ml of 30 percent H₂SO₄. Titrate immediately with N/10 Na₂S₂O₃ to a cream colored end point. The titration difference between that for the paste sample and the blank gives the ml of N/10 Na₂S₂O₃ equivalent to the reduced copper and the reducibles calculated as dextrose. This value is obtained from a table. The calculation for percent sugars is as follows:

$$\% \text{ reducing sugars} = \frac{\text{gm dextrose} \times 100}{\text{wt. of sample} \times \% \text{ solids}}$$

Example: for a 2.0 gm sample

$$\begin{array}{l} \text{titer of blank} \quad 38.0 \text{ ml N/10 Na}_2\text{S}_2\text{O}_3 \\ \text{titer of sample} \quad \underline{35.1 \text{ ml}} \\ \qquad \qquad \qquad 2.9 \text{ ml} \end{array}$$

from table 2.9 = .0091 gm dextrose

$$\% \text{ reducing sugars} = \frac{.0091 \times 100}{2.0 \times .25} = 1.82$$

English Clay was used as the pigment make-up. The dispersant was TSPP. A common non-complex coating was desired to facilitate lab methods. The coating was made up at 40 percent solids for the purpose of simplifying dispersion and making draw downs. The starch was added while hot and draw downs made while the entire coating was still hot. Four sheets of paper were coated with each batch. All sheets were conditioned in a temperature and humidity controlled room prior to the surface strength tests. IGT pick tests were run to determine the effect of the various sugar contents of the starch adhesive. The results of these tests are given in Table II and illustrated with respect to sugar content and enzyme additions in Graphs II and III respectively. (see pp. 18 & 19)

TABLE II

<u>Sample No.</u>	<u>Ink No.</u>	<u>IGT Scale</u>	<u>ft./min. (Pres.50)</u>	<u>ft./min.(Pres.25)</u>
Base Sheet	7	B	560	----
1	7	B	265	----
2	7	B	580	----
3	7	B	510	270
4	7	B	550	210
5	7	B	220	----
6	7	B	565	230
7	7	B	230	----
8	7	B	430	----

It was hoped that one ink and one IGT setting would permit acceptable tests for all of the sheets. It can be seen from Table II, however, that an IGT pressure variation occurred. This was necessary because samples 3, 4, and 6 gave very indeterminate tests with a pressure of 50 kg. With a pressure of 25 kg. these particular samples picked quite clearly although the pick itself was very fine.

Theoretically, the correct results could be anticipated. As the sugar content of the adhesive increases, the binding power should decrease. Therefore, the pick values should be lower with those sheets coated with the higher sugar content adhesives. Percent solids could also make a difference when related to the adhesive strength of the starch. At high solids coating and low adhesive strengths pick values would be very low.

The pick results of this experiment do not correspond to theory and are very poor and inconclusive. Graph IV plots ideal points from the collected data and illustrates what should have happened. Graphs II and III illustrate what did happen. No specific reason is available for the failure to achieve the expected results. Possible effects are draw down technique, temperature variations during the starch cook resulting in unusual activity of the enzyme, poor agitation especially during the more viscous period of the cook, poor representative samples for testing, and inherent variations of the IGT Pick Tester -- and the ink in particular.

CONCLUSION

The results did not satisfy the object of this experiment. It was hoped that the trials would be able to demonstrate a definite relationship between percent reducing sugars in the starch and pick values of coated papers using this starch, but this correlation could not be established.

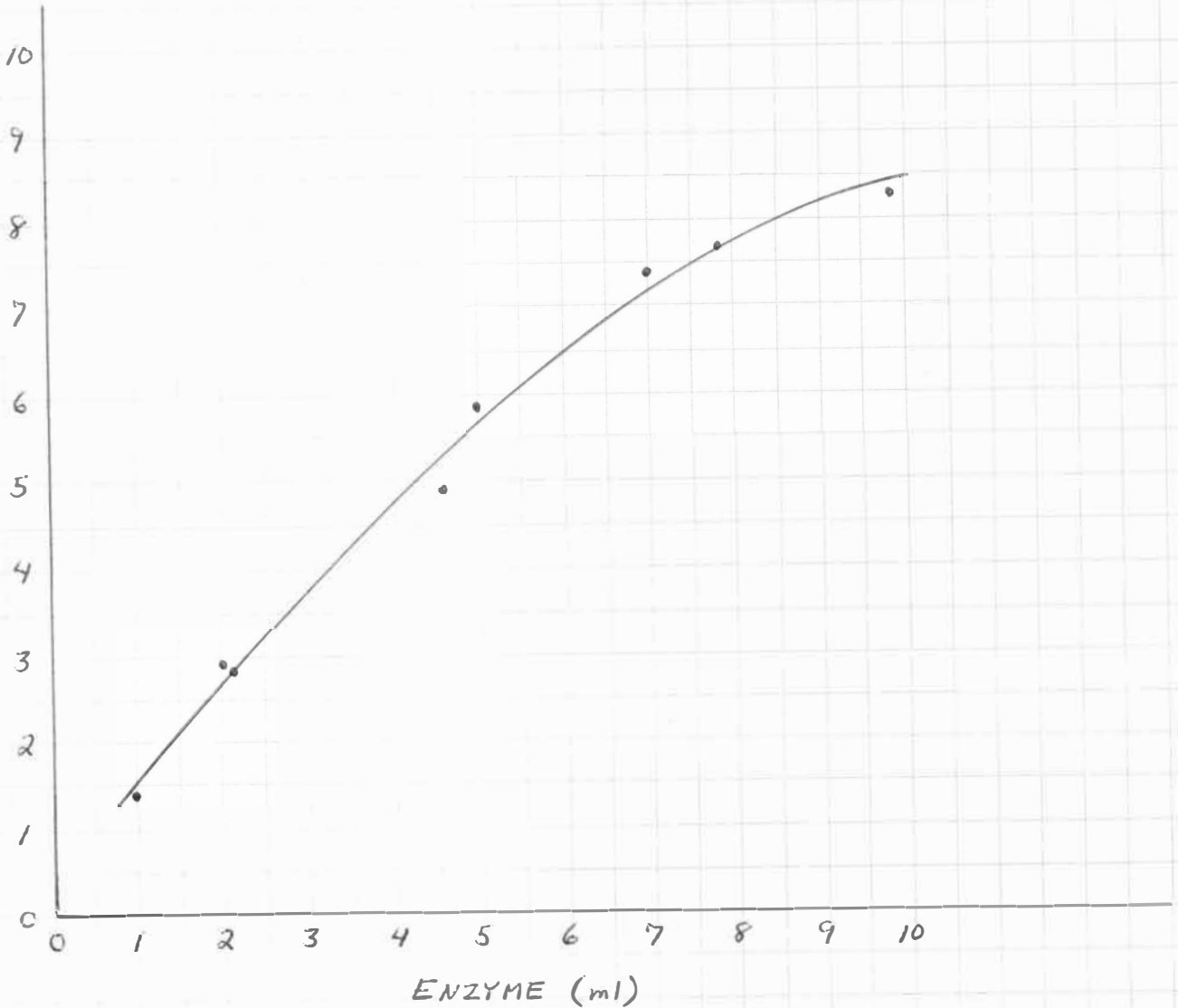
RECOMMENDATIONS

If this experimental analysis were to be extended, it would be advisable to do the following:

1. Find a heat source that could effectively maintain temperature throughout a cook.
2. If possible, locate a double propeller mixer or find a more efficient type of mixer. (One that will continue to operate effectively even during the gel period of a starch cook.)
3. Place more emphasis on viscosity.
4. Make draw downs with the coating at one particular temperature in each case and also run a solids test on the coating. During this research solids tests were run on the starch slurry but not on the coating mixture. This may have been an expensive oversight.

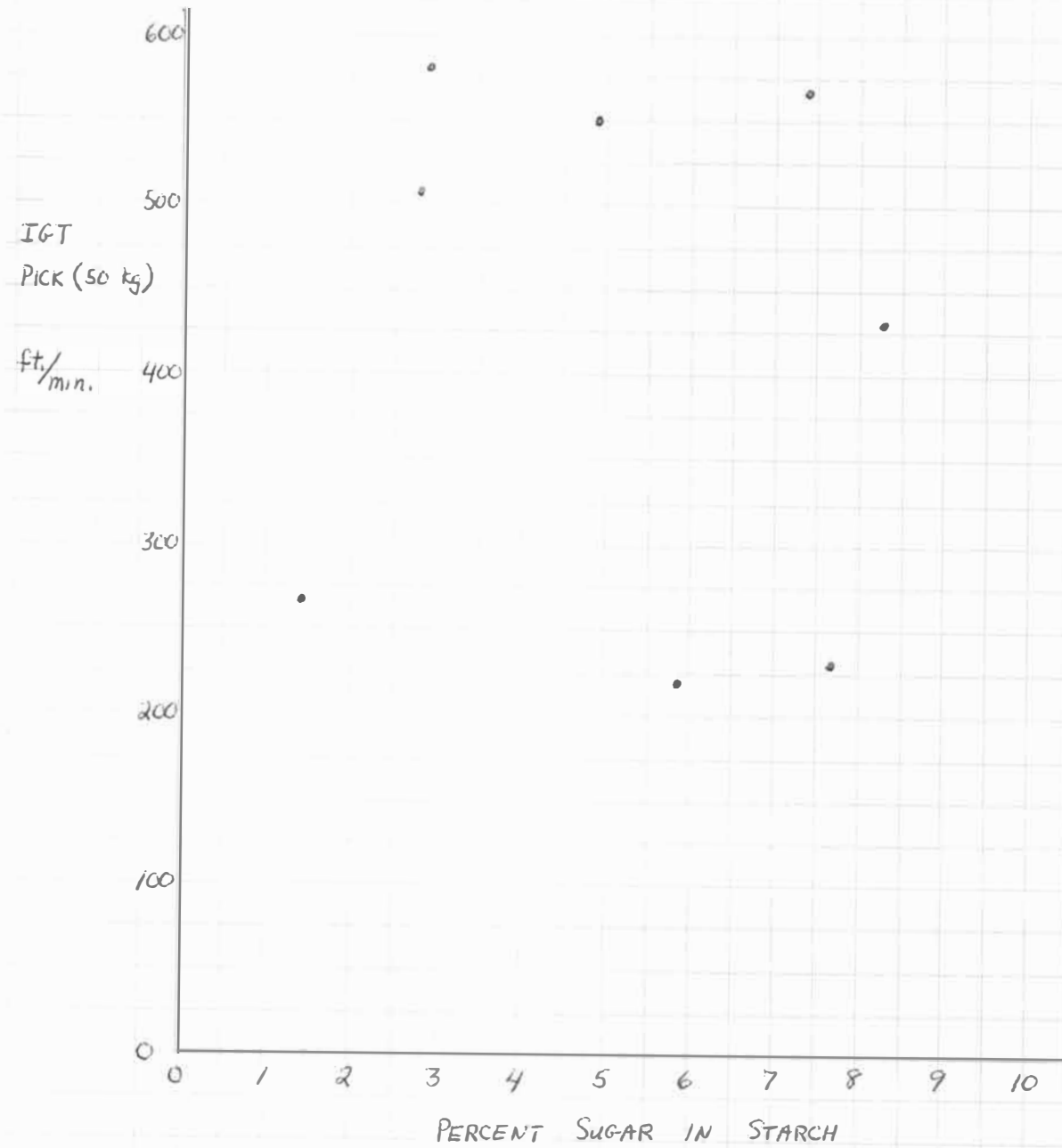
GRAPH I

PERCENT SUGAR VS ENZYME ADDITIONS

PERCENT
SUGAR

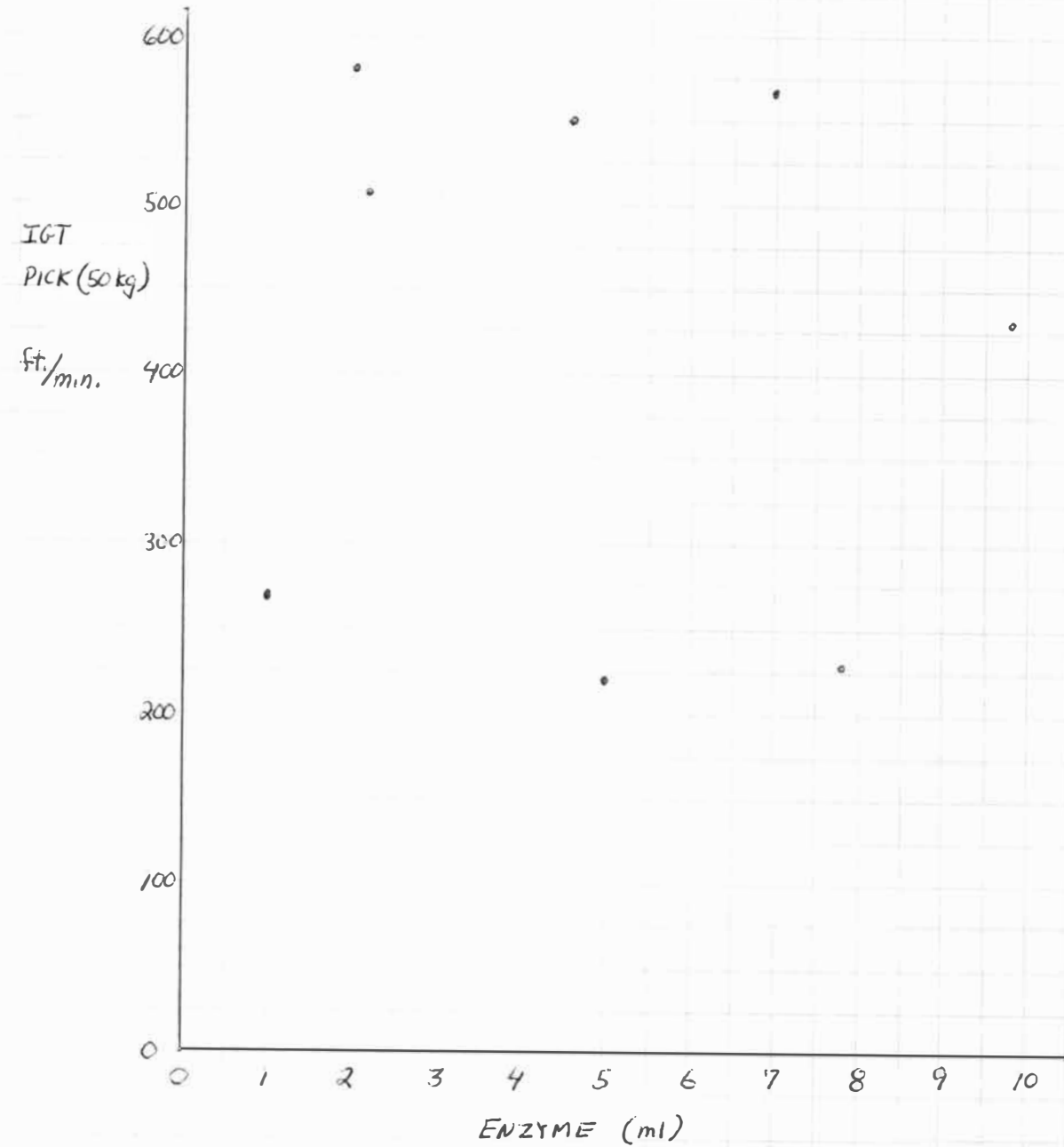
GRAPH II

PERCENT SUGAR VS IGT PICK



GRAPH III

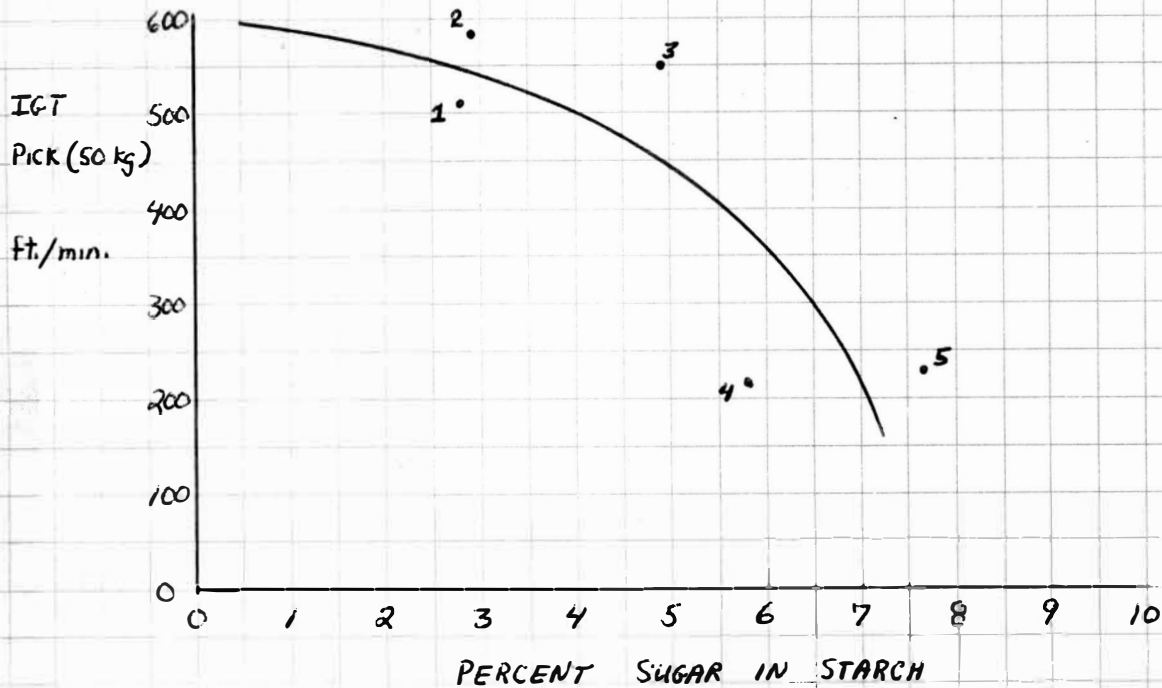
ENZYME VS IGT PICK



GRAPH IV

IDEAL PLOT

PERCENT SUGAR vs IGT PICKS



CORRESPONDING TABLE

<u>POINT NO.</u>	<u>RELATED COOK NO.</u>	<u>% SUGAR</u>	<u>APPROPRIATE PICK VALUE</u>
1	3	2.8	510
2	2	2.9	580
3	4	4.9	550
4	5	5.8	220
5	7	7.7	230

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HELPFUL SOURCES

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