EXTRUSION-COOKING OF WHEAT STARCH: EFFECT OF pH AND EMULSIFIERS

BY

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Approved by:

Paul A Seib
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To my parents and

Isabelita de Neffré

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I. INTRODUCTION

Pregelatinized wheat starches are most valuable when used in foods. Food manufacturers generally desire the following properties for a pregelatinized starch:

1) rapid dispersion in cold water to form a smooth paste,
2) high viscosity of the paste at low percent of solids, and
3) minimal loss of viscosity when the paste is subjected to shear, heat or acid.

Pregelatinized starches are generally produced by cooking on heated drum rolls. The method produces a starch which hydrates quickly, gives a thick paste at low solids but is subject to lumping. Drum cooking however, produces gelatinized starch at a slow rate and with a large consumption of energy. In addition, small drifts in operating conditions around the drum produce significant changes in the finished product (Powell, 1967).

An alternate technique to produce pregelatinized starches is the extrusion-cooking process. That process has three advantages: 1) high production rate, 2) cooking with small amounts of water, and 3) ease of cooking with additives. However, the process has the disadvantage of giving a product that generally produces a paste of low viscosity. High mechanical shear forces during extrusion processing apparently destroy the granular structure of a starch (Powell, 1967). Thus, the thickening power of an extrusion-cooked product is probably due almost entirely to a molecular dispersion of amylose and amylopectin.

It is well known that emulsifiers complex with regular starches when the two materials are heated in an aqueous medium. Complexing has important implications because it represses swelling and solubilization of a starch (Van Lonkhuysen et al., 1976; Osman et al, 1961). Amylograms of starch heated with emulsifiers show increased pasting temperatures and generally lower paste consistencies (Krog, 1973). Microscopic examination of starch-emulsifier pastes has shown that the granular structure of a starch is more stable in the presence of many complexing agents (Van Lonkhuysen et al. 1976; Miller et al. 1973).

At the molecular level iodine binding and X-ray studies (Krog, 1971; Lagendik et al., 1970) have demonstrated that the starch complex is due to the non-polar part of a surfactant molecule entering into the cavity formed inside the amylose helix.

One of the purposes of this study was to determine if surfactants could be used to modify the properties of wheat starch during extrusion-cooking. It was thought that perhaps some of the granular structure of the starch-emulsifier complex might survive the short-time cooking process. In addition, precooked complexes of starch might have useful properties for the food technologist.

Four emulsifiers were chosen for study, which, in increasing order of hydrophilic character, are as follows: distilled monoglycerides (DMG), ascorbyl palmitate (AP), sodium stearoyl-2-lactylate (SSL) and polyoxyethylene sorbitan monostearate (PSM). Three of the emulsifiers (DMG, AP and PSM) are already used in starch-based foods. Ascorbyl palmitate is used sparingly in starchy foods because it is expensive.

Wheat starch was chosen for study because that starch is increasing in supply due to the growth of the gluten processing industry. The wet milling of wheat or flour to isolate gluten gives much larger quantities of wheat starch than of gluten.

Since corn starch is much cheaper than wheat starch in the United States, unique products must be made from wheat starch.

Another purpose of this study was to examine the effect of pH on the extrusion-cooking of wheat starch. This work was needed because several of the emulsifiers were expected to change the pH of the moistened wheat starch before extrusion.

Several properties of starches were measured to determine the effects of emulsifiers and pH on the precooked products. These included pasting curves on the Amylograph, water-solubility, pH, and the rate of aqueous dispersion. The effects of the emulsifiers on extrusion rate and power consumption were also determined.

Few studies have been reported on the extrusion-cooking of prime starches. In 1972, Lawton et al., presented a study on the effect that extrusion variables have on the gelatinization of corn starch. From a mathematical model of the laboratory-scale extrusion operation, they determined that the important variables affecting gelatinization were extrusion temperature, screw speed, screw geometry and moisture content of the starch. They reported a strong interaction between moisture and temperature on gelatinization.

Stearns (1974), studied many of these variables on the extrusion-cooking of wheat starch with a 3/4" diameter extruder (L/D = 25/1). In comparison to drum-cooked wheat starch, he found that extrusion-cooking gave pregelatinized starches with a higher percentage of water solubles, more acidic pH values, lower viscosity in dimethyl sulfoxide solution, and a greater degree of browning. Stearns also reported that interactions between temperature and moisture affected expansion of the starch leaving the extruder. He found optimum expansion at 175°C and 19% moisture.

Charbonniere et al., (1973) using X-ray techniques found that extruded wheat and corn starches showed only disorganized structures (devoid of type-A, B, C, or V patterns) when the extrusion temperature was about 70°C, but at higher temperatures a new structure was formed. That structure was the same for both starches and was similar to the type-V crystalline pattern of dry or wet amylose. They also reported that extruded amylomaize and waxy starches showed the new structure even at low temperatures. On the contrary, extruded tapioca and potato starches had an entirely disorganized structure whatever the temperature used.

In 1975, Mercier and Pfeillet, reported the changes in properties that several cereal starches underwent upon extrusion-cooking at different temperatures and moisture content. Corn, waxy corn, rice, wheat and amylomaizes starches with 51 and 61% of amylose were studied. Using the amylograph, these workers observed the final paste viscosities (50°C) of extruded waxy corn, wheat and rice starch reached a maximum value of 215-380 B.U. after extrusion at ∿100°C. On the other hand, the final paste viscosity of the extruded normal corn decreased regularly. The pasting curves of the extruded products from the high amylose starches remained almost identical to the curve of the uncooked control. The water solubles of corn and wheat starch steadily increased with extrusion temperature, whereas those of waxy corn decreased. Water solubles of high amylose starches increased only at extrusion temperatures of 200^{0}C. In general, the amount of soluble starch was found to increase with increasing extrusion temperature and with decreasing moisture content of the starch.

By determining the amount of water-soluble carbohydrates and its enzymic degradation, these authors found that the solubilized starch in extruded corn starch occurred in its macromolecular form without formation of maltooligosaccharides. Their studies further indicated that the susceptibility of extruded starches to bacterial α-amylase increased with increasing of extrusion temperatures. No difference in the initial rate of amylolysis was detected for the several extruded starches, except for high-amylose starches which reacted slower. The authors also reported that at extrusion temperatures above 70^{0}C, expansion, water-soluble carbohydrates, and susceptibility to α-amylase decreased as the amylose content of the starch increased. They noted that under the same conditions of extrusion, waxy corn starch gave the most water-solubles followed by corn, wheat, rice and high amylose starches.

Extrusion-cooking of potato starch (Mercier, 1977) showed that an increase in extrusion temperature and moisture content of the starch produced an increase in the water solubles. The ethanol-soluble (80% aqueous ethanol) carbohydrate fraction with a d.p. < 14 increased when the extrusion temperature increased and the moisture content decreased. Enzymatic studies on the ethanol-soluble fraction suggested that there was a preferential breakdown of amylose during the extrusion-cooking of the potato starch to produce linear maltooligosaccharides.

Most recently, Mercier et al. (1978) reported on the extrusion of cassava starch. Those authors reported that cassava starch which had been extrusion-cooked with 0.5% stearic acid or monoglycerides had excellent freeze-thaw stability. Such products might be used to replace chemically modified starches in frozen and refrigerated foods.

II. MATERIALS AND METHODS

A. MATERIALS

1. Cereal Starches

Prime wheat starch and drum-cooked pregelatinized wheat starch was obtained from Midwest Solvents Co. Inc., Atchison, Ks.

Prime corn starch was donated by A.E. Staley Manufacturing Co., Decatur, Ill.

Commercial drum-cooked corn starch was donated by National Starch & Chemical Corporation, Bridgewater, New Jersey.

Amylopectin was isolated from wheat starch and was a gift from W. Atwell, Kansas State University.

2. Emulsifiers

Distilled Monoglycerides (DMG)were obtained from Eastman Kodak Co., Rochester, N.Y. The material was prepared from saturated edible animal fat and contained 90% monoglycerides and 5% diglycerides.

Sodium stearoyl-2-lactylate (SSL) was obtained from Patco Products, Inc., Kansas City, Mo.

Polyoxyethylene (20) sorbitan monoestearate (PSM) was obtained from ICI United States Inc., Wilmington, Deleware.

Ascorbyl palmitate (AP) was obtained from Hoffmann-La Roche, Nutley, New Jersey.

B. METHODS

1. Preparation of starch-emulsifier blends

To obtain a uniform blend of the emulsifier and starch, a premix (100g) was prepared as follows. One hundred grams of starch (wheat or corn) was placed in a 1 liter round bottom flask and suspended in _ca_. 400 ml of a mixture of chloroform-ethanol (2:1). Then 0.25 g, 0.5g, or 0.75 g of the desired emulsifier which had been previously dissolved in _ca_. 100 ml of the solvent, was added.

The solvent was removed under reduced pressure and the dry premix was added to wheat or corn starch in a 3000 ml plastic bag. The amount of corn or wheat starch was calculated to give 0.25, 0.50 and 0.75% emulsifier on a dry weight basis. The bag was inflated with air, sealed, and shaken by hand ∿ 10 min. The blends were stored in plastic bags at $4^{o}C$, and were used within one day after blending.

2. _Test for homogeneity of the starch-emulsifier blends_.

The uniformity of the emulsifier-starch blends was tested for two of the four blends. The blends tested were those with distilled monoglyceride and ascorbyl palmitate. The other two blends were assumed to have the same uniformity. Triplicate samples (10 g each) of a starch-surfactant blend were taken following a quartering procedure (Dedrick, 1924). A 2:1 mixture of chloroform-ethanol (50 ml) was added, and the mixture was stirred 10 min and centrifuged at 700 g for 10-15 min. The clear supernatant was filtered (Whatman paper #4) and the filtrate collected in a tared 150 ml beaker. The residue was extracted once again using 10 ml of the mixed solvents. The combined extracts were evaporated in a fume hood at $25^{o}C$, and the beakers were heated ($105^{o}C$) to constant weight. The extraction of prime wheat starch alone constituted a blank.

The percent of emulsifier was calculated using the expression:

$$\text{Emulsifier \%} = \left(\frac{W1}{Ws} - \frac{W2}{Wo}\right) \times 100$$

where:

W_1 = weight of extract from the starch-emulsifier blend.

W_2 = weight of extract from the starch without emulsifier.

Ws = weight of starch-emulsifier blend on dry basis.

Wo = weight of starch on dry basis.

3. Tempering of wheat starch to different pH's

Solutions of phosphate salts and hydrochloric acid - aqueous potassium chloride were added to temper wheat starch to pH 3.0-9.0. The starch was tempered to 19% moisture for all samples, and the pH of the tempering solution was adjusted to give the desired final pH of the tempered starch. Table 1 shows the composition and pH of the tempering solutions used, as well as the pH of the tempered starch. Beginning with starch at 12% moisture, 90 ml of tempering solution was added to one kilogram of wheat starch to produce 19% moisture at the desired pH.

TABLE 1

COMPOSITION AND pH OF SOLUTIONS USED TO TEMPER WHEAT STARCH TO 19% MOISTURE AT DIFFERENT pH's.

Tempering Solution	Composition[a]	Solution's pH	Starch[b] pH
A	90 ml. HCl + 10 ml. KCl	0.59	3.0
B	60 ml. HCl + 10 ml. KCl	0.77	3.4
C	35 ml. HCl + 10 ml. KCl	0.96	4.4
D	91 ml. H_3PO_4 + 19 ml. Na_2HPO_4	1.80	5.4
E	25 ml. HCl + 10 ml. KCl	1.15	6.2
F	10 ml. H_3PO + 30 ml. Na_2HPO_4	3.00	6.5
G	70 ml. Ha_2HPO_4 + 30 ml. NaH_2PO_4	7.00	7.5
H	55 ml. Na_3PO_4 + 45 ml. Na_2HPO_4	11.60	8.3
I	97 ml. Na_3PO_4 + 3 ml. Na_2HPO_4	12.10	9.0
Control	Deionized water	---	7.6

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[a] Where necessary, solutions were made up to 100 ml. with deionized water. Concentrations of KCl and HCl solutions were 0.5M, whereas the concentrations of H_3PO_4, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 solutions were 0.1 M.

[b] The pH of the tempered starch was measured on 5 g of starch in 50 ml of water.

In general, the quantity of water or tempering solution needed to adjust the starch (1,000 g.) to a desired moisture level was calculated using the formula:

$$\underset{(g)}{\text{Water to be added}} = 1000 \times \frac{(\%\text{ desired moisture} - \%\text{ sample moisture})}{(100 - \%\text{ desired moisture})}$$

The starch samples were tempered to the desired moisture level using the procedure described by Stearns (1974).

4. Extrusion Process

a) Brabender Laboratory Extruder.

The extrusion equipment used in this study was a laboratory single screw extruder, Model 2403, manufactured by C.W. Brabender Co. of South Hackensack, New Jersey. The extruder specifications are as follows:

Barrel diameter	1.905 cm.
Barrel length	47.625 cm.
Length/diameter ratio	25:1
Number of heated zones	3
Watts per Zone	1000
Type of cooling	air
Compression ratios	
Screw #5	5:1
Screw #3	3:1
Rod shape die, Diameter 1/8"	3.175 mm.
Rod shaped die, Diameter ¼"	6.350 mm.

The stainless steel screws were fitted with a torpedo of 35^0 at the discharge end, to fill the large void volume leading into the die. The extruder was fed using a force-feeder (Model No. 114) manufactured by C. W. Brabender.

b) Extruder operating conditions.

1. The extruder was assembled and plugged in.
2. The heating zones were switched on and the temperatures were set on start up conditions as follows:

Feeder block	Water cooled
Zone One	Air cooled (30^{0}C)
Zone Two	100^{0}C
Zone Three	160^{0}C

3. When the zones reached temperature and the die-cap nozzle reached a temperature of ∿80°C, the extruder was ready for start up.
4. The screw was turned on and the screw speed adjusted to 100 RPM. The feeder was turned on, and adjusted at 18 in its scale.
5. To prevent plugging on start up, wheat flour of about 22% moisture was slowly fed into the feeder.
6. When the wheat flour started to come out of the extruder, the temperatures of zones two and three were adjusted to the desired levels.
7. The tempered wheat starch or blend was fed into the extruder. After uniform flow and equilibrium product temperature was established throughout the system (∿5-10 min.), the product sample was taken. About 700 g. of sample was collected and placed in a sealed polyethylene bag for storage.
8. Between extrusion of the different samples, tempered starch (19.0%) was extruded to minimize the possibility of interaction of the different batches in the barrel. After 5 minutes the new sample was fed into the extruder and the step 7 was followed.
9. While the sample was being taken the following readings were recorded: screw speed, amperage consumption and temperature of the three zones.

c) Production rate

When equilibrium during extrusion was thought to have been reached, two one-minute samples of the extruded product were collected. The samples were weighed, ground in a Stein mill and their moisture content determined following the A.O.A.C. Method 14.004 (1970). The production rate, on dry basis, was calculated in kg/hr using the equation:

$$\text{Production rate (kg/hr)} = \frac{60 \times W \times (100-h)}{1000}$$

where: W = weight of sample collected for one minute, kg

h = moisture content of collected sample, %

5. Sample preparation for analysis

Approximately 300 g. of each sample was pre-ground in a Waring-Blendor, and then finely ground in a Stein Laboratory Mill, model M-1, for one and a half minutes. The temperature was maintained below 30°C. The finely ground sample was sieved through a U.S. No. 50 wire and No. 100 wire to give two fractions designated -50W + 100W and -100W. Those samples were placed in plastic bags for storage at room temperature.

6. Moisture determination

Moisture determinations were made following the A.O.A.C. Method 14.004 (1970).

7. Expansion

Expansion was measured as the ratio of the product diameter to die diameter. That ratio is defined as the expansion index. Ten random diameter readings were taken on each sample using a ruled caliper. Each reading was the average between the largest and the smallest values found on each one of the ten rod-shaped samples. The mean of the ten observations was used as the expansion index for that sample.

8. pH determination

The pH measurements were made on a Beckman Expandomatic SS-2 pH meter which had been standardized with pH 4 buffer. Two different procedures were followed depending on the samples:

a) Prime and extruded starches. - Four grams of sample was dispersed in 50 ml. of distilled water, and the pH was taken on this slurry. Two pH determinations were made for each sample.

b) Pastes from amylograph. - Ten gram of paste was removed from the amylograph at the end of a pasting-curve determination. The sample was dispersed in 50 ml of distilled water and the pH measured.

9. Color determination

Reflectance color was measured by the Agtron Model 500A reflectance meter, which measures relative spectral reflectance. Two wavelengths were used. 436 (blue) and 540 (green). When samples had a particle size less than 147 microns (-100W), standardized discs Nos. 44 and 90 were used for the blue region and standardized discs Nos. 71 and 90 for the green region. Standardization was checked before reading each sample. To obtain duplicates in color readings, two replicate samples of 10 g from each sample were taken.

10. Paste viscosity

Hot paste viscosity was measured in a Brabender Amylograph-Viscograph, No. 400, Type DC-2. The instrument was equipped with a 700 cm.gm head, and the bowl rotated at 75 rpm. Two main methods were used according the type of sample analyzed, which differed in the use or not of carboxymethylcellulose (CMC). Four procedures of a third method (industrial method) were studied. Those procedures differed in the stirring given to the sample-water slurry before addition of the slurry to the amylograph bowl and in the heating system used in the determination.

a) Method for prime starch-emulsifier blends with CMC. - A final suspension of each prime starch-emulsifier blend containing 9% solids (w/v) on dry basis, in 450 ml of deionized water containing 0.8% (w/v) of carboxymethylcellulose (CMC) was prepared as follows. In a 500 ml beaker fitted with a magnetic stirbar was placed 250 ml of deionized water and a portion (∿ 1 g) of the CMC. The beaker's content was transferred into a Waring-Blender, and the rest of CMC was added together with the sample during continuous agitation. After stirring ∿ 1-2 min all the materials were in suspension and the slurry was transferred to the amylograph bowl. The heating cycle was standardized to heat from 35°C to 95°C, (at constant rate of 1.5°C per minute) and to hold at 95°C for 15 minutes.

b) Method for extruded samples. - A suspension of a ground extruded sample of 9% solids on d.b. (w/v) in 450 ml of deionized water was prepared using the following procedure. Three hundred ml of deionized water was placed in a 500 ml beaker and the weighed amount of sample was slowly added portionwise to the water with continuous stirring. When the suspension in the beaker became too viscous to stir with the magnetic stirrer, the beaker's contents was added to the Waring-Blender cup. After stirring one minute, the resultant slurry was rinsed quantitatively into the amylograph bowl and sufficient water added to bring the total to 450 ml. The heating cycle was heating from $30^{o}C$ to $95^{o}C$, ($1.5^{o}C$/min) followed by holding 15 min at $95^{o}C$ and then cool from $95^{o}C$ to $50^{o}C$ ($1.5^{o}C$/min).

c) Industrial method for pregelatinized starches. -

METHOD A. To 460 g of distilled water in a Waring-Blender was added forty grams (5% m.b.) of pregelatinized or extrusion-cooked starch. The suspension was stirred rapidly for ∿ 1 min. and the resultant slurry was poured into the amylograph bowl which was heated from $30^{o}C$ to $95^{o}C$ at a rate of $1.5^{o}C$ per minute, using cooling water to help control the bowl temperature.

METHOD B. Same as Method A, except that cooling water was not circulated through the cooling coils during heating. Therefore, the rate of heating was not constant.

METHOD C. To 460 g of distilled water in a 600 ml beaker was added forty grams (5% m.b.) of pregelatinized starch. The suspension was stirred gently with a spatula until it appeared homogeneous. After that time, the paste was stirred an additional 4 min with the spatula. The paste was then poured into the amylograph bowl. The temperature control cycle was set to heat from 30 to $95^{o}C$ at a rate of $1.5^{o}C$ per minute. Cooling water was circulated through cooling coils.

METHOD D. This method is the one used by some industries. The procedure is the same as Method C, except that cooling water was not circulated through cooling coils during heating.

11. Cold paste viscosity and shear-thinning of a cold-paste. Cold paste viscosity was measured with a Brookfield Synchrolectric viscometer, model LVT, using a No. 2 spindle at 60 rpm. The calibration of the Brookfield viscometer was checked using standard viscosity solutions provided by Brookfield Co., Stoughton, Mass. A suspension of a ground precooked product (-50W + 100W) of 6% solids on dry basis (w/v) in 120 ml of distilled water was prepared as follows. All the water was placed in a 150 ml beaker containing a stir bar. The sample was added rapidly to the water while stirring, which was stopped as soon as all the sample had been added (5 to 10 sec). The spindle of the viscometer was introduced into the suspension, and after 5 seconds, the spindle of the viscometer was turned on and the viscosity reading was taken. That viscosity was considered as the viscosity at zero-time stirring. The spindle was then withdrawn, the magnetic stirrer turned on, and after five seconds the stirrer was again turned off. The viscosity of the suspension was measured as before. This procedure was repeated for the following stirring times: 10, 15, 20, 30 and 60 seconds and 2, 3, 5, 10, 45 and 60 minutes. In some cases, readings of viscosity were recorded after several hours of stirring. Measurements were always made on duplicate samples to obtain an average viscosity. The readings were converted to centipoise units using the Brookfield conversion chart.

12. Water solubility

A 5.0 g sample of ground (-50W + 100W) precooked starch was slowly added to 175 ml of distilled water in a 250 ml centrifuge bottle. The water was stirred as the sample was added to prevent formation of clumps. The suspension was stirred 30 min with a magnetic stirrer. After that time, the stir bar was removed, rinsed with 25 ml water, and the suspension centrifuged 5 min at 700 G. Duplicate aliquots (10.0 ml) were taken from the top of the supernatant and each one was placed in a Petri dish previously dried and weighed. The Petri dishes were put in a forced air oven at 105°C and dried for four hours. Duplicate 5.0 g samples of all starches were extracted.

$$\% \text{ of water solubles} = \frac{(W_2 - W_1)\ (2000)}{5 - (5 \times h)}$$

where W_2 = weight of Petri dish with solids after drying (g.)

W_1 = weight of empty Petri dish (g.)

h = moisture content of the sample, %.

13. Ferricyanide number and dextrose equivalents

The dextrose equivalents of extruded samples were calculated on the basis of the ferricyanide number determination (Schoch, 1964).

14. Spectral properties of iodine-complexes of extrusion-cooked starches.

The spectral properties of the iodine complexes were determined using a modification of the method of Williams et al. (1970). One hundred mg of starch that had been extrusion-cooked with or without emulsifiers was placed in a 100 ml volumetric flask. One ml of ethanol was added to wet the solids, followed by 50.0 ml of water. The mixture was shaken on a table-top shaker for 30 min at 25°C. After that time, the mixture was made to volume with distilled water. The suspension filtered through Whatman paper #4 and a 50 ml aliquot was pippeted from the filtrate, into a 100 ml volumetric flask. After adding 5 ml of 0.1 N hydrochloric acid and 0.5 ml of a 0.2% iodine reagent solution, the volume was diluted to 100 ml with water and the absorbance of the colored solution was determined as a function of the wavelength, using a Beckmann OB-G spectrophotometer.

When the amylopectin-iodine complex was measured, the amylopectin was first dissolved in 10 ml of 0.5 M aqueous potassium hydroxide and then made to volume (100 ml) as above. A 5.0 ml aliquot of that solution was treated as above to form the amylopectin-iodine complex.

15. Stereoscopic microscopy

Stereoscopic micrographs were taken of extrusion-cooked starch samples to show the differences in "grain" or cell structure obtained by extrusion at different temperatures and moisture levels. For viewing, the rod-shaped extrudates were cut into short cylinders with a height of ∿ 8.0 mm. Photographs were taken in a Wild Heerbrug Stereoscopic microscope, Switzerland, using a magnification of 6x. The upper light had a setting of 5 while the light under the specimen had a setting of 11.0. The film was Kodak high intensity black and white.

16. Statistical analysis

In determining the characteristics of the various extrusion-cooked starches, two main sources of error are present. First, the error due to the variability of the extrusion process itself, and second, the variation due to the different analytical methods. The errors involved were determined for only one of the extrusion-cooked starches. It is assumed the errors involved in the extrusion of other samples are of the same order of magnitude.

When an emulsifier is added to starch prior to extrusion, a third source of error is introduced, namely, the preparation of the wheat starch-emulsifier blend.

To examine the reproducibility of the data, wheat starch and wheat starch - 0.5% SSL were extrusion-cooked on five and four different days, respectively. All the analytical methods were applied to all nine samples. An analysis of variance on the data given an indication of the main sources of error.

A one way analysis of variance was run on the data of the extruded samples of wheat starch and the wheat starch-SSL blend. The Least Significant Difference (LSD) at 95% probability level was calculated for all the analysis performed.

In some determinations, such as hot-paste viscosity, no replications were done. However, several runs were made on one sample on four or five different days. From those runs confidence intervals of 95% probability were calculated.

III. RESULTS AND DISCUSSION

A. EFFECT OF EXTRUSION pH ON EXTRUDATE PROPERTIES.

Early in this study, when emulsifiers were added to wheat starch, it was noticed that the pH of an extruded blend was variable. A search of the literature revealed no one had previously reported the effect of pH on the properties of extruded starch. Consequently, a series of wheat starch samples with pH values ranging from 3.0 to 9.0 were extruded to study the influence of extrusion pH on the expansion index, water solubility, production rate, color, hot paste viscosity, cold water viscosity, reducing value and pH change during extrusion.

Figure 1 (page 60) shows that the expansion index was practically constant in the pH range from ∿ 4.4 to 9.0. But expansion decreased sharply as the pH of the inlet starch fell below ∿pH 4.4.

This effect can be explained by the thinning of the starch due to acid hydrolysis of starch during extrusion. By thinning the starch, the thermoplastic mass leaves the die as a much less viscous fluid. The lower viscosity combined with the availability of more free water to produce more steam at the die gives an extrudate with very thin cell walls. But the diameter of the rod-shaped extrudate is small because the walls of the cells are too weak to retain much of the flashing water vapor.

As expected the pH of the extrudate product is affected by the pH of the inlet feed material. Figure 2 shows that when the feed inlet was acidic there was a slight rise in the pH of the extrudate product. On the contrary, when the inlet feed starch had a basic pH, there was a decrease in pH, which was greater as the pH value of the feed increased.

The presence of atmospheric carbon dioxide during the extrusion process could possibly explain the pH-change observed during extrusion. Carbon dioxide is pumped into the extruder together with starch. Some amount of that carbon dioxide dissolves to neutralize some of the base. Base may also be consumed by saponification of lipids that contaminate the starch, or by alkaline degradation of starch (BeMiller, 1967).

The color of the extruded starch samples was measured using an Agtron reflectance meter. The higher the reflectance value the lighter the color. Figures 3 and 4 for green and blue color respectively, show that the lower the pH of the inlet feed, the lighter is the color of the extrudate product. The commercial sample of pregelatinized wheat starch had an Agtron color value of 96.0 in the blue mode and 97.0 in the green mode, indicating that the extruded samples underwent more browning during their processing than did the commercial starch, except for starch extruded below pH 4.4.

Figure 5 is a color photograph showing how browning of the extrudate increases as the pH of the inlet starch increases.

The brown color of the extruded products can be caused by both a caramelization of sugars and by a Maillard reaction between the amino acids present in the protein contaminant of the starch and the carbohydrate. Both types of reactions are known to be accelerated by high temperature, basic pH, and by the presence of phosphate ions. (Ellis, G. 1959).

The pH affects not only the properties of the product, but also influences the operation of the extruder. Figure 6 shows that the output rate (kg/hr) maintained a constant value through the pH range of 3.4 to 9.0. This means, the pumping efficiency of the screw and the flow through the die were not affected between those pH values. But there was a significant reduction in the production rate at pH 3.0.

The second curve in Fig. 6 shows the amperage* per Kg per hr (energy consumed per unit production) as it varied with pH. It can be seen that there was a decrease in the energy used for a unit of production in the pH region from 3.0 to 4.4. This fact may be explained by the lower viscosity of the paste at pH 3.0 and 3.4 due to partial acid hydrolysis. The lower the viscosity of the paste inside the barrel, the lower the amount of energy needed to pump the product out the die (Tadmor and Klein, 1970). Except for the region of low pH values, the viscosity of the starch-water system inside the extruder is probably the same at the different pH values studied; therefore similar amounts of energy are needed.

The amylograph curves in Figure 7 illustrate the effect of pH on the hot paste viscosity of prime wheat starch. The amylogram curves are seen to be similar for prime starch cooked at pH values from 4.4 to 9.0. When cooking was done below pH 4.4, the peak viscosity was less, shear-thinning was greatly increased, and the setback viscosity on cooling to 50°C was significantly reduced. This fact supports the proposed hypothesis concerning the reduced viscosity of starch extruded at pH 3.0 and 3.4.

The amylograms of the extrusion-cooked starches are shown in Fig. 8. Once again, there was no significant difference between the amylograms of the control and the amylograms of the extrusion-cooked samples when extrusion had been done at pH 4.4 to 9.0. Only the samples obtained from extrusion at pH 3.0 and 3.4 exhibited lower viscosities.

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*An increase in current consumption is directly proportional to the power required at a constant speed. The voltage across the armature of the motor drive of the extruder is 90 v D.C. at 100 rpm.

Because of the small amounts of material produced by the laboratory-scale extruder, a new technique using the Brookfield viscometer was devised to determine some of the pasting properties of the pregelatinized starches on approximately 8.0 g of sample. In the method, I wished to obtain data on (i) the rate of hydration of extruded products, (ii) their maximum viscosity, and (iii) their viscosity-stability to shearing.

Before giving the results of the new test, it might be best to first review the current theory of the thickening power of starch. The viscosity of a starch paste is a function of several factors: the degree of gelatinization, the availability of starch molecules to hydration, the degree of chain cleavage of starch molecules, and the residual aggregation of starch molecules as they were deposited in the native granule. It is probable that those metastable aggregates are eventually broken apart and separated into hydrated molecules by continual stirring.

Those factors controlling starch paste viscosity depend in turn on the effects of the cooking process on the starch granule and on its starch molecules. If amylose and amylopectin molecules in starch have been substantially degraded, the precooked starch will display very little swelling, and it will hydrate rapidly with simultaneous release of much soluble material. Consequently, the viscosity of its paste will be small to null.

Even when molecular degradation is small, a pregelatinized starch can still give a reduced viscosity compared to a freshly made paste. It seems that the gelatinization of a starch granule in water causes the "melting" of the crystalline zones in the granule as evidenced by the change in X-ray diffraction patterns. The melting is probably accompanied by the introduction of some water molecules between the chains of amylose and amylopectin. If the gelatinized granule is quickly dried with no agitation, such as on a drum dryer, then the granular structure remains partially intact. A film-dried granule will retain much of the structure of the granule as it was laid down in nature. Rehydration of that type of pregelatinized granule will proceed somewhat along the same path as hydration of the native granule. However, the structural features of the native granule gradually disappear during continual heating and shearing of a starch paste.

If a starch granule is sheared during gelatinization, such as in the extrusion process, a greater percentage of the native structure is disrupted than in drum cooking. Thus, extrusion cooking gives a starch whose viscosity is closer to the lower limit of viscosity for that starch. The lower limit of viscosity is reached when the amylose and amylopectin are fully separated and surrounded by water molecules. The paste viscosity is thicker when those molecules remain somewhat entangled or associated with each other, as they occur in the native granule. Starch pastes continue to thin upon stirring because the continual breakdown of residual granular structure, and because of the thixotropic nature of starch (due to allignment of molecular chains along the lines of stress). Of course, any treatment that depolymerizes amylose and amylopectin molecules leads to an easier breakdown of the native starch structure, and also to a lower limiting viscosity of the starch paste.

Figure 9 indicates that the cold paste viscosities of the extruded products decreased as the extrusion pH decreased. An inlet-feed starch of pH 3.0 gives an extrudate product with a very low, cold-water viscosity (14.5 centipoises at the maximum). That product solubilizes ($\sim$90%) in water almost instantly. Such properties indicate again the high degree of degradation the starch suffered upon extrusion under strongly acidic conditions. The products obtained by extrusion at pH 4.4 and 5.4 had a higher viscosity than the sample obtained at pH 3.0. The maximum viscosity (88 centipoises for pH 4.4 and 115.5 centipoises for pH 5.4) was attained by those two samples after 30-60 seconds stirring. On the other hand, the more viscous samples obtained at higher pH reached their maximum viscosity ($\sim$225 cps) between two and three minutes stirring. No significant differences were found for the cold paste viscosities in the first five minutes of stirring for the samples extruded at pH 6.2, 7.6 and 9.0 (Fig. 9). These results seem to indicate possible structural differences between the samples extruded at pH 4.4 - 5.4, and those extruded at neutral or basic pH.

The data in Figure 10 shows that products of high solubility (80-90%) can be produced with extrusion pH's of 3.0 and 3.4. The solubility of the extruded starch decreased sharply somewhere between pH 3.4 and 4.4 (from 81% to 50%). Extrusion at pH 4.4 to pH 9.0 changes the solubility of the product slightly (50% to 40%).

The data in Table 2 shows there was no change in the Dextrose Equivalent (D.E.) of the samples extruded at pH 4.4 to 9.0 compared to the D.E. of the blank sample of prime wheat starch. However, at pH 3.4 there was an increase in D.E., and at pH 3.0 the extrudate sample has a D.E. of 7.5, or an average chain length of $\sim$13.

These results indicate that it is possible to use extrusion cooking to produce maltodextrins, which could be incorporated in foods with an acidic pH such as pizza sauces and other tomato-based products. The biggest problem might be the accelerated wear on the metal of the extruder.

B. EXTRUSION COOKING OF WHEAT STARCH WITH EMULSIFIERS

A series of wheat starch, emulsifier blends were extruded to study the influence of emulsifiers on the extruded starch's expansion, water solubility, color, hot paste viscosity, cold water viscosity, and pH. The effect of the emulsifiers on production rate and energy required for extrusion were also examined. Four different commercial emulsifiers were used at levels of 0.25, 0.50, and 0.75%. The emulsifiers were chosen to represent a range of hydrophilic-lipophilic balance (HLB). They were as follows: a distilled monoglyceride (DMG), which is a non-ionic surfactant with an HLB 4 (Stutz et al., 1973); sodium stearoyl-2-lactylate (SSL),which is an anionic surfactant with an HLB of ~6-7; ascorbyl palmitate (AP) which is theoretically an anionic surfactant but which is practically insoluble in water (Cort, 1974); and polyoxyethylene sorbitan monoestearate (PSM), which is a nonionic surfactant with HLB 14 (Stutz et al. 1973).

The levels of the four emulsifiers are reported in weight percent in this study. Differences in the behaviour of starch with varying levels of surfactant could be due to differences in the surfactants' formula weights. The formula weights of the four surfactants studied here are approximately as follows: DMG 395 g; SSL 449 g; AP 414 g; and PSM 1006 g. Thus, 0.5% PSM contains half the number of molecules of 0.5% AP.

When the effects of a minor component on the behavior of a wheat starch is to be studied, it is important that that minor component be uniformly distributed in the starch. The homogeneity of distribution of two or the four emulsifiers used in this study was checked by extraction of several random samples of the blends. The data in Table 3 shows that the emulsifiers did indeed give a uniform distribution at the lowest level of emulsifier added.

The pH of the starch-emulsifier blends before extrusion varied from 6.5 to 7.5 depending on the emulsifier used. The addition of SSL or AP gave slightly acidic pH values, whereas DMG and PMS gave slightly alkaline values (Table 18, Appendix 1). The effect of pH on extrusion of wheat starch was already examined in detail in the preceding section. The results showed that extrusion of wheat starch was not affected between pH 4.4 and 9.0. It can be concluded that the effects of emulsifiers on extrusion cooked wheat starch are not due to changes of pH, but rather are due to interactions between the starch and an emulsifier.

Figure 11 shows the effect that each emulsifier had on the production rate during the extrusion of wheat starch. At 0.25%, DMG and AP did not produce a significant change in the rate of production, but they did reduce the power requirements, as indicated by a reduction in the amperage (Fig. 12). SSL produced a slight increase in output at 0.25%, but gave no significant decrease in amperage. PSM at 0.25% caused a sharp reduction in both output and power consumption.

At a level of 0.5%, all emulsifiers produced a decrease in production rate (Fig. 11). PSM gave the lowest production rate (0.62 kg/hr), while SSL gave the highest (2.77 kg/hr). It should be noted that during duplicate extrusion runs at 0.5% PMS, surging occurred during extrusion. The unstable extrusion condition could not be eliminated by increasing or decreasing the screw speed.

At 0.75%, all emulsifiers reduced the output to approximately one half that of the control run (1.4 kg/hr vs 2.9 kg/hr, Table 4 and Fig. 11).

Figure 12 shows the motor-drive energy needed to produce one kilogram of product containing various emulsifiers. In a control run with wheat starch alone, the energy required for extrusion at 100 rpm and 19% moisture was 2.82 amp. hr/kg (Table 4). In general, all four emulsifiers lowered the energy needed to extrude starch. One notable exception was PSM at 0.5%. The curves for SSL, AP and DMG in Figure 12 show that the energy requirements go through a minimum as the level of emulsifier is increased in the starch. However, PSM exhibited an anomalous behaviour, its curve gave two minima (Figure 12).

A hypothesis is presented in the next few paragraphs to try to explain the changes in energy requirements with changes in emulsifier and its level of addition. First, the case of SSL will be considered as a model for the action of three of the emulsifiers studied (DMG, SSL, and AP).

At 0.25% level the emulsifier molecules complex with starch during extrusion and decrease the amount of water solubles. The complexed and relatively insoluble amylose molecules exist as very finely divided particulate matter in the swollen gel phase. These particles are assumed to have little effect on the viscosity of the starch gel. The net effect is that a greater amount of free water molecules exist in the starch gel and therefore the viscosity of the melt phase decreases in the presence of strong starch complexing agents. Since the viscosity is decreased, the energy required for extrusion also decreases. A highly viscous melt requires more energy to transport it down the barrel and expel it through the die.

But there is one other effect that a surfactant can have on a starch paste. If all the surfactant is not complexed with starch, the uncomplexed portion can act as a lubricant inside the barrel. A reduction of the surface friction at the barrel's surface will greatly decrease the pumping efficiency of the extruder. Drag flow normally dominates the flow of material through a laboratory-scale extruder (Harmann and Harper, 1972). The pressure created at the die does oppose the drag flow, but pressure flow is normally small in extruders with shallow flights. However, if the friction between the barrel's surface and the feed material is low, the pressure forces at the die push the material back towards the inlet of the extruder. Thus, surfactants can cause "slippage" at the barrel surface. Under that condition, material is not advanced efficiently toward the die as the screw turns.

At 0.25% SSL, almost all of the surfactant is apparently complexed with starch. The reduction in the viscosity of the starch paste is dominant, and the energy needed for extrusion is reduced (Figure 12). But increasing the level of SSL to 0.5% and 0.75% apparently supplies extra molecules of SSL or other surfactant molecules besides those complexed with starch. Thus, "slippage" becomes important at 0.5 and 0.75% SSL, and the energy requirements for extrusion increase.

Polyoxyethylene sorbitan monostearate behaves differently than AP, SSL and DMG*. Slippage is apparently a serious problem at 0.5%

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*AP, SSL and DMG could also have double minima curves, but not enough levels were tested to detect them.

PSM. During extrusion at 0.5% PSM, the extruder exhibited surging, and the flow was unstable. When the level of PSM was increased to 0.75%, extrusion became normal again and energy requirements decreased. The behavior at 0.5% PSM remains unexplained.

The effects of emulsifiers on the expansion index of extruded wheat starch are shown in Figure 13. The expansion of an extruded cereal product is important because the cellular structure or "grain" of the product plays an important role in the eating texture of a food. In general, expansion of the extruded product decreased upon addition of an emulsifier. Closer examination of the curves in Figure 13 show that each type of emulsifier had a slightly different effect on the expansion index.

At 0.25%, all emulsifiers produced a decrease in expansion, but the effect was greatest in the cases of AP and SSL. At 0.5%, the downward trend of expansion changed, and sodium stearoyl 2-lactylate and ascorbyl palmitate produced significant increases in expansion when compared to those observed at 0.25%. At 0.75%, all emulsifiers except PSM reduced expansion. Ascorbyl palmitate gave the lowest expansion.

The general reduction of expansion caused by the emulsifiers appears to be due to their ability to complex with starch, especially the amylose fraction.

When starch complexes with an emulsifier, its solubility is reduced (Gray and Schoch, 1962). Soluble starch is important in forming the viscous medium which traps the water vapor in cells as the cooked starch leaves the extruder. If the viscosity decreases too much, the cell walls do not set rapidly enough upon leaving the extruder and they rupture during expansion.

The interaction between starch and each emulsifier is different, depending on its molecular structure. The molecular structure also controls it's hydrophilic-hydrophobic balance, to a large extent.

Polyoxyethylene sorbitan monoestearate is a relatively hydrophilic surfactant (HLB 14), and it is known to exhibit less tendency to complex with amylose than DMG (Krog, 1971; Osman et al, 1961). The more hydrophobic surfactants are expected to form the strongest complexes with amylose, due to the hydrophobic character of the inside surface of the amylose helix. Thus at equal weight percentages, PSM is not as effective as AP, SSL or DMG in reducing the expansion of starch during extrusion. The action of SSL _versus_ that of AP or DMG also support the hypothesis. In general, SSL showed less effect on expansion than the more hydrophobic AP and DMG.

Distilled monoglycerides and polyoxyethylene sorbitan monostearate had little effect on the pH of the extruded starch (Fig. 14). However, SSL and AP caused the pH of the product to decrease. At 0.75% AP, for example, the extruded product had pH 5.3 compared to pH 7.1 for the control. These results could be expected due to the somewhat acidic nature of SSL and AP.

Figures 15 and 16 illustrate the effect of the emulsifiers on the Agtron green and blue color of the extrudate starch. SSL showed a tendency to give a product with a lighter color than the other three emulsifiers at all levels. The SSL products were almost all lighter in color than the control. DMG and AP gave products that were more brown than the control. The color increased as the percent of DMG or AP increased. At 0.25%, PSM produced a more brown product than the control, while at 0.50% and 0.75% it gave a product with a color approximately the same as that of the control.

The color of the extruded starch is probably controlled by two factors, the pH and the residence time of the starch in the extruder. Since the pH and residence time varied inconsistently with the different emulsifiers, it is difficult to explain the color differences.

The percentage of water extractables (25°C) in the extruded products sharply decreased when any of the four emulsifiers was present in the inlet feed starch (Figure 17). At 0.25% emulsifier, the solubility of all products was about 20%, whereas the control starch gave about 45% of water solubles. The lowest solubility of all products (about 10% solubles) occurred at 0.5% SSL and 0.5% AP. At 0.75% the products had solubilities ranging from 13 to 20%.

The solubility of the extruded products are undoubtedly related to three variables; the pH, the residence time in the extruder, and the degree of complexing with an emulsifier. The last factor probably dominates, whereas the other two factors cause minor variations in the amount of water extractables.

A blend of wheat starch with 0.5% SSL at pH 3.0 was extruded at the same conditions as a blend of wheat starch - 0.5% SSL to study the effect of emulsifiers at low extrusion pH. The product extruded at pH 3 gave 86.5% of water solubles, whereas the SSL control gave 19% solubles. These results, together with those obtained with an inlet feed starch of pH 3.0 without emulsifier (89% water solubles), indicate that at low pH, the hydrolysis reaction overrides the complexing action of the emulsifier.

Another important property of extrusion-cooked starches is their pasting characteristics. The Brabender Amylograph is the conventional instrument used to examine the pasting properties of starch. When using the amylograph, one can add carboxymethylcellulose (CMC) to a paste to observe subtle viscosity changes that occur during gelatinization at the early stages of swelling of a starch granule. This material is also useful to study the effects that emulsifiers have on the rheological characteristics of the starch-water system. In a control run, a suspension of prime wheat starch in water (5.5% solids d.b.) in presence of 0.8% CMC gave a similar amylogram to that reported by Miller et al. (1973). However, to accentuate the possible differences between the control and the wheat starch-emulsifier blends prepared in this work, a higher concentration of solids was used (9% d.b.).

The differences in the amylose-complexing ability of the emulsifiers used in this study can be demonstrated by examining pasting curves on prime wheat starch using the CMC technique (Figures 18, 19, 20). Ascorbyl palmitate appears to have the greatest complexing ability among the emulsifiers used. Therefore, AP would be expected to give the greatest reduction in paste viscosity during extrusion. SSL and DMG showed similar and intermediate complexing power with wheat starch. Polyoxyethylene sorbitan monostearate had the least effect on the gelatinization and pasting curves of prime wheat starch.

A closer examination of the curves in Figures 18-20 reveal some interesting differences in the interaction of the four emulsifiers with prime wheat starch. AP is unique in that it delays both the initial gelatinization and swelling of wheat starch, and reduces its hot paste viscosity (95°C). In addition, AP at 0.75% appears to largely eliminate the first stage swelling of wheat starch granules. On the other hand, SSL and OMG have little effect on the hot-paste viscosity, but they do delay gelatinization and swelling. In contrast, polyoxyethylene monostearate (PSM) only slightly delays gelatinization and swelling on wheat starch, and it has no effect on hot-paste viscosity at 0.25% and 0.50%. But at 0.75%, PSM does reduce hot paste viscosity. The latter observation may help explain the sudden decrease in energy requirements for the extrusion of wheat starch with 0.75% PSM as compared with 0.5% PSM.

From Figures 18-20, one can see that PSM has the lowest complexing ability of the four emulsifiers, possibly because it has the highest hydrophylic character. This means that PSM would be more prone to cause slippage if added to starch prior to extrusion.

The amylograph was also used to study the pasting properties of extruded wheat starch-surfactant blends (Fig. 21, 22, 23). The curves in Figs. 21-23 were obtained after Waring blending of the pastes and normal operation of the temperature control of the amylograph. The control curve is extrusion-cooked wheat starch with no emulsifiers. The extrusion cooked (gelatinized) starches all gave much lower viscosities than prime wheat starch (Figures 18, 19, 20). Wheat starch that had been extruded with OMG, SSL or AP gave pregelatinized pastes with similar properties. However the product obtained by extruding starch with PSM behaved differently. Starch pregelatinized with SSL, AP and OMG (0.25% - 0.75%), as well as PSM (0.25%), showed reduced cold-paste viscosities (Figures 21, 22, 23). However, a cold-paste viscosity higher than that of pregelatinized control was obtained when starch was extrusion cooked with 0.75% PSM (Figure 23).

Another series of amylograph curves were obtained to help determine whether complexing of the emulsifiers with starch occurred during the extrusion process or during the amylograph tests. A control sample of extrusion-cooked starch containing no emulsifier was placed in the amylograph with the various surfactants. The results are shown in Figure 24. At a level of 0.75%, PSM and DMG when added to the control extruded product, gave higher viscosities than when either surfactant was co-extruded with wheat starch at a level of 0.75%. Furthermore, the results show that PSM can be used to increase the viscosity of extrusion-cooked starch. These results suggest that a starch-surfactant complex is formed during the extrusion process.

To confirm complex formation, iodine complexes of extrusion-cooked starches were examined (Mercier, 1978). The results of this series of experiments are shown in Figures 25 and 26. Extrusion-cooked starch without emulsifier (control) in Figure 25 gave a peak absorption for its iodine-amylose complex at λ max = 620 nm, which is almost identical to λ max = 624 nm reported by Banks and Greenwood (1975). The iodine complex of amylopectin from wheat starch showed λ max = 580 nm. In theory, complexing of the amylose fraction of wheat starch with a surfactant should effectively precipitate the amylose fraction and prevent subsequent formation of a complex with iodine (Krog, 1971). In that case, the deep blue color (λ max = 624 nm) of the iodine complex of the free starch shifts towards a purple color (λ max = 580 nm), indicating an iodine complex with an amylose-deficient starch. Such effect is clearly seen in Figure 26, where the λ max of all starches co-extruded with emulsifiers shifted towards the 580 nm region (purple color). Furthermore, addition of PSM at 0.75% to the control sample of extruded starch (Fig. 25) did not affect the color of the iodine-starch complex (compare control curve *vs* control + PSM 0.75%). Addition of distilled monoglycerides at 0.75% to the control sample resulted in approximately one-half the complexing of DMG obtained during extrusion.

The present work was undertaken to determine if extrusion cooking of wheat starch with an emulsifier could give a product in which the granular structure of starch was partially preserved. The hot-paste viscosities (95°C) of the pregelatinized starches (Fig. 21-23) containing SSL, AP or DMG indicate that no granular structure survives extrusion-cooking. It should be recalled that AP greatly reduced the hot-paste viscosity of prime wheat starch and SSL or DMG did not (Figures 18, 19, 20). That uniqueness of AP was not observed in the hot pastes of the extrusion-cooked starches (Figures 21, 22, 23).

The cold paste viscosity is the most important part of the amylogram when comparing pregelatinized starches. To complement the amylogram evaluation, the cold-water viscosity of several samples of pregelatinized starches were studied using the Brookfield viscometer. This method, as described in the Materials and Methods section, gives an indication of the rate of hydration of the starch, its degree of gelatinization, degree of chain cleavage, and residual aggregation of starch molecules as they occurred in the native granule.

Figure 27 shows that during the initial stages of pasting the cold-water viscosity of wheat starch co-extruded with a surfactant decreased as the concentration of emulsifier increased. It also indicates that the stirring time needed to attain the maximum viscosity depends on the type of emulsifier. The control as well as those samples extruded with DMG and SSL required about two minutes stirring, but those containing PSM needed between five and ten minutes stirring.

When the samples in Fig. 27 were stirred for 1 hr, the viscosities of the control starch and the 0.25% SSL decreased to 116 cps and 89 cps, respectively, while the viscosities of the 0.5% PSM and 0.75% PSM samples increased to 120 cps and 113 cps, respectively. The viscosities of the 0.5% DMG or SSL remained unchanged.

C. EFFECT OF SCREW COMPRESSION RATIO, OIE OPENING AND 0.5% S.S.L ON THE EXTRUSION OF WHEAT AND CORN STARCH.

In this part of the work two extrusion variables were examined for their effects on extrusion-cooking of wheat and corn starch, both with and without 0.5% S.S.L. The two variables were compression ratio* (5 to 1, and 3 to 1) and rod-die diameter (¼ and 1/8 of inch). The inlet moisture content, temperature and screw speed were kept constant at 18.5%, 175°C and 100 rpm, respectively. The following effects were monitored; production rate and the product's expansion, water solubility, hot paste viscosity, cold-water viscosity, and pH.

Table 5 indicates that under the fixed extrusion conditions above mentioned, increasing the die diameter decreased expansion by 37-48% for both wheat and corn starch. Addition of 0.5% SSL also decreased expansion by 1 to 8% in the case of wheat starch, and by 4.6 to 20.3% in the case of corn starch. Apparently, starch extruded from a larger die collapses more after it leaves the die, because of its added mass and because of less water flashing off. In addition, a smaller die gives a higher pressure drop across the die opening, thereby creating greater expansion forces in the smaller die. The SSL probably complexes with amylose, which removes amylose molecules from solution, and therefore gives weaker cell walls.

The compression ratio of the screw appeared to have little effect on expansion except for corn starch through a ¼" die and corn starch plus 0.5% S.S.L, through a 1/8" die. Wheat and corn starch expanded

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*Screw Compression ratio is defined as the ratio of the channel depth at the end of metering zone to the channel depth at the beginning of feeding zone.

equally well at a compression ratio of 5:1, but wheat starch expanded 1.5-13.0% better than corn starch at a compression ratio of 3:1.

In general, the screw compression ratio did affect the motor-energy needed for extrusion. The channel depths are greater for the 3:1 than the 5:1 screw. The pressure-flow term is of greater importance as channel depth increases. Thus, as predicted by theory more energy is required to push one kilogram of starch through the extruder with a 3:1 rather than a 5:1 screw.

Table 6 shows that the production rate of wheat starch through a 1/8" or ¼" die was not affected by a change of screw compression ratio. This fact shows that the die is the bottle-neck in those extrusion runs. The added pumping capacities of the 3:1 screw over the 5:1 screw is not needed to satisfy the volumetric flow capacity of the dies. But different results were obtained when wheat starch was extruded in the presence of 0.5% SSL. Production rate decreased when a 3:1 screw was used instead of a 5:1 screw. Apparently the 3 to 1 screw was less efficient at pumping due to "slippage" caused by SSL.

The results with corn starch (Table 6) show that the production rate was always greater with a 3:1 screw compression ratio than with a 5:1. In contrast to results with wheat starch (Table 6 and Fig. 11) the addition of 0.5% SSL to corn starch increased production over the control. The energy required for extrusion of corn decreased the same as with wheat starch when SSL was co-extruded with the starch. But the energy reduction for corn seemed somewhat larger than for wheat.

One observation with corn starch is difficult to explain. Using a 5 to 1 screw, the production rate dropped when the die size was increased from 1/8" to ¼". The same phenomenon was observed using a

3 to 1 screw. It is possible that more shear-thinning occurred with the faster flow through the 1/8" die, therefore production rate was much faster through the smaller die-opening than through the ¼" die opening.

By comparing the production rate between wheat and corn starch, under the same conditions as in Table 6, it can be seen that the production rate for wheat starch was about 25% higher than for corn starch except for the combination of SSL and a 3 to 1 compression ratio. The energy consumed per unit output was often the same or lower for corn starch than for wheat starch.

The percentage of water solubles of the extrusion-cooked products from corn starch was always higher than the products from wheat starch, both with and without emulsifier (Table 7). The presence of emulsifier produced in both starches a sharp reduction in the percentage of water solubles. The percentage solubles was about 73% for extruded corn starch and about 43% for extruded wheat starch. In the presence of 0.5% SSL, the percentage of water solubles was about 41% for the extruded corn starch-emulsifier blend, and about 19% for the extruded wheat starch-emulsifier blend. Our results support the observations of Mercier and Pfeillet (1975), who reported that under the same conditions of extrusion, corn starch becomes more soluble than wheat starch. The reduction of water solubles caused by SSL is slightly different for wheat starch (about 56%) than for corn starch (about 44%).

These precooked starches containing SSL can be expected to give short pastes with little set-back upon cooling. They would behave as waxy maize starches, but would not possess the long or stringy character of waxy starches. For that reason, wheat starch precooked or complexed with SSL might be used to produce instant-starch puddings with cold or warm liquids. Because the amylose is completely complexed, the precooked starch-complex might also display freeze-thaw stability. Mercier (1978) has demonstrated such freeze-thaw stability for extrusion-cooked tapioca starch containing stearic acid or monoglycerides.

Table 8 shows that there was a slight decrease in the pH of extrusion-cooked wheat starch compared to inlet wheat starch, but a slight increase in the case of extrusion-cooked corn starch. Neither the screw compression ratio nor the die diameter influenced the pH of extruded product. The pH of corn starch is lower than that of wheat starch possibly because sulfur dioxide is used in the wet processing of corn.

The amylograms of extruded wheat starch in Figure 28, reveals that screw compression ratio and die diameter had only a slight influence on the pasting curves of the extrusion-cooked wheat starch. However, as discussed previously, extrusion-cooking of wheat starch with 0.5% SSL gave a complexed product with a modified pasting curve. The complex began to dissociate at 80°C, and at 95°C all the extruded starches had essentially the same viscosity.

Figure 29 shows the amylograms of extruded corn starch products. The viscosity of extruded corn starch was not affected by the screw compression ratio or the die diameter, in presence or absence of emulsifier.

A slight reduction in the viscosity of the extruded products was observed when the corn starch was precooked with 0.5% SSL. These amylograms agree with the water-solubility data for corn and wheat starch precooked with 0.5% SSL (Table 7). It will be recalled that the solubility of the extruded wheat starch-SSL blend was lower than that of the extruded corn starch-SSL blend. The greater degree of complexing of SSL with wheat starch results in a larger decrease in viscosity of wheat starch precooked with SSL (Figure 28) than in corn starch precooked with SSL (Figure 29). This effect is more clearly seen in Figure 30 which also shows the generally lower viscosities of extruded corn starch.

This result is surprising since it is well known that prime corn starch generally gives a stronger pasting curve than prime wheat starch. The opposite seems to be true of precooked wheat and corn starch. It is unlikely that the lower pH of the corn starch causes the reduced viscosity. The pH of the starch must drop below 4.0, as shown in Figure 1, before pH affects viscosity.

A comparison of the viscous properties of the pregelatinized starches obtained by drum-cooking and by extrusion-cooking is necessary to determine if the extruded products are similar to drum-cooked starches. The conditions under which a starch granule is cooked on steam-heated rolls are different from those used during extrusion cooking. In the latter case, the starch granule is subjected not only to hydro-thermal action, but also to shear stresses. Shearing disrupts and tears apart starch granules, thereby causing a decrease in the swelling power and in the viscosity of a starch paste.

The effect of shear is evident in the case of corn starch as shown in Figure 29. The commercial drum-cooked product exhibited a greater viscosity than all of the extruded corn starches examined in this work.

Figure 31 shows the pasting curves of commercial drum-cooked, of commercial extrusion-cooked, and of laboratory extrusion-cooked wheat starch. The drum-cooked starch displayed a slightly greater viscosity than the two extruded products.

After most of the amylograph data had been collected in this work, it came to our attention (Hoseney, 1978) that the pasting characteristics of pregelatinized starches can be tested by several different procedures using the Brabender amylograph.

Four methods were used to compare the pasting curves obtained on one sample of pre-gelatinized wheat starch. All curves were measured using 40g (5% m.b.) in 450 ml of water, but the method of suspending the starch in water was different and so was the method of heating the paste.

Method A: In this method, the pregelatinized starch was added quickly to water being stirred rapidly in a Waring blender. The slurry was poured into the Amylograph bowl, which was heated at a rate of 1.5°C/min using cooling water to help control the bowl temperature.

Method B: Same as Method A, except that cooling water was not circulated through the cooling coils during heating.

Method C: The pregelatinized starch and water were stirred gently by hand and the paste poured into the Amylograph bowl. Cooling water was circulated through cooling coils.

Method D: (Industrial method) Same as Method C, except that cooling water was not circulated through cooling coils during heating.

The results of using these four methods on a pregelatinized wheat starch (commercial drum-cooked) are shown in Figure 32. Curves C and D showed that rapid stirring of the pregelatinized starch in the Waring blender reduced the paste consistency from 400-600 B.U. (curves C and D) to 100-200 B.U. (curves A and B). When cooling water was not circulated in the cooling coil, the starch pastes were thicker and displayed a pasting peak at a higher temperature than when the cooling water was used. Apparently the starch underwent more intense thermal treatment with the cooling mechanism off, allowing slightly higher swelling.

The four curves in Figure 32 all converged as the temperature of the pastes reached 95°C for a few minutes. This shows that the viscosity of the molecular species in the extruded and drum-cooked starches are the same. The higher viscosity of the drum-cooked starch is due to residual granular structure rather than lower molecular degradation.

Amylograms of the KSU extrusion-cooked wheat starches (control) were obtained using Methods A and D from 30-95°C (Figure 33). Once again, the viscosity of the starch paste was always higher using Method D (industrial method) than when using Method A, except at 95°C where the viscosities were equal. The largest difference was observed at 30°C, where the Method D gave 220 B.U. and Method A 140 B.U. However, the two methods gave approximately the same shape of amylograms. Therefore, if two pregelatinized starches are compared, differences in the two starches can be determined using Method A or D, but Method D is a more sensitive procedure than Method A. Either Method A or D could be used to test the properties of pregelatinized starches for many uses, since the ultimate viscosity of the paste can be determined at 95°C. Most uses of pregelatinized starches include pumping or other forms of shearing that reduce the viscosity of a paste to that due to the molecules.

Several other extruded wheat starches were also tested for their pasting properties using the industrial method D. These amylograms are shown in Figure 34. From those curves, one would deduce the following arrangement of the starches in decreasing order of cold paste viscosity; drum-cooked starch > extrusion-cooked wheat starch > extrusion-cooked blend of wheat starch - 0.5% PSM > extrusion-cooked blend of wheat starch - 0.5% SSL > extrusion-cooked blend of wheat starch - 0.75% AP. The same order was obtained using Method A, as is shown in Figures 22 and 23.

To be useful, pregelatinized starches must hydrate and swell rapidly in cold water. The Brookfield viscometer was used in this work to measure the rate of hydration of various starches. (See Materials & Methods p. 18). Differences in hydration rates also provide information on differences in the structures of pregelatinized starches as it was already mentioned in the Section A of the thesis.

Figure 35 shows that extrusion-cooked wheat starch (obtained with a extrusion temperature 175°C, 100 rpm, screw compression ratio 5 to 1 and die diameter 1/8") rehydrated very rapidly, attaining full hydration in about two or three minutes. At that time, the maximum viscosity (220 B.U.) was reached, after which time the viscosity decreased exponentially as stirring of the paste was continued for one hour. On the contrary, the drum-cooked product rehydrated slowly. Even after one hour of stirring by the magnetic bar, the viscosity of the drum-cooked product was still increasing. After two minutes stirring the viscosity of the drum-cooked product was less than that of the extruded one (about 75 cps vs 220 cps), but was larger after one hour (about 150 cps vs 115 cps). The viscosities of the drum-cooked and extrusion-cooked corn starches followed a similar pattern to that of wheat, but the corn starches had a much lower viscosity (maximum viscosity: 62 cps).

These results confirm the hypothesis of the structure of the pregelatinized starch granule, postulated early in Section A of this thesis. The structure of the pregelatinized starch granule obtained by drum cooking retains some of the structure of the native granule; therefore the hydration is somewhat slower as water gradually penetrates a tight system of hydrogen bonds. In the case of extrusion-cooked starches, which contains a random arrangement of amylose and amylopectin molecules, water quickly penetrates and hydrates the less-ordered structure. Therefore, the viscosity of the extrusion-cooked product rises quickly as the ground starch particles rapidly swell. Continued stirring gradually disperses the swollen particles into individual molecular species, causing a loss in viscosity as the suspended swollen particles disappear.

Our results also indicate the native structure of the corn starch granule is more easily disrupted than that of the wheat starch granule (Fig. 35).

The changes in viscosity of the drum-cooked and extrusion-cooked wheat starch were studied during a period of twenty-four hours of stirring in water at 25° (Figure 36). The drum-cooked product continuously swelled for about 12 hours, after which time it reached its maximum viscosity (about 200 cps). Afterwards, there was a slow decrease in the viscosity due to some shear thinning effect caused by the stirring. The extruded product, after an initial rapid increase in viscosity over the first three minutes of stirring, lost viscosity for the next three hours, at which time it seemed to level off. But after 8 hrs of continuous stirring, the viscosity began to increase again and maintained this trend even at the 24 hours. This increase could be due to a reassociation of the polymer molecules during stirring. Thus, it may be possible to use extruded starches for thickening power if their pastes could be stirred for 24 hr prior to use. In any event, it appears again that the ultimate viscosity of drum-cooked and extrusion-cooked wheat starches are of the same order of magnitude.

D. EFFECT OF EXTRUSION TEMPERATURE AND MOISTURE CONTENT OF WHEAT STARCH ON THE CELL STRUCTURE OF THE EXTRUSION-COOKED PRODUCT.

Several authors (Mercier and Pfeillet, 1975; Stearns, 1973; Lawton, 1972) have already reported the strong dependence of the expansion of extruded starch on extrusion temperature and the moisture content of the starch. However not much has been reported on the "grain" or cell structure of extruded starches. It is obvious that the internal structure of extruded starch may vary even though expansion remains constant.

In the following preliminary study, four arbitrary classifications of the grain or cell structure of extrusion-cooked wheat starch were established. The four classes of grain structure were used to assign cell structure to products made by extrusion of wheat starch samples at moisture contents of 19%, 22% and 25%, and at temperatures of 65, 100, 125, 150 and 175°C. At the same time, the effect of moisture and temperature was also measured on the current drawn by the motor drive, and on the cold-water viscosity of the extrusion-cooked products.

Table 9 shows that the lower the extrusion temperature or the lower the moisture content, the higher the energy consumption (indicated by the amperage). Lower extrusion temperature and lower moisture obviously give a more viscous paste in the extruder which gives high currents in the motor drive.

Lower extrusion temperatures and moistures in the starch also favor higher production rates (Table 9). The high viscosity of a "melt" in an extruder favors higher production rates for two reasons, (1) "Slip" is reduced at the barrel surface. and (2) the back-pressure flow is less significant in the volumetric flow through an extruder channel when viscosity is high (Squires, 1958). However, power consumption increases with higher viscosity. Thus, the energy required to produce a kg of product should go through a minimum as viscosity (temperature or moisture) of a starch decreases. At 22% and 25% moisture a minimum amount of energy is found when the extrusion temperature is 125^{o}C (Table 9).

The cell structures of the extrusion-cooked products were examined using the stereoscopic microscope. Four classes of structures were chosen as typical of almost all the extruded starches.

Figure 37 illustrates the characteristics of the four classes as viewed by a stereoscopic microscope using bottom illumination.

Structure 1: This structure is a glassy solid containing no gas cells.

Structure 2: This material is mostly a glassy solid containing a few very large gas cells with thick walls.

Structure 3: This type of structure has a greater number of cells than structure 2 and somewhat thinner cell walls.

Structure 4: This structure has a fine grain with a honeycomb-like structure and thin, lacy cell walls.

At constant screw speed (100 rpm), die opening (1/8 inch), and compression ratio (3:1), temperature seemed to have the predominant effect on the grain of extruded wheat starch over the moisture level of 19-25% (Table 10). Structure 1 was obtained at the lowest extrusion temperature of 65^{o}C. At that temperature, the extruder works well to form wheat starch into a solid gelatinized product, which could be subsequently cooked by other methods. Structure 4 was obtained at the highest extrusion temperature of 175^{o}C; structures 2 and 3 were obtained at ∿ 125°C and 150°C, respectively.

From Table 10 the following hypothesis is presented concerning the mechanism of expansion of extrusion-cooked wheat starch. At temperatures of 65-95°C, there occurs only gelatinization of the wheat starch which produces a molten paste. No steam is exhausted at the die, therefore there is little or no expansion (Structure 1). From 100°C to 125°C some steam is formed, depending on the moisture level of the starch. The steam produces some pockets or bubbles inside the thick starch paste. The low amount of steam limits the expansion to give a few thick-walled cells characteristic of structure 2. At even higher temperatures of 125-150°C, a greater number of bubbles or pockets of steam are formed as the cooked starch leaves the die. On flashing of the steam, smaller cells with thinner cells are formed (Structure 3). When the extrusion temperature and moisture content of the starch are optimum, like at 175°C and 19% moisture, there is a uniform distribution of smaller steam bubbles inside the molten material. Naturally, on releasing the steam, a large number of cells with thin cell walls are formed (Structure 4). Structure 3 can also be created at 175°C if too much moisture is present in the paste. The higher moisture allows bubbles to coalesce, and fewer cells are created.

The rate of hydration of extrusion-cooked wheat starch depends on its cellular structure. Structures 3 and 4 hydrate rapidly to give the highest initial viscosities. Structure 2 hydrates more ~~more~~ slowly. The product with Structure 1 could not be ground for testing along with the other samples used in Figure 38. Structure 1 gives a very hard and vitreous solid upon cooling after leaving the extruder.

The experiments on expansion show how the crunchiness of a wheat-based food can be controlled. The lower the expansion, the more dense and crunchy the final product can become. The greater the expansion, the easier will be the mastication and solubilization of the pre-cooked products.

IV. SUMMARY OF CONCLUSIONS

1) Extrusion-cooking of wheat starch in the range of pH 4.0 to 9.0 gave products with very similar properties. However, browning became more intense as pH increased. Drastic changes occurred as extrusion pH was lowered below 4.0. The water solubility increased and the degree of polymerization dropped sharply.

2) Co-extrusion of wheat starch at 175°C and 19% moisture any of the following emulsifiers, distilled monoglycerides (DMG), ascorbyl palmitate (AP), sodium stearoyl-2-lactylate (SSL), and polyoxyethylene sorbitan monostearate (PSM) gave a pregelatinized starch with a sharp reduction in water solubles, expansion index and production rate. The presence of emulsifier lowered the motor-drive energy required for extrusion of wheat and corn starch.

3) Cold paste viscosities of wheat starch co-extruded with DMG, AP or SSL decreased as the percentage of the emulsifier in the cooked blend was increased. However, PSM produced extruded wheat starch of greater thickening power than starch extruded without any emulsifier.

4) The granular structure of starch was more severely damaged during extrusion-cooking than during the drum-cooking, even when starch was co-extruded with surfactants that complexed with the starch.

5) Stirring an aqueous suspension of extrusion-cooked wheat starch for 24 hr at 25° slowly increased the viscosity of the mixture.

On the other hand, stirring a suspension of drum-cooked wheat starch caused the viscosity of the medium to increase and then slowly decrease. After 8 hr stirring the paste of the drum-cooked starch was ∿75 cps more viscous than that of the extrusion-cooked sample. After 24 hr, the difference was 25 cps and narrowing.

6) Under the same extrusion-cooking conditions, corn starch gave an extruded product with a higher percentage of water solubles and a lower hot and cold paste viscosity than extruded wheat starch, even in presence of 0.5% SSL. The corn starch granule appears more fragile to hydrothermal processing than the wheat starch granule.

7) The temperature of extrusion had the greatest effect on the cell structure or "grain" of wheat starch when it was extrusion-cooked at 19-25% moisture. A dense rod of pregelatinized wheat starch with no gas cells was produced by extrusion at 65-95°C. A product of maximum expansion with thin-walled cells was produced at 175°C and 19% moisture.

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FIGURE I

EXPANSION INDEX vs INITIAL pH FOR WHEAT STARCH

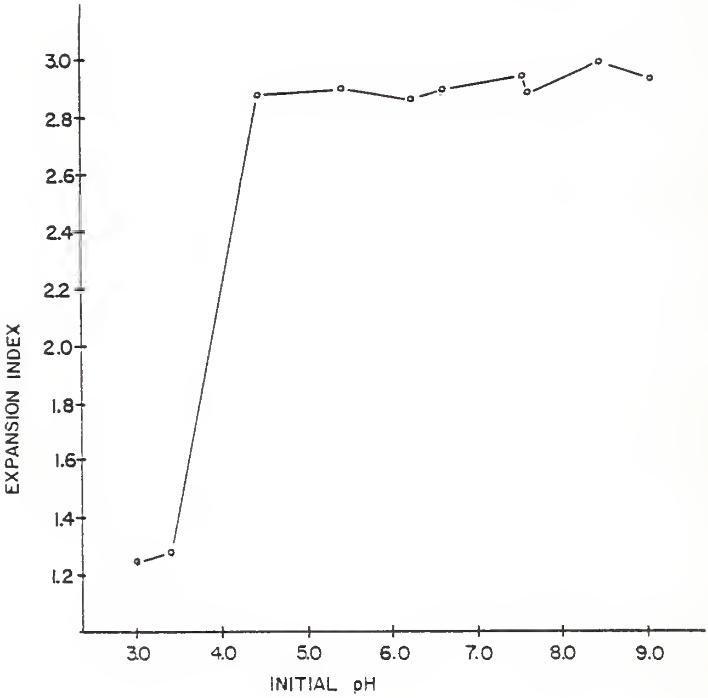


FIGURE 2

CHANGE OF pH DURING EXTRUSION vs INITIAL pH

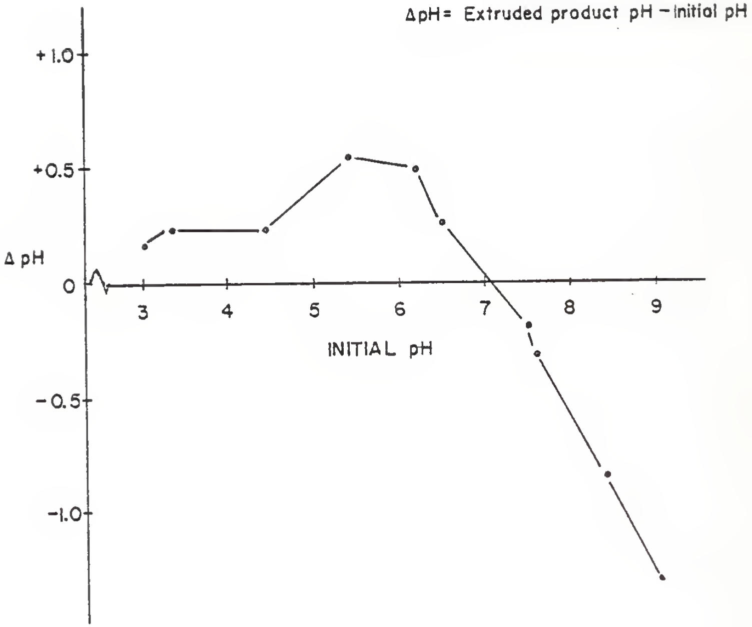


FIGURE 3

AGTRON GREEN COLOR vs INITIAL pH

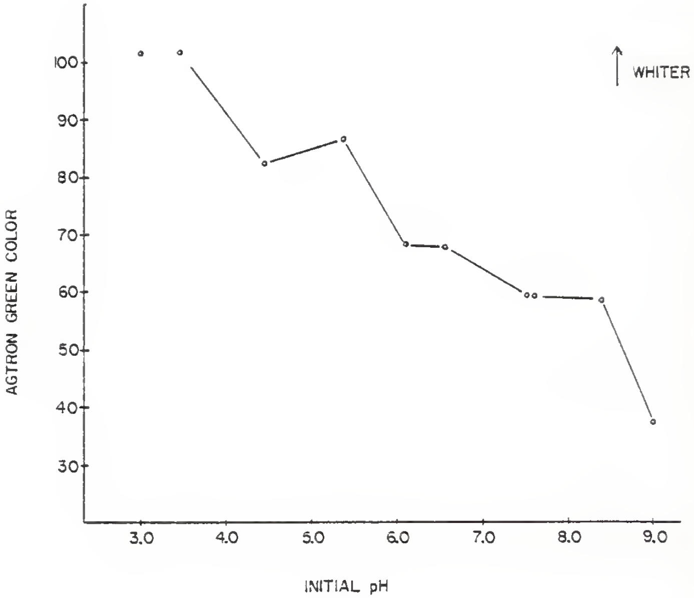


FIGURE 4

AGTRON BLUE COLOR *vs* INITIAL pH

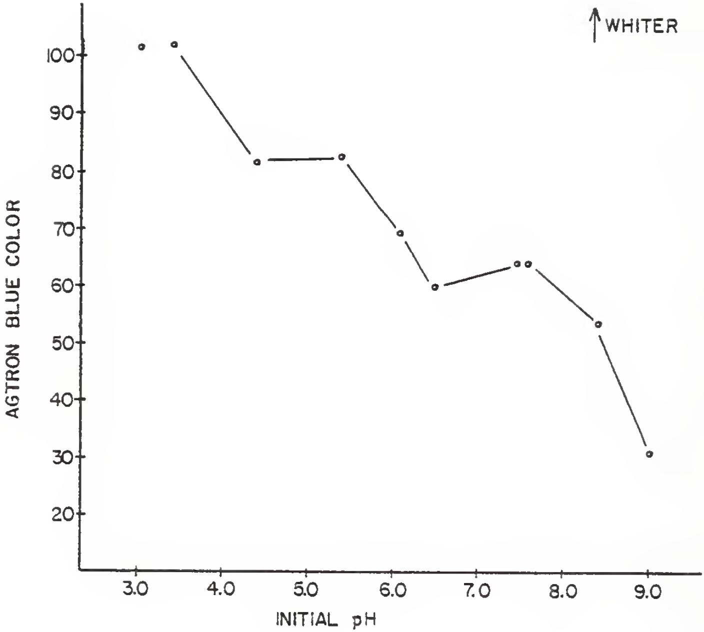


FIGURE 5

EFFECT OF EXTRUSION pH ON THE COLOR OF EXTRUDED WHEAT STARCH

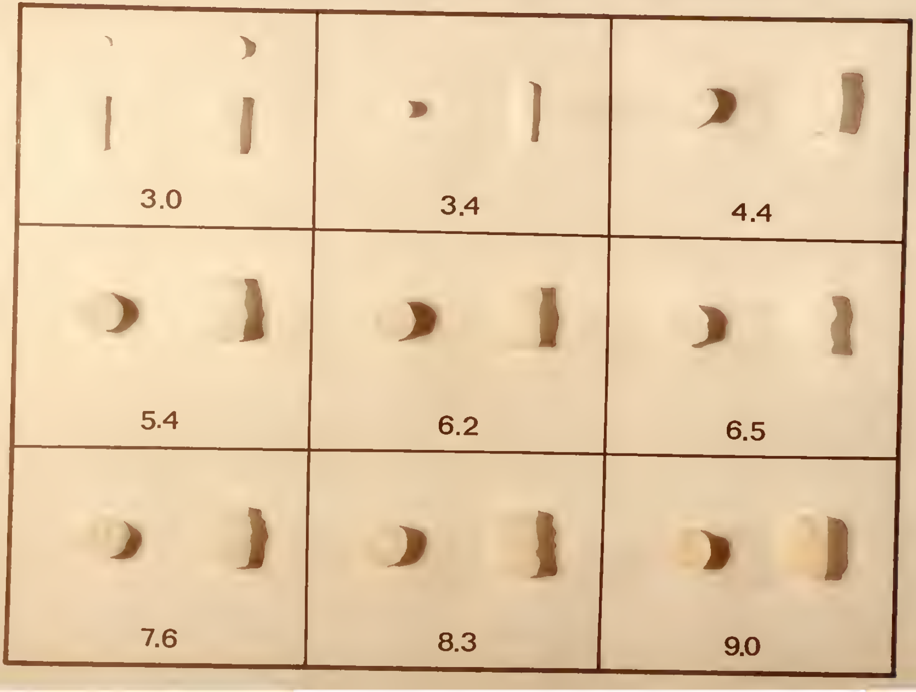


FIGURE 6

EFFECT OF INITIAL pH ON PRODUCTION RATE

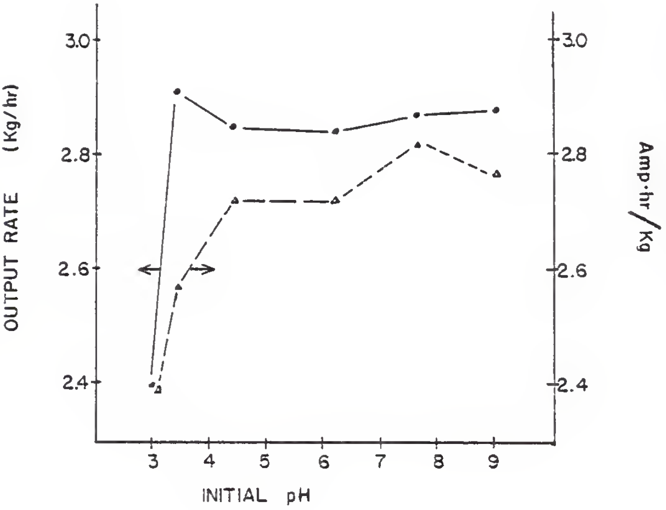


FIGURE 7

EFFECT OF pH ON PRIME WHEAT STARCH AMYLOGRAMS

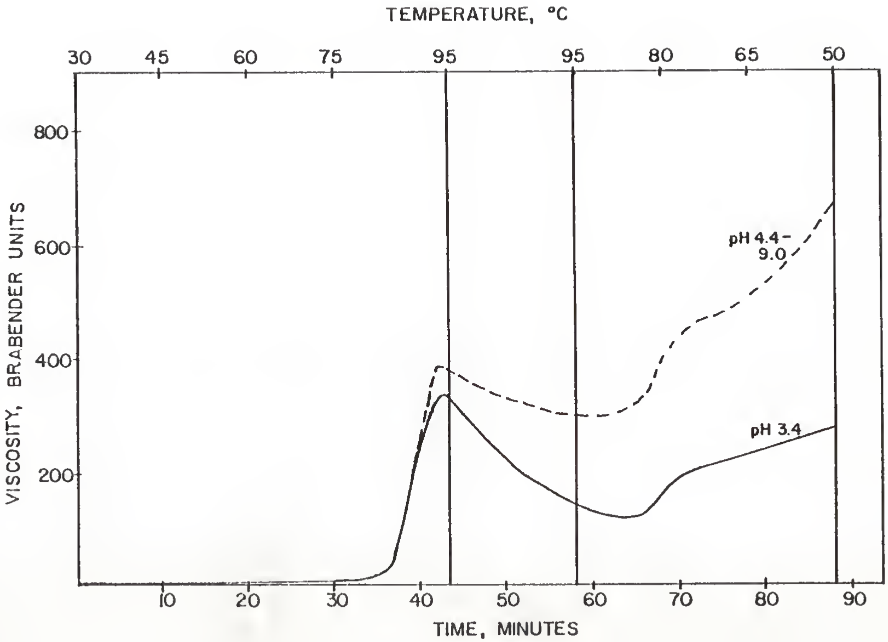


FIGURE 8

EFFECT OF INITIAL pH ON AMYLOGRAMS OF EXTRUSION COOKED WHEAT STARCH

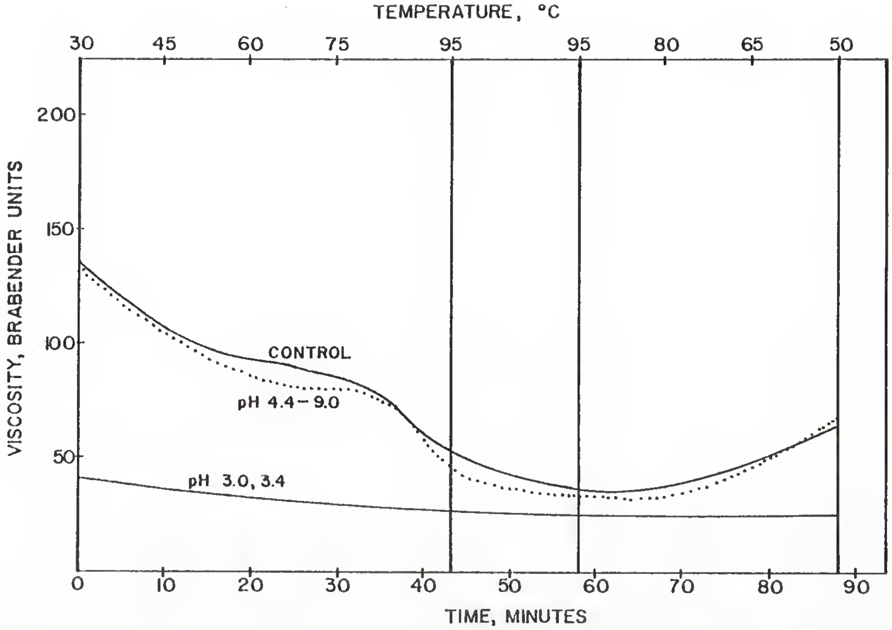


FIGURE 9

COLD WATER, BROOKFIELD VISCOSITY AS A FUNCTION OF STIRRING TIME
EFFECT OF INITIAL pH ON COLD WATER VISCOSITY OF EXTRUSION COOKED WHEAT STARCH

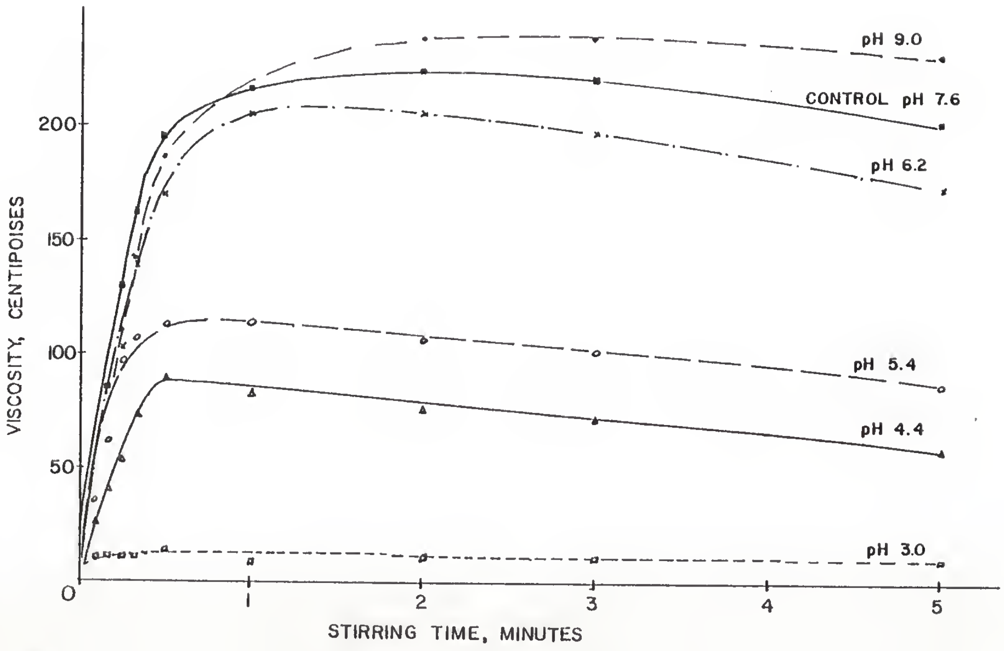


FIGURE 10

WATER SOLUBILITY vs INITIAL pH

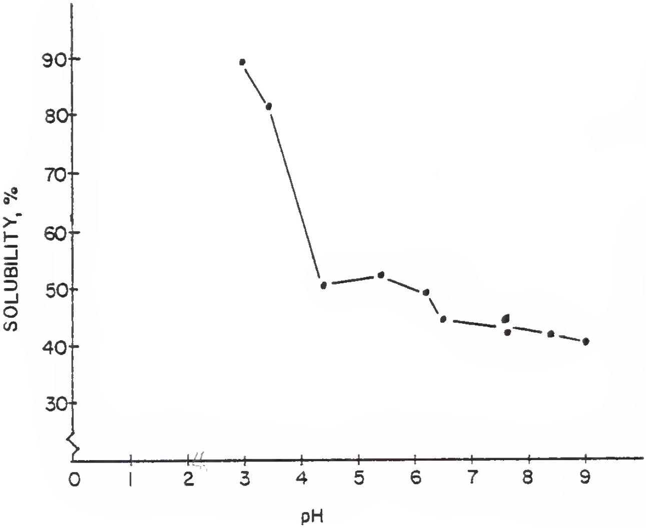


FIGURE II

OUTPUT RATE vs LEVEL OF EMULSIFIER

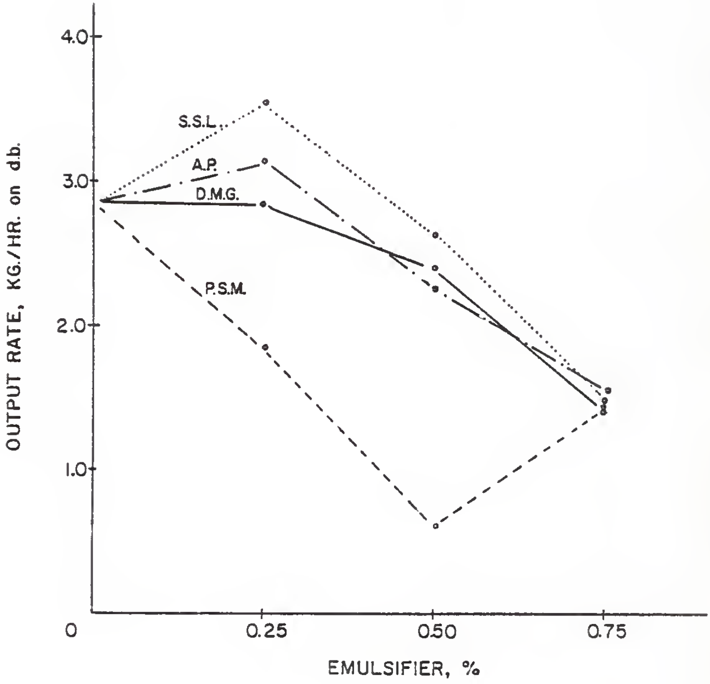


FIGURE 12

ENERGY CONSUMPTION vs LEVEL OF EMULSIFIER

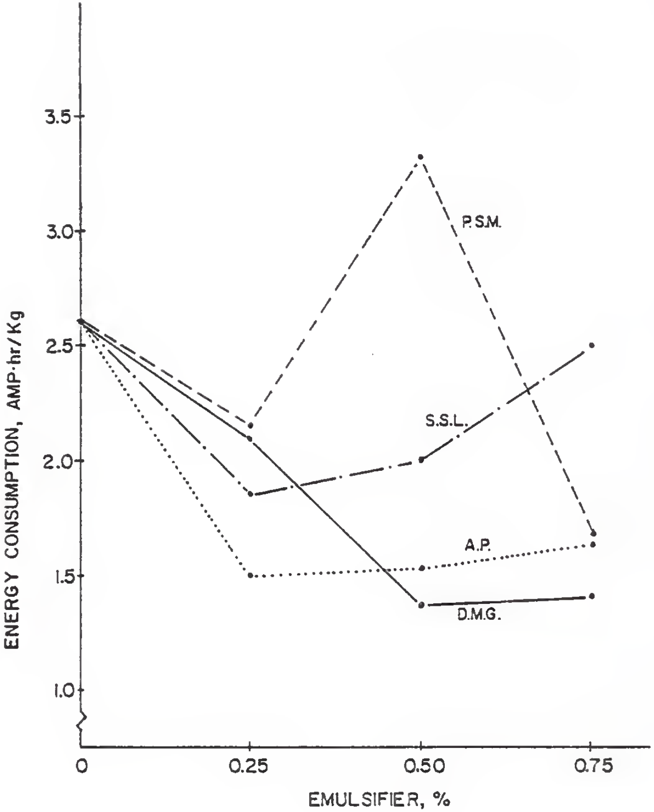


FIGURE 13

EXPANSION INDEX vs LEVEL OF EMULSIFIER

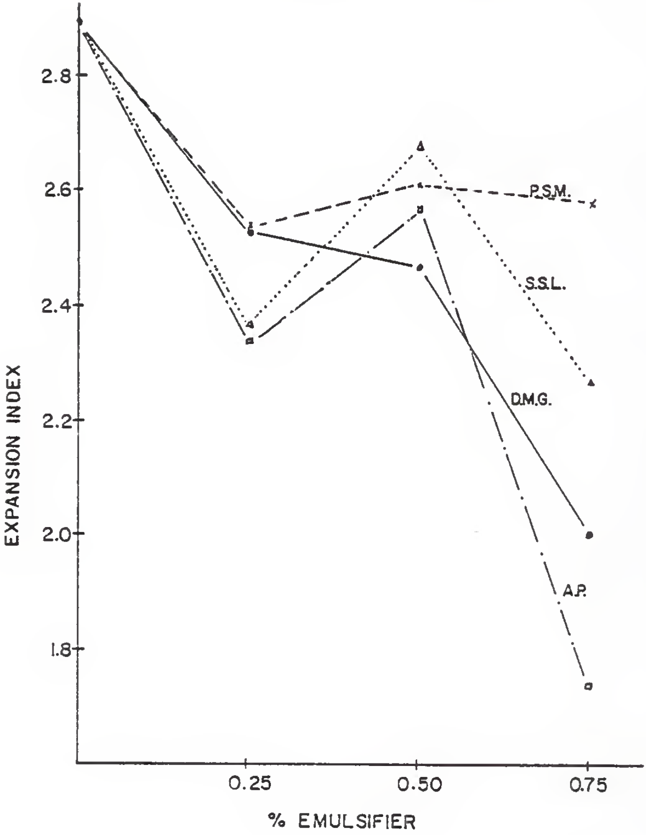


FIGURE 14

pH OF EXTRUSION COOKED PRODUCT vs LEVEL OF EMULSIFIER

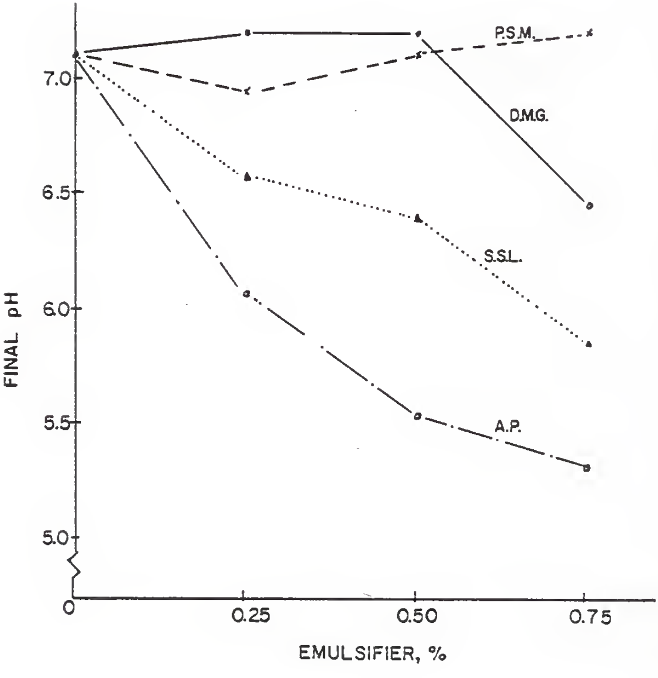


FIGURE 15

AGTRON GREEN COLOR vs LEVEL OF EMULSIFIER

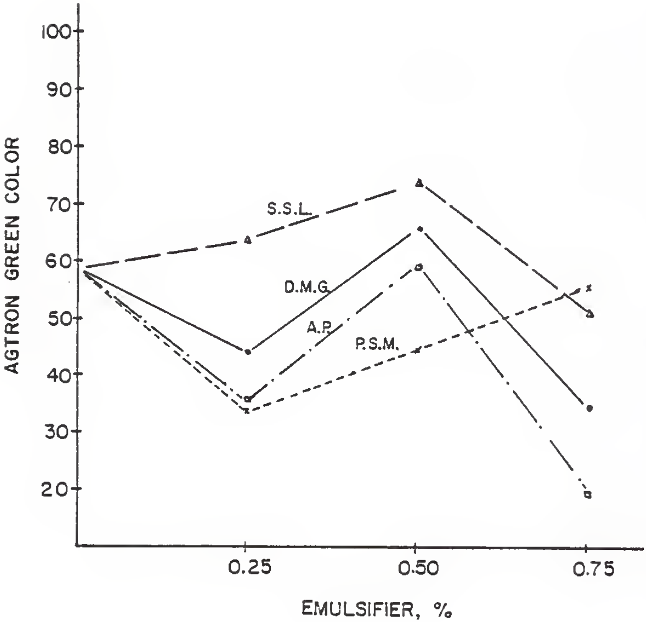


FIGURE 16

AGTRON BLUE COLOR vs LEVEL OF EMULSIFIER

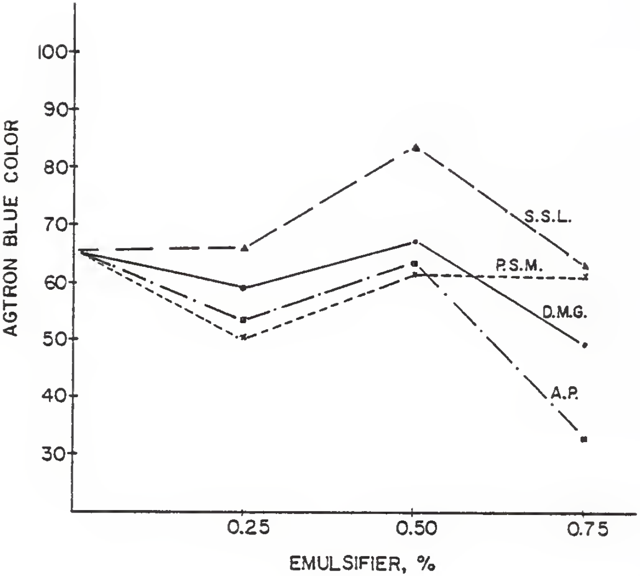


FIGURE 17

WATER SOLUBILITY OF EXTRUSION COOKED PRODUCTS *vs* LEVEL OF EMULSIFIER

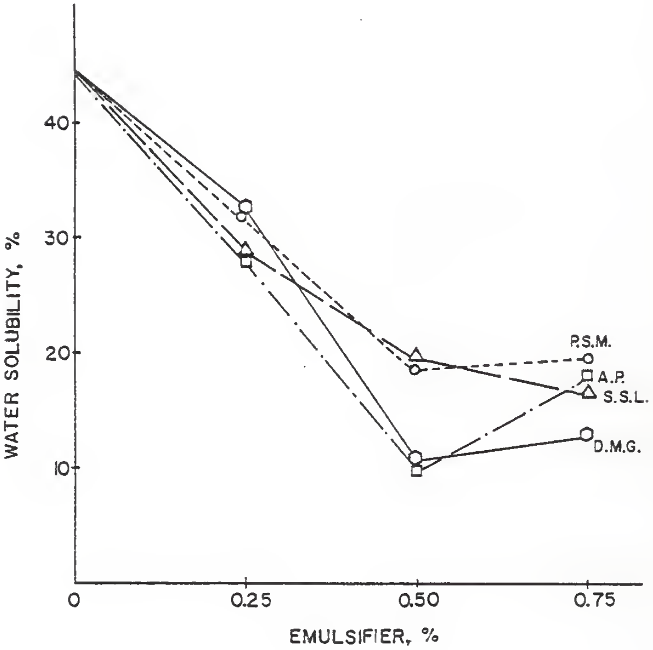


FIGURE 18

EFFECT OF 0.25% EMULSIFIER ON WHEAT STARCH AMYLOGRAM
Determined at 9% solids (d.b.) and 0.8% Carboxymethylcellulose

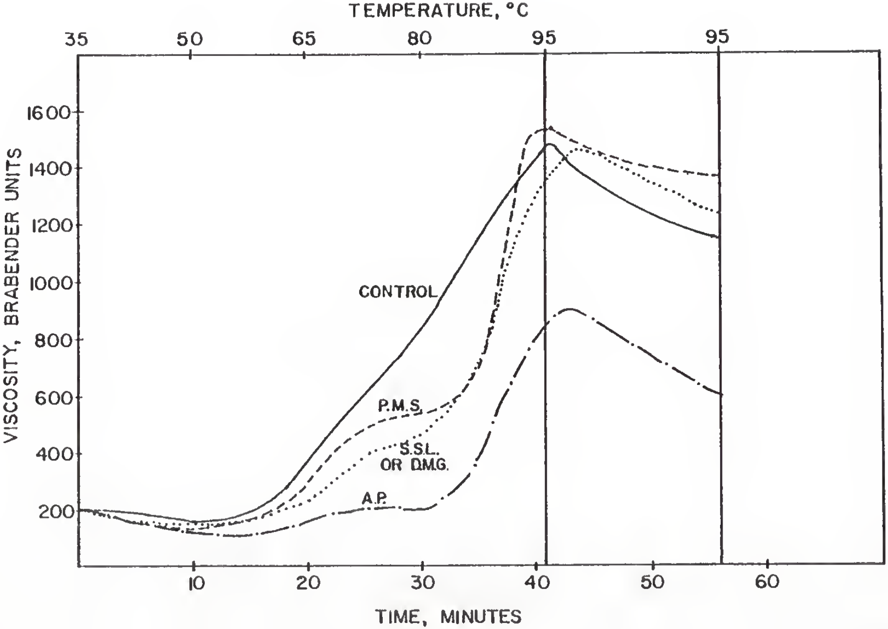


FIGURE 19

EFFECT OF 0.50% EMULSIFIER ON WHEAT STARCH AMYLOGRAM

Determined at 9% solids (d.b.) and 0.8% Carboxymethylcellulose

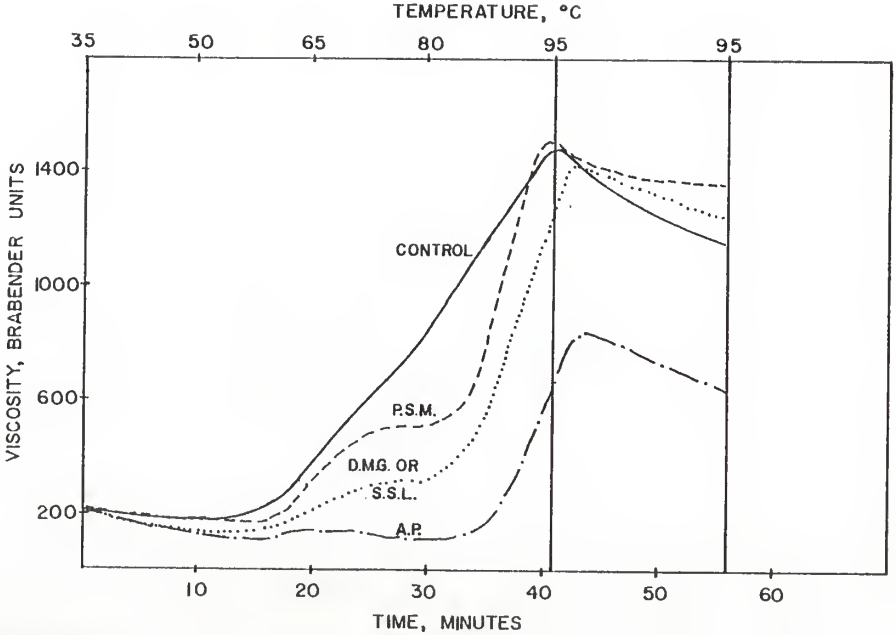


FIGURE 20

EFFECT OF 0.75% EMULSIFIER ON WHEAT STARCH AMYLOGRAM CURVES

Determined at 9% solids (d.b.) and 0.8 % corboxymethylcellulose

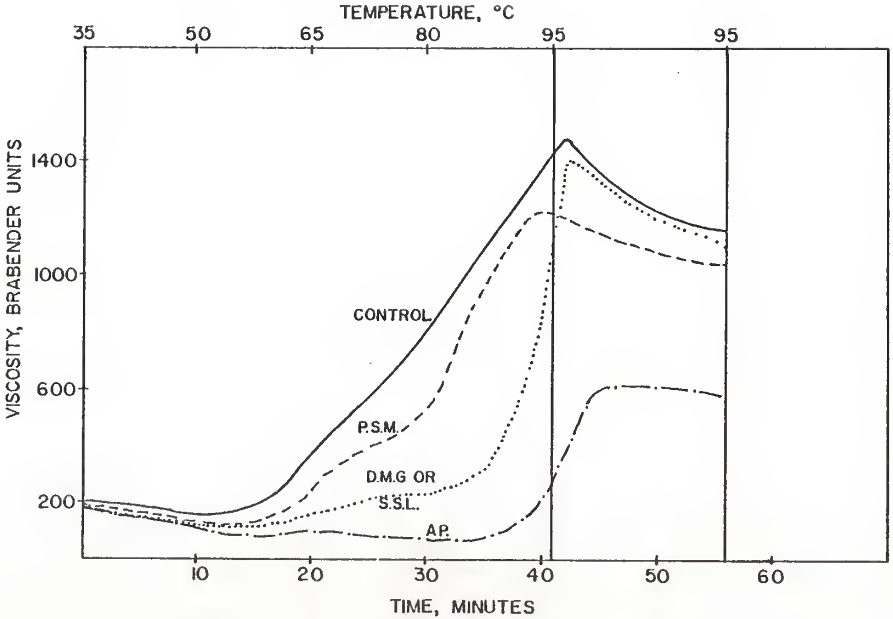


FIGURE 21

EFFECT OF 0.25% EMULSIFIER ON AMYLOGRAMS (9% solids on d.b.) OF EXTRUSION COOKED BLENDS OF WHEAT STARCH AND EMULSIFIERS

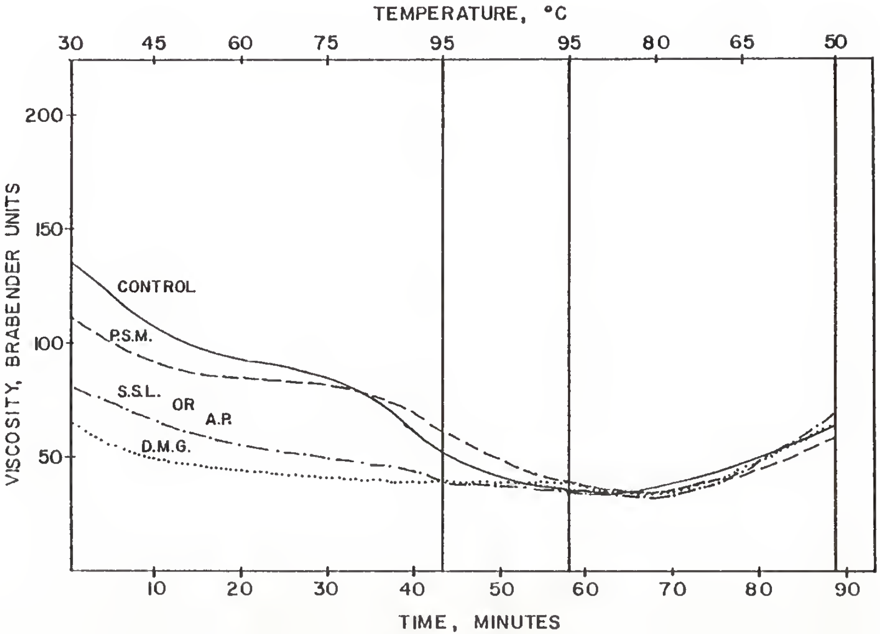


FIGURE 22

EFFECT OF 0.50% EMULSIFIER ON AMYLOGRAM CURVES OF EXTRUSION COOKED WHEAT STARCH EMULSIFIER BLENDS, 9% solids on d.b.

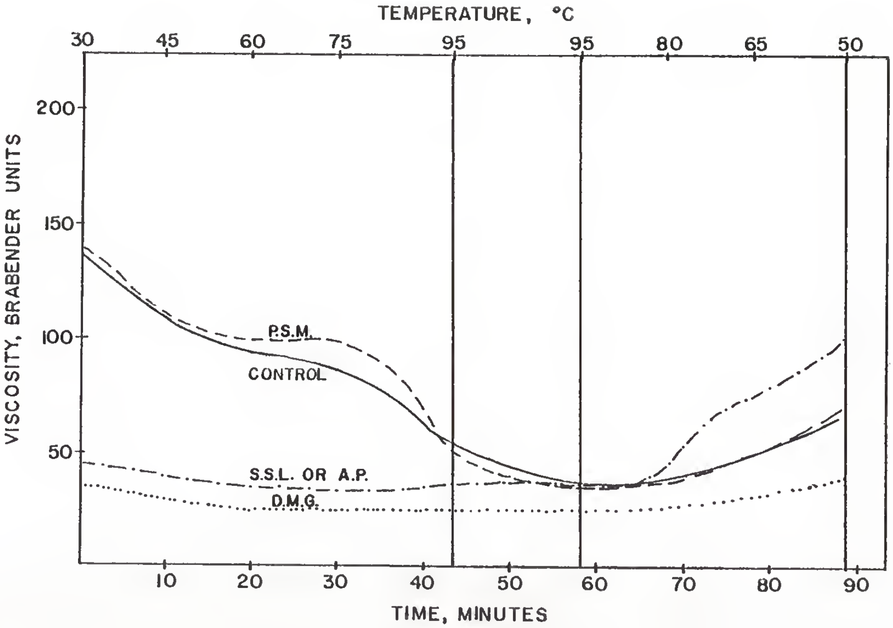


FIGURE 23

EFFECT OF 0.75% EMULSIFIER ON AMYLOGRAM CURVES OF EXTRUSION COOKED WHEAT STARCH–EMULSIFIER BLENDS (9% solids)

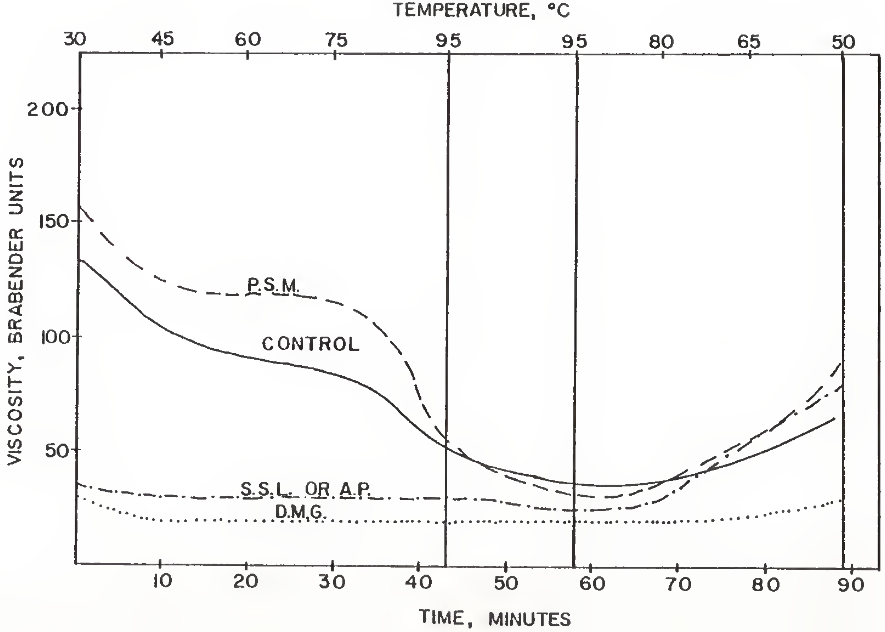


FIGURE 24

COMPARISON OF AMYLOGRAMS AMONG EXTRUSION COOKED BLENDS OF WHEAT STARCH EMULSIFIER AND EXTRUSION COOKED WHEAT STARCH PLUS 0.75% EMULSIFIER – 9% d.b.

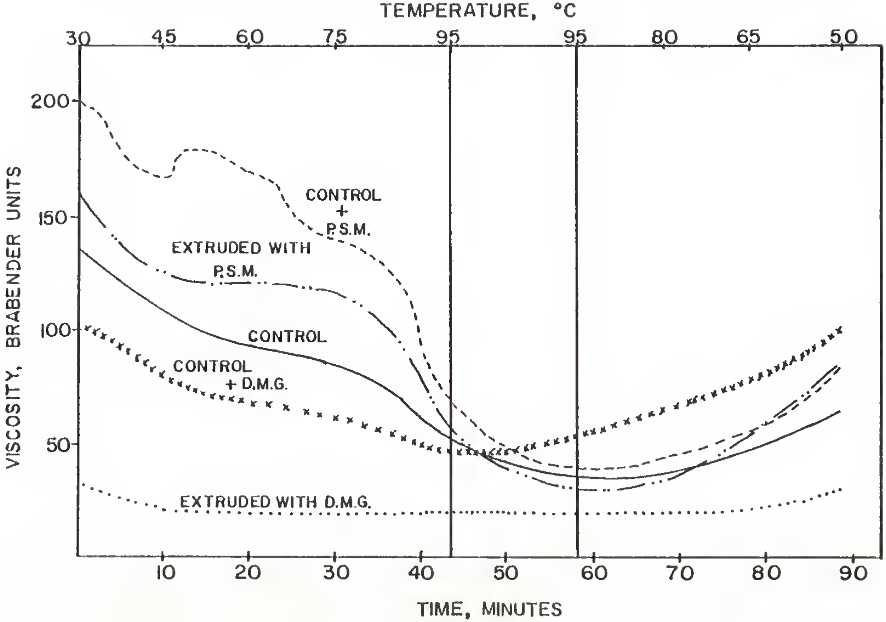


FIGURE 25

ABSORBANCE OF IODINE COMPLEXES OF EXTRUSION–COOKED STARCHES WITH AND WITHOUT EMULSIFIERS

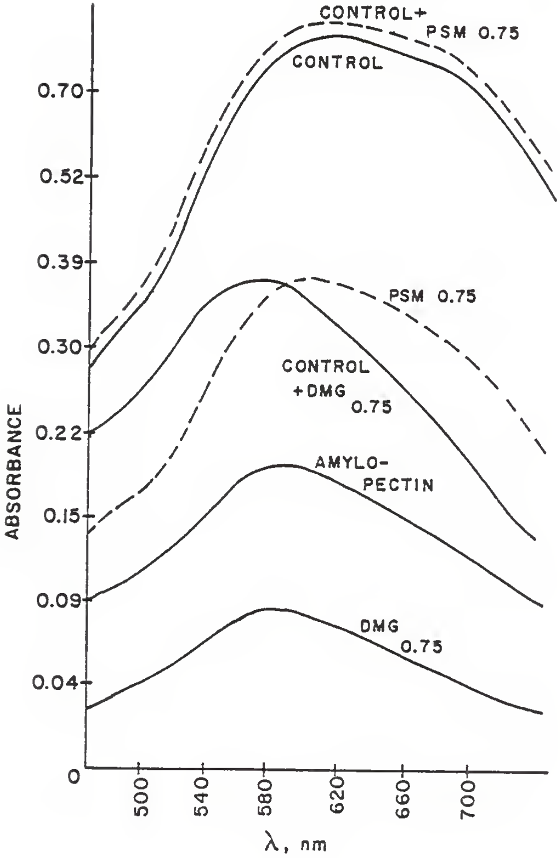


FIGURE 26
ABSORBANCE OF IODINE COMPLEXES OF EXTRUSION-COOKED STARCHES WITH AND WITHOUT EMULSIFIERS.

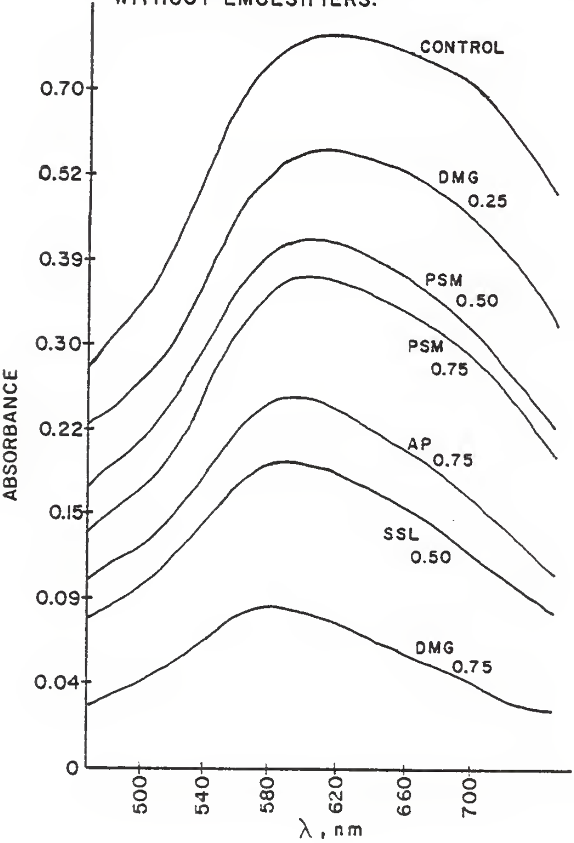


FIGURE 27

COLD WATER VISCOSITY CURVES OF SOME EXTRUSION-COOKED BLENDS OF WHEAT STARCH AND EMULSIFIER

—Brookfield Method—

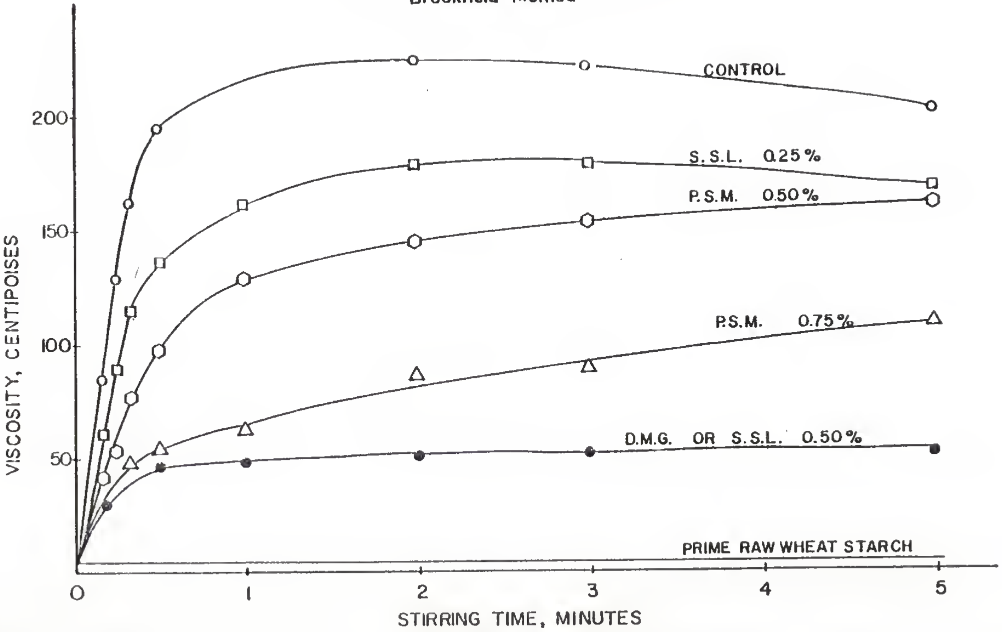


FIGURE 28

EFFECT OF SCREW COMPRESSION RATIO, DIE OPENING AND 0.5% S.S.L. ON AMYLOGRAMS OF EXTRUSION-COOKED WHEAT STARCH

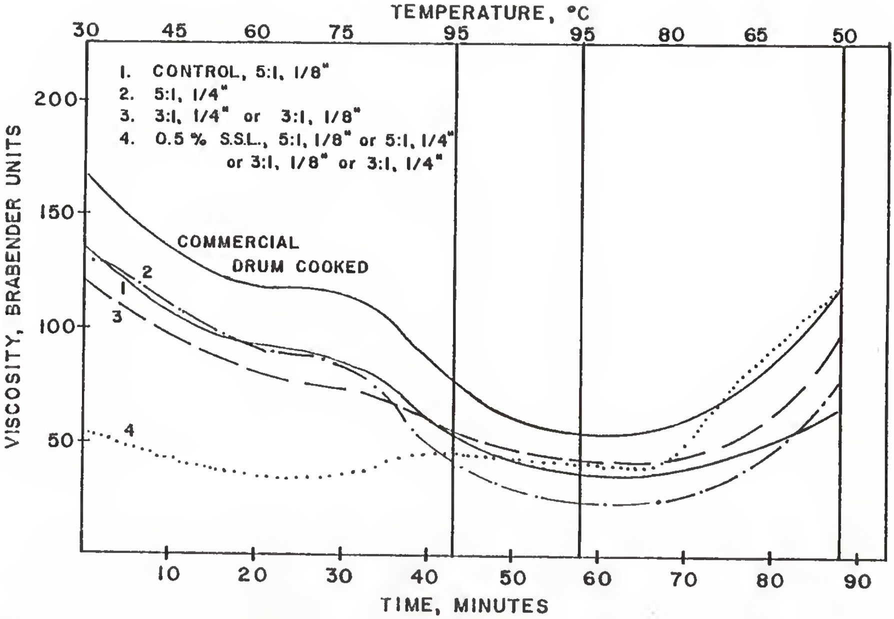


FIGURE 29

EFFECT OF SCREW COMPRESSION RATIO, DIE OPENING AND 0.5% S.S.L. ON AMYLOGRAMS OF EXTRUSION-COOKED CORN STARCH

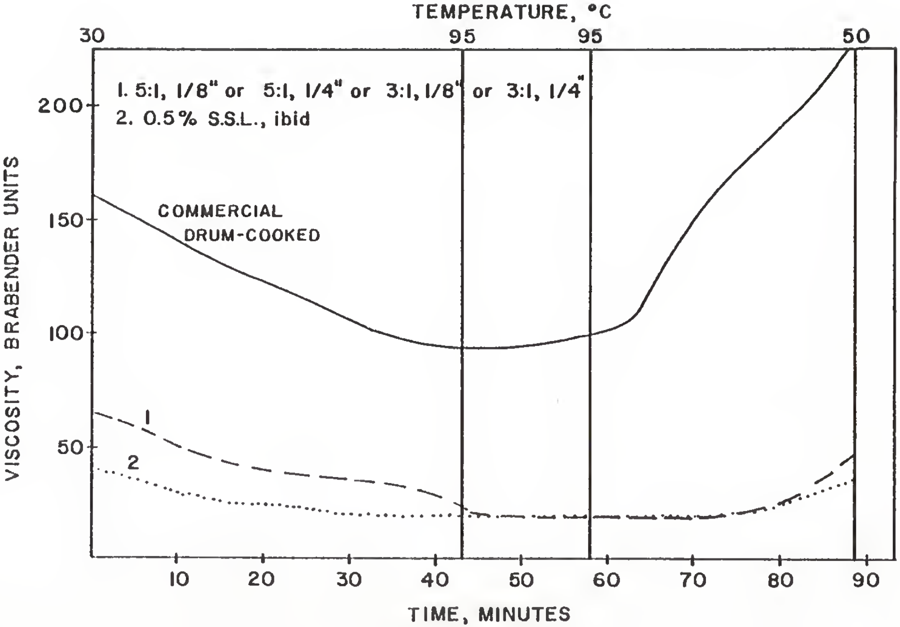


FIGURE 30

EFFECT OF SCREW COMPRESSION RATIO, DIE OPENING AND 0.5% S.S.L. ON COLD WATER VISCOSITY CURVES OF EXTRUSION-COOKED WHEAT AND CORN STARCH

—Brookfield Method—

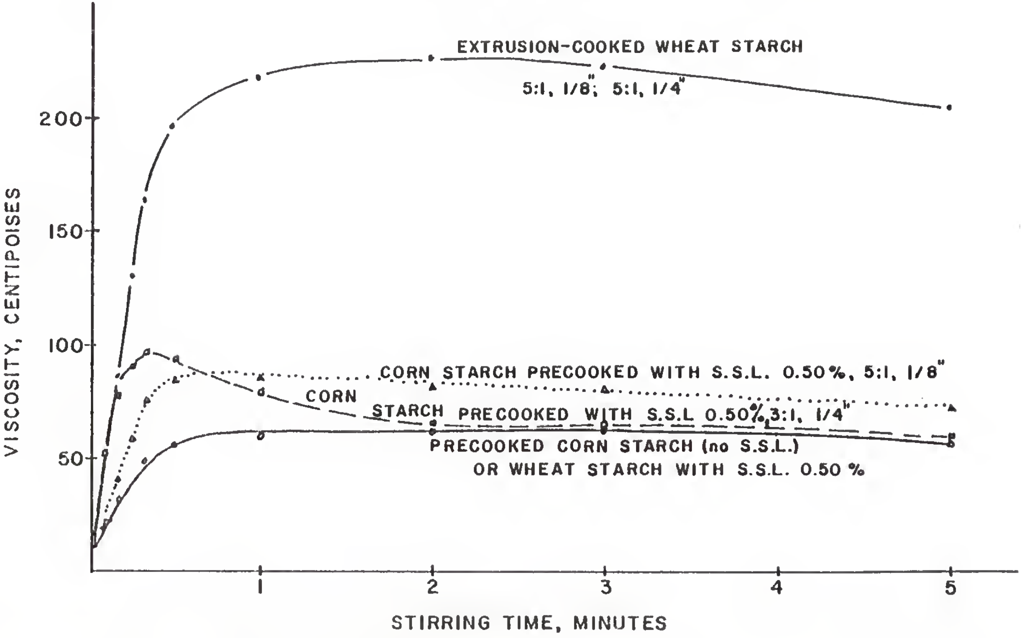


FIGURE 31

COMPARISON AMONG AMYLOGRAMS OF COMMERCIAL DRUM-COOKED COMMERCIAL EXTRUSION AND LABORATORY EXTRUSION-COOKED WHEAT STARCH

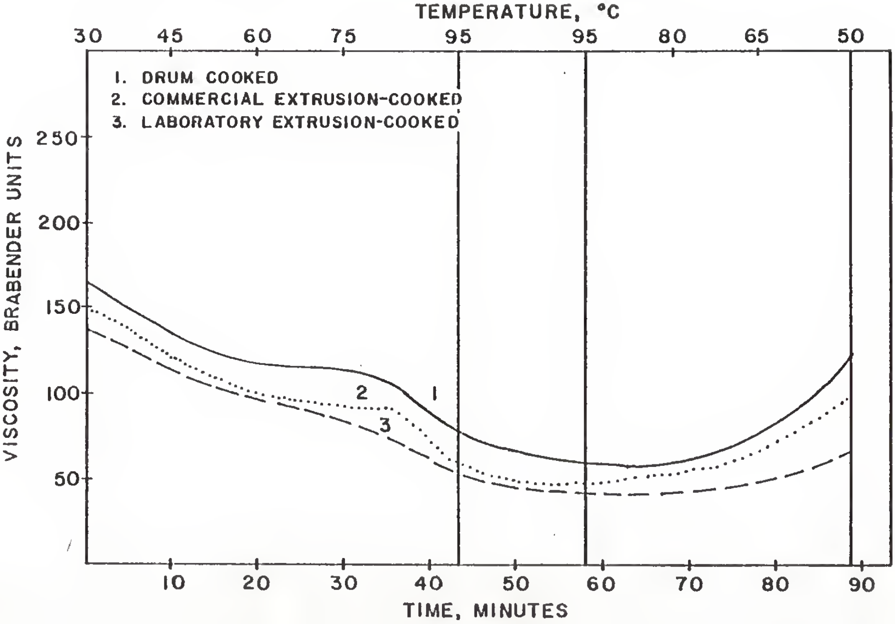


FIGURE 32

EFFECT OF PREPARARATION OF THE DRUM-COOKED STARCH—WATER SLURRY ON AMYLOGRAMS BOTH WITH AND WITHOUT USE OF COOLING WATER IN THE TEMPERATURE CONTROL SYSTEM

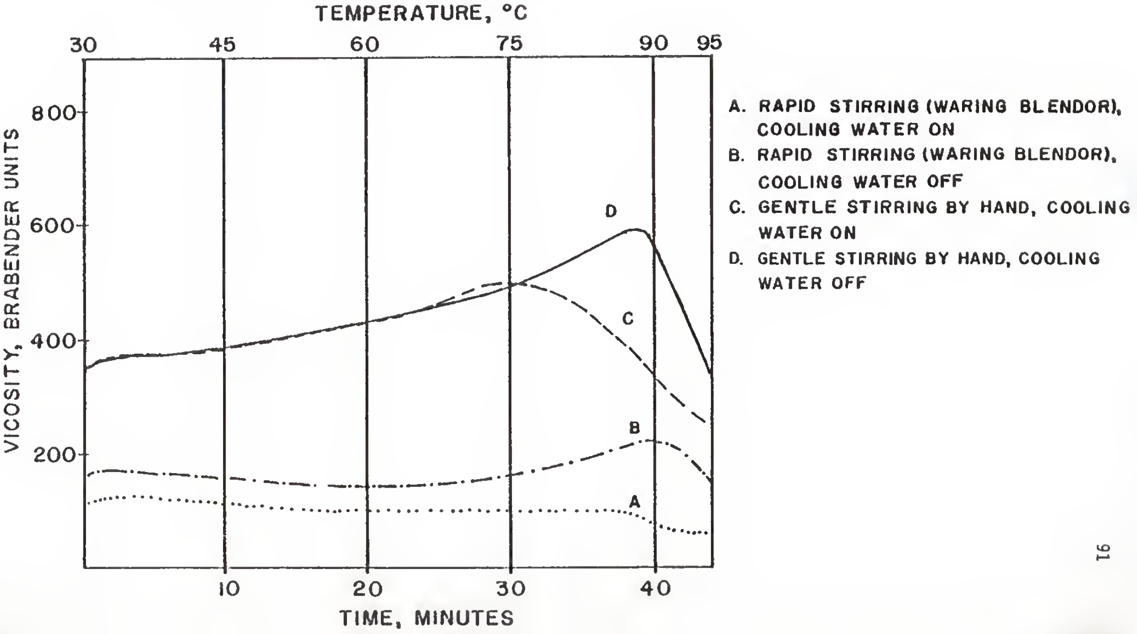


FIGURE 33

COMPARISON BETWEEN AMYLOGRAMS OF EXTRUSION-COOKED WHEAT STARCH (control) OBTAINED BY USING THE INDUSTRIAL METHOD AND THIS WORK (**Method A**)

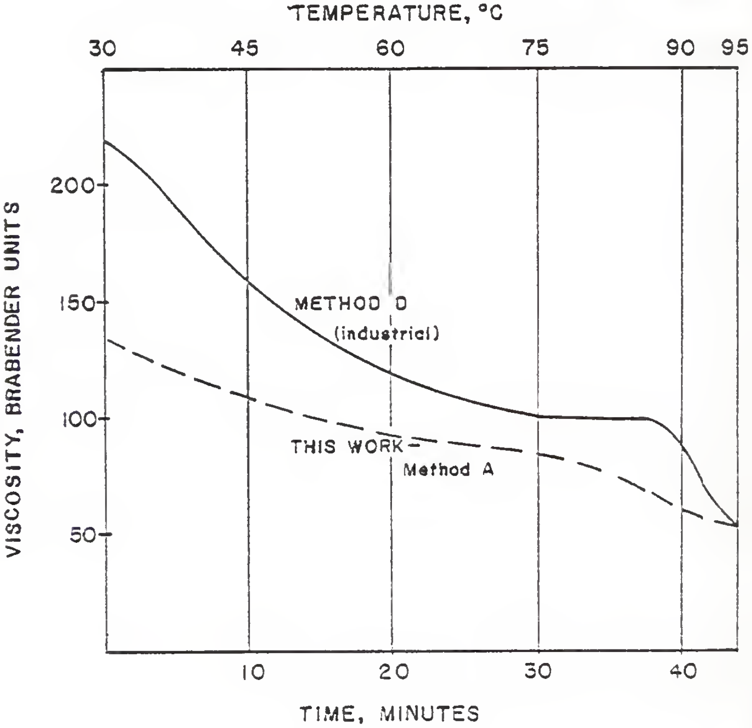
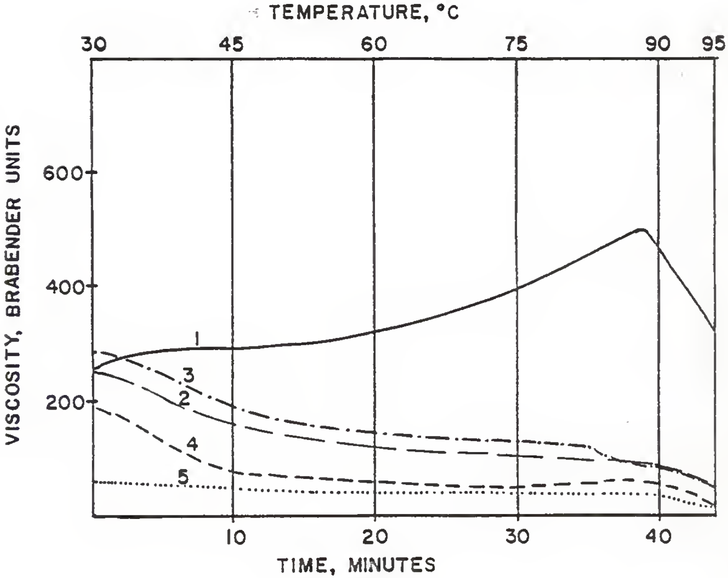


FIGURE 34

AMYLOGRAMS OF COMMERCIAL DRUM-COOKED AND LABORATORY EXTRUSION-COOKED WHEAT STARCH

Method D (industrial)



1-COMMERCIAL DRUM-COOKED
2-LAB. EXTRUDED 5:1, 1/8 or 5:1, 1/4 or 3:1, 1/8 or 3:1, 1/4
3-LAB. EXTRUDED STARCH + 0.50 % P.S.M.
4-LAB. EXTRUDED STARCH + 0.50 % S.S.L.
5-LAB. EXTRUDED STARCH + 0.75 % A.P.

FIGURE 35

COMPARISON OF COLD WATER VISCOSITY CURVES BETWEEN LABORATORY EXTRUSION-COOKED, COMMERCIAL & DRUM-COOKED CORN AND WHEAT STARCHES

—Brookfield Method—

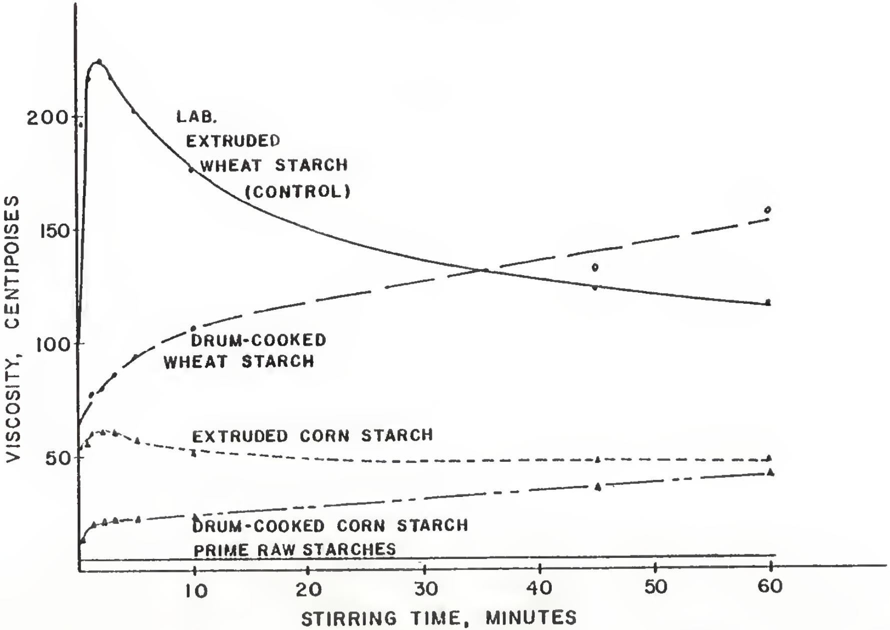


FIGURE 36

COLD WATER VISCOSITY CURVES OF COMMERCIAL DRUM-COOKED AND LABORATORY EXTRUSION-COOKED WHEAT STARCH

— Brookfield Method —

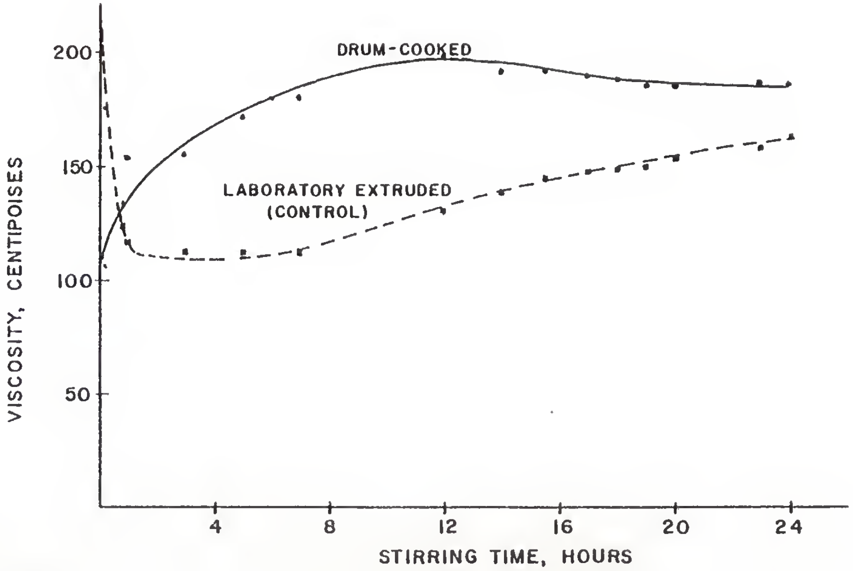
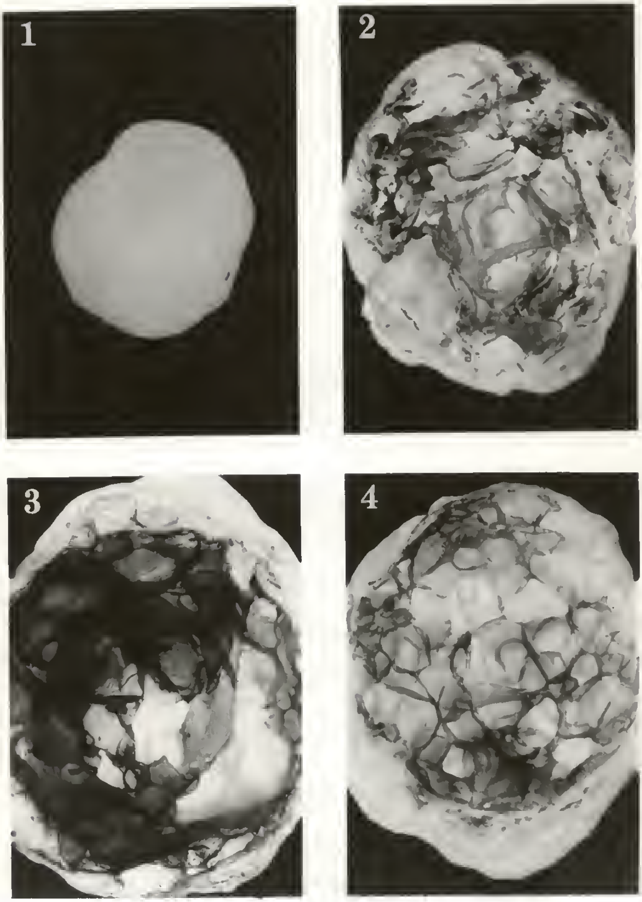


Figure 1

TYPICAL CELL STRUCTURES ("GRAIN") OF EXTRUSION-COOKED WHEAT STARCH *



#1 at <100°C

#2 at 125°C

#3 at 150°C

#4 at 175°C

FIGURE 38

CELL STRUCTURE OF EXTRUSION-COOKED WHEAT STARCH

<u>vs</u> COLD WATER VISCOSITY — Brookfield Method

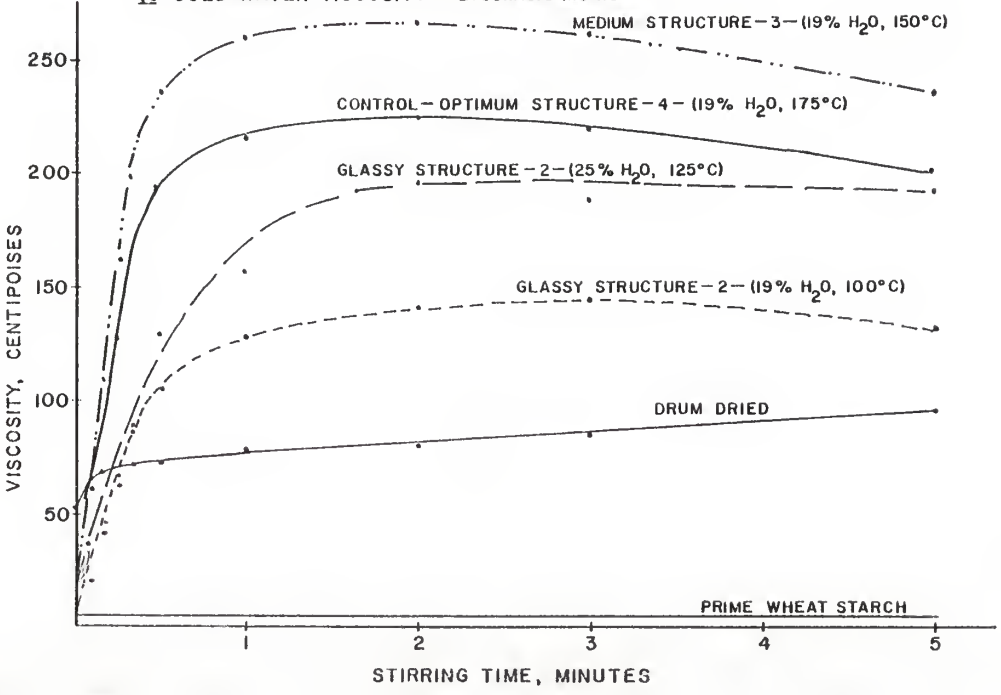


Table 2

INFLUENCE OF EXTRUSION pH ON DEXTROSE EQUIVALENT (D.E.) OF EXTRUDED SAMPLES

Extrusion pH	F.N.[a]	D.E.
Prime raw starch	0.22	1.03
9.0	0.20[b]	0.96
7.5	0.22[b]	1.06
7.6(control)	0.24[b]	1.17
5.4	0.22[b]	1.06
4.4	0.20[b]	0.96
3.4	1.68	8.02
3.0	7.50	35.86

---

[a] Ferricyanide Number (See Materials and Methods #13)

[b] Not significantly different from the blank sample of prime starch.

Table 3

TEST OF HOMOGENEITY OF EMULSIFIER BLENOED WITH WHEAT STARCH[a]

Emulsifier	Theoretical Percent in Sample	Percent found in Sample[b]	Average[c] Recovery%
Distilled Monoglyceride	0.25	0.23	92.0
		0.21	
		0.24	
Ascorbyl palmitate	0.25	0.21	89.2
		0.21	
		0.23	
		0.23	

---

[a] Each data represent a different replication with a quartered sample of 10 g. each.

[b] The recovery method gave a standard deviation of 0.01%.

[c] Average recovery % = $\frac{\text{Percent extracted from sample}}{\text{Theoretical percent in sample}} \times 100$

Table 4

INFLUENCE OF EMULSIFIER CONCENTRATION ON PRODUCTION RATE

Sample	Level,%	Production rate, Kg/hr (d.b.)	Amperage Consumption, Amps	Energy Consumption Amp.hr/kg
Raw Starch(s)		2.87	8.10	2.82
S + DMG	0.25	2.85	6.0	2.10
	0.50	2.41	3.3	1.35
	0.75	1.42	2.0	1.41
S + S.S.L	0.25	3.57	6.7	1.89
	0.50	2.78	5.5	1.99
	0.75	1.44	3.6	2.50
S + AP	0.25	3.16	4.7	1.50
	0.50	2.28	3.5	1.53
	0.75	1.53	2.5	1.64
S + PSM	0.25	1.85	4.0	2.16
	0.50	0.62	2.0	3.31
	0.75	1.43	2.4	1.66

Table 5

INFLUENCE OF SCREW COMPRESSION RATIO, DIE DIAMETER ON EXPANSION INDEX OF EXTRUDED PRODUCTS FROM WHEAT AND CORN STARCH[a]

EXPANSION INDEX

STARCH	Compression Ratio 5:1 Die Diameter 1/8"	 1/4"	 3:1 Die Diameter 1/8"	 1/4"
WHEAT STARCH	2.39	1.82	2.90	1.73
WHEAT STARCH + 0.5% SSL	2.66	1.72	2.61	1.63
CORN STARCH	2.94	1.74	2.86	1.51
CORN STARCH + 0.5% SSL	2.55	1.46	2.28	1.44

a) Screw speed 100 rpm; Temperature of Zone 3: 175°C:
Temperature of Zone 2 : 100°C for wheat starch and 110°C for corn starch.
Moisture percent of samples before extrusion: 18.5%

Table 6

INFLUENCE OF SCREW COMPRESSION RATIO AND DIE DIAMETER ON PRODUCTION RATE OF WHEAT AND CORN STARCH

STARCH	Screw Compression Ratio	Die Diameter, inches	Production Rate, Kg/hr (d.b.)	Current, amp.	Energy per Kg product Amp-hr/Kg
WHEAT STARCH	5:1	1/8	2.87	8.10	2.82
		1/4	2.93	8.50	2.90
	3:1	1/8	3.02	10.25	3.39
		1/4	2.85	12.00	4.21
WHEAT STARCH + 0.5% SSL	5:1	1/8	2.58	5.50	2.13
		1/4	2.92	4.75	1.63
	3:1	1/8	2.09	5.50	2.63
		1/4	2.21	6.00	2.72
CORN STARCH	5:1	1/8	2.03	6.00	2.96
		1/4	1.62	4.75	2.93
	3:1	1/8	2.29	7.50	3.27
		1/4	2.14	7.00	3.27
CORN STARCH + 0.5% SSL	5:1	1/8	2.19	4.50	2.06
		1/4	2.32	5.50	2.37
	3:1	1/8	3.05	3.75	1.23
		1/4	3.34	3.25	0.97

Table 7

INFLUENCE OF SCREW COMPRESSION RATIO AND DIE DIAMETER ON WATER SOLUBILITY OF WHEAT AND CORN STARCH[a]

SOLUBILITY, %

STARCH	Compression Ratio			
	5:1		3:1	
	Die Diameter		Die Diameter	
	1/8"	1/4"	1/8"	1/4"
WHEAT STARCH	44.38	44.69	40.51	41.43
WHEAT STARCH + 0.5% SSL	24.25	21.16	16.85	15.37
CORN STARCH	69.75	74.34	70.68	79.38
CORN STARCH + 0.5% SSL	40.92	43.19	36.88	43.45

a) Screw speed: 100 rpm: Temperature of Zone 3: 175°C
Temperature of Zone 2: 100°C for wheat starch and 110°C for corn Starch.
Moisture percent of samples before extrusion: 18.5%

Table 8

INFLUENCE OF SCREW COMPRESSION RATIO AND DIE DIAMETER ON THE pH OF EXTRUDED PRODUCTS FROM WHEAT AND CORN STARCH[a]

pH UNITS

STARCH b)	Compression Ratio			
	5:1		3:1	
	Die Diameter		Die Diameter	
	1/8"	1/4"	1/8"	1/4"
WHEAT STARCH	6.95	6.90	6.80	6.70
WHEAT STARCH + 0.5% SSL	6.20	6.20	6.10	6.20
CORN STARCH	4.60	4.60	4.60	4.60
CORN STARCH + 0.5% SSL	5.30	5.30	5.30	5.30

a) Screw speed:100rpm; Temperature of Zone 3:175°C
Temperature of Zone 2: 100°C for wheat starch and 110°C for corn starch
Moisture percent of samples before extrusion: 18.5%

b) pH of samples before extrusion; Wheat starch 7.60 , Wheat starch with 0.5% SSL 6.70; Corn starch 4.55; Corn starch with 0.5% SSL 5.25

Table 9

INFLUENCE OF BARREL TEMPERATURE AND MOISTURE CONTENT ON THE OUTPUT RATE OF EXTRUDATE[a]

Moisture Content %	Zone Temperatures, °C		Production Rate[b)] Kg/hr, m.b.	Current, amperes	Energy per Kg product Amp-hr/Kg
	Z_2	Z_3			
19	65	65	3.48	9.0	2.6
	100	100	3.13	6.5	2.1
	100	125	2.98	5.7	1.9
	100	150	2.75	5.0	1.8
	100	175	2.97	4.5	1.5
22	65	65	2.58	7.2	2.8
	100	100	2.07	5.5	2.7
	100	125	2.13	5.5	2.6
	100	150	1.80	5.2	2.9
	100	175	1.74	4.5	2.6
25	65	65	1.71	6.7	3.3
	100	100	1.32	4.5	3.4
	100	125	1.64	3.5	2.1
	100	150	1.41	3.5	2.5
	100	175	1.47	4.0	2.7

a) Temperature of Zone 1 (30° C) was kept constant. Z_2: Zone 2; Z_3: Zone 3. Screw speed 100 rpm. Die diameter 1/4 inch Screw compression ratio: 3:1

b) Data given in Kg/hr of extruded product as is, since some of the samples could not be ground by its extreme hardness.

Table 10

EFFECT OF EXTRUSION TEMPERATURE AND MOISTURE CONTENT OF WHEAT STARCH ON THE CELL STRUCTURE[a] OF THE EXTRUDED PRODUCT[b,c]

Zone Temperature, °C Z_2	65	100	100	100	100
Moisture Content,% Z_3	65	100	125	150	175
19	1 (1.4)[d]	2 (1.7)	3 (2.0)	3 (2.2)	4 (1.8)
22	1 (1.3)	2 (1.3)	3 (1.6)	3 (1.9)	3 (1.3-1.8)
25	1 (1.1)	1 (1.3)	2 (1.5)	3 (1.5)	3 (1.1-1.7)

a) Classification of cell structure based on visual observation
Scale: 4. Closed structure, thin cell walls, uniform honeycomb like structure.
3. Medium open structure,thick cell walls, not uniform structure.
2. Glassy structure with large open cells of very thick walls
1. Entirely glassy structure. No gas cells.

b) Screw speed: 100 rpm;,Die diameter: 1/4 "; Compression ratio 3:1

c) Temperature of Zone 1: 30°C. It was kept constant.
Z_2: Temperature of Zone 2
Z_3: Temperature of Zone 3

d) Number in parenthesis are expansion indexes.

APPENDIX I

Table 11

INFLUENCE OF EXTRUSION pH ON EXPANSION

Initial pH	Buffer	Diameter, mm[a]	Expansion Index[b]
3.02	HCl-KCl	3.98	1.25
3.02[c]	HCl-KCl	6.96	2.19
3.45	HCl-KCl	4.10	1.29
4.40	HCl-KCl	9.14	2.88
5.40	H_3PO_4-NaH_2PO_4	9.25	2.91
6.18	HCl-KCl	9.11	2.87
6.50	H_3PO_4-NaH_2PO_4	9.25	2.91
7.50	Na_2HPO_4-NaH_2PO_4	9.35	2.94
7.60(control)	none	9.19	2.91
8.40	Na_3PO_4-Na_2HPO_4	9.62	3.00
9.05	Na_3PO_4-Na_2HPO_4	9.34	2.94

[a] Mean of ten observations

[b] Expansion index = Product diameter/Die diameter

[c] Bimodal behavior of sample during extrusion.

Table 12

CHANGE OF pH DURING EXTRUSION

Initial pH	Final pH	Δ pH[a]	pH after pasting
3.02	3.16	+0.14	3.60
3.45	3.64	+0.21	4.00
4.40	4.61	+0.21	4.75
5.40	5.97	+0.57	5.75
6.18	6.67	+0.51	6.25
6.50	6.78	+0.28	6.05
7.50	7.20	-0.29	6.77
7.60(control)	7.21	-0.39	6.40
8.40	7.52	-0.87	6.80
9.05	7.75	-1.30	7.00

[a] Δ pH = final pH - initial pH

Table 13

INFLUENCE OF EXTRUSION pH ON PRODUCTION RATE

Extrusion pH	Production rate Kg/hr	Moisture in sample after flashing and cooling, %	Water lost by flashing and cooling %	Current consumption amp	Energy Consumption Amp.hr/kg
3.02	2.40	7.2	61.2	5.75	2.39
3.40	2.91	9.3	49.8	7.50	2.57
4.40	2.85	8.8	52.4	7.75	2.72
6.18	2.84	10.2	45.1	7.75	2.73
7.60	2.87	9.6	47.9	8.10	2.82
9.05	2.88	9.0	51.2	8.00	2.77

All samples extruded at 175°C, 100 rpm, and 18.5% moisture, using 1/8" die cap and compression ratio of 5 to 1.

Table 14

INFLUENCE OF EXTRUSION pH ON AGTRON COLOR OF EXTRUDED PRODUCT

(Particle size: -100W)

pH	Green (71-90)	Blue (44-90)
3.02	>100	>100
3.45	>100	>100
4.40	82.3	81.5
5.40	87.2	82.7
6.18	68.3	69.7
6.50	68.0	60.5
7.50	59.8	63.8
7.60	60.4	65.4
8.40	58.5	53.8
9.05	37.5	31.0

Table 15

EFFECT OF pH OF EXTRUSION ON THE PASTING CHARACTERISTICS OF THE EXTRUDED SAMPLE

	VISCOSITY (B.U.) at				
pH	30°C	95°C	15 min at 95°C	50°C	Observations
5.4	110	40	30	70	no peak
6.5	110	40	30	70	"
7.5	110	30	20	60	"
7.6(control)	138	52.5	40	80	"
8.4	150	70	60	60	"
9.05	120	40	20	60	"
Raw starch	10	350	290	650	Peak
Starch at pH 5.4	10	380	300	680	Peak

Table 16

INFLUENCE OF pH ON WATER SOLUBILITY OF EXTRUDED PRODUCT

Initial pH	%S (gr/100gr)[a]
3.02	89.77
3.45	81.15
4.40	50.11
5.40	52.09
6.18	49.28
6.50	44.32
7.50	39.57
7.60	44.38[b]
8.40	41.53
9.05	40.71

---

[a] Mean of four replications

[b] Mean of five different extrusions

Table 17

INFLUENCE OF EMULSIFIERS ON EXPANSION

Sample	Level, %	Diameter, mm	EI[a]
S + DMG	0.25%	8.02	2.53
	0.50%	7.83	2.47
	0.75%	6.47	2.04
S + S.S.L	0.25%	7.53	2.37
	0.50%	8.56	2.68
	0.75%	7.20	2.27
S + AP	0.25%	7.43	2.34
	0.50%	8.16	2.57
	0.75%	5.54	1.74
S + PSM	0.25%	8.02	2.53
	0.50%	8.28	2.61
	0.75%	8.17	2.57
Raw Starch	--	9.24	2.89

---

[a] Expansion index

Table 18

pH CHANGE DURING EXTRUSION-COOKING OF WHEAT STARCH - EMULSIFIER BLENDS.

Sample	Level, %	Initial pH	Final pH	pH after Pasting
Prime Starch		7.6	7.11	6.75
	0.25	7.21	7.20	6.45
DMG	0.50	7.07	7.20	6.65
	0.75	7.37	6.47	6.58
	0.25	6.94	6.57	6.15
SSL	0.50	6.85	6.40	6.34
	0.75	6.77	5.85	6.28
	0.25	6.76	6.06	5.25
AP	0.50	6.73	5.54	5.17
	0.75	6.56	5.37	5.43
	0.25	7.24	6.95	6.55
PSM	0.50	7.15	7.11	6.43
	0.75	7.50	7.20	6.77
Commercial Extruded Wheat Starch			7.70	
Commercial Drum-Cooked			6.03	

Table 19

VISCOAMYLOGRAPHIC CHARACTERISTICS OF WHEAT STARCH-EMULSIFIER BLENDS

BLEND		FIRST SWELLING STAGE				SECOND SWELLING STAGE			
	% Emulsifier	Viscosity at 35°C	Initial Temp. a) °C	Viscosity at Initial Temp. B.U.	Mid-point Viscosity b) B.U.	Initial Temp. °C	Viscosity at Initial Temp. B.U.	Peak at 95°C B.U.	15 min at 95°C B.U.
WHEAT STARCH (Control)	-	200	58.5	180	610	79.5	760	1470	1160
WHEAT STARCH + DMG	0.25	205	60.5	155	380	80.5	410	1430	1430
	0.50	195	61.2	150	310	81.0	310	1430	1220
	0.75	140	60.5	110	200	85.1	200	1400	1100
WHEAT STARCH + SSL	0.25	200	61.0	155	410	81.0	475	1450	1240
	0.50	210	61.0	160	350	83.0	390	1300	1200
	0.75	170	62.9	130	240	85.4	265	1300	1230
WHEAT STARCH + AP	0.25	200	61.0	120	200	82.5	200	900	620
	0.50	210	60.5	120	130	86.5	130	840	650
	0.75	180	60.8	90	80	92.3	70	610	580
WHEAT STARCH + PSM	0.25	230	60.5	160	510	83.5	540	1530	1370
	0.50	220	60.0	160	500	82.5	500	1500	1360
	0.75	180	60.0	130	430	80.9	530	1220	1040

a) Equal to gelatinization temperature.

b) Mid-point viscosity is defined as the viscosity read at middle of the first swelling stage, which occurs at 74-75°C

Table 20

INFLUENCE OF % EMULSIFIER ON COLOR OF THE EXTRUDATE PRODUCT[1]

Sample		Blue (44-90)	Green (71-90)
Raw Starch		>100	>100
Extruded wheat starch		65.5	58.9
S + DMG	0.25%	59.0	44.3
	0.50%	67.5	66.0
	0.75%	49.5	35.3
S + PSM	0.25%	50.8	34.5
	0.50%	61.5	44.8
	0.75%	61.2	56.5
S + S.S.L.	0.25%	66.3	64.0
	0.50%	77.8	74.3
	0.75%	63.0	51.5
S + AP	0.25%	53.5	36.0
	0.50%	63.5	59.3
	0.75%	32.8	20.0

[1] Particle size: -100W

Table 21

INFLUENCE OF EMULSIFIERS ON WATER SOLUBILITY OF EXTRUDED PRODUCT

Sample	Level, %	%S (gr/100gr)
Raw Starch (Control)		44.38
S + OMG	0.25%	32.56
	0.50%	10.60
	0.75%	12.97
S + S.S.L.	0.25%	28.08
	0.50%	19.52
	0.75%	16.08
S + AP	0.25%	27.62
	0.50%	9.94
	0.75%	18.09
S + PSM	0.25%	32.00
	0.50%	18.59
	0.75%	19.97
Commercial Extruded Starch	1	13.42
Commercial Drum Dried Starch	1	13.55
" " " "	2	6.61

Table 22

INFLUENCE OF THE TYPE AND PERCENT OF EMULSIFIER ON THE HOT PASTE VISCOSITY OF EXTRUDED WHEAT STARCH-EMULSIFIER BLENDS.

		VISCOSITY, B.U., at			
Emulsifier	% Emulsifier	30°C	95°C	15 min at 95°C	50°C
Control Wheat Starch	none	138.8	52.5	37.5	67.5
OMG	0.25	65.0	40.0	35.0	70.0
	0.50	30.0	30.0	30.0	40.0
	0.75	30.0	20.0	20.0	30.0
S.S.L.	0.25	80.0	40.0	35.0	65.0
	0.50	50.0	40.0	40.0	100.0
	0.75	40.0	25.0	25.0	70.0
AP	0.25	75.0	40.0	30.0	70.0
	0.50	45.0	50.0	40.0	130.0
	0.75	35.0	30.0	30.0	80.0
PSM	0.25	110.0	60.0	40.0	65.0
	0.50	145.0	50.0	40.0	75.0
	0.75	160.0	55.0	50.0	90.0

Table 23

INFLUENCE OF SCREW COMPRESSION RATIO AND DIE DIAMETER ON THE HOT PASTE VISCOSITY OF EXTRUDED PRODUCTS FROM WHEAT AND CORN STARCH

STARCH	Screw Compression Ratio	Die Opening, inches	VISCOSITY, B.U. at 30° C	95°C	15 min at 95°C	50°C
WHEAT STARCH	5:1	1/8	140	59	44	82
		1/4	130	40	25	80
	3:1	1/8	140	50	40	90
		1/4	120	55	45	105
WHEAT STARCH + 0.5% SSL	5:1	1/8	55	35	30	95
		1/4	55	45	40	120
	3:1	1/8	55	35	30	130
		1/4	50	55	50	130
CORN STARCH	5:1	1/8	60	20	20	50
		1/4	55	20	20	50
	3:1	1/8	50	20	20	35
		1/4	70	30	20	50
CORN STARCH + 0.5% SSL	5:1	1/8	40	20	20	30
		1/4	40	20	20	35
	3:1	1/8	45	20	20	45
		1/4	40	20	25	40

Table 24

COLD WATER BROOKFIELD VISCOSITY OF COMMERCIAL DRUM DRIED AND LABORATORY EXTRUDED WHEAT STARCH AS A FUNCTION OF STIRRING TIME

Stirring time hrs	Viscosity, Centipoises	
	Drum Dried	Lab Extruded
0	51.8	4.8
0.16	106.8	175.5
0.75	133.0	124.3
1.00	158.0	116.2
3.00	155.5	112.5
5.00	172.5	112.5
6.00	180.5	112.0
7.00	180.5	112.5
12.00	198.0	130.0
14.00	193.0	138.0
15.50	193.0	145.0
17.00	190.5	147.5
18.00	188.0	148.0
19.00	185.5	150.0
20.00	185.5	152.0
23.00	188.0	157.5
24.00	187.0	165.5

Tables 25 - 40

STATISTICAL ANALYSIS OF EXTRUDED WHEAT STARCH AND BLEND WITH 0.5% SSL

APPENDIX II

Table 25

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN EXPANSION INDEX OF EXTRUSION-COOKED WHEAT STARCH.

DATA IN EXPANSION INDEX

	DAY				
Replication	1	2	3	4	5
1	3.11	2.86	2.77	2.90	2.82
2	2.79	2.83	2.87	2.88	2.99
3	2.87	2.84	2.90	2.82	2.83
4	2.96	2.96	2.83	2.97	2.95
5	2.97	2.87	2.84	2.94	2.82
6	2.94	2.82	2.81	2.79	2.91
7	3.19	2.76	2.85	2.95	2.94
8	3.05	2.90	2.83	2.90	2.79
9	3.17	2.76	2.88	2.90	3.03
10	2.96	2.88	2.86	2.91	2.83
Mean	3.00	2.85	2.84	2.90	2.89

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	0.1606	0.0401
Within	45	0.2852	0.0063
Total	49	0.4458	

Mean = 2.89

SD = 0.03

$LSD_{95\%}$ = 0.07

Table 26

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN SOLUBILITY OF EXTRUSION COOKED WHEAT STARCH.

DATA IN PERCENT

Replication	1	2	3	4	5
1	44.51	43.51	41.30	46.88	44.76
2	44.18	43.04	41.32	48.10	46.48
3	44.16	43.01	42.15	46.43	47.15
4	43.79	42.53	42.06	47.01	46.30
Mean	44.16	42.77	41.70	47.10	46.17

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	81.65	20.41
Within	15	6.72	0.448
Total	19	88.37	

Mean = 44.38

SD = 0.48

$LSD_{95\%}$ = 1.00

Table 27

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN pH OF EXTRUSION-COOKED WHEAT STARCH.

DATA IN pH UNITS

Replication	1	2	3	4	5
1	7.35	7.18	7.35	6.92	7.18
2	7.36	7.20	7.38	6.98	7.20
Mean	7.35	7.19	7.36	6.95	7.19

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	0.2269	0.0567
Within	5	0.0027	0.0005
Total	9	0.2296	

Mean = 7.21

SD = 0.02

$LSD_{95\%}$ = 0.06

Table 28

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN PRODUCTION RATE OF EXTRUSION-COOKED WHEAT STARCH.

DATA IN KG/HR

Replication	1	2	3	4	5
1	2.72	2.87	2.78	2.87	2.96
2	2.80	2.90	2.88	2.95	2.99
Mean	2.76	2.88	2.83	2.81	2.97

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	0.0531	0.01327
Within	5	0.0123	0.00246
Total	9	0.0654	

Mean = 2.87

SD = 0.05

$LSD_{95\%}$ = 0.13

Table 29

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AMPERAGE CONSUMPTION OF EXTRUSION-COOKED WHEAT STARCH

DATA IN AMPERES

Replication	1	2	3	4	5
1	7.0	8.0	8.0	7.5	7.5
2	8.0	9.0	9.0	8.5	8.5
Mean	7.5	8.5	8.5	8.0	8.0

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	1.4	0.35
Within	5	2.5	0.50
Total	9	3.9	

Mean = 8.10

SD = 0.7071

$LSD_{95\%}$ = 1.82

Table 30

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AGTRON BLUE COLOR FOR EXTRUSION-COOKED WHEAT STARCH.

DATA IN AGTRON UNITS

Replication	1	2	3	4	5
1	64.5	68.5	68.5	62.5	62.0
2	64.5	68.5	69.5	63.0	63.0
Mean	64.5	68.5	69.0	62.7	62.5

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	77.6	19.4
Within	5	1.125	0.225
Total	9	78.725	

Mean = 65.44

SD = 0.474

$LSD_{95\%}$ = 1.22

Table 31

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AGTRON GREEN COLOR FOR EXTRUSION-COOKED WHEAT STARCH.

DATA IN AGTRON UNITS

Replication	1	2	3	4	5
1	63.0	62.5	56.5	59.0	58.5
2	64.0	63.5	58.5	59.5	59.5
Mean	63.5	63.0	57.5	59.2	58.8

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	4	56.10	14.025
Within	5	3.625	0.725
Total	9	59.725	

Mean = 60.4

SD = 0.851

$LSD_{95\%}$ = 2.2

Table 32

DATA, STANDARD DEVIATION AND 95% CONFIDENCE INTERVAL FOR DAY TO DAY CHANGES IN HOT PASTE VISCOSITY OF EXTRUSION-COOKED WHEAT STARCH

	VISCOSITY (8.U.) AT			
Day	30°C	95°C	15' at 95°C	50°C
1	125	45	30	50
2	155	80	60	80
3	130	35	25	60
4	145	50	35	80
Mean:	138.8	52.50	37.5	67.5
SD:	13.8	19.4	15.5	15.0
$CI_{95\%}\pm$:	19.1	26.9	21.6	20.8

Table 33

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN EXPANSION INDEX OF EXTRUSION-COOKED WHEAT STARCH + 0.5% S.S.L. BLEND

DATA IN EXPANSION INDEX

	Day			
Replications	1	2	3	4
1	2.54	2.73	2.67	2.78
2	2.75	2.66	2.66	2.72
3	2.63	2.65	2.83	2.52
4	2.69	2.66	2.62	2.64
5	2.68	2.72	2.80	2.53
6	2.70	2.54	2.84	2.54
7	2.73	2.77	2.91	2.74
8	2.66	2.72	2.75	2.90
9	2.57	2.69	2.64	2.61
10	2.80	2.83	2.70	2.66
Mean	2.68	2.70	2.74	2.66

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	0.03573	0.012
Within	36	0.3351	0.009
Total	39	0.3708	

Mean = 2.68

SD = 0.04

$LSD_{95\%}$ = 0.09

Table 34

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN SOLUBILITY OF EXTRUSION-COOKED WHEAT STARCH + 0.5% SSL

DATA IN PERCENT

Replication	1	2	3	4
1	14.46	21.05	19.98	24.87
2	13.91	20.05	20.23	24.43
3	14.52	17.89	20.83	23.90
4	14.50	17.36	20.68	23.81
Mean	14.35	19.08	20.43	24.25

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	200.66	66.88
Within	12	10.65	0.885
Total	15	211.31	

Mean = 19.52

SD = 0.67

$LSD_{95\%}$ = 1.45

Table 35

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO TO DAY CHANGES IN pH OF EXTRUSION-COOKED WHEAT STARCH + 0.05% S.S.L. BLEND

DATA IN pH UNITS

Replication	1	2	3	4
1	6.20	6.45	6.54	6.39
2	6.24	6.45	6.58	6.40
Mean	6.22	6.45	6.56	6.39

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	0.1207	0.0402
Within	4	0.0017	0.0004
Total	7	0.1224	

Mean = 6.40

SD = 0.02

$LSD_{95\%}$ = 0.06 pH units

Table 36

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN PRODUCTION RATE OF EXTRUSION-COOKED WHEAT STARCH + 0.5% S.S.L. BLEND

DATA IN KG/HR

Replication	1	2	3	4
1	3.06	2.48	2.98	2.50
2	2.98	2.60	2.75	2.86
Mean	3.02	2.54	2.86	2.68

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	0.2647	0.088
Within	4	0.1016	0.025
Total	7	0.3663	

Mean = 2.78

SD = 0.15

$LSD_{95\%}$ = 0.44 Kg

Table 37

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AMPERAGE CONSUMPTION EXTRUSION-COOKED WHEAT STARCH + 0.5% S.S.L. BLEND (DATA IN AMPERES)

Replication	1	2	3	4
1	5.0	5.0	5.0	5.5
2	6.0	6.5	6.0	5.0
Mean	5.5	5.7	5.5	5.2

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	0.25	0.0833
Within	4	2.25	0.5625
Total	7	2.50	

Mean = 5.5

SD = 0.75

$LSD_{95\%}$ = 2.08 amperes

Table 38

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AGTRON BLUE COLOR EXTRUSION-COOKED WHEAT STARCH + 0.5% SSL BLEND(DATA IN AGTRON UNITS)

Replication	1	2	3	4
1	71.5	82.5	75.0	81.5
2	72.0	83.0	76.5	80.5
Mean	71.8	82.8	75.7	81.0

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	151.094	50.364
Within	4	1.875	0.4687
Total	7	152.969	

Mean = 77.8

SD = 0.68

$LSD_{95\%}$ = 1.90

Table 39

DATA, ANALYSIS OF VARIANCE, STANDARD DEVIATION AND L.S.D. FOR DAY TO DAY CHANGES IN AGTRON GREEN COLOR EXTRUSION-COOKED WHEAT STARCH + 0.5% S.S.L. BLEND (DATA IN AGTRON UNITS)

Replication	1	2	3	4
1	65.5	85.0	71.5	75.0
2	67.0	84.0	70.0	76.0
Mean	66.3	84.5	70.8	75.5

Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Between	3	365.75	121.916
Within	4	3.25	0.8125
Total	7	369.0	

Mean = 74.3

SD = 0.901

$LSD_{95\%}$ = 2.3

Table 40

COLD WATER BROOKFIELD VISCOSITY OF EXTRUSION-COOKED SAMPLES OF WHEAT AND CORN STARCH

SAMPLE	VISCOSITY (centipoises) *vs.* STIRRING TIME												
	seconds						minutes						
	0	5	10	15	20	30	1	2	3	5	10	45	60
WS[a], pH 3.0	6.8	11.8	13.0	11.8	11.8	14.3	9.3	11.8	10.5	13.0	9.3	12.3	13.0
WS, pH 4.4	0.0	25.5	40.5	53.0	73.0	88.0	83.0	75.5	73.0	64.3	53.0	45.5	50.5
WS, pH 5.4	0.0	35.5	61.8	95.5	106.8	115.5	115.5	106.8	100.5	85.5	78.0	61.8	58.0
WS, pH 6.2	1.8	33.0	63.0	103.0	139.3	168.0	205.5	205.5	196.0	173.0	141.8	100.5	88.0
WS, pH 7.5	0.3	23.0	61.8	93.0	131.8	178.0	206.8	250.5	246.8	233.0	183.0	139.3	136.8
WS, pH 9.0	11.8	30.5	75.5	108.0	141.8	185.5	219.3	239.3	239.3	230.5	205.5	140.5	131.8
WS+ 0.25% SSL	11.8	41.8	61.8	89.3	115.5	135.5	161.8	174.3	178.0	170.5	145.5	98.0	89.3
WS+ 0.50% SSL	1.5	20.5	30.5	41.8	45.5	46.8	49.3	51.8	51.8	50.5	49.3	43.0	43.0
WS+ 0.50% DMG	5.8	25.5	26.8	36.8	39.3	41.8	44.3	46.8	45.5	44.3	40.5	39.3	41.8
WS+ 0.50% PSM	8.0	19.3	43.6	57.4	76.8	97.5	127.4	144.3	152.4	158.6	158.6	135.5	128.0
WS+ 0.75% PSM	0.0	5.5	30.5	40.5	46.8	54.3	63.0	85.5	88.0	108.0	114.3	103.0	113.0
WS,3:1[b],1/8[c]	18.0	30.5	64.3	101.8	158.0	189.2	238.0	253.0	248.0	223.0	174.2	119.3	103.0
WS+ 0.50% SSL 3;1, 1/4	10.5	33.0	35.5	41.8	45.5	49.3	56.5	60.5	60.5	61.8	56.7	43.0	43.0
WS, 19% H_2O, 100°C, (2)[d]	8.0	20.5	46.5	64.3	88.0	106.8	128.0	140.5	143.0	133.0	119.3	88.0	88.0
WS, 25% H_2O, 125°C, (2)[d]	5.5	34.3	44.3	66.8	86.8	129.3	155.5	195.5	189.3	194.3	174.3	121.8	118.0
WS, 19% H_2O, 150°C, (3)[d]	13.0	65.5	108.0	161.8	199.3	235.5	263.0	271.8	266.8	235.5	185.5	109.3	110.5

* a,b.c,d) See footnote next page

Table 40 (Continued)

SAMPLE	VISCOSITY (centipoises) vs. STIRRING TIME												
	seconds						minutes						
	0	5	10	15	20	30	1	2	3	5	10	45	60
Drum-cooked CS e)	14.3	16.8	15.5	18.0	19.3	23.0	19.3	20.5	21.8	21.8	21.8	35.5	40.5
CS,5:1^{b},1/8^{c}	1.5	20.5	33.0	38.0	49.3	55.5	59.3	60.5	61.8	56.8	51.8	48.0	49.3
CS,3:1^{b}, 1/4^{c}	13.0	31.8	45.5	50.5	54.3	54.3	54.3	51.8	51.8	50.5	48.0	44.3	41.8
CS + 0.5% SSL 5:1, 1/8	5.5	18.0	41.8	58.0	75.5	84.3	84.3	80.5	78.0	73.0	65.5	53.0	50.5
CS + 0.5% SSL 3:1, 1/4	14.3	53.0	78.0	90.5	94.3	91.8	78.0	69.3	63.0	58.0	54.3	45.5	44.3
Drum-cooked WS a)	51.8	66.8	70.5	71.8	74.3	74.3	78.0	80.5	85.5	94.3	106.8	133.0	158.0
WS- Control 1^{f}	11.5	24.3	66.8	108.0	131.8	164.3	189.3	203.0	196.8	180.5	150.5	109.3	101.8
WS- Control 2^{f}	3.6	56.2	106.8	155.5	191.2	211.2	219.3	206.2	200.6	179.9	161.2	111.8	112.4
WS- Control 3^{f}	0.0	40.5	88.3	137.4	183.0	225.5	248.0	262.4	256.2	231.8	200.5	136.2	128.3
WS- Control 4^{f}	0.0	44.3	79.3	113.7	153.1	183.0	211.8	227.4	227.4	215.6	189.9	139.9	122.4
WS CONTROL Mean	4.8	41.3	85.3	128.6	164.7	196.0	217.1	224.0	220.2	201.9	175.5	124.3	116.2
SD^{g}	8.7	12.3	11.9	17.5	12.6	12.8	10.4	10.1	9.4	6.5	1.9	8.8	4.3
LSD^{h}	24.18	34.2	33.1	48.6	34.9	35.7	28.8	28.0	26.0	17.9	5.2	24.6	11.9

* Each data represents the average of two determinations

a) WS: Wheat starch
b) Screw Compression Ratio
c) Die Diameter (inches)
d) Moisture content, Extrusion temperature and cell structure classification respectively
e) CS: Corn starch
f) Extrusion-cooked wheat starch with no emulsifiers or acid added. pH 7.6 Number refer to different experiments.
g) SD: Standard Deviation of WS-Controls
h) LSD: Least Significant Difference at 95% probability level.

EXTRUSION-COOKING OF WHEAT STARCH: EFFECT OF pH AND EMULSIFIERS

by

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B. S., Universidad Nacional de Colombia, 1973

AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Prime wheat starch was extrusion-cooked with four different emulsifiers at three levels (0.25, 0.50, and 0.75%) using a laboratory-scale extruder having a 3/4 inch diameter and a length to diameter ratio of 25 to 1. The effect of the emulsifiers on the following properties of the cooked starch were examined: pasting curve in the Brabender Amylograph, pH, water solubility, color and degree of expansion. The four emulsifiers included distilled monoglycerides (DMG), ascorbyl palmitate (AP), sodium stearoyl 2-lactylate (SSL) and polyoxyethylene sorbitan monostearate (PSM).

All the surfactants produced a sharp reduction in the water solubles, expansion, and production rate of the cooked starch. The cold-paste viscosity of starches extrusion-cooked with DMG, AP, or SSL decreased as the surfactant percentage increased, except with PSM, which produced the opposite effect. The emulsifiers generally decreased the energy required for extrusion except when they apparently caused "slip" at the barrel surface.

In another series of extrusion runs, wheat starch was cooked at 175°C at pH values ranging from 3.0 to 9.0. As the extrusion pH increased, the extruded starch was more brown in color and gave a higher paste viscosity. The water solubility of the extruded starch increased sharply when cooked at pH $\leq$ 3.5 compared to pH 4.0. At pH 3.0 and 175°C the extrudate was approximately 90% water-soluble and had an average degree of polymerization of about 13.

Extrusion-cooked corn starch was more soluble than extrusion-cooked wheat starch even in the presence of 0.5% SSL.

The cell structure ("grain") of extrusion-cooked wheat starch was affected most by the extrusion temperature and moisture.