FUNCTIONALITY OF NONFAT DRY MILK AND MILK REPLACERS IN SPONGE CAKES

by

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This thesis is dedicated to all of the people who have supported me and inspired me to succeed.

To Mom and Dad

and to ...

... the Beast; Squeege and Barb; Madge and Jurhh; Oz (the demon of heavy metal mania) and Murhh; Paul John; Linda and Betty; McVey; Wild Bill; Doug B; Cash and Slowww Motion; Ronnie (who wouldn't leave K-Who); Twad and Patty; Jock and Dori; Peter and Co; the Polish Prince; Frizz and Suze-eye; Nad and Red; Food Face and Sweet Baby; Mark and Steph and Jack and Lil; Papa John and Mama Rosa; Ziggie; Bionic Bob; Mike and Mary Kay; Joe Toad; Mark and Marion; Kur and Monica; Chef Hef; K. Ball and Debbie; Phlebitis too; Greg (Super Hawk) and Debbie; Don and Mary N.; Dr. Ron P.; Danny, Gary, Steve and Ed; Hombre and Leslie; Big Irish Bob and Mrs. C.; Mr. and Mrs. K; Loose and Margie; H. T. and Elsie; Joe and Virginia; Willie and Nancy; Bets, Jeri, Mark, Hugh and Kevin; Raj, Prakash, Steve, Hassan and Vic and Tai-Lee; Larry Aljeers; and last but not least, my two good friends, Charlie and Jack Daniels.

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INTRODUCTION

Because of the high cost of nonfat dry milk (NFDM), milk replacers have assumed great importance in the baking industry. Milk replacers are defined here as ingredients that are substituted for NFDM. Ideally they are less expensive than NFDM, while hopefully maintaining the functional properties of NFDM. Generally, milk replacers are available as all-dairy blends, cereal-dairy blends and all-cereal blends. In at least one application however, it was shown that the overall functionality of replacers were inferior to NFDM.

Recent work at Kansas State has shown that in a certain type of cake, milk replacers cannot be successfully substituted for NFDM. Sigsworth (1980) showed that when sponge cakes were made with replacers in a formula representative of a popular snack cake, the test cakes were inferior to the control, with NFDM, in terms of overall cake quality. Sigsworth (1980) did not find deleterious effects when milk replacers were utilized for white layer cakes. Since sponge-type snack cakes represent a large percentage of the cake consumed in this country, the problem has economic overtones.

In considering the relative inability of milk replacers to function in sponge cakes, we hypothesized that the gelatinization of starch was affected by the replacers. The rationale behind this hypothesis is the finding of Sigsworth (1980), that milk replacers lowered the percentage of starch gelatinization in sponge cakes, as measured by the method of Chiang and Johnson (1977). It is reasonable to assume that anything affecting the gelatinization of starch will have an effect on the structure of the final product.

The objectives for this study were:

1. To identify some probable reasons for the relative inability of milk replacers to function in sponge cakes.

2. To gain additional information about the role of NFDM in cakes.

3. To apply the amylograph and differential scanning calorimeter to the study of cake batters.

The results of the investigation are presented in this thesis.

REVIEW OF LITERATURE

Milk and Milk Replacers in Baking

Milk or milk products, as used in bakery foods, serve at least two general purposes. One of these purposes is nutritional. It is widely accepted that milk is an excellent source of protein, vitamins, and minerals. The amino acid pattern of cereal proteins are well complemented by milk proteins, cereal proteins being limiting in lysine and tryptophan while milk proteins are high in both of these amino acids (Singleton and Robertson, 1974). Combining these two protein sources into a bakery product yields a food of better nutritional quality than the same product without milk. In fact, Pedraja (1965) reported that the biological value of nonfat dry milk (NFDM) is exceeded only by that of whole egg. This is in agreement with the findings of Singleton and Robertson (1974).

Milk is also a very good source of calcium and phosphorus. Pedraja (1965) stated that these two minerals are present not only in liberal quantity, but are in readily utilizable form. Regarding vitamins, he stated that milk contains all of the water soluble vitamins. Riboflavin is present in large quanity, while thiamin and niacin are present in significant amounts. Fat soluble vitamins are present in whole milk, but are found in trace amounts only in NFDM.

In addition to the nutritional properties, milk also serves functional purposes in baked products. Kirk (1971) has outlined a list of functional contributions provided by NFDM in various bakery foods. These functions include: Increased absorption; buffering value; lactose color reaction; tenderizing effect; improved body and resilience of crumb. This is in agreement with Pyler (1973), who added that in bread, NFDM also affects mixing requirements, fermentation rate, and bromate requirements. For cakes, Pyler (1973a) maintained that NFDM falls mainly into the categories of structure former and drier, and, to a lesser degree, is a flavorer, directly and, indirectly by promoting crust browning. Craig and Colmey (1971) also label milk solids as structure building ingredients.

When considering replacer substances for NFDM, one must design products that have the desired functionality for a particular application. They must also be less expensive than the product that they are designed to replace. A wide array of products are marketed as milk replacers. As was stated, milk replacers fall into two basic categories. These are the all-dairy blends and the cereal-dairy blends. Kirk (1973) breaks these categories down to the following: (1) "reconstructed milks," which are whey-caseinate blends; (2) liquid or dry blends of whey with NFDM or buttermilk; (3) wet or dry blends of whey with either (1) or (2) above and (4) sweet dairy whey for the all-dairy types. The cereal-dairy replacers were identified as: (5) wet or dry blends of whey-soy or whey-soy-milk and (6) dry blends of whey-corn flour-milk. Among the major differences in these products, in terms of typical analysis, are in the percentages of protein, lactose and minerals present.

Kirk (1973) pointed out that the process used to manufacture the products will cause a difference in functionality. For example, products that are blended as liquids and then spray dried perform better than do products of similar composition, in which the ingredients are dried separately, then blended.

Craig and Colmey (1971) stated that whey has a tenderizing effect, unlike NFDM or casein, which were labeled as structure builders. These authors do not indicate whether the tenderizing effect is due to the presence of lactose or minerals in the whey fraction, or has to do with the nature of the protein.

Casein, the protein which is coagulated to make cheese, exists as a micelle (Craig and Colmey, 1971). In milk replacers, casein is used in the calcium or sodium caseinate form which is water soluble and has a high water binding capacity, hence absorption is enhanced.

In cereal-dairy replacers, soy protein is the major cereal involved. These replacers have protein levels similar to that for NFDM.

In terms of functionality, milk replacers generally perform well in most applications. Best (1967) reported that cakes made with whey solids had better volume, finer grain, and better texture than cakes made with NFDM. Hanning and De Goumois (1952) concluded that cakes made with dried whey were superior to cakes made with NFDM with respect to moistness and flavor. Additionally, they found an interaction between whey and fat, namely that cakes made with lower fat content could be made of equal or better quality than cakes of higher fat content, if the lower fat cakes had the addition of 15% whey. This may be important when considering using milk replacers in cakes that contain no fat.

Soy flour and the cereal-dairy replacers also are reported to find success as substitutes for NFDM. Turro and Sipos (1970), reported that a specially processed soy flour could be used as a complete or partial replacement for NFDM in cakes. Their work included pound, sponge, devils food, and yellow layer cakes. In white layer cakes, they reported that crumb color is slightly affected. They noted that some formula changes were required to successfully use soy flour as a complete replacer for NFDM in cakes.

Gelatinization of Starch During Cake Baking

Gelation, according to Howard (1972) is the most important stage in cake baking. According to this investigator, during this stage, the batter changes from "a fluid, aerated emulsion to a solid, porous structure," involving the absorption of most of the "free" water present in the system. Additionally, Howard (1972) stated that this is the point at which the gelatinization properties become important to the structural properties of the baked cake. It is therefore useful to discuss gelatinization, particularly as it relates to cake baking.

D'Appolonia et al. (1978) recognize that gelatinization is the term applied to the sequence of changes that occur when starch is heated in an aqueous medium. The sequence involves a very rapid swelling of the individual granules and the concomitant loss of birefringence. The swelling occurs over a temperature range for the sample of starch, due to the range of sizes of the native granules. During the time that the granules are swelling with increasing heat, they are also imbibing water. This imbibition and corresponding swelling causes the apparent viscosity of the suspension to increase greatly.

In a cake batter, much more than starch and water are present. All of the components of the batter have the ability to affect the gelatinization character of starch. Depending upon how gelatinization is affected, the result can exert a positive or negative influence on the final product.

Several workers have studied the effect of different factors on gelatinization. Anker and Geddes (1944) studied the effect of starch concentration on gelatinization temperature and viscosity. They found only a slight difference in the temperature at which the peak viscosity occurred but found much greater differences in the value of the peak viscosity. Sandstedt et al. (1960) examined the effects of salt on the gelatinization of wheat starch and found that salt solutions not only changed the temperature at which gelatinization began, but also changed the character of the entire course of gelatinization. Miller and Trimbo (1965) determined that when sucrose is added to a flour and water suspension, the suspension must be heated to a higher temperature to register a viscosity change on the amylograph, compared to flour and water alone. They found that glucose had a similar effect, but to a different degree. They concluded that anything that causes the batter to allow earlier gelatinization would improve the quality of the cake. Therefore, less sucrose in the cake would cause early gelatinization, as would increasing the water level and as would partial replacement of the sucrose with glucose.

Mizukoshi et al. (1979) found that the wheat proteins and other components of wheat flour did not affect the gelatinization of wheat starch. Osman (1967) indicated that the pH of the system has relatively little effect on the viscosity. This is in agreement with Miller and Trimbo (1965).

Thermodynamics of Starch Gelatinization

The gelatinization of starch has been studied not only from a rheological point of view, but has been given thermodynamic consideration as well, the latter research involving Differential Thermal Analysis. As instrumentation and techniques improved, a method of thermal analysis called Differential Scanning Calorimetry (DSC) came to the fore. Since the original work of Stevens and Elton (1971), a host of other workers have employed DSC techniques to study various aspects of gelatinization.

Stevens and Elton (1971) reported on characteristics of gelatinization for different types of starch, including wheat, rice, maize, and potato. They found that the different starches caused differences in the shape of the thermogram and in the value of the heat of gelatinization, which is generally referred to as ΔH, or the enthalpy of gelatinization. They were able to group the samples according to increasing ΔH and found the order to be: cereal less than root less than tuber. The samples also showed differences in the temperatures at which the peak in the thermogram occurred. Stevens and Elton (1971) included in their work the effect of starch damage, particle size and percentage of amylose and amylopectin in the sample. They found that as the percentage of starch damage increased, ΔH increased; that particle size had no bearing on ΔH; and that high amylopectin starch had higher corresponding ΔH values than did normal and high amylose starches. This work set the stage for other researchers to apply DSC techniques to the study of starch gelatinization. Eliasson _et al_. (1981), Donovan and Mapes (1980), Biliaderis _et al_. (1980), Kugimiya _et al_. (1980), Wootton and Bamunaurachchi (1979) and Donovan (1977) are a few of the most recent papers describing this application of DSC.

Donovan (1977) studied angel cakes, concentrating on denaturation of egg protein and starch gelatinization as affected by such factors as sucrose concentration and amount of foam whipping. He determined "that the starch and protein form the cake structure by being denatured in the same temperature range." Wootton and Bamunaurachchi (1979) studied the thermodynamic properties of native and modified starches. For native starches, they found some agreement with Stevens and Elton (1971). Much of their data was quite different, however. These dissimilarities were explained by differences in experimental conditions.

Regarding the modified starches, Wootton and Bamunaurachchi (1979) included substituted wheat starches, crosslinked wheat starches and acid cut starches, as well as pregelatinized, oxidized, and dextrinized wheat starches. For all of these treatments, there was a decrease in the ΔH value compared to native starch. The thermogram temperatures for the treatments were very close to those for the native starch, with peak temperature showing the most differences.

In a subsequent report, Wootton and Bamunaurachchi (1979a) described gelatinization behavior as affected by heating rate and moisture level. They showed a decrease in ΔH values when heating rates increased from $8^{o}C$ to $32^{o}C$ per minute. The onset temperature of the peak also decreased with increasing heating rate. These workers also studied the effect of the water to starch ratio for the system. Their findings showed that as the water to starch ratio increased, the ΔH value increased. The correlation coefficient for these data was $r = 0.99$ for the range studied.

The work of Eliasson (1980) dealt with the effect of water content on gelatinization. This research showed two, and in some cases three endothermic peaks, which is in agreement with Donovan (1977). The first peak did not change with water content but the temperature at which the second and third peaks occurred did vary with water content. Eliasson (1980) showed that when enough water is present, the second peak disappears and that as the water level decreases, the peaks shift toward higher temperatures.

Eliasson (1980) maintained that scanning rate did not explain the appearance of the second and third peaks. Eliasson *et al.* (1981) determined that the thermal appearance of the second and third peaks may be related to the distribution of lipids in the starch. They found that the second peak of the endotherm changed greatly when the lipids were extracted. This is in agreement with Kugimiya *et al.* (1980) who showed that the size of the endotherm decreased with lipid extraction.

MATERIALS AND METHODS

Materials

A yellow sponge formula was used in this study. The formula is given in Table I.

Flour used in the study was Softasilk® cake flour, provided by General Mills, Inc. The proximate composition of the flour is as follows:

Protein: 9.8% Moisture: 12.1% Ash: 0.32% Fat: 0.73%

Lowheat nonfat dry milk (NFDM) was used in the control. The milk replacers used were of the whey-caseinate (WC) type, the whey-soy (WS) type, spray dried sweet whey (SW), calcium caseinate (CC) and defatted soy flour (SF). Table II gives the typical analysis of NFDM and the various milk replacers. Table III gives the label declaration for the specific replacer blends used. Milk replacers were used as 100% replacement for NFDM. For the experiment, we debated the point of optimizing the formula for each replacer, but decided to avoid this in order to keep the formulae on a constant solids basis.

For part of the experiment, two emulsifiers were used. Their compositions are as follows: Emulsifier A: Hydrated Sorbitan Monostearate and Polysorbate 60 (45%), propylene glycol, hydroxylated lecithin, and potassium sorbate. Emulsifier B: Hydrated Mono- and Diglycerides, Polysorbate 60 (11.3%), and sorbitan monostearate (11.3%); with phosphoric acid, sodium propionate, and sodium benzoate. The water level

Table I

YELLOW SPONGE FORMULA

Ingredient	Baker's Percent
Flour	100.0
Granulated Sugar	106.0
Salt	2.7
Dairy Component	10.0
Whole Egg Solids	10.4
Baking Powder	5.0
Soy Flour (1.5% Fat)	1.7
Emulsifier	A: 2.0 B: 0.5[1]
Water	A: 102.0 B: 106.0[2]

[1]Indicates that Emulsifier A was used at 2.0% or Emulsifier B was used at 0.5%.

[2]102.0% water corresponds to use of Emulsifier A. 106.0% water corresponds to use of Emulsifier B.

in the formula was adjusted for the different emulsifiers, to yield the optimum cake.

Methods

Batter Mixing Procedure. All of the ingredients, except whole egg solids and emulsifier, were weighed, then sifted together. The dry ingredients were placed in the 5-quart bowl of the Hobart N-50 mixer. A wire whip was used for the mixing and ice water was used to keep the batter temperature between 68^{o}F and 70^{o}F. The egg solids were weighed separately and were rehydrated with 65% of the water. The emulsifier was added and the entire contents were mixed for one minute at speed one. The bowl was scraped and the batter mixed for two minutes at speed two. The remaining 35% of the water was added, the bowl scraped and the batter mixed at speed one for one minute. The bowl was scraped and the batter mixed two minutes at speed three.

Specific Gravity Measurement. The specific gravity of the batter was determined by filling a metal cup of known volume with batter immediately after mixing. Excess batter was struck off with the edge of a spatula. The cup with batter was then weighed. By knowing the batter volume, the weight of an equal volume of water and the batter weight, one can calculate the specific gravity of the batter. Specific gravity is a dimensionless number.

Baking Procedure. The baking method follows. 255 grams of the batter was scaled into 6 inch round pans. These were baked at 375^{o}F for 28 minutes in a Reed reel oven. After 30 minutes of cooling, the cakes were removed from the pans. The depanned cakes were then allowed to cool

TABLE II

TYPICAL ANALYSIS OF MILK/REPLACERS

Milk/Replacer	Protein %	Moisture %	Ash %	Fat %
NFDM[1]	36.0	3.0	8.2	0.7
Whey-Caseinate A[2]	27.7	4.0	8.2	1.7
Whey-Caseinate B[3]	28.0	4.0	5.0	1.0
Whey-Soy A[2]	27.8	4.0	8.7	1.5
Whey-Soy B[4]	21.0	5.0	8.0	1.0
Calcium Caseinate[5]	90.0	3.0	6.0	0.7
Sweet Whey[6]	12.5	4.0	8.0	1.0
Defatted Soy Flour[7]	50.4	6.6	6.0	1.3

[1]Pedraja, R. The Bakers Digest 39(5):46(1965).

[2]Technical Bulletin, Kraft Foods, Industrial Foods Division.

[3]Technical Bulletin, DMI, Inc., 6-17-80.

[4]Technical Bulletin, DMI, Inc., 12-15-80.

[5]Dairy Research Inc., Dairy Based Ingredients for Food Products.

[6]Lampert, L. Modern Dairy Products. Chap. 12, p. 192. Chemical Publishing Co: New York (1975).

[7]Technical Bulletin, Archer Daniels Midland Company.

for an additional 30 minutes. After this period, the weight and volume of the cakes were recorded. Volume measurement was done by rapeseed displacement. Following this, the cakes were scored with respect to crust and crumb characteristics.

Cake Scoring Procedure. The cooled cakes were sliced vertically in half. The parameters scored were crust color, cake symmetry or shape, crumb grain, and crumb texture. These subjective parameters were evaluated by the experimenter and major professor. The scoring system used was a simple system, with values of satisfactory, questionable, and unsatisfactory. For cases that were difficult to categorize, a (+) or (-) sign was used.

Amylograph Procedure A. In this series of tests, flour plus NFDM or replacer, to total 80 grams was slurried in 460 ml. of distilled water. Milk or replacer represented 10% of the total solids weight. 360 ml. of the water was added to the solids and the suspension was agitated in a flask, 200 shakes per minute for 30 seconds. The suspension was poured into the amylograph bowl, then the remaining 100 ml. of water was used to rinse the flask. The rinsings were then added to the amylograph bowl. The amylograph was operated in the normal fashion, the temperatures increasing from 30°C to 95°C, by 1.5°C per minute. A sample of flour and water without a dairy component was included in this series.

Amylograph Procedure B. In an attempt to determine whether milk replacers affect starch swelling, the following amylograph procedure was employed. A complete batter was mixed and 350 grams of the batter was scaled into the amylograph bowl. The amylograph had been previously adjusted to operate at 25 RPM, the normal speed being 75 RPM. Cooling

TABLE III

LABEL DECLARATION FOR MILK REPLACERS
(BLENDS ONLY)

Whey-Caseinate A:	Whey, sodium caseinate, nonfat dry milk, lecithin, calcium phosphate and calcium oxide.
Whey-Caseinate B:	Whey, nonfat dry milk and sodium caseinate.
Whey-Soy A:	Whey, soy protein, sodium phosphate, lecithin and calcium oxide.
Whey-Soy B:	Whey, soy protein concentrate, calcium caseinate and calcium phosphate.

water was used to prevent evaporative moisture losses. The amylograph was operated through the normal temperature range of $30^{o}C$ to $95^{o}C$, increasing $1.5^{o}C$ per minute. When the temperature reached $95^{o}C$, the temperature program was held while the bowl continued turning with the chart running. The amylograph operated thus until the pen recorded 1000 B.U. on the chart. In this series, only emulsifier B was used.

Differential Scanning Calorimeter Procedure. For this portion of the experiment, the Perkin-Elmer DSC-2, with Scanning AutoZero and Intra Cooler II was used. The DSC had been previously calibrated against standards of distilled water and indium. The baseline was checked daily and was adjusted as necessary. In doing the calorimetry work, it was necessary to use incomplete batters, i.e. they lacked baking powder. At elevated temperatures, the gas produced by the leavening agents could potentially force open the hermetically sealed sample pans.

To obtain the DSC data, a sample of batter ranging from 9 to 13 milligrams was introduced into an aluminum sample pan, was hermetically sealed and then weighed. Weighing was done on a Cahn 21 Automatic Electrobalance. The sample then was introduced into the sample holder of the instrument. The DSC was programmed to scan between $280^{o}K$ and $400^{o}K$ or $7^{o}C$ and $127^{o}C$. The scanning rate selected was $10^{o}K$ per minute and the range was set at 1 mcal. per second-inch.

The output signal of the DSC was fed to a Perkin-Elmer chart recorder. Chart speed was set at 20 millimeters per minute. The curve drawn by the recorder pen was used to determine several important parameters. These parameters are the transition temperature, the enthalpy of gelatinization and differences in the amount of water available for gelatinization. The area under the curve was determined by means of a Compensating Polar Planimeter. An indium standard was run, so as to obtain information needed for the enthalpy calculation. For this portion of the experiment, both emulsifiers A and B were used. Additionally, a series was run in which the batter lacked emulsifier. An example of a typical thermogram appears in the Results section of this thesis.

RESULTS AND DISCUSSION

Baking Tests.

Both emulsifiers A and B were used in the baking tests, in addition to NFDM and milk replacers. Tables IV through VII summarize the data obtained in the baking tests.

Table IV shows the specific gravity of the batters, measured just prior to baking the cakes. All treatments are significantly different from NFDM at a 99% confidence level.

In addition to all the milk replacer treatments being different from the control, the average specific gravity within either emulsifier is different as well. These differences are significant at a 99% confidence level. This indicates that the emulsifier used exerted an effect on the specific gravity. Additionally, there was an interaction between the treatments and the emulsifiers. The effect of the treatments was larger than the effect of the interaction, yet was not as large as the effect of the emulsifiers. Nonetheless, Table IV shows only the treatment effects, based on the analysis of variance. From the data in this table, it was concluded that the effect of milk replacers on specific gravity was to increase the specific gravity compared to the control.

Considering the effect of the replacers, it was noted that certain replacers were easier to incorporate into batters than others. Presumably, this was due to a difference in the hydration capacity of the

TABLE IV

SPECIFIC GRAVITY OF BATTER[1,2]

Treatment	Emulsifier A	Emulsifier B
NFDM	.708	.845
Whey-Caseinate A	.763**	.979**
Whey-Caseinate B	.748**	.933**
Whey-Soy A	.765**	.939**
Whey-Soy B	.748**	.970**
Calcium Caseinate	.808**	.896**
Sweet Whey	.747**	.961**
Soy Flour	.808**	.972**
Average	.762	.941

[1]Average of 3 replicates

[2]Key to symbols:
** = 99% confidence level

various replacers. This presumption was based on personal observations made during the batter mixing process. The soy flour and calcium caseinate replacers were much more difficult to incorporate than all other replacers.

Regarding the effect due to the emulsifiers, two points need to be made. First, the emulsifiers were used at different levels, each level being chosen because it gave the optimum control cake, based on a series of test bakes. Second, the difference in the composition of the emulsifiers should be considered. It is pointed out that emulsifier A contained Hydrated Sorbitan Monostearate and Polysorbate 60 (45%), propylene glycol and hydroxylated lecithin, whereas emulsifier B contained Hydrated Mono- and Diglycerides, Polysorbate 60 (11.3%), and sorbitan monostearate (11.3%). The gist is that the emulsifiers themselves may have different water binding capacities.

Table V shows the effect of milk replacers on the specific volume of the cakes. In the case of either emulsifier, NFDM was responsible for the largest specific volume.

Compared to control, all treatments with emulsifier A were significantly different at a 99% confidence level, with the exception of sweet whey, which was significant at a 90% confidence level. In the case of emulsifier B, the confidence levels ranged from 99% to no significance, the latter being the case for calcium caseinate and whey-soy A. This may lead one to believe that the emulsifiers exert an effect on the specific volume. Such is not the case, however.

The analysis of variance showed that the effect of the emulsifiers was significant at less than a 90% confidence level, which is considered

TABLE V

SPECIFIC VOLUME OF CAKES[1,2]

Treatment	Emulsifier A	Emulsifier B
NFDM	3.53	3.53
Whey-Caseinate A	3.37**	3.44†
Whey-Caseinate B	2.89**	2.46**
Whey-Soy A	3.32**	3.45NS
Whey-Soy B	2.71**	2.41**
Calcium Caseinate	3.22**	3.49NS
Sweet Whey	3.43†	3.44†
Soy Flour	3.30**	3.26**
Average	3.22	3.19

[1]Average of 3 replicates

[2]Key to symbols:
- † = 90% confidence level
- * = 95% confidence level
- ** = 99% confidence level
- NS = No significant difference

not significant. No evidence of an interaction between treatments and emulsifiers was detected. Therefore, the decreased specific volume was due only to the presence of milk replacers. It is noted that the overall average specific volume for either emulsifier series differs by only .03 cc/g.

Table VI and VII detail the scoring data for the cakes made with the different emulsifiers. Table VI indicates that cakes made with emulsifier A did not show a large difference between NFDM and the various replacers. This is denoted by the number of satisfactory scores given. Whey-soy A produced cake that was equal in score to the control. Whey-caseinate A produced cake that was very nearly equal in score to the control. All cakes containing emulsifier A were seen to have unsatisfactory shape. In all cases, this shape was due to the cake collapsing, giving a flat-topped appearance. Because emulsifier A was not effective at showing the differences that had been reported earlier (Sigsworth, 1980), emulsifier B was tested.

Table VII provides the score data for cakes containing emulsifier B. It is seen that only when the cakes contained NFDM did the product have satisfactory scores for all parameters. Whey-caseinate A produced the best cake of all cakes containing milk replacers, nonetheless, this replacer warranted questionable ratings at best. All other cakes were judged as having at least one unsatisfactory parameter. The cakes made with whey-soy B were unsatisfactoy for all parameters judged. Shapes of the cakes, as they correspond to the assigned scores, were well rounded for satisfactory, slightly rounded for questionable and sunken for those called unsatisfactory.

TABLE VI

Summary Of Scores For Cakes Made With Emusifier A[1,2]

Treatment	Shape	Crust Color	Grain	Texture
NFDM	U	S	S	S
Whey-Caseinate A	U	S	Q	S
Whey-Caseinate B	U	S	U	U
Whey-Soy A	U	S	S	S
Whey-Soy B	U	S	U	U
Calcium Caseinate	U	Q	U	U
Sweet Whey	U	S	S	S
Soy Flour	U	U	S	U

[1]2.0% Emulsifier A used

[2]Average of 3 replicates

TABLE VII

Summary Of Scores For Cakes Made With Emulsifier B[1,2]

Treatment	Shape	Crust Color	Grain	Texture
NFDM	S	S	S	S
Whey-Caseinate A	Q+	Q	Q	Q
Whey-Caseinate B	U	Q	U	U
Whey-Soy A	Q+	Q	Q+	U
Whey-Soy B	U	U	U	U
Calcium Caseinate	S	U	U	S
Sweet Whey	Q+	Q	Q-	U
Soy Flour	S	U	U	U

[1]0.5% Emulsifier B used

[2]Average of 3 replicates

The crust color was either satisfactory or unsatisfactory for the cakes containing emulsifier A. The cakes containing soy flour and calcium caseinate had little crust color development. In the cakes containing emulsifier B, the control was the only cake with satisfactory crust color. Calcium caseinate and soy flour again gave cakes with little crust color development. Whey-soy B was unsatisfactory because the crust color was too dark. All cakes receiving a questionable rating had some browning, but were still light compared to the control.

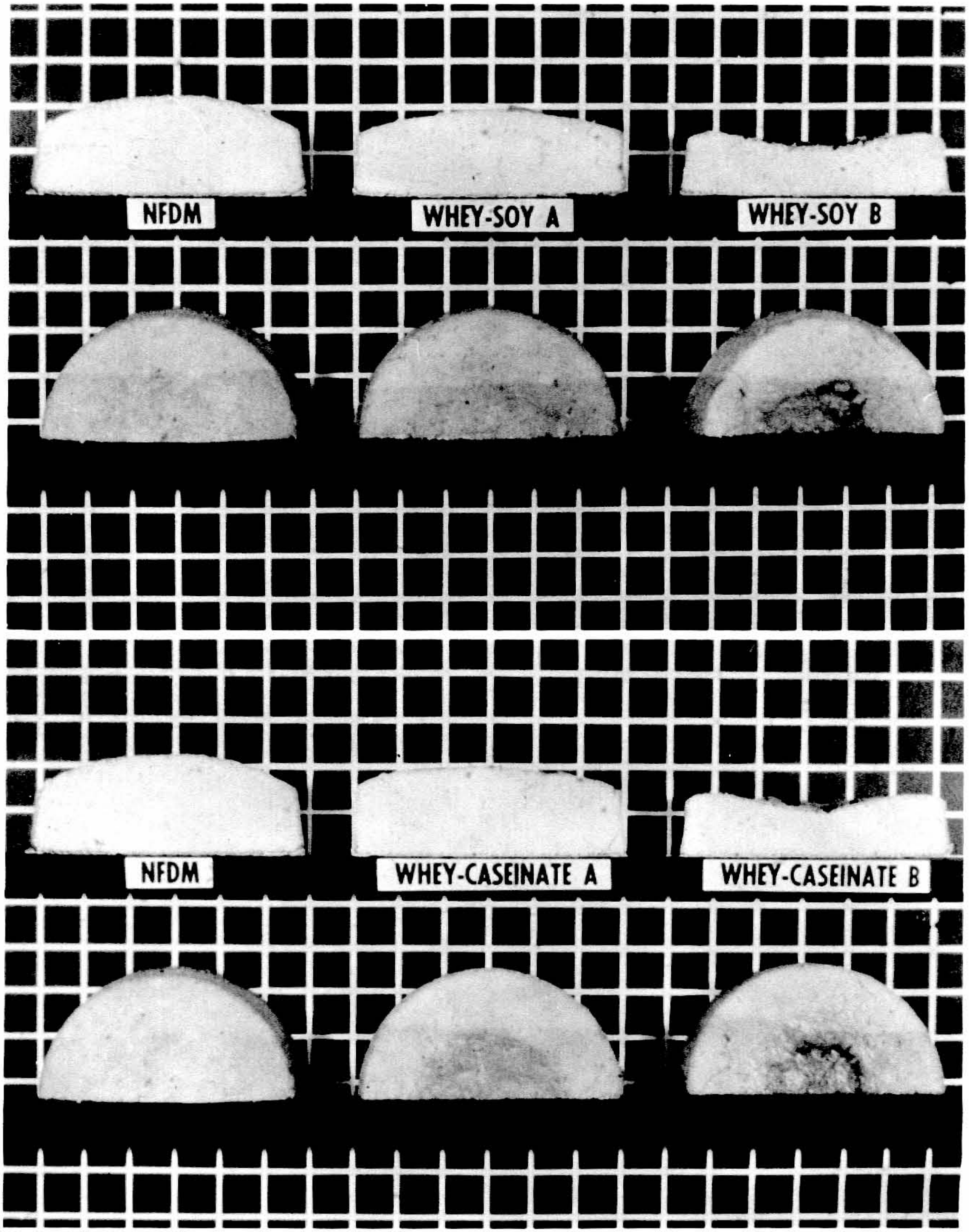
The effect of the replacers on the grain of the cake was not as obvious with emulsifier A as with emulsifier B. Emulsifier A made a greater number of cakes with a satisfactory grain than did emulsifier B, where only the control had satisfactory grain. The control had a fine grain with small air cells and thin cell walls. The unsatisfactory grain was very open with large air cells and thick cell walls. Texture followed grain score rather closely, with the open, unsatisfactory grain giving a coarse, unsatisfactory texture. Conversely, the satisfactory, fine grain was accompanied by a satisfactory, soft texture. Fig. 1 is a series of photographs ~~of the~~ cakes made with the various replacers and NFDM. These cakes were made with emulsifier B.

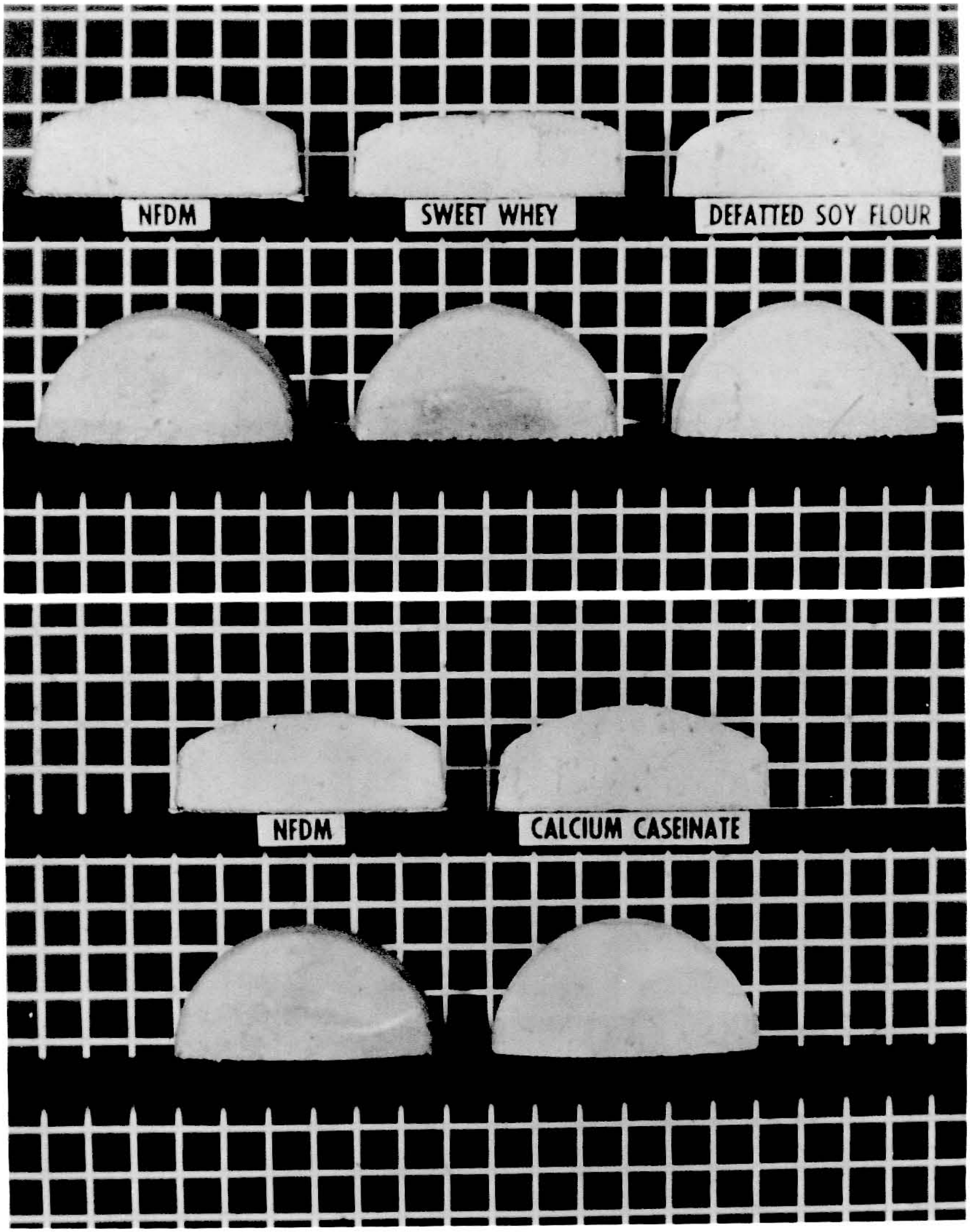
The results of the baking tests are in agreement with the findings of Sigsworth (1980). These results reinforce his conclusion, that sponge cakes made with milk replacers are inferior in quality to cakes made with NFDM.

Amylograph Procedure A.

The results of amylograph procedure A, involving a flour-water-dairy

Fig. 1. Cakes made with emulsifier B.


NFDM
WHEY-SOY A
WHEY-SOY B
NFDM
WHEY-CASEINATE A
WHEY-CASEINATE B


NFDM
SWEET WHEY
DEFATTED SOY FLOUR
NFDM
CALCIUM CASEINATE

component suspension, are given in Table VIII. Included with the data for NFDM and milk replacers are values for a cake flour-water suspension, without a dairy component.

Table VIII shows that adding a dairy component to the flour-water suspension caused a decrease in the peak viscosity. Peak viscosities for all suspensions containing a dairy component were significantly different (99% confidence level) from the flour-water suspension. These results are in agreement with those of Sigsworth (1980), who also noted that lactose raised the peak viscosity of a flour-water suspension, lactose being a major constituent of whey.

The peak time value for the flour-water suspension was seen to fall within a range of values for the treatments. This finding does not agree with Sigsworth (1980), who showed that NFDM and milk replacers decreased the temperature (or time) of the peak. The reason for this discrepancy is not clear, but perhaps the difference lies in the nature of the two cake flours used in the different studies. Most notable is the difference in the peak viscosities for the flour-water suspensions in the Sigsworth (1980) and present studies, i.e., they differ by nearly 400 B. U. Nevertheless, with the exception of whey-soy A, all peak times for treatments were significantly different from the peak time for the flour-water suspension (90-99% confidence level).

Comparing the values for the control to the milk replacers, Table VIII shows that the general trend was for the milk replacers to decrease the peak viscosity, but only to a very slight extent. Hence, it most cases the decrease was not significant. Sweet whey was seen to significantly increase the peak viscosity. This trend is in agreement with

TABLE VIII

AMYLOGRAPH PROCEDURE A[1,2]

Treatment	Peak Viscosity (B. U.)	Peak Time (min.)
NFDM	336.7	36.2
Whey-Caseinate A	346.7[NS]	36.3[NS]
Whey-Caseinate B	326.7[NS]	40.3**
Whey-Soy A	321.7*	37.5*
Whey-Soy B	328.3[NS]	40.3**
Calcium Caseinate	330.0[NS]	37.0[NS]
Sweet Whey	351.7*	40.3**
Soy Flour	316.7**	36.8[NS]
Flour-Water	496.7**	38.0**

[1]Average of 3 replicates

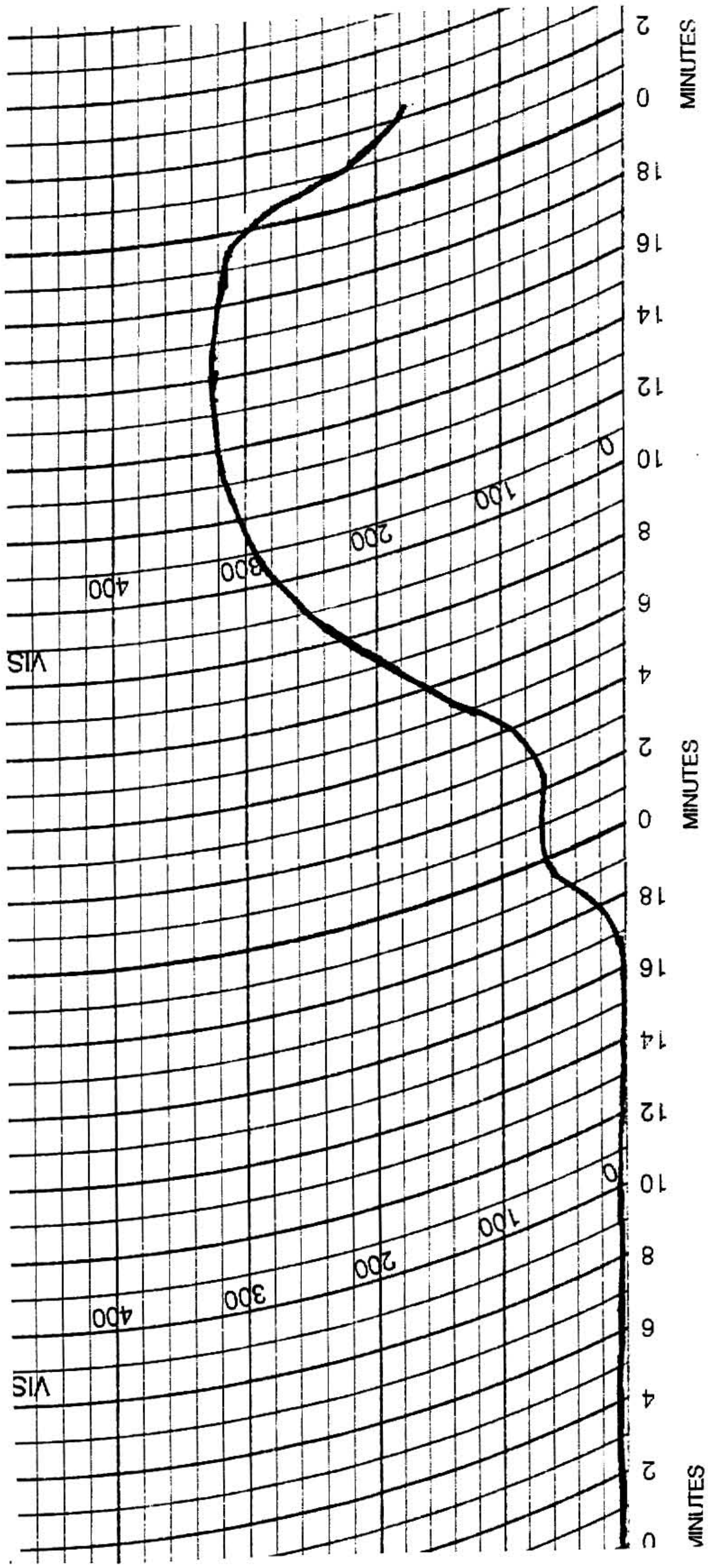
[2]Key to symbols:
* = 95% confidence level
** = 99% confidence level
NS = No significant difference

Sigsworth (1980), although he showed a wider range of differences in his study. Again, it is speculated that this may be due to differences in the two flours used. It is not surprising that sweet whey has a larger associated viscosity than does the control. The proportionately larger amount of lactose in the suspension with sweet whey would increase competition for water, thereby increasing the concentration of starch (Sigsworth, 1980).

The present study shows that milk replacers increase the time of the peak, *significantly* in some but not all cases. This too is in agreement with Sigsworth (1980), and again, he showed a wider range of differences in the peak temperatures he reported. Sweet whey was significantly different from the control, presumably due to the large amount of lactose. It is widely accepted that sugars delay gelatinization, e. g., Miller and Trimbo, (1965). Calcium caseinate and soy flour are not different from the control and presumably this is because these replacers do not contain the sugars that are present in whey containing substances.

Calcium caseinate was seen to be responsible for a unique amylogram, as seen in Fig. 2. The present study indicates a plateau at approximately the same temperature that the former study showed a brief viscosity increase. Sigsworth (1980) attributed this to the aggregation of casein micelles. There is no reason to believe that the same logic does not apply here. A difference in the curves from the two studies, is that in the present study, the viscosity does not decrease from the plateau, whereas in the former study, the viscosity does decrease before gelatinization begins.

Fig. 2. Amylogram of flour, water and calcium caseinate. (Amylograph procedure A).


MINUTES
0
2
4
6
8
10
12
14
16
18
VIS
0
100
200
300
400

Amylograph Procedure B.

Amylograph procedure B, which involved heating a batter in the amylograph, was used to determine whether milk replacers affect starch swelling. The resulting amylogram was somewhat difficult to interpret; indeed the literature does not report any work of this nature that the experimenter could find. Therefore, rather than quantify the amylograms, it was decided that the best way to explain the results would be to characterize the NFDM amylogram, then compare the amylograms of the milk replacers to NFDM.

Fig. 3 shows a family of curves obtained from procedure B. The curve labeled "Replacer" is typical of the curves obtained for the whey-caseinate blends, the whey-soy blends and sweet whey. The curve for soy flour was not included, so as to maintain clarity.

Considering the three curves together, some basic commonalities are established. First, all batters exhibit a sharp decrease in viscosity early in the heating period. This is attributed to shear thinning. Second, all batters exhibit a rather sharp viscosity increase, beginning about 40 minutes into the heating period. Aside from these similarities, the curves have some important differences.

The curve for NFDM shows that shear thinning proceeds for approximately 26 minutes. After this time, the viscosity immediately begins to increase, reaching a plateau at approximately 32 minutes. It is suspected that this first rise in viscosity corresponds to the early stage of gelatinization. In the first stage of gelatinization, granule swelling begins (Miller *et al.*, 1973). The plateau exists until about 38 minutes have elapsed, after which time the viscosity begins a fairly rapid increase, followed by, at 43 minutes, an extremely sharp increase in apparent viscosity. It should be noted that at the point where the extremely sharp increase begins, the batter apparently begins to solidify. Therefore, the final viscosity increase may be misinterpreted, due to the presence of solid material in the amylograph bowl.

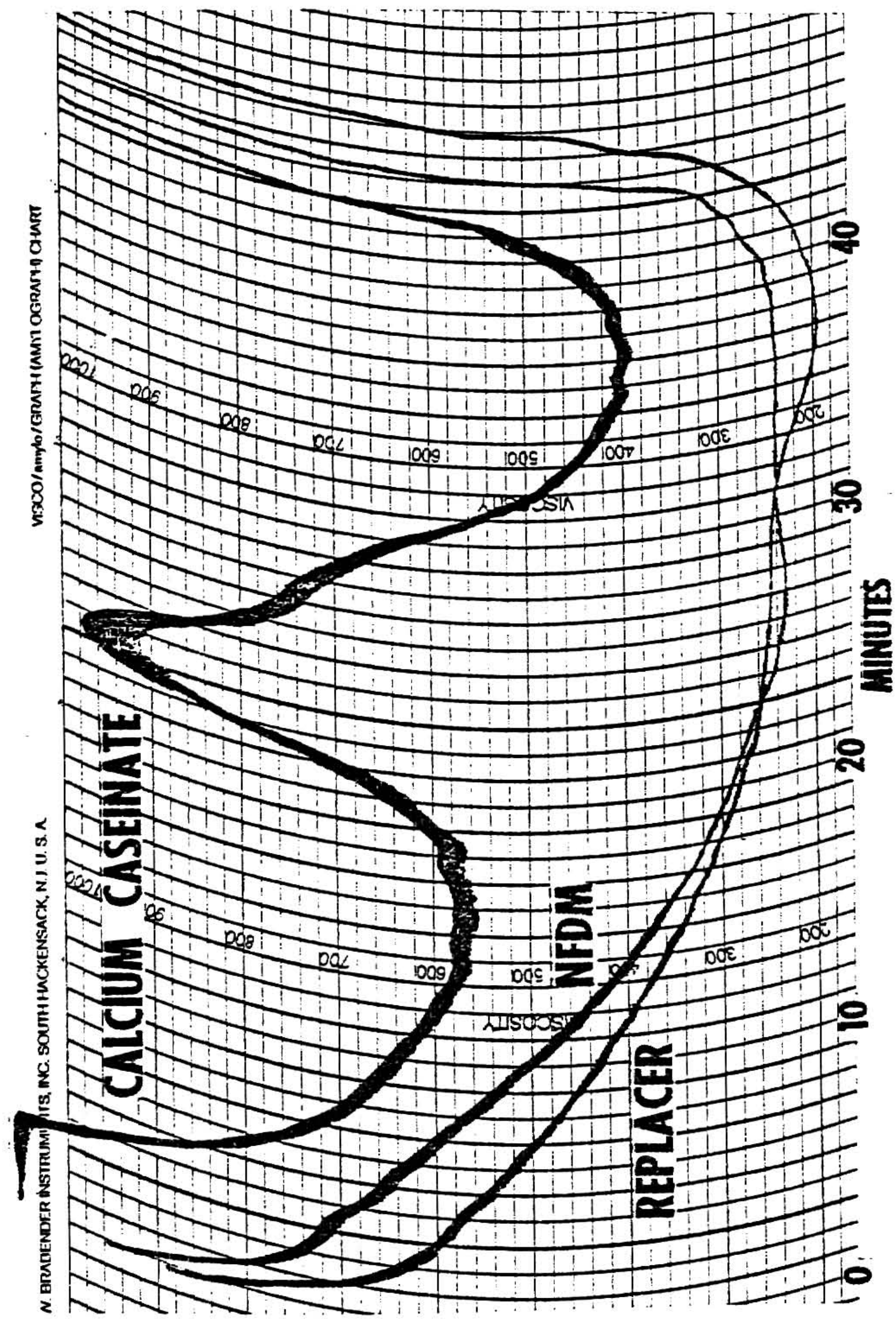
The replacer curve represents the general shape of the curves that were obtained for all milk replacers except soy flour and calcium caseinate. While the basic shape is characteristic, the timing of the peaks and troughs varies for the different milk replacers. This curve shows shear thinning proceeding as in the case of NFDM. Shear thinning is then interrupted by a plateau. Following the plateau is another decrease in viscosity before the final rise in viscosity. The important difference is the sequence of events, which is:

NFDM: Shear thinning: Increase: Plateau: Increase.

Replacer: Shear thinning: Plateau: Decrease: Increase.

The nature of the second decrease in viscosity for milk replacers is unclear. Perhaps it is due to additional shear thinning. Alternatively, it may be due to the milk replacers modifying the starch granules. At the point in time at which the plateau is occurring for NFDM (and the decrease is occurring for replacers), the swelling of granules has been shown by Miller _et al_. (1973) to be unrelated to amylograph viscosity. They showed that the major increase in amylograph viscosity of a starch-water suspension was due to the formation of a filamentous network of exudate released from the granules. Hence it may be inaccurate to associate the decreased viscosity with impaired starch swelling.

Fig. 3. Amylograms of cake batters.
(Amylograph procedure B).


CALCIUM CASEINATE
NFDM
REPLACER
MINUTES
0
10
20
30
40
VISCOSITY

Prior to the plateau for NFDM, the time at which viscosity is increasing, is a time where granule swelling is reflected by amylograph viscosity. Therefore, it is important to identify that which causes the premature plateau for replacers, as well as to identify the cause of the second viscosity decrease.

The curve for calcium caseinate shows a large peak that begins after approximately 17 minutes. Not surprisingly, this corresponds to the rise in viscosity that is seen in Fig. 2. The magnitude of the increase in Fig. 3 is somewhat surprising, however. Calcium caseinate also appears to begin its final viscosity increase about 2 minutes earlier than do either NFDM or the replacers.

We may summarize the difference in viscosity development between batters containing NFDM and milk replacers as follows. NFDM containing batters begin to increase in viscosity much earlier than do milk replacer containing batters. This increase occurs at a time in which granule swelling is reflected by viscosity. Replacer containing batters however, do not cause a viscosity increase in the granule swelling period, although the plateau may be due to granule swelling. Nonetheless, NFDM containing batters exhibit a tendency to become more viscous while replacer containing batters exhibit a tendency to become less viscous, all prior to the final viscosity increase.

Viscosity change in batter during the early cake baking stages is a dynamic and complex phenomenon. Any change in the batter system that affects viscosity will undoubtedly reflect in starch gelatinization changes and hence in changes in finished cake quality. Thus the observed differences in batter viscosities due to the use of milk replacers compared to NFDM are relatively subtle, but occur at a critical point in the cake baking process. This behavior of the milk replacers may be a primary reason whey they lack all the functionality of NFDM, but further evidence is required to prove this point conclusively.

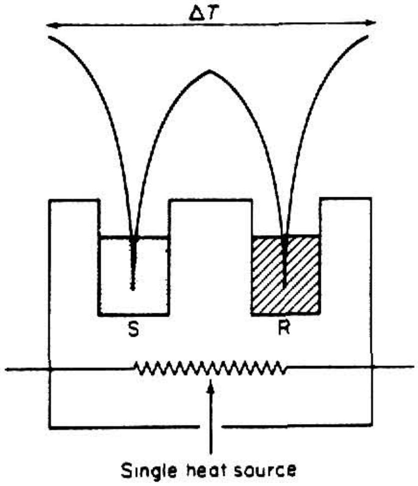
Differential Scanning Calorimeter Studies.

The DSC was used to determine the energy associated with the phenomenon of gelatinization and to determine the temperature at which this phenomenon occurs. Before discussing the data obtained however, a brief description of the operation of the instrument is in order. The following quote from McNaughton and Mortimer (1975), is helpful.

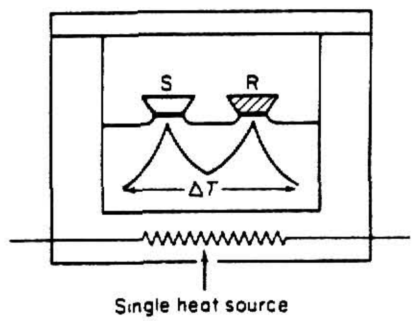
"The purpose of differential thermal systems is to record the difference between the enthalpy change that occurs in a sample and that in some inert reference material, when they are both heated." Differential Thermal Analysis (DTA) is one such thermal analysis system, DSC being the other major system. The major difference in these systems is the manner in which the sample and reference are heated. In DTA, the sample and reference are heated by a single heater, whereas in DSC, the sample and reference have individual heat sources. Fig. 4 illustrates these differences.

As the sample and reference are heated, an endothermic or exothermic reaction occurs and a temperature difference between the sample and reference results. The DSC functions to keep the sample and reference at the same temperature, and the amount of energy required to ensure this event is proportional to the signal fed to the recorder (McNaughton and Mortimer, 1975).

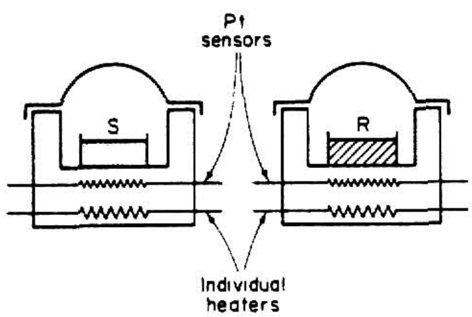
Fig. 4. Schematic diagrams comparing thermal analysis systems (McNaughton and Mortimer, 1975).



(a) Classical DTA



(b)'Boersma'DTA



(c) DSC

Fig. 5 shows a typical DSC thermogram for the batter system used in this study. The thermogram shows a single endothermic transition. This peak is believed to correspond with the gelatinization of starch. It is conceivable that the denaturation of protein could also contribute to the appearance of this peak, however, it is consistent with the literature to accept the peak as being due to gelatinization. Interpretation of the data in this study is based on this assumption.

In analyzing a thermogram, the area under the curve is used to calculate the enthalpy of the transition. A key point in the thermogram is the onset temperature or transition temperature. This point is dependent on the nature of the sample, unlike the peak temperature, which is dependent on the size of the sample. Fig. 6 shows these differences. Both the curve area and the onset temperature are found by extrapolating the base line and the leading edge of the endotherm. Additionally, the trailing edge of the peak and the baseline after the transition are extrapolated for the area determination.

Examination of the data in Table IX reveals several important points. Foremost is the enthalpy difference between milk replacers and control. The analysis of variance showed that the control had a significantly smaller enthalpy associated with gelatinization than did the milk replacers. This was true regardless of the emulsifier used. In most cases, a 99% confidence level was observed for this trend. However, because of the few select cases where this confidence level was not observed, an overall confidence level of 95% should be associated with this trend.

In the three cases where there was no significance found, a different milk replacer was responsible for each case. In the no emulsifier

Fig. 5. Thermogram of sponge-type cake batter.

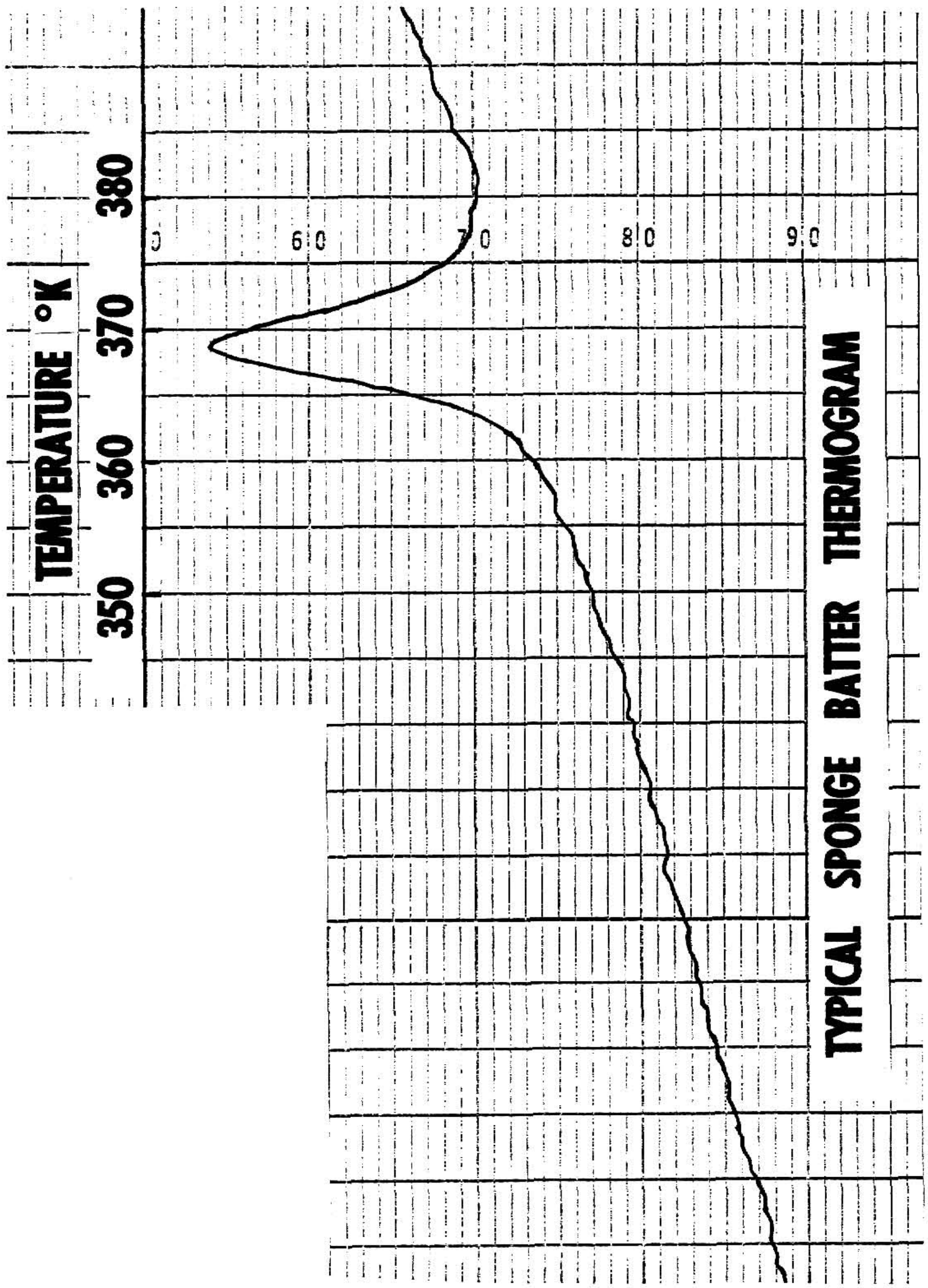
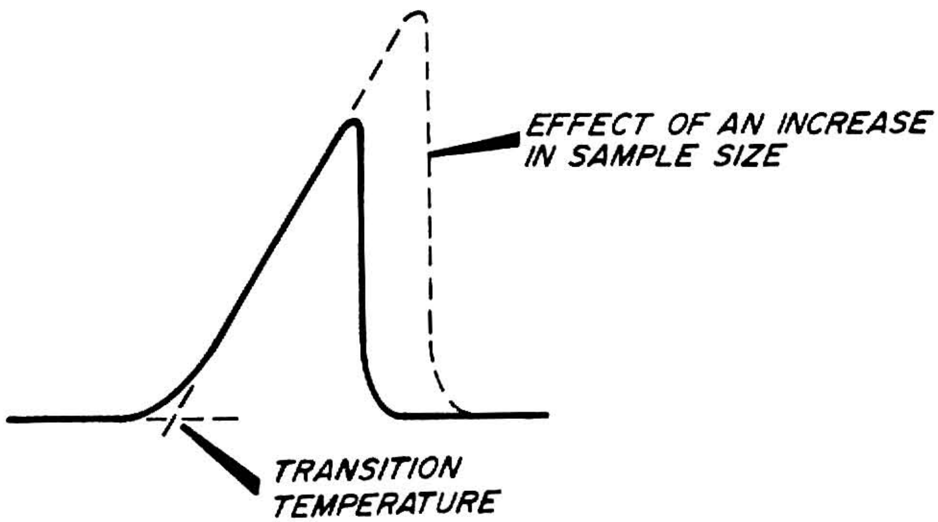

TEMPERATURE °K
350
360
370
380
60
70
80
90
TYPICAL SPONGE BATTER THERMOGRAM

Fig. 6. Thermogram showing transition temperature and sample size effect (The Perkin-Elmer Company, Operation Manual for the DSC-2).



Determination of Transition Temperature series, whey-soy A was not different from NFDM. For emulsifier A, whey-caseinate B was not different from NFDM and in the emulsifier B series, calcium caseinate was not different from the control. The analysis of variance indicated that there was an interaction between the emulsifiers and the replacers, and possibly this explains the lack of significance in these cases.

The interaction between emulsifiers and treatments is also evident in the average enthalpy value for any emulsifier series. The average enthalpy for emulsifier A is significantly different from the average for emulsifier B and the no emulsifier series at a 99% confidence level. The average for emulsifier B is not significantly different from the no emulsifier series. The effect of the emulsifiers may be due not only to their water binding nature but also to the nature of their interaction with starch.

These results support the findings of Sigsworth (1980), who showed that milk replacers significantly reduced the percentage of starch gelatinized in sponge cakes. It is reasonable that if batters containing milk replacers have a higher energy requirement for gelatinization than do batters containing NFDM, then for a given amount of energy, i.e., a fixed time constraint in which gelatinization should occur, then a smaller percentage of the starch should gelatinize. It is possible that competition for water is a factor involved.

In Table X it is shown that generally, the transition temperature is not affected by the treatment, i.e., milk replacers do not significantly affect the point at which gelatinization begins. An exception to this seems to be calcium caseinate, which is significantly different

TABLE IX

ENTHALPHY OF GELATINIZATION[1,2,3]
(cal/g)

Treatment	No Emulsifier	Emulsifier A	Emulsifier B
NFDM	2.93	2.72	2.92
Whey-Caseinate A	2.99*	2.81**	2.97†
Whey-Caseinate B	3.02**	2.76NS	3.04**
Whey-Soy A	2.97NS	2.80**	3.10**
Whey-Soy B	3.00*	2.78*	3.08**
Calcium Caseinate	3.03**	2.77†	2.92NS
Sweet Whey	3.13**	2.80**	3.03**
Soy Flour	3.10**	2.80**	3.10**
Average	3.02	2.78	3.02

[1]Average of 3 replicates

[2]Key to symbols:
† = 90% confidence level
* = 95% confidence level
** = 99% confidence level
NS = No significant difference

[3]Enthalpy values based on starch in cake batter (flour in batter assumed to contain 77% starch).

from the control in the cases of emulsifiers A and B, yet is not different for the no emulsifier series.

Gelatinization is known to occur over a range of temperature in starch. As seen in Fig. 5, the endothermic transition occurs over a range of temperature as well. Recalling that Miller and Trimbo (1965) stated that anything causing earlier gelatinization of starch would exert a positive influence on the structure of the cake, would lead one to believe that milk replacers might cause a delay in gelatinization of starch in the batter. However, such a delay is not indicated from this study.

The lack of effect from the replacers on transition temperature appears to disagree with the results of amylograph procedure A. The discrepancy may be explained by the following. The DSC is more sensitive to changes in the batter system than is the amylograph. Further, the DSC measures changes in energy where the amylograph measures changes in viscosity. Therefore, in terms of energy, the onset temperature is not delayed by utilization of milk replacers but in terms of granule swelling and viscosity, a delay may be indicated, as evidenced by the data obtained from the two amylograph procedures.

The analysis of variance shows that there was an interaction between the emulsifier and the milk replacer. This was reflected in the average onset temperature for the emulsifiers. All of these average temperatures are significantly different from each other. Emulsifier A is different from emulsifier B and the no emulsifier series at a 99% confidence level. Emuslifier B is different from the no emulsifier series at a 90% confidence level.

TABLE X

ONSET TEMPERATURE[1,2]
(^{o}K)

Treatment	No Emulsifier	Emulsifier A	Emulsifier B
NFDM	363.7	364.5	363.2
Whey-Caseinate A	364.3^{NS}	364.1^{NS}	363.6^{NS}
Whey-Caseinate B	363.5^{NS}	364.6^{NS}	363.4^{NS}
Whey-Soy A	363.5^{NS}	363.9^{NS}	364.0*
Whey-Soy B	363.4^{NS}	364.7^{NS}	363.7^{NS}
Calcium Caseinate	363.5^{NS}	362.9**	362.3*
Sweet Whey	363.4^{NS}	364.8^{NS}	363.4^{NS}
Soy Flour	363.5^{NS}	363.0**	363.2^{NS}
Average	363.6	364.1	363.3

[1]Average of 3 replicates

[2]Key to symbols:
* = 95% confidence level
** = 99% confidence level
NS = No significant difference

The conclusion from this data is that milk replacers, in some manner, raise the amount of energy required for gelatinization of starch in the cake batter. Further, since milk replacers do not appear to delay the onset of gelatinization, delayed gelatinization is probably not responsible for the deleterious effect of milk replacers in sponge cakes.

CONCLUSION

NFDM has been shown to perform satisfactorily in sponge cakes while milk replacers were shown to yield unsatisfactory cakes. The unsatisfactory response of milk replacers was manifest in the specific volume, crust color, shape, grain and texture of the final product. It was hypothesized that starch gelatinization was affected by the replacers in a different manner than NFDM affects gelatinization. All batter ingredients have the ability to affect gelatinization to some degree.

This study found that milk replacers significantly increased the batter specific gravity, compared to NFDM. This was true regardless of the emulsifier used. Conversely, the milk replacers showed a tendency to reduce the specific volume of the final product, yielding dense cakes in most cases. Again, the emulsifier used was not a factor.

Two amylograph procedures were used. Procedure A involved a flour-water-dairy component suspension. The results indicated a general trend to reduce the peak viscosity very slightly, compared to the control. Additionally, procedure A showed that peak time was increased only in certain cases. A significant trend was not indicated.

Amylograph procedure B, run with complete batters, showed that milk replacers may affect starch swelling in the first stage of gelatinization.

Changes in granule size are known to affect amylograph viscosity and such changes occur during the first stage of gelatinization. NFDM containing batters showed an increase in viscosity immediately following the shear thinning stage, while milk replacers showed a tendency to reduce batter viscosity during the same period. Additionally, the replacers caused a second decrease in viscosity that the NFDM containing batters did not exhibit. While this second decrease is not associated with the granule swelling period, a reduction in viscosity at a critical period may certainly contribute to defects in the cake.

Differential scanning calorimetry results indicated that milk replacers significantly increased the amount of energy required for gelatinization of starch in the batter compared to NFDM. This supports an earlier finding, that replacers lowered the percentage of starch gelatinization in sponge cakes. The DSC also indicated that the onset of gelatinization was not delayed, except in the case of calcium caseinate. This seems to agree with the peak time trend for amylograph procedure A, where no significant trend was established.

The lack of complete functionality of milk replacers, appears then to be at least partially due to an increased energy requirement for gelatinization, as well as to impaired granule swelling in the early stage of gelatinization. Certainly, additional factors must contribute to the problem and only further investigation will lead to a complete understanding of the problem.

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FUNCTIONALITY OF NONFAT DRY MILK
AND MILK REPLACERS IN SPONGE CAKES

by

PATRICK JOSEPH MCCLUSKEY

B. S., Kansas State University, 1979

AN ABSTRACT OF A THESIS

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1982

ABSTRACT

Various types of milk replacers have been utilized by the baking industry in the production of bakery foods as a means of reducing the cost of ingredients. Evidence indicates that replacing nonfat dry milk (NFDM) is more difficult in some cake systems than in others. For example, replacing NFDM in sponge cakes is difficult because of deleterious effects on the volume, grain and texture of the finished product.

The purpose of the present study was to elucidate factors involved in the lack of full functionality of the replacers. The replacers employed in this study were: whey-caseinate blends, whey-soy blends, calcium caseinate, sweet whey and defatted soy flour. NFDM was used as the control. Data was obtained by amylograph studies, baking tests and differential scanning calorimeter studies.

The amylograph studies indicated that milk replacers may affect starch swelling in the first stage of gelatinization. Differences were seen in the shape of the amylograms obtained for NFDM compared to the replacers. The baking tests showed that milk replacers lowered the volume of the cakes and raised the specific gravity of the batters.

Differential scanning calorimeter studies showed that milk replacers significantly increased the amount of energy associated with gelatinization of starch in the batter, compared to NFDM. There was no evidence that milk replacers delayed the onset of gelatinization, compared to NFDM.