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## Differences in Picking Properties Between Casein and Soya Proteins

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DIFFERENCES IN PICKING PROPERTIES BETWEEN  
CASEIN AND SOYA PROTEINS |

by

Shinya Takekawa  
/l

A Thesis Presented to the  
Faculty of the Paper Technology Department  
in Partial Fulfillment of  
the Requirement for the  
Degree of Bachelor of Science

Western Michigan University

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Shinya Takekawa

## ABSTRACT

In this paper, the various picking properties are discussed at first, then in the experiment the fundamental differences between soya protein and casein in picking strength were studied.

Since it is considered that the penetration of the adhesives in a coating mixture into the base paper is important in picking, the picking strength of casein and soya protein were evaluated in functions of the beating level, sizing level and the amount of the adhesives. Whole experimental data were treated with the statistical method.

The results indicate that with the Wax test, the soya protein and casein have almost equal picking strength, however with IGT test, the values of the soya protein are less than that of casein by around three percent. It is also found that the IGT test evaluation in picking is better than the Wax test.

## INTRODUCTION

It is well known that the sheet needs a good surface strength to give good printing. The weak surface strength causes not only inferior printing on sheets but also inferior running on presses, particularly at high speed printing machines.

Although some troubles concerning the surface strength are decreasing because of the great improvement of the adhesives, we still have many problems. We can improve its surface strength with increased amounts of adhesives, but it is not only not economical, but also it affects badly the other printability or properties of the sheets.

It may be concluded that the paper makers are looking for the adhesives that have the following:<sup>1</sup>

1. High binding power proportional to the total cost of the adhesives. (Purchase price plus expense for preparation.)
2. High barrier efficiency.
3. Best properties to meet the end use of the surface-treated products.

In this paper, the various picking properties are discussed as the surface strength and the adhesive properties of casein and isolated soy proteins in coated papers are studied. Because of unstable price in market and quality of casein, the isolated soy proteins seem to have a bright future, because they have the advantage of close chemical control in large modern chemical plants.

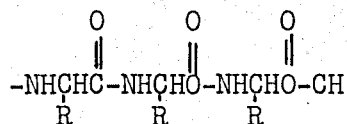
## I. CASEIN AND ISOLATED SOY PROTEIN

There are two types of proteins in paper coating industry, casein and isolated soy protein. They will be discussed individually.

### Casein

Caseins have been used in the coating industry for a long time in spite of some disadvantages such as difficulties to make high solids percentages of color, and the brittleness of film. However, they have advantages such as very good adhesive strength and pigment binding power, and easily attainable insolubility.

Casein is a globular amphoteric phospho-protein, heterogeneous in nature, and compound of polypeptides. The simple proteins are linear copolymers of  $\alpha$ -amino acids in which the units are linked by peptide (amide) linkages.



where R may be  $-\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{C}_6\text{H}_5$ ,  $-(\text{CH}_2)_4-$ ,  $\text{NH}_2$ , etc.

Since proteins contain basic amino groups and acidic carboxyl groups, they have amphoteric properties. Thus, casein forms soluble salts with the alkalies, and the acids such as  $\alpha$ -hydroxy acids. Casein is also very reactive with organic reagents such as formaldehyde and acid anhydrides. They form crosslinks between two parts of the molecules.

From the physical standpoint of view, the strong adhesive power of casein comes from its high degree of polarity.

Some physical constants and properties are as follows:<sup>2</sup>

Molecular weight	33,600-375,000
Particle shape	Approx. globular
Particle diam. (in milk)	20-140 $\mu$
Isoelectric point	4.6
Dielectric constant	8.0
Equilibrium moisture content at 25°C	8% at 20% R.H. 12% at 50% R.H. 17% at 80% R.H.
Solubility in water alone at 5°C	0.05g. per liter
at 25°C	0.11g. per liter
Specific gravity	1.21-1.31
Sodium caseinate	1.42

### Isolated Soya Proteins

In the United States, the first significant amount of soya proteins for paper coating industry became available in 1937. Since this time, great improvement has been made since the soya proteins have the distinct advantage of being processed in modern plants of chemical industry. Now the following types of commercial soya proteins are available in the market: unhydrolyzed types ("unmodified", or "undenatured"), hydrolyzed types of high, medium, low, and extra low viscosity grades, chemically modified types (acylated, hydrolyzed) and enzyme-digested types (extensively hydrolyzed, not suitable for adhesive purposes). These different types of proteins are discussed by Bain.<sup>5</sup>

Biologically, commercially used varieties of soya bean contain about 40 percent protein and 20 percent oil. The beans are cracked, dehulled, flaked, and the oil is removed by hexane extraction, before the flakes are suitable for protein productions.



It is said that soya proteins are very similar to milk casein in its properties. Soya bean proteins are of the class of proteins known as globulins. Because the molecules are very large, they do not produce "true" solutions but a colloidal solution. Soya protein is an "acidic" protein because nearly 30 percent of its weight is due to glutamic and aspartic acid. Thus, it is soluble in aqueous alkaline solutions. Other chemical groups comprising the side chains such as phenolic, hydroxyl, etc., contribute to adhesive strength characteristics of the protein.<sup>3</sup>

Some physical constants and properties of soya protein are as follows:<sup>4,5</sup>

Molecular weight		
Unhydrolyzed types		295,000-380,000
Medium-low viscosity grades		90,000-110,000
Low viscosity grades		50,000- 60,000
Particle shape		
Unhydrolyzed types		a slightly flattened sphere
Medium-low viscosity grades		football-like in shape
Low viscosity grades		rodlike in shape

The properties of commercially available hydrolyzed soya proteins:

Moisture	8 -10%
Protein (as shipped)	87-90%
pH of aqueous slurry	4 - 5
Ash	< 2.5
Petroleum ether-soluble material	< 0.3
Particle size	to pass 40-mesh screen
Dry storage stability	excellent

#### Differences in Picking Strength Between Casein and Soya Protein

The differences in Dennison Wax tests among various adhesives including casein and soya protein are shown in a book.<sup>17</sup> However, the conditions of the experiment are not available. These results, however, indicate that soya protein is approximately equal to casein in Dennison Wax tests.

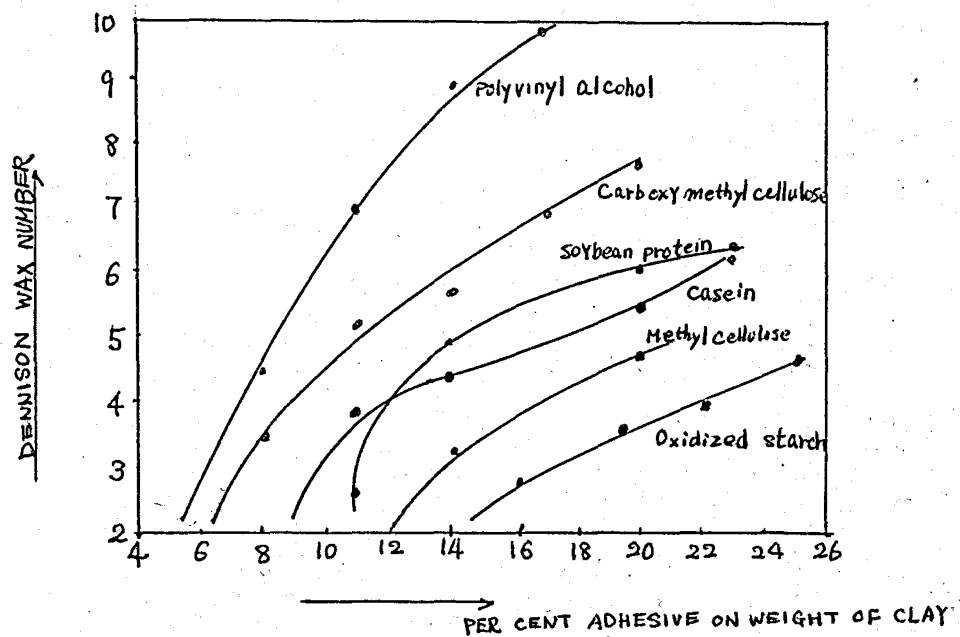


FIG. I-1. Comparison of adhesives for pigment bonding strength

## II. PICKING PROPERTIES AND ITS TESTING

According to the recent definitions of terms and illustrations that have been prepared by the Surface Strength Subcommittee of the Tappi Graphic Arts Committee, the following 12 terms are defined in picking:<sup>6</sup>

1. Surface Strength of Paper
2. Picking
3. Dry Pick
4. Wet Pick
5. Fiber Pick
6. Coating Pick
7. Blister Pick
8. Rupture Pick
9. Wet Rub
10. Piling
11. Linting
12. Dusting

Since the picking properties in paper are affected by many factors as they are discussed later, it is very difficult to determine the surface strength with one testing instrument. The simplest method is the Dennison Wax test. This method is useful if we evaluate the same kinds of sheets, however, it is said that this method is not useful if we evaluate the different kinds of sheets such as fine papers and coated papers. Because in printing, the picking is affected not only by these static picking in paper, but also by the speed of printing machines and by the tackiness of ink. The best way to evaluate the picking of the sheet is to print them. Thus, the evaluation of the surface strength is more useful in IGT, LFT and Hercules-Brookfield where the surface strength is measured dynamically.

The other disadvantages of the Dennison Wax test are as follows:<sup>7</sup>

1. In latex coating, the waxes are solubilized by the adhesive vehicle so that the adhesive strength of latex coating can not be accurately determined.

2. The strength of the coating can not defined in fundamental units.

Although there are some limitations which are described by Hemstock,<sup>7</sup> it is said that the IGT printability tester can be successfully used for measuring the pick strength of pigment coatings. Some limitations are as follows:

1. The picking strength of coating is expressed only as a proportionality of a viscosity-velocity product.
2. Some errors come from variations in backing and specimen roughness, undriven ink disk, the stretching of specimen, and oil penetrations into the specimen.

As is was mentioned before, there are many characters of picking. Expressing it another way, the bond or picking properties of paper is a function of:<sup>8</sup>

1. Strength of base stock, rupturing fiber-to-fiber bonds when a stress has been placed upon the product.
2. Adhesion of coating to stock, or strength of glue and/or its adhesion to coated and uncoated surfaces.
3. Internal strength of coating.

In this paper, the picking is restricted to express the second phenomenon. This picking may be related to the following items which are going to be discussed later:

1. Water retention properties in coated paper.
2. Strength of sizing of the base paper.
3. Density of the base paper.
4. Viscosity and solid percent of the coating color.
5. Drying rate of the coating.
6. Mixture of adhesives such as casein or soya protein to latex adhesives.

### III. FACTORS OF THE PICKING

The most important factor that affects on the picking is the binder migration in the coated sheet of the paper. The binder migration is the process in which the coating color is set by drying. It is important to know these migration properties from the stand points of not only economical usage of the binder, but also the adsorbency and pattern of the finished products. The previously listed five factors are related to this binder migration particularly. These will be discussed in the given order.

#### 1. Water retention properties in coated paper.

The binder migration has very close relationship with water retention of coatings. Frost showed the relationship between the Dennison Wax test and water retention using starch.<sup>9</sup> It was indicated that because of this excellent relationship shown is Fig. 1, it is possible to predict a wax test by measuring water retention before a sheet is coated.

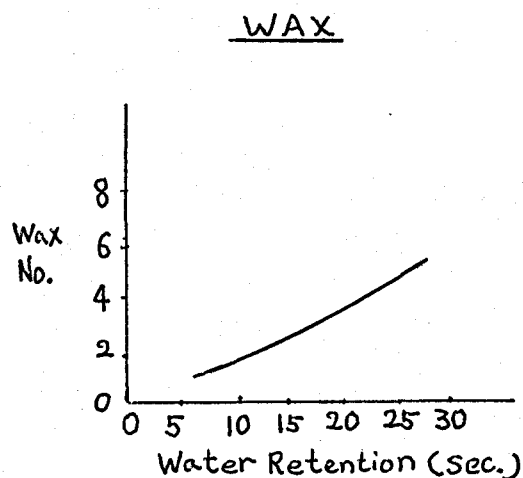


FIG. 1

In another study, Hagerman studied the latex which was not so great water retention that the casein or the starch had. It is also found that the picking resistance is increased as the water retention of latex is increased by adding the methyl-cellulose.<sup>10</sup>

#### 2. and 3. Strength of sizing and density of the base paper.

It is predicted that the binder migration is affected by the density of the sheet, and sizing of the sheet. In coating base paper, the application

of the internal sizing means that it not only protects from splitting or blistering which occurs between fiber bonding in coated paper, but also it controls the penetration of the adhesive of coating into the base paper. Thus, by using internal sizing, we can control the picking strength of the coated paper.

Early Casey and Libby studied the effect of density on wax test, ink receptivity, and penetration of the starch into base paper.<sup>11</sup> They concluded that although there was no significant difference in the depth of penetration on the high density and low density sheets, the wax number was appreciably increased as the density of the base paper was increased, when they used the same amount of sized paper (0.5 percent rosin and 1.25 percent alum). In different sizing level test, they found that the decrease in wax test which occurred in the low density sheets was greatest in the sheets of high rosin content, and this was explained as follows: it could be caused by differences in penetration although it might be a general weakening of the sheet brought about the rosin.

As the example of the migration of the adhesive into the base paper, Lavender studied it by using soya proteins. The coating was prepared with various cutting agents and he applied it to raw stock either the porous absorbent raw stock or the dense paper.<sup>2</sup> The results show that the porous absorbent raw stock requires approximately 25 percent more protein than the dense paper.

Adhesive Strength of Coated Papers.<sup>2</sup> (Dennison Wax Tests)

Amount of medium viscosity of protein	12%	12%	15%	15%	18%	18%
Type of rawstock	Porous	Dense	Porous	Dense	Porous	Dense
Dispersion of protein with;						
5% NaOH, pH 9.7	4.8	7.0	6.5	9.35	9.0	10.65
15% Na <sub>2</sub> CO <sub>3</sub> , pH 9.3	6.15	7.7	7.25	9.5	9.35	11.1
15% NH <sub>4</sub> OH, pH 9.1	5.9	6.9	6.7	9.1	8.4	10.65
15% Borax pH 7.3	4.2	6.65	6.55	8.4	7.15	9.75
20% Borax pH 7.9	6.0	7.35	6.80	9.2	8.45	10.60

4. and 5. Viscosity and solid percent and drying rate of the coating.

Viscosity of the color and drying rate is also very significant factor of the binder migration. Low solids, low viscosity colors are more prone toward migration, especially when subjected to high drying rates, than are high solids colors.<sup>6</sup>

(12)  
Heiser and Cullen studied the redistribution of the latex during the drying. They used 100 parts of coating grades clay and 20 percent of Dow Latex binder. The low solids coating was applied with an air knife and the high solid coating was applied with the puddle type trailing blade coater. The results are shown in Fig. 2.

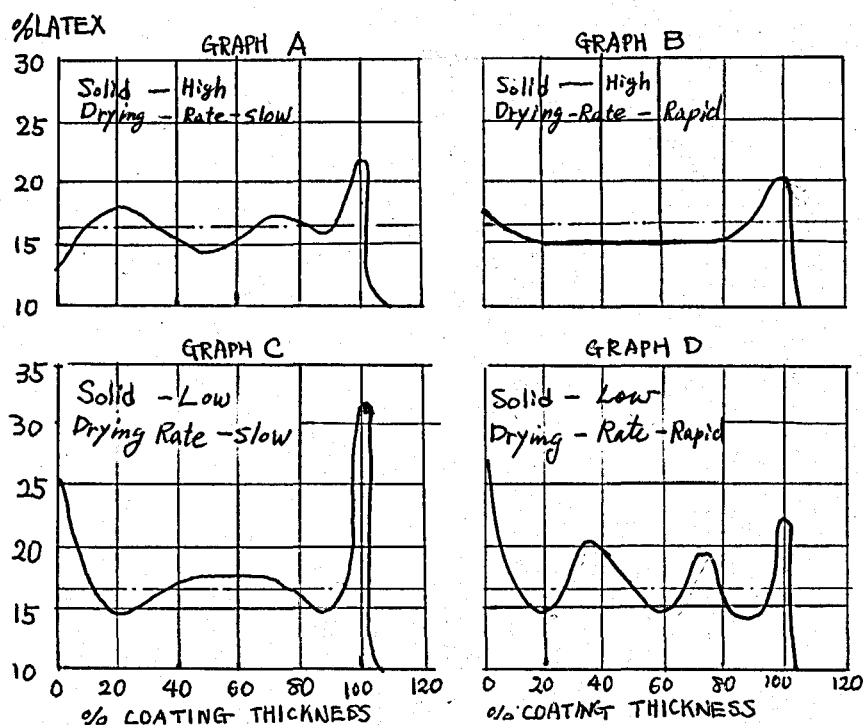


Fig. 2. Redistribution of the Latex in Coated Paper

They indicate that the binder migration is greater in low solids percent than in high solids percent, and if the drying rate is slow, the binder goes to the base stock side (Substructure), while at fast drying rate the migration occurs in two directions; towards the substructure and toward the coating surface. The degree of migration to the surface is proportional to the drying rate. More migration occurs as the drying rates is increased.

Some relationships among the Dennison Wax tests and viscosities which are provided with various kinds of alkali are prepared by Calvert.<sup>4</sup> The table shows that the effect of the type of alkali on a medium viscosity soya protein on coating color properties. The coating colors are at 45 percent solids with 15 parts of protein on 100 parts of a fine particle size clay.

Effect of Amount and Type of Alkali

Type and Percentage of Alkali	Clay Coating Mix Viscosity at 30°C (cp)	Clay Coating Mix pH at 30°C	Adhesive Strength (Wax No.)
<b>NH<sub>4</sub>OH</b>			
4.5	372	7.24	3.8
7.5	355	8.45	4.6
10.0	340	8.77	4.2
12.5	330	8.95	5.0
15.0	325	9.80	4.9
<b>NaOH</b>			
2.0	670	6.58	2.9
2.5	584	7.00	3.3
3.0	528	7.72	4.5
3.5	548	8.60	4.8
4.0	492	9.12	4.6
<b>Borax</b>			
15.0	490	7.52	4.0
20.0	631	7.85	5.1
25.0	600	8.08	4.8
30.0	650	8.18	5.2
35.0	645	8.51	5.5



6. Mixture of adhesives such as casein or soya protein to latex adhesives.

In the coating industry, synthetic latices have been investigated for use as paper coating adhesives, particularly since the time of World War II. Because of the many advantages, the use of latex is now well accepted. Some of the advantages are as follows: high solid percent in low viscosity, improved gloss, flexibility, moisture resistant, more uniform coated paper, and improved printability.

Avery studied the picking strength in various ratios of styrene and butadiene.<sup>14</sup> He found that 50 percent styrene and 50 percent butadiene had maximum strength in the ranges where the ratios of styrene to butadiene are 50 to 50, and 90 to 10.

In case of casein coating color, at some ranges (for example, the ratio of styrene and butadiene is more than 70 to 30 as shown in Fig. 3) its picking strength is lower than that of casein color where only casein is used as a binder. The following figure shows IGT tests results which is done at the following conditions:

Adhesive ----- 18%  
The ratio of casein  
to latex - 1:2  
The solid line indi-  
cates ratios of styrene and  
butadiene in latex.

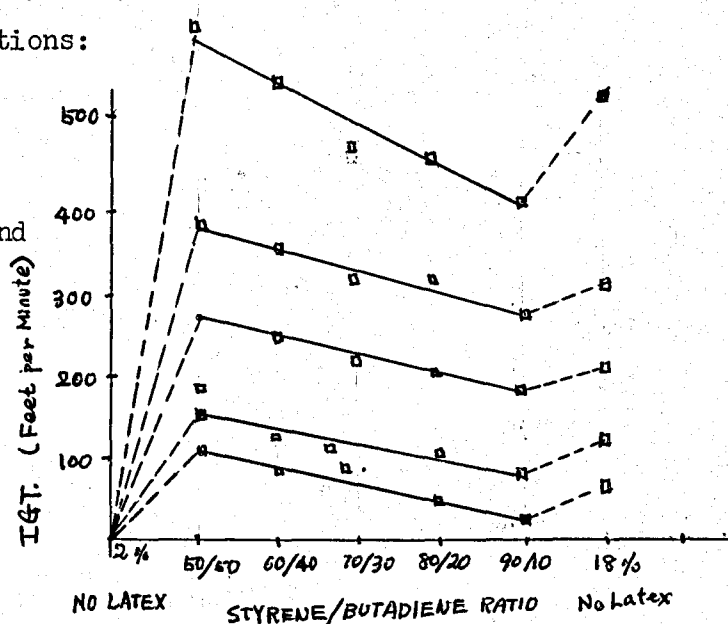


Fig. 3 Effect of Adhesive

In another studies, in the case of Dow Latex (S-B Latex) and casein, the results show that the picking strength (IGT test) increases as the ratios of latex increases as shown in Fig. 4.<sup>13</sup> However, in case of acrylic latex (Rhoplex), the maximum picking strength exists somewhere in the mixtures of acrylic and alpha protein.<sup>15</sup> It suggests that at certain blends, a synergistic effect exists between the acrylic emulsion and other water soluble binders that produce greater bonding strength than is obtainable from either binder material alone. The relations are shown in Fig. 5.

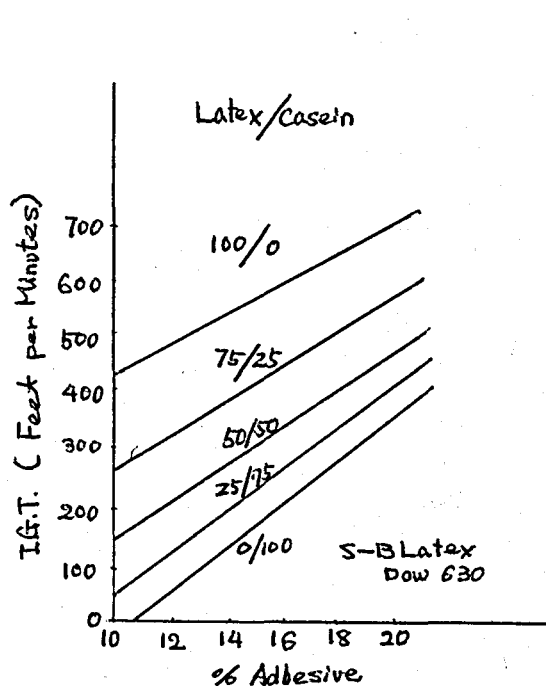


Fig. 4. Picking Strength in S-B Latex and Casein Color.

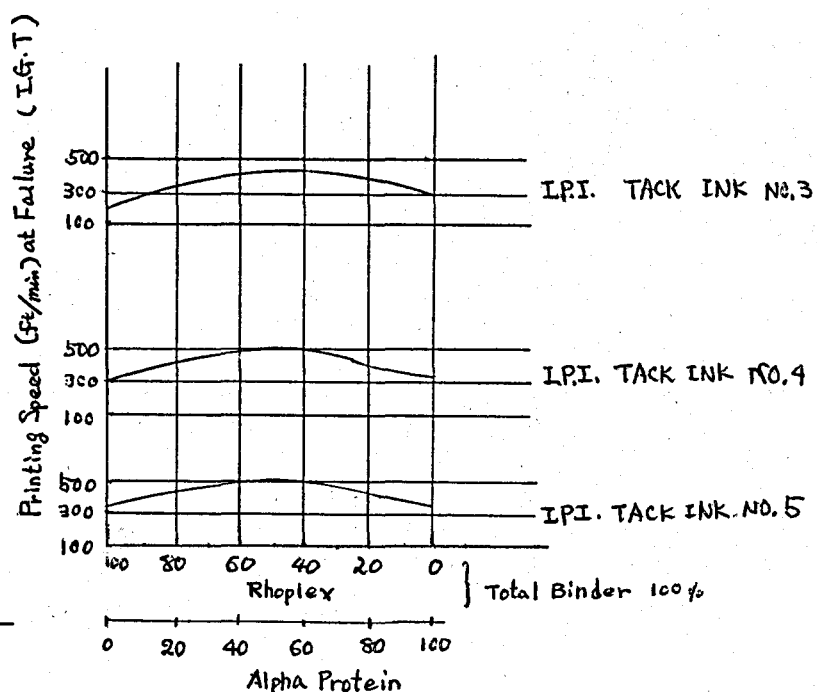


Fig. 5. Picking Strength in Acrylic Latex and Soy Protein Color.

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### Experiment Schedule (I)

The main object of this experiment is to determine what differences there may be in picking strength between casein and soya protein.

Since there are a large number of factors which affect the picking strength, it would be impossible to study all of them. The importance of the penetration of adhesives in a coating mixture into the base stock in picking evaluations and the differences of the casein and soya protein in picking strength were studied on basis of the following:

1. Different size levels of base paper, such as 0 percent and 1.5 percent.
2. Different beating levels of base paper using H.W. Bl. Kraft, such as 644cc CEF, 333cc CSF and 116cc CSF.
3. Different adhesive strength, such as 12 percent, 15 percent, and 18 percent on clay.

In order to get a better understanding of the relations among them, these experimental results were treated statistically.

In evaluation of the coated paper, the water retention properties and the study of the depth of the migration of adhesive were given up because of the shortage of time.

### Procedure

#### (1) Preparation of Handsheets

The fibrous furnish used in making the handsheets was 100 percent hardwood bleached kraft. The pulp was beaten by following the TAPPI standard procedure and the stock was prepared at the levels of 644cc CSF, 333cc CSF and 116cc CSF.

When the pulp was sized, the sizing was done as follows: The prepared rosin solution which was 5.0 percent and alum solution which was 5.0 percent

were added to the pulp up to 1.5 percent rosin on the pulp and 2.5 percent alum on the pulp. The stock suspension was around 1.60 percent or 1.76 percent depending on the beating levels. The stock suspension was stirred for around 5 minutes after rosin and alum solution were added.

The all handsheets were prepared in the laboratory, using the Noble-Wood sheet machine. The standard procedures of this sheet machine were followed.

The basis weight of the sheet was about 37#/25 x 38-500 (54.5g/m<sup>2</sup>). After drying, the sheet was calendered lightly to get good surface properties.

## (2) Preparation of Coating Mixtures

The clay used was HT clay, so that no dispersing agent was used. The clay was dispersed at first up to around 75 percent solid content by using high speed mixer, then later it was diluted to the figures stated later.

The casein solution or soya protein solutions were prepared by cooking 150 grams of casein or soya protein for about 20-30 minutes at 130°-140°F. The ingredient is as follows: (both casein and soya protein are the same process)

For one batch,

Water	830 gr
Casein or Soya protein	150 gr
NH <sub>4</sub> OH (28%)	18cc

After cooking casein or soya protein solution to the room temperature, and correcting for the water which was evaporated during the cooking, the adhesive solution was added to prevent casein shock by using a stirring rod. Both casein and soya protein were prepared on the levels of 12, 15, and 18 percent adhesive strength based on the weight of clay.

### (3) Preparation of Coated Samples and Their Evaluations

All samples were coated, using the wire-wrapped coating rods numbered 6 or 8, depending on the viscosity of the coating color. The weights of coating applied were around 10#/25 x 38-500 per side. In applying the coating the rod was placed upon the surface of the sheet close to one end. The coating mixture was poured in a line ahead of the rod, then the rod was drawn across the surface of the sheet. Finally, the surface was air dried. The coated sheets were calendered using four nips at 1280 pli.

The coated sheets were tested for the strength of the coating by means of the Dennison Wax pick test according to the TAPPI standard procedure (T 459m-45), and also they were tested by using IGT testing machine as indicated in TAPPI. All sample sheets were conditioned according to the TAPPI standard. Also, both picking and IGT testers were operated under conditions of constant temperature and relative humidity.

### Experimental Schedule (II)

In order to study the effects of the sizing, beating and amount of adhesives, or the interaction among them, the following factorial experimental schedule was used.

Factors	Key	Levels		
		1	2	3
Sizing	B	0.0%	1.5%	
Amount of Adhesive	C	12%	15%	18%
Beating	A	116cc CSF	333cc CSF	644cc CSF

For both casein and soya protein, the same procedures were used.

The experimental numbers are as follows:

		A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>
B <sub>1</sub>	C <sub>1</sub>	1*	2	3
	C <sub>2</sub>	4	5	6
	C <sub>3</sub>	7	8	9
B <sub>2</sub>	C <sub>1</sub>	10	11	12
	C <sub>2</sub>	13	14	15
	C <sub>3</sub>	16	17	18

\*The number indicates the experimental number. For example, #1 is the combinations of A<sub>1</sub> (the beating level is 116cc CSF), B<sub>1</sub> (sizing level is zero percent), and C<sub>1</sub> (12 percent of adhesive either casein or soya protein).

### Calculations of the Data

Analysis:

$$S_A = \frac{1}{6} (\text{Sum of } A_1)^2 + (\text{Sum of } A_2)^2 + (\text{Sum of } A_3)^2 - CT$$

$$S_B = \frac{1}{9} (\text{Sum of } B_1)^2 + (\text{Sum of } B_2)^2 - CT$$

$$S_C = \frac{1}{6} (\text{Sum of } C_1)^2 + (\text{Sum of } C_2)^2 + (\text{Sum of } C_3)^2 - CT$$

$$S_{AB} = \frac{1}{3} (A_1B_1)^2 + (A_1B_2)^2 + (A_2B_1)^2 + \text{-----} - CT$$

$$S_{AC} = \frac{1}{2} (A_1C_1)^2 + (A_1C_2)^2 + (A_1C_3)^2 + \text{-----} - CT$$

$$S_{BC} = \frac{1}{3} (B_1C_1)^2 + (B_1C_2)^2 + \text{-----} - CT$$

$$\text{Where } CT = \frac{(\text{Sum of Total})^2}{18}$$

$$SE = S_O - S_A - S_B - S_C - S_{AxB} - S_{AxC} - S_{BxC}$$

Where  $S_O$ : Sum of Squares (Total)

$$S_{AxB} = S_{AB} - S_A - S_B$$

$$S_{AxC} = S_{AC} - S_A - S_C$$

$$S_{BxC} = S_{BC} - S_B - S_C$$



Factor	S	Degree of Freedom	V	F <sub>o</sub>	F Distribution F95%	Contribution
A	$S_A$	2	$\frac{S_A}{2}$	$(S_A/2)/(S_E/4)$	$F_{2,4}$	$S_A/S \times 100$
B	$S_B$	1	$S_B$	$S_B/(S_E/4)$	$F_{1,4}$	$S_B/S \times 100$
C	$S_C$	2	$S_C/2$	$(S_C/2)/(S_E/4)$	$F_{2,4}$	$S_C/S \times 100$
AxB	$S_{AxB}$	2	$S_{AxB}/2$	$(S_{AxB}/2)/(S_E/4)$	$F_{2,4}$	$S_{AxB}/S \times 100$
AxC	$S_{AxC}$	4	$S_{AxC}/4$	$(S_{AxC}/4)/(S_E/4)$	$F_{4,4}$	$S_{AxC}/S \times 100$
BxC	$S_{BxC}$	2	$S_{BxC}/2$	$(S_{BxC}/2)/(S_E/4)$	$F_{2,4}$	$S_{BxC}/S \times 100$
E	$S_E$	4	$S_E/4$			
Total	S	1:7				100%

## Experimental Data

## Coating Color

1. Solid percent in coating color		Viscosity at 25.5°C	pH
casein 12%	43%	3300 at poise	8.2
15%	40%	3100	8.4
18%	41%	4950	8.7
soya protein 12%	47%	242	8.8
15%	48%	368	8.8
18%	43%	198	8.7

## RESULTS I (Soya Protein)

IGT Tester (unit: ft/min)

The ink used: #3.

Table I

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	117 (110-125)	90 (85-90)	63 (60-70)
	C <sub>2</sub> 15%	302 (290-320)	262 (250-280)	153 (150-160)
	C <sub>3</sub> 18%	600 >600	310 (280-310)	324 (310-340)
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	116 (110-120)	80 (75-85)	48 (40-55)
	C <sub>2</sub> 15%	150 (140-160)	108 (90-120)	73 (70-75)
	C <sub>3</sub> 18%	300 (290-300)	263 (260-270)	115 (110-130)

\*In this experiment, the values obtained above are the mean of at least five readings.

\* The parentheses indicates the ranges between maximum and minimum.

## RESULTS II (Casein)

IGT Tester (unit: ft/min)

The ink used: #3

Table II

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	220 (210-230)	166 (160-190)	92 (90-100)
	C <sub>2</sub> 15%	423 (410-450)	345 (340-350)	206 (200-210)
	C <sub>3</sub> 18%	600	471 (460-490)	278 (210-280)
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	166 (150-200)	139 (130-155)	78 (75-85)
	C <sub>2</sub> 15%	218 (170-280)	155 (150-160)	110 (100-140)
	C <sub>3</sub> 18%	408 (380-430)	305 (280-340)	173 (150-200)

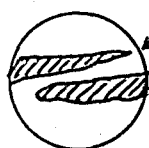
## RESULTS II (Soya Protein)

Dennison Wax Pick Test

Table III

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub>	C <sub>1</sub> 12%	4.6 (3.6-5.0)	4.5 (4.0-4.5)	4.4 (4.0-4.8)
size	C <sub>2</sub> 15%	7.7 (7.6-8.0)	7.9 (7.6-8.2)	7.3 (7.2-7.6)
0%	C <sub>3</sub> 18%	9.7 (9.4-10.0)	8.4 (8.0-8.8)	9.3 (9.0-9.4)
B <sub>2</sub>	C <sub>1</sub> 12%	4.8 (4.0-5.0)	3.1 (2.8-3.6)	less 2 less 2
size	C <sub>2</sub> 15%	6.7 (6.4-7.5)	5.6 (5.0-6.0)	5.2 (4.8-5.8)
1.5%	C <sub>3</sub> 18%	7.9 (7.8-8.0)	6.9 (6.8-7.0)	6.6 (6.2-7.0)

\* The values obtained above are the mean of at least five readings. The picking strength was evaluated as follows. The highest numerical designation of the wax that does not disturb the surface of the paper plus some amount of area fraction which is left from the next wax number. For example, the highest wax number 5, and suppose that #6 were used and the surface was disturbed. In this case, it is evaluated around 5.6.



The surface of the wax.

A part of the surface of the sheet which sticks on the wax.

The parentheses indicates the ranges evaluated.

## RESULTS IV (Casein)

Dennison Wax Pick Test

Table IV

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	5.7 (5.4-6.0)	4.9 (4.8-5.0)	3.3 (3.0-4.4)
	C <sub>2</sub> 15%	7.9 (7.8-8.0)	7.6 (7.4-7.8)	6.6 (5.8-7.2)
	C <sub>3</sub> 18%	9.4 (9.2-9.6)	9.8 (9.6-10.0)	9.9 (9.8-10.0)
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	4.9 (4.8-5.0)	4.8 (4.6-5.0)	2.6 (2.2-3.8)
	C <sub>2</sub> 15%	6.9 (6.8-7.0)	6.7 (6.6-7.0)	6.0 (5.8-6.2)
	C <sub>3</sub> 18%	8.0 (7.8-8.0)	7.9 (7.6-8.0)	7.8 (7.6-8.0)

## Analysis of the data (from Table I) and Discussion

## (1) Soya Protein (IGT Testing)

From Table I, the following table is obtained by subtracting 100 in soya protein experiment.

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	17	-10	-37
	C <sub>2</sub> 15%	202	162	53
	C <sub>3</sub> 18%	500	210	224
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	16	-20	-52
	C <sub>2</sub> 15%	50	8	-27
	C <sub>3</sub> 18%	200	163	15

Evaluation - Table V

		Degree of Freedom	V	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	55,046	2	27,523	0.62	6.94	11.2
S <sub>B</sub>	38,211	1	38,211	0.92	7.71	7.8
S <sub>C</sub>	165,892	2	82,946	2.00	6.94	33.8
S <sub>AxB</sub>	16,423	2	8,211	0.20	6.94	3.3
S <sub>AxC</sub>	18,000	4	4,500	0.16	6.39	3.7
S <sub>BxC</sub>	31,613	2	15,806	0.38	6.94	6.4
S <sub>E</sub>	165,913	4	41,488			33.8
Total	491,138					100.0%

## Soya Protein (IGT Testing)

When B is kept constant, we know the main effect of A and C.

(1)  $B_1 = 0\%$  sizing

	A <sub>1</sub> 116	A <sub>2</sub> 333	A <sub>3</sub> 644
C <sub>1</sub> 12%	17	-10	-37
C <sub>2</sub> 15%	202	162	53
C <sub>3</sub> 18%	500	210	224

$$CT = \frac{1}{9} (\text{Total})^2 = 193,897$$

$$S_A = \frac{1}{3} (\text{Sum of } A_1)^2 + (\text{Sum of } A_2)^2 + (\text{Sum of } A_3)^2 - CT$$

$$= 41,309$$

$$S_C = \frac{1}{3} (\text{Sum of } C_1)^2 + (\text{Sum of } C_2)^2 + (\text{Sum of } C_3)^2 - CT$$

$$= 155.155$$

$$S_T = \text{Sum of square} - CT$$

Table VI

		D of F	V	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	41,309	2	20,654	3.03	6.94	18.5%
S <sub>C</sub>	155,155	2	77,577	11.35	6.94	69.4%
S <sub>E</sub>	27,334	4	6,833			12.1%
S <sub>T</sub>	223,798					100.0%



## Soya Protein (IGT Testing)

$$(2) B_1 = 1.5\%$$

	A <sub>1</sub> 116	A <sub>2</sub> 333	A <sub>3</sub> 644
C <sub>1</sub> 12%	16	-20	-52
C <sub>2</sub> 15%	50	8	-27
C <sub>3</sub> 18%	200	163	15

The calculation is the same.

Table VII

	S	D.F	V	F <sub>0</sub>	F <sub>0.95</sub>
S <sub>A</sub>	18,706	2	9,393	6.30	6.94
S <sub>B</sub>	35,150	2	17,575	12.02	6.94
S <sub>E</sub>	5,846	4	1,461		
S <sub>T</sub>	59,602				

## (2) Casein (IGT Testing)

From Table II, we can get the following table by subtracting 200 in casein experiment.

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub>	C <sub>1</sub> 12%	20	-34	-108
size	C <sub>2</sub> 15%	223	145	6
0%	C <sub>3</sub> 18%	400	271	78
B <sub>2</sub>	C <sub>1</sub> 12%	-34	-61	-122
size	C <sub>2</sub> 15%	18	-45	-90
1.5%	C <sub>3</sub> 18%	208	105	-27

Evaluations - Table VIII

	S	Degree of Freedom	V	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	101,470	2	50,735	3.95	6.94	24.9%
S <sub>B</sub>	61,133	1	61,133	4.76	7.71	14.9%
S <sub>C</sub>	158,234	2	79,122	6.16	6.94	38.8%
S <sub>AxB</sub>	4,911	2	2,460	0.19	6.94	1.2%
S <sub>AxC</sub>	15,281	4	3,820	0.29	6.39	3.7%
S <sub>BxC</sub>	16,279	2	8,140	0.64	6.94	4.0%
S <sub>E</sub>	51,438	4	12,859			12.5%
Total						100.0%

## Casein (IGT Testing)

When B is kept constant, we know the main effect of A and C.

(1)  $B_1 = 0\%$  sizing

	A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
C <sub>1</sub> 12%	20	-34	-108
C <sub>2</sub> 15%	223	145	6
C <sub>3</sub> 18%	400	271	78

$$C_{1T} = \frac{(\text{total})^2}{9} = 111,333$$

$$S_A = \frac{1}{3} (\text{Sum of } A_1)^2 + (\text{Sum of } A_2)^2 + (\text{Sum of } A_3)^2 - CT$$

$$= 75,316$$

$$S_C = \frac{1}{3} (\text{Sum of } C_1)^2 + (\text{Sum of } C_2)^2 + (\text{Sum of } C_3)^2 - CT$$

$$= 125,254$$

$$S_T = \text{Sum of square} - CT$$

Table IX

		(D.F.)	(V)	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	75,316	2	37,658	15.62*	6.94	35.5%
S <sub>C</sub>	127,254	2	63,627	26.40*	6.94	60.0%
S <sub>E</sub>	9,642	4	2,411			4.5%
S <sub>T</sub>	212,202	8				100.0%

## Casein (IGT Testing)

(2)  $B_1 = 1.5\%$ 

	A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
C <sub>1</sub> 12%	-34	-61	-122
C <sub>2</sub> 15%	18	-45	-90
C <sub>3</sub> 18%	208	105	-27

Table X

	S	D.F.	V	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	31,985	2	15,993	11.19*	6.94	37.60%
S <sub>C</sub>	47,269	2	23,634	16.58**	6.94	55.70%
S <sub>E</sub>	5,718	4	1,429			6.70%
S <sub>T</sub>	84,972					100.0%

## (3) Soya Protein (Wax Testing)

From Table III, we can get the following table by subtracting  $l_4$  in soya protein experiment.

		A <sub>1</sub> 116cc	A <sub>2</sub> 333cc	A <sub>3</sub> 644cc
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	0.6	0.5	0.4
	C <sub>2</sub> 15%	3.7	3.9	3.3
	C <sub>3</sub> 18%	5.7	4.4	5.3
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	0.8	-0.9	-2
	C <sub>2</sub> 15%	2.7	1.6	1.2
	C <sub>3</sub> 18%	3.9	2.9	2.6

Table XI

	S	Degree of Freedom	V	F <sub>0</sub>	F <sub>0.95</sub>	Contribution
S <sub>A</sub>	3.96	2	1.98	0.086	6.94	2.4%
S <sub>B</sub>	12.50	1	12.50	0.56	7.71	7.5%
S <sub>C</sub>	55.82	2	27.91	1.22	6.94	33.3%
S <sub>AxB</sub>	1.77	2	0.88	Neg.	6.94	1.5%
S <sub>AxC</sub>	1.10	4	0.27	Neg.	6.39	0.6%
S <sub>BxC</sub>	0.53	2	0.26	Neg.	6.94	54.7%
S <sub>E</sub>	91.94	4	22.98			
Total	167.62					100.0%

## (4) Casein (Wax Testing)

From Table III, we can get the following table by subtracting 5 in casein experiment.

		A <sub>1</sub> 116	A <sub>2</sub> 333	A <sub>3</sub> 644
B <sub>1</sub> size 0%	C <sub>1</sub> 12%	0.7	-0.1	-1.7
	C <sub>2</sub> 15%	2.9	2.6	1.6
	C <sub>3</sub> 18%	4.4	4.8	4.9
B <sub>2</sub> size 1.5%	C <sub>1</sub> 12%	-0.1	-0.2	-2.4
	C <sub>2</sub> 15%	1.9	1.7	1.0
	C <sub>3</sub> 18%	3.0	2.9	2.8

Table XII

	S	Degree of Freedom	V	F <sub>0</sub>	Contribution
S <sub>A</sub>	4.17	2	2.09	0.16	3.3%
S <sub>B</sub>	5.01	1	5.01	0.38	3.9
S <sub>C</sub>	59.50	2	29.75	2.26	47.2
S <sub>AxB</sub>	0.02	2	0.01		0.1
S <sub>AxC</sub>	3.41	4	0.85		2.7
S <sub>BxC</sub>	1.35	2	0.67		1.1
S <sub>E</sub>	52.63	4	13.16		41.7
	126.09				100.0%

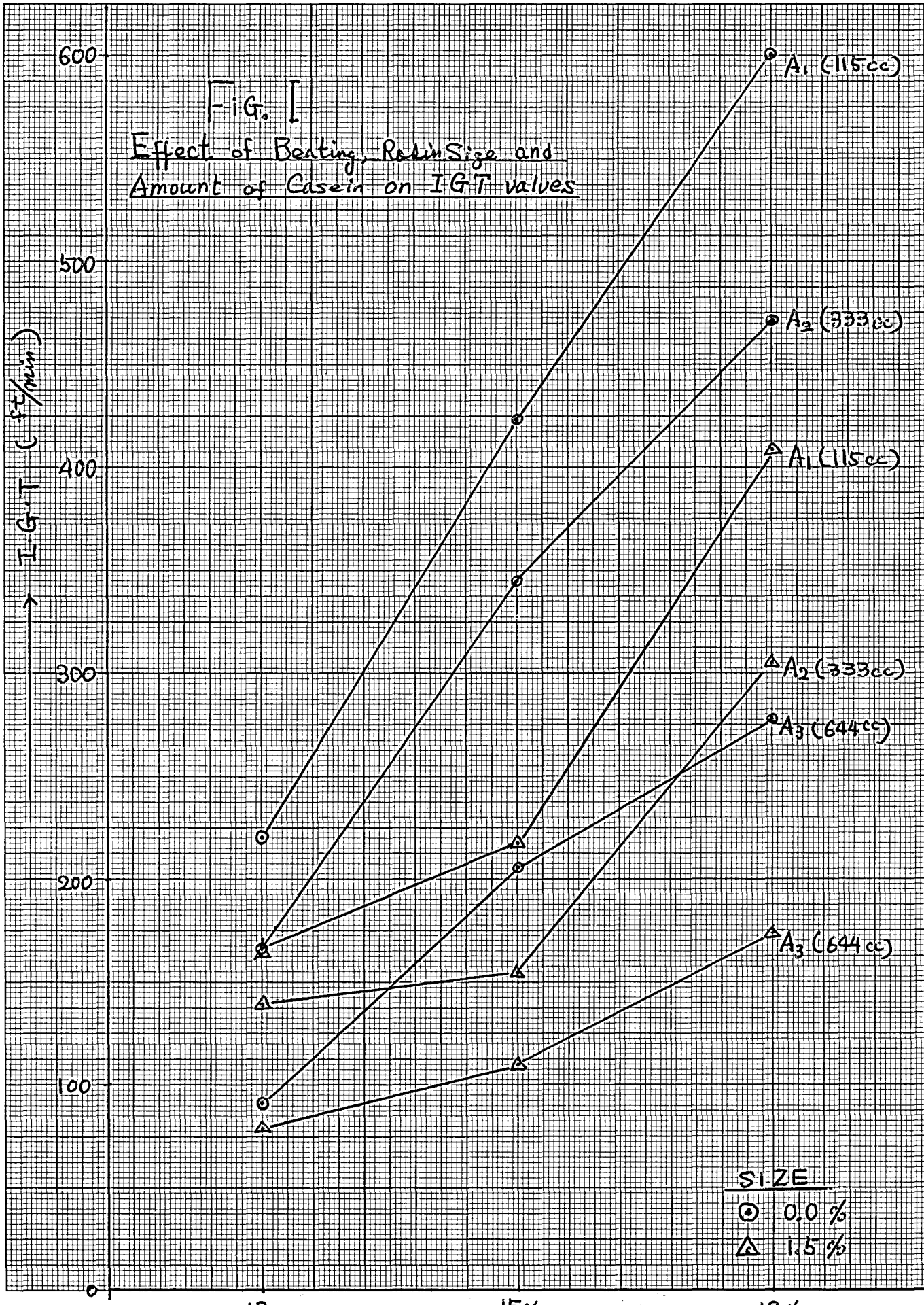
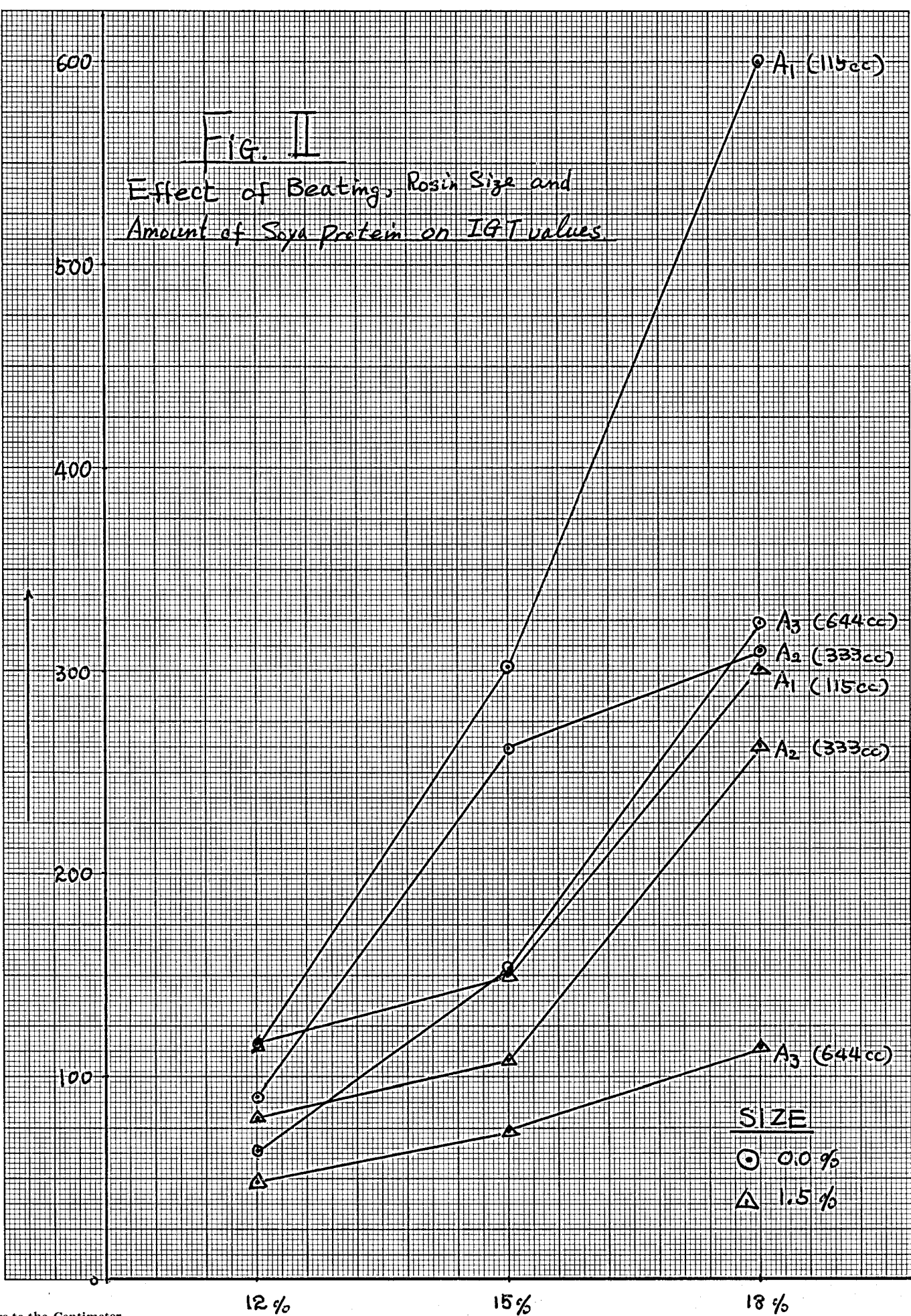


FIG. II  
Effect of Beating, Rosin Size and  
Amount of Soya Protein on IGT values



SIZE  
 ○ 0.0 %  
 △ 1.5 %



Fig. III

Effect of Beating, Rosin Size  
and Amount of Soya Protein  
on Wax Number.

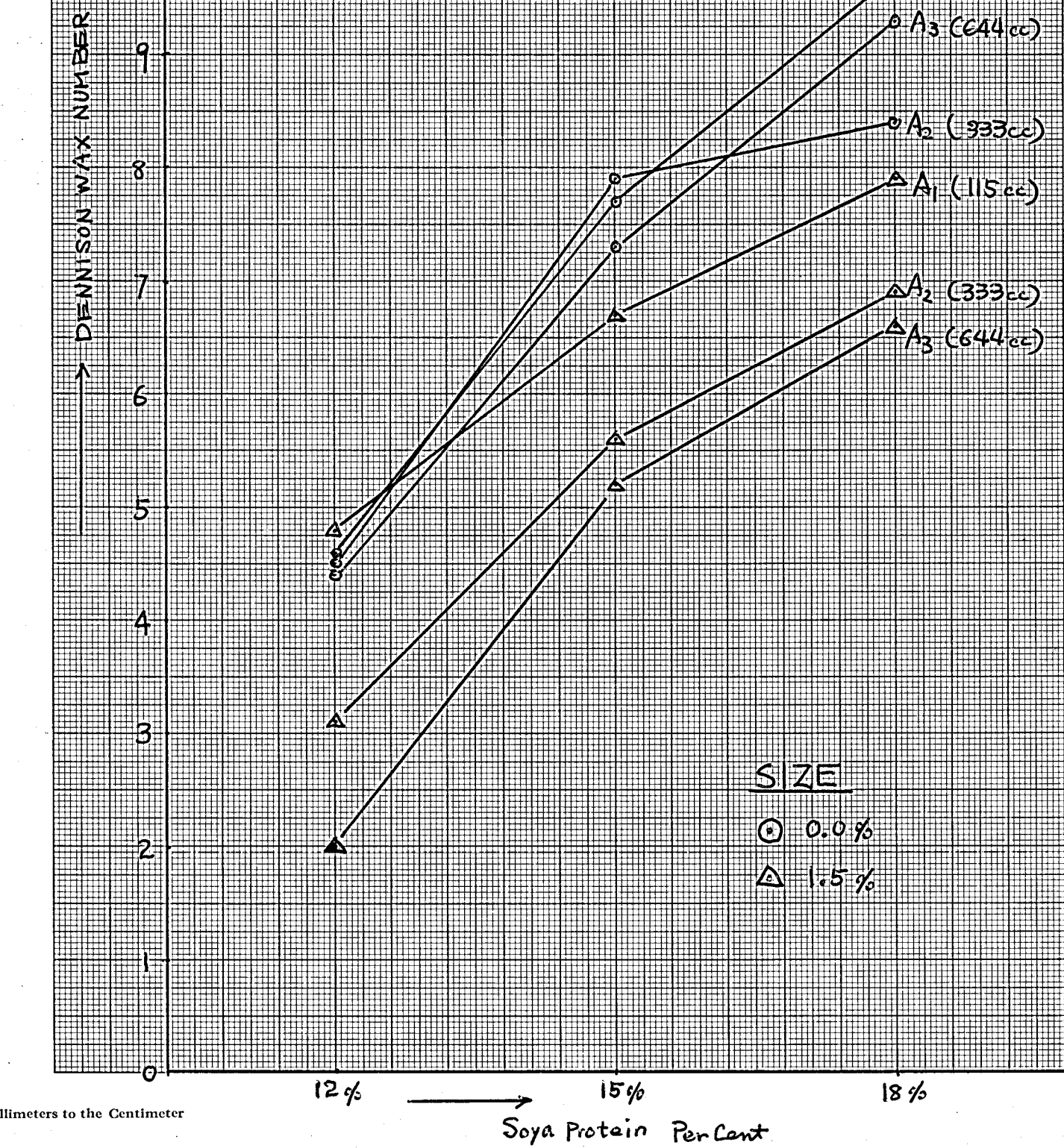
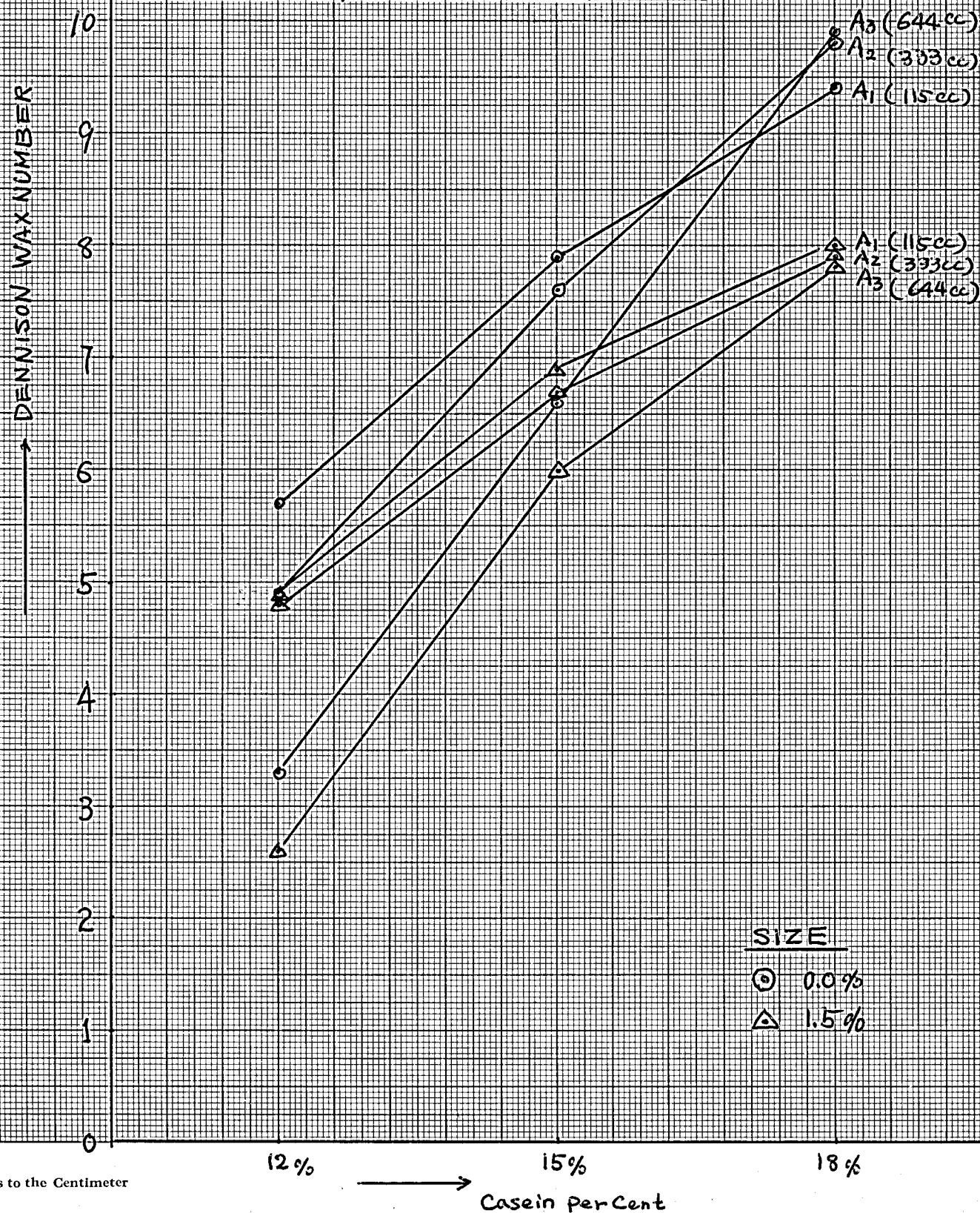


Fig. IV

Effect of Beating, Resin Size  
and Amount of Casein on WAX Number



### I. IGT Test Evaluations

The experiment was carried out to determine the effects of densities of the sheets (or beating levels), amounts of adhesive applied, and sizing. None of them showed a predominant effect on the values of the IGT test, but they depended on all of them.

Table V shows in the soya protein experiment, the amount that the protein contributes to the IGT values around 34 percent, and the beating levels affect around 11 percent and the differences of sizing levels affect only around 8 percent. Table VIII shows in the casein experiment, the amounts of adhesive affect around 39 percent, the beating levels affect around 25 percent and the differences of size levels affect around 15 percent. This means that in IGT test, the values of soya proteins were less affected by beating and sizing than were those of casein.

As shown above, in both sized or non-sized paper, the amount of adhesive applied gives more important effects than the differences of the beating levels or sizing levels. In the soya protein experiment, however, once the paper is sized, the beating levels are also fairly important as shown in Table VII, while in the case of casein adhesive, both sized or non-sized paper was affected by the differences of beating levels. As a whole, if we neglect the differences of sizing levels, the values of IGT test were appreciably increased as the amount of adhesive increased at 95 percent of reliability, and the differences of beating levels affect more in casein adhesive than in soya protein adhesive.

The interaction effects of these three factors were not so important, but some relations may exist between the sizing and the beating levels

according to the calculation shown in Table V or Table VIII. These are completely negligible to compare with the experimental errors.

In IGT testing (or even Wax test), it is very difficult to conclude the differences in picking strength between soya protein and casein, because there are lots of errors among experimental values. In another words, the experiment itself is not accurate enough to find these differences. However, on the graph shown Figure I or Figure II, it may be concluded that casein may be used at 3 percent less than that of the soya protein to get the same IGT strength values.

## II. Wax Test Evaluations

In the Wax test, this picking strength was mainly affected by the amount of adhesive used rather than two other factors as shown in Table XI or XII. The relations were shown in Figure III and Figure IV, and we know that all values are close enough among the differences of sizing and beating levels. It may be concluded that there are no differences in picking strength between casein and soya protein within the experimental errors.

### III. IGT Testing and Wax Test

When we compare the values obtained in IGT test and Wax test, we know that the IGT testing method indicates better relationships in picking strength than the Wax test. In other words, we can get less variables in IGT testing than Wax test.

Although it is said that the Wax test evaluates the strength of the coating film much more than the strength of the fiber bonding strength, the experiment in Wax test indicates that it is not necessarily so. For example, in the Wax test, the maximum value was obtained at 18 percent adhesive (both soya, casein), unsized and medium beaten paper. It appears that any factor which reduces the strength of the sheet also reduces the wax number. Thus, addition of size, or unbeaten pulp or severely beaten pulp reduce the wax number also.

## CONCLUSIONS

1. As far as the picking strength, the casein and soya protein have almost equal picking strength with the Wax test within the experimental errors. However, with the IGT test, casein may be used at 3 percent less than that of the soya proteins to get the same IGT strength values.
2. In the IGT test, the differences of beating and sizing level are greater with the casein adhesive than with the soya protein.
3. The better evaluation values are obtained in IGT test than Wax test.
4. Soya protein has lower viscosity than casein, thus we can make high solid content color easily.
5. The following statistical analysis seems to be justifiable on the data presented.