FORMULATION AND EVALUATION OF IMITATION EVAPORATED MILK

By

Abdulrahman Abdulla Al-Saleh

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Food Science and Human Nutrition

1984

ABSTRACT

FORMULATION AND EVALUATION OF

IMITATION EVAPORATED MILK

By

Abdulrahman Abdulla Al-Saleh

This study was undertaken to develop an imitation evaporated milk utilizing sweet whey, sweet cream buttermilk and other milk by-products. Additionally, this study compares the new product to normal evaporated milk.

Two methods were used to produce imitation evaporated milk: a) by direct-formulation (mixing the ingredients without evaporation) and b) by evaporation (fluid-base). Sweet cream buttermilk, sweet whey, isoelectric casein, and soybean oil were used to prepare the imitation evaporated milk. In addition, corn syrup solids were added to direct formulation milk to increase total solids.

The addition of disodium phosphate and sodium citrate increased the stability of imitation evaporated milk as determined with heat and alcohol test, whereas the addition of calcium ions decreased it. The addition of ascorbic acid (0.10% w/v) or sodium hexametaphosphate (0.10% w/v) inhibited the development of browning in direct-formulation product (D-F), whereas (0.15% w/v) of ascorbic acid, and (0.15% w/v) of sodium hexametaphosphate was required to

prevent the browning defect in the fluid-base (F-B).

The D-F product possessed normal heat stability and a low level of discoloration. The F-B product exhibited enhanced flavor, body, and mouth feel, but was accompanied by an increase in discoloration which could be lessened by the addition of ascorbic acid or sodium hexametaphosphate.

To the memory of my beloved Father and Mother.

ACKNOWLEDGMENTS

I would like to express appreciation to my professor, Dr. J.R. Brunner, Professor of Food Science, for his continuous and patient advice throughout my graduate program.

Special appreciation is expressed to Dr. L.E. Dawson, Professor of Food Science, Dr. A.M. Pearson, Professor of Food Science, and to Dr. E.S. Beneke, Professor of Botany and Plant Pathology, for serving on my guidance committee.

A special thanks to Ursula Koch for her continual assistance in the laboratory.

TABLE OF CONTENTS

TABLE OF CONTENTS (CON'T)

TABLE OF CONTENTS (CON'T)

LIST OF TABLES

LIST OF TABLES (CON'T)

LIST OF FIGURES

INTRODUCTION

Evaporated milk is a commercially sterile, concentrated milk containing not less than 7.9% (w/w) fat and not less than 25.9% (w/w) total solids. Its primary advantage lies in its convenience, relatively long shelf life, and low cost. Thus, the world population of evaporated milk has increased from 1969 to 1981 (See Table 1). The primary purposes of the study were to develop an imitation evaporated milk product and to compare the new product with normal evaporated milk.

By utilizing materials such as sweet cream buttermilk, sweet whey, isoelectric casein, and partially hydrogenated soybean oil it should be possible to formulate imitation evaporated milk. Thus, the following advantages would be achieved: 1) a utilization of whey (by-product of cheese manufacture), 2) a development of local industries e.g. vegetable oil production, cheese production, 3) and the elimination of the need to refrigerate milk products during transportation, especially in developing countries.

Table 1. World Production of Evaporated Milk[a]

Area	Years			
	1969-1971[c]	1979	1980	1981
World	4,540,704[b]	4,648,310	4,685,397	4,749,160
N. America	1,620,165	1,347,425	1,340,030	1,353,665
S. America	135,700	167,374	160,825	180,400
Asia	427,013	582,474	616,900	642,073
Europe	1,809,295	1,880,482	1,892,100	1,923,210
Australia	79,670	88,626	88,281	77,212

[a] From FAO Production Yearbook, V. 35, 1981.

[b] MT = million tons.

[c] Average annual production of evaporated milk.

LITERATURE REVIEW

Recombined Evaporated Milk

Recombined, filled, and imitation milks have gained an increasingly important role in the marketplace, especially in supplying large population areas with milk and milk products. Recombined milk products are derived by combining non-fat milk solids with one of the sources of milk fat. These mixtures may be packaged with or without water. Filled evaporated milk is produced by combining skimmed milk with any fat or oil other than milk fat. Imitation milk products are simulated products which have no conventional products in their formulation. Lactose, demineralized whey solids, and sodium caseinate are not considered as milk products (Lampert, 1975).

While the method of manufacturing varies slightly, the composition should meet legal standards. Kieseker (1982) reviewed the literature on the formulation and manufacture of recombined evaporated milk. Water is heated to 45-55^{o}C in preparation for the dispersion of skim milk powder by using a high speed blade. Liquid fat is then added. The preheating and homogenization temperature is usually 55-60^{o}C. The homogenization pressure varies in the range of 2000-2500

psi on the first stage, followed by 500 psi at the second stage. Fat stability in the product is increased by increasing the pressure of homogenization. The goal is to ensure fat dispersion. Failure to achieve a stable fat dispersion results in fat separation. The addition of citrate, phosphate or calcium ions is required to stabilize the protein against the effects of heat denaturation during sterilization. However, the addition of these salts should be kept at minimum levels since they adversely affect flavor when used in high concentrations.

Kieseker (1982) found that the main problem encountered during the production of recombined and filled milks is the possibility of protein coagulation during sterilization.

Alyer (1969) described a method for the preparation of artificial milk and found out that solubilizing acid casein at pH values in excess of 9.0 had a detrimental effect on the caseinate, probably because of its effect on the sulphur amino acids. Additionally, he reported that acid casein imparted better keeping qualities to artificial milk than neutral sodium caseinate and does not form sediment in the presence of normal levels of calcium ions.

Factors Effecting Heat Coagulation of Evaporated Milk

The principal problem in the manufacturing of evaporated milk is heat coagulation which occurs during the sterilization process. The heat process effects the salt and protein components of milk and causes a heavy body and

precipites the milk protein. The effect of heat upon various constituents of milk has been studied extensively (Hunziker, 1949; Sommer and Hart, 1926). The time and temperature of heating are primarily responsible for producing the changes that occur during heating.

Hunziker (1949a) reviewed the factors affecting the heat stability of evaporated milk and identified two main types of problems: 1) those which effect the properties of the milk, and 2) those influencing the efficiency of manufacturing. The first group includes: a) acidity of milk (the hydrogen ion concentration and titratable acidity). Any increase in the acidity decreases the heat stability. b) The milk proteins. Hunziker (1949a) agreed with Webb (1935) that the problem of heat stability can be attributed to the nature of the calcium caseinate system and c) the salt-balance which includes the cations (calcium and magnesium) and the anions (phosphate and citrate). The second group includes: a) a forewarming temperature below the boiling point (190-210^{o}F) for 10-25 minutes is adequate for enhancing the heat stability of evaporated milk; b) the heat coagulation temperature decreases as degree of concentration increases; c) a high homogenization pressure lowers the heat stability of evaporated milk; and d) heating after concentration of 150^{o}C (302^{o}F) with no holding produced maximum stability.

Sommer and Hart (1919) reported that the milk salts constitute the main factor in heat coagulation of fresh

milk. Contrary to this, Rogers, Deysher, and Evans (1921) concluded that the salts of milk are a minor factor in determining coagulation time, due to the rearrangement of acid-base relations in the condensing process. They also concluded that there is no definite relationship between the true acidity (hydrogen ion concentration) of the milk before sterilization and the coagulation temperature of evaporated milk. Sommer and Hart (1922) criticized this conclusion, stating that they failed to find any relationship between the coagulation of evaporated milk and the salt-balance. They speculated on the inadequancy of the analytical method utilized by the Rogers group. Holm, Webb and Desher (1932) observed that the salt-balance as determined by analysis of milk has no direct relation to the heat stability of fresh milk or its evaporated products.

Millory (1915) found that when milk was heated there was a slight increase in titratable acidity. Maxcy and Sommer (1954) reported that factors influencing the heat stability were a) forewarming, b) homogenization, c) concentration, d) presence of rennet-producing organisms, e) acid and pH, f) albumin and globulin content, g) relative concentration of ions, h) total ion or salts concentration, and i) possible differences in the casein components.

Dejongh (1978) stated that increasing the solids-not-fat concentration from 16 to 18 percent reduced the heat stability from 57 to 42 minutes at 120^{o}C. They also demonstrated that increasing the fat concentration from 8%

to 10% reduced the coagulation time from 49 to 39 minutes at 130°C. Newslead, Conaghan and Sanderson (1976) showed that evaporated milk prepared from concentrated whey com bined with milk fat had a distinct heat stability/pH relationship.

Correlation between the Alcohol Test and Heat Coagulation

The alcohol test is one of the tests used in the evaporated milk industry to detect suitability of milk for the sterilization process. Some investigators, such as Dahlberg and Garner (1921) and Sommer and Binney (1923), reported that this test is reliable for detecting the quality of milk. Others, such as Anne, Beton and Albery (1926) reported that the alcohol test is not reliable.

Ayers and Johnson (1915) mentioned that the addition of acid to milk would change dibasic phosphate, which is present in milk, to a state in which it is possible to precipitate the casein by alcohol. They considered milk from a single cow to be abnormal if it showed a positive alcohol reaction. A positive alcohol test with mixed milk was attributed to bacterial action, but they did not show a definite relationship between the number of bacteria in milk and the alcohol test.

Dahlberg and Gerner (1921) stated that the alcohol test showed possibilities of being a reliable and practical test for determining the quality of milk for condensing. Sommer and Binney (1923) reported that the salts of milk have an

important effect on alcohol coagulation. A slight increase in calcium or magnesium caused a positive alcohol test, whereas an increase of phosphate, citrate, chloride and sodium did not result in a positive alcohol test.

Anne, Bentin and Albery (1926) stated that whether the alcohol test is negative or positive does not prove anything relative to the heat stability of milk. Changing alcohol positive milk to alcohol negative by adding citrate or other buffers does not increase the stability unless a critical combination of salt-balance and pH is approached. This condition was found in the majority of samples, which they studied at or near the point where the milk is negative to 70 percent alcohol and positive to 75 percent alcohol. White and Davis (1958) reported that the most important factor governing the stability of the caseinate complex in milk to alcohol is the concentration of bivalent cations. Deman and Batra (1964) found that alcohol test values increased with the addition of phosphate or citrate. These anions act in similar ways in complexing calcium ions and thus increasing milk stability.

Forewarming of Evaporated Milk

The time of milk coagulation at a given temperature varies with the nature of the forewarming treatment. It is known that the forewarming temperature has a great effect on the stability of evaporated milk. Sommer (1923) stated that the effect of forewarming was largely due to the

precipitation of milk albumin (whey proteins), since the albumin content of milk has an affect upon its coagulation. He suggested that the forewarming treatment decreased the coagulating tendency by promoting the precipitation of soluble calcium. Webb and Bell (1942) found that the heat stability of evaporated milk of 26% total solids content was increased as much as six times that of control samples when forewarmed to 95°C (203°F) for 10 minutes.

Bell and Webb (1943) concluded that the heat stability of evaporated milk may be greatly increased by high temperature forewarming to 95°C (203°F) for 10 minutes without any effect upon the color. Deysher, Webb and Holm (1929) stated that the heat treatment of milk affects the heat stability of evaporated milk. Temperatures up to 70°C for 10 minutes decreased the heat stability while higher temperatures increased it. Bell, Curran and Evans (1944) reported that the forewarming treatment of only 65°C (149°F) for 10 minutes did little to increase heat stability.

Hunziker (1949b) stated that forewarming fluid milk was the most common method for inducing increased heat stability in evaporated milk. Rose (1962) found that forewarming milk at 120°C for 10 minutes decreased milk pH by about 0.09 and lowered the pH at which maximum heat stability occurs by about 0.16. He also found that the behavior of an individual milk after forewarming depends upon its original ph relative to the pH at maximum heat stability.

Griffin, Hickey, and Chandler (1976) reported that preheating tends to increase the heat stability of milk when the pH of milk is lower than the pH of maximum heat stability. When the pH of the milk is greater than that of the maximum heat stability, forewarming tends to reduce the heat stability. Pearce (1979) concluded that the only effect of forewarming was to change the pH of maximum heat stability from about 6.6 to 6.5.

Newstead, Conaghan, and Baldwin (1979) noted that when forewarming was carried out following both homogenization and evaporation, no increase in heat stability was induced by the forewarming treatment. When milk was forewarmed after either homogenization or evaporation, the evaporated milk was considerably less heat stable than normally processed milk in which forewarming treatment preceded homogenization. Sweetsur and Muir (1980) showed that the combination of a suitable stabilizer, such as Na_2HPO_4, and forewarming could induce a large increase in the heat stability of both skim and concentrated skim milk.

Sweetsur and Muir (1982) found that the heat stability of concentrated milk could be enhanced to the greatest extent by high temperature forewarming (145^{o}C for 5 sec.), two-stage of homogenization, and addition of sodium phosphate.

Newstead and Baucke (1983) stated that the greatest heat stability of the raw skim milk was obtained by using forewarming treatments of 110 - 120^{o}C for 120-240 sec.

Effect of Milk Salts on Heat Stability of Evaporated Milk

Milk salts play an important role in the heat stability of evaporated milk. The successful manufacture of evaporated milk is largely dependent on the ionic equilibrium (cations and anions) of salts and the way they affect the stability of the calcium caseinate complex.

Sommer and Hart (1919) concluded that casein required a definite optimum calcium content for maximum stability, and that the calcium content of casein is controlled by the concentration of phosphates, citrates, and magnesium. Benton and Albery (1926) found that there was an optimum balance of buffer salts and pH within a pH range of 6.58 - 6.65. The salt-balance was the most important factor, but outside the optimum pH range, pH had a greater influence on stability.

Sommer and Hart (1926) showed that calcium and magnesium on the one hand, and phosphate and citrates on the other hand, have opposite effects on heat coagulation; an excess of either one of these two ionic groups will cause the coagulation. To prevent heat coagulation of the milk, it should have a proper balance of salts (cations and anions). They found that in some of the milk, addition of a suitable amount of disodium phosphate or sodium citrate, and in other samples by the addition of calcium acetate or magnesium chloride. They explained that the reason for the difference between the heat coagulation of the unconcentrated milk and that of evaporated milk was due to the

precipitation of salts, and concomitant increases in the hydrogen ion concentration. Holm, Webb, and Deysher (1932) showed that there was an increase in heat stability of milk as the concentration of magnesium and calcium became greater.

Seeks and Smeets (1948) stated that precipitation of fresh milk was due to increased calcium ion activity which could be corrected by the addition of sodium citrate. Zittle, Dellamoneca, and Custer 91957) concluded that both phosphate and citrate act by binding calcium, which in the case of phosphate leads to the formation of insoluble calcium phosphate. In the case of a calcium-phosphate/ calcium caseinate complex, an excess of calcium precipitated both calcium caseinate and tricalcium phosphate.

Evenhuis and DeVaries (1957a) reported that the binding capacity of casein for calcium in a given milk is related to the composition of the milk protein, the citrate content, and its heat treatment. Evenhuis and DeVaries (1957b) found that the composition of collodial calcium phosphate was always the same when precipitated at pH values of 6.7, 8.0 or 9.0, possessing a (Mg + Ca)/P ratio of about 1.60. They concluded that milk with high citrate and low phosphate contents, together with a low collodial calcium phosphate content, could be unstable to heat (Evanhuis 1957).

Zittle and Pepper (1958) reported that $CaCl_2$-induced aggregation of casein occurred in two stages: an immediate aggregation upon the addition of $CaCl_2$ followed by a period of gradual aggregation. The principle function of calcium

in casein aggregation is a ramification of its effect on the hydration and charge of the casein complex. Zittle, Della-monica, Ruddard and Custer (1957) found that both heated and unheated B-lactoglobulin in the presence of calcium bound the same amount of calcium in the pH range of 6 to 8. Sub-sequently, Dellamonica, Custer, and Zittle (1958) observed that a dilute solution of B-lactoglobulin (1%) was not precipitated by calcium chloride when heated in the pre-sence of casein. The reason for this, they postulated, was that the casein reduced the concentration of calcium chloride available to the B-lactoglobulin.

Rose (1961a) concluded that the maximum heat stability of milk in the pH range of 6 to 8 was significantly cor-related with the following salt ratios: a) soluble calcium/ soluble inorganic phosphorus, b) calcium ions/soluble inorganic phosphorus, and c) soluble magnesium plus soluble calcium/soluble citrate plus soluble inorganic phosphorus. Rose (1961b) observed that by increasing the calcium con-tent, the maximum heat stability was decreased, and by increasing the phosphate content there was an increase in the maximum heat stability. This effect, however, was reversed at high levels of phosphate. Rose (1962) also noted that the removal of collodial phosphate from milk by dialysis or acidification increased heat stability.

Deman and Batra (1964) showed that when 60 mg/100 ml of calcium was added to skim milk the ratio of ionic to soluble calcium shifted from 0.56 to 0.64, and the ratio of soluble

to toal calcium shifted from 0.33 to 0.42. This indicated that only one quarter of calcium ions remained in the ionic form. They also found that the destabilizing effect of adding 10 mg/100 ml of calcium ions was counteracted by approximately 60 mg of added citrate. Zittle (1969) reported that k-casein was not precipitated by heating in the absence of calcium ions, but k-casein was precipitated when calcium ions were subsequently added.

Wedit (1981) pointed out that the commonly used heat treatment i.e., preheating, pasteurization, and sterilization, increased the sensitivity of the whey proteins to calcium ions and caused denaturation of the whey protein so that the susceptibility of whey proteins to denaturation depends on the presence of calcium ions.

Horne and Parker (1981) reported that the addition of Ca would lead to higher concentration of colloidal calcium phosphate and such addition leads to reduced Etoh stability. They also reported that the addition of phosphate would increase colloidal phosphate, or Ca phosphate itself, but did not have an equivalent effect. Phosphate, at the level added, had no observable effect on Etoh stability, while Ca phosphate had a destabilizing effect.

Browning of Evaporated Milk

Evaporated milk usually has a darker color than fresh whole milk; a ramification of the prolonged heat treatment of evaporated milk. For many consumers, evaporated milk

should possess very little brown color.

Experimental studies on the factors causing color formulation in evaporated milk are very limited. There are two types of browning involved in the browning of evaporated milk: a) the Maillard-type or amino-sugar browning; and b) the caramelization of lactose. Most investigators support the first type (Jenness and Patton, 1959a). Therefore, lactose and casein are the two major constituents involved in the browning of evaporated milk.

Webb and Holm (1930) reported that these changes in color were due to the effect of heat; whether during storage, sterilization or forewarming. Hunziker (1949c) stated that the lactose-protein reaction was responsible for the dark color of milk. The NH_2 group combines with the CHO group of lactose, leaving the acid group free, which causes a reduction in the pH and the eventual formation of a colored product.

Jenness and Patton (1959b) reviewed the following factors which effect browning in the fluid milk system: a) properties of milk; b) total solids concentration; c) heat treatment; d) pH; e) oxygen; f) storage time and temperature; g) various added compounds; and h) processing steps of forewarming and sterilization. They reported that as the concentration of milk solids, the concentration of lactose, and the pH increased, browning increased. From a stability point of view, as the stabilizer level was increased the color intensity increased. This was attributed to a shift in pH due to the alkaline stability salts.

EXPERIMENTAL

Materials and Methods

The principal chemicals used in this study are listed below. The water used was distilled. The chemicals used in the calcium determination, sodium acetate and sodium chloride, were purchased from Mallinckrodt, Inc.; ammonium purpurate was purchased from Sigma Chemical Company; sodium citrate and disodium ethylenediamine tetraacetate were obtained from Fisher Scientific Company; phosphoric acid was purchased from J.T. Baker Chemical Co.; calcium chloride and potasium chloride were obtained from Mallinckrodt.

The standard titration solution was prepared by dissolving 10 grams of disodium ethylenediamine tetraacetate and 2 grams of sodium hydroxide pellets in water which was made to one liter. The solution was standardized against a standard solution of $CaCl_2$ to be equivalent to approximately 1.0 mg of calcium per milliliter (Jenness, 1953). Calcium indicator was prepared by grinding 100 grams of sodium chloride and 0.2 grams of ammonium purpurate into an intimate mixture.

Chemicals used in browning studies include ascorbic acid purchased from Mallinckrodt, and sodium hexametaphosphate obtained from the Fisher Scientific Company.

An anion exchange resin was used to prepare an ion exchange column. The column was backwashed with water and several portions of IN sodium acetate followed by rinsing with distilled water.

A superspeed centrifuge, Servall Type SS-1, was used to obtain ultrafiltrate product for ionic calcium determination. Centrifuge tubes (50 ml) were fitted with a perforated plexiglass platform and support ring served as a support for specimens placed in Visking tubing bags.

A laboratory-size Delaval Separator was used to separate cream from pasteurized milk. A Logeman Laboratory Homogenizer Model C-8 was used to homogenize the imitation evaporated milk preparations. Photomicrographs of the fat phase in imitation evaporated milks were produced with a Microstar, series 10, American Optical Co. Microscope equipped with a poloroid camera.

An oil bath equipped with a thermoregulator ($\pm$ 1°C) and mixer was used for temperature stability evaluations. Temperatures ranging from 118°C (245°F) to 132°C (270°F) were used. Capped Pyrex tubes (15 ml) were employed as sample holders, fitted with Septum-Cap Teflon discs, 13 mm inside diameter.

Formulation and Manufacturing Procedures

Preparation of Sweet Cream Buttermilk and Sweet Whey

The main constituents used in the manufacture of imitation evaporated milk were: sweet whey, sweet cream buttermilk, soybean oil, and isoelectric casein. The major steps involved in producing sweet whey and sweet cream butter milk are shown in the schematic diagram (See Figure 1). The raw milk was obtained from the MSU dairy barn.

There is no accurate test for determining the heat stability of raw milk which will predict with certainty the coagulation tendency of the manufactured product. However, an alcohol test can be used to distinguish abnormal milk. Raw milk used to produce sweet whey and sweet cream buttermilk had a pH 6.58 and a negative alcohol test.

Total solids determination was accomplished by using a Mojonnier Milk Tester. The Babcock method was used to determine the fat content (See Table 2).

Table 2. Properties of sweet cream buttermilk and sweet whey

	Property				
Product	pH	TS%	Fat%	Total Calcium	Calcium ions
				mg%	
Sweet cream buttermilk	6.58	9.66	0.36	70	18
Sweet whey	6.47	6.50	--	14	3

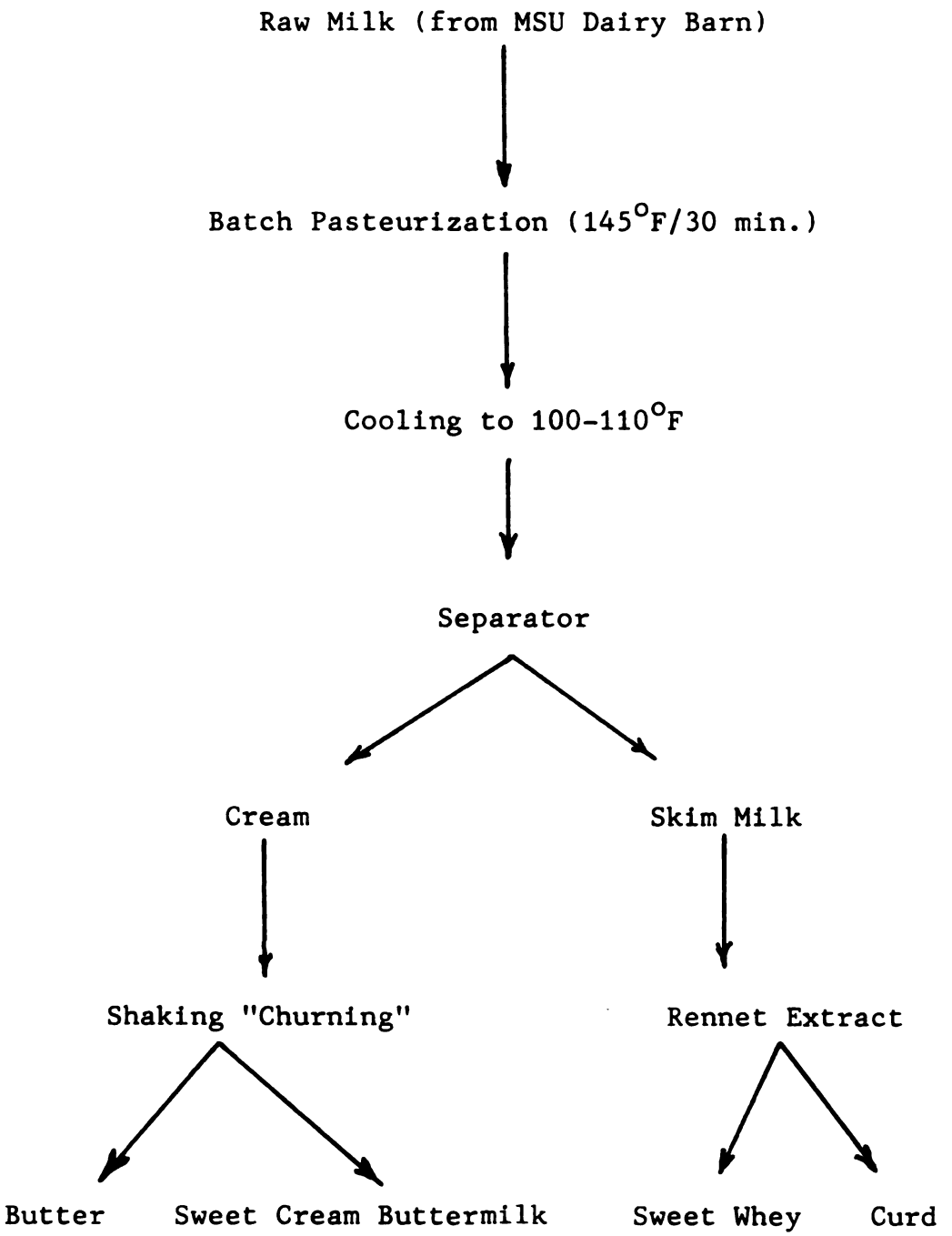


Figure 1. Schematic representation of the procedure employed for producing sweet cream buttermilk and sweet whey.

Two methods were used to manufacture imitation evaporated milk: an evaporative-concentration (fluid-base) method and a direct formulation procedure. For both methods the same ingredients were used except that in the direct-formulation method, corn syrup solids were used to balance the carbohydrate composition.

Direct-formulation Imitation Evaporated Milk

The formulation of the components used in the direct method consisted of 50% (V/V) sweet whey and 30% (V/V) sweet cream buttermilk. By calculating the shortage of milk ingredients, the amount of soybean oil, isoelectric casein, and corn serum solids required to achieve a legal composition (25.9% TS and 7.9% fat) was determined. Data in Table 3 show the calculation procedure for formulating the direct method imitation evaporated milk.

Mixing of the ingredients was carried out by increasing the pH of the whey to 8.0 with a mixture of KOH/NaOH (4:1) prior to the addition of isoelectric casein. This operation was accomplished at a low temperature to reduce the degradation of casein. The pH was neutralized to 6.7 with H_3PO_4. Then, the sweet cream buttermilk was added and the mixture was divided into three portions. The first part of the mixture was not heated, the second part of the mixture was forewarmed to 87.5°C (190°F) for five minutes and the third part of mixture was forewarmed to 93.5°C (200°F) for ten minutes. This was done to compare the effect of the

Table 3. Calculations for the manufacture of direct formulation imitation milk.

	Fat	Protein	Lactose or CSS[a]	Salts
	---------- % ----------			
50% Sweet cream buttermilk[b]	0.18	1.8	2.35	0.35
30% Sweet whey[c]	--	0.21	1.41	0.21
Total	0.18	2.01	3.76	0.56
Desired	7.9	6.8	9.03	
Need	7.72	4.79	5.27	
	Oil	IEC[d]	CSS[e]	

[a]Corn syrup solids.

[b]Sweet cream contains 0.36% fat, 3.6% protein, 4.7% lactose and 0.7% salts.

[c]Sweet whey contains 0.7% protein, 4.7% lactose, and 0.7% salts.

[d]IEC: isoelectric casein.

[e]CSS: corn syrup solids.

forewarming treatment. This mixture was cooled to 38.5°C (100°F). Corn syrup solids were added and the mixture cooled to 4°C (40°F).

The non-fat solids content of the direct-formulation product was determined to ascertain that the level of solids was not less than 18%. The formulated milk was warmed to 65°C (150°F) and partially hydrogenated soybean oil (mp 92°F) was added while stirring. Two stage-homogenization

(2,000/500 psi) was accomplished at 65°C (150°F). This direct-formulation product was cooled immediately after homogenization to 22°C (70°F) and stored at 4°C (40°F) for subsequent experiments.

Alternately, the same procedure was followed to produce a direct-formulation product, but with 20% (V/V) of sweet cream buttermilk, and 80% (V/V) of sweet whey. The product which was produced by this formula tested and looked like whey, thus, it was rejected.

Fluid-base Imitation Evaporated Milk

To manufacture imitation evaporated milk by this approach, the following procedure was followed. The formula consisted of 80% (V/V) of sweet whey, 20% (V/V) sweet cream buttermilk, and 3% (W/V) of isoelectric casein.

The pH of the whey was increased to 8.0 with KOH/NaOH (4:1) and the prescribed amount of isoelectric casein was dissolved at low temperature. Upon complete dissolution of the isoelectric casein, the pH was neutralized to 6.7 with H_3PO_4. Then, sweet cream buttermilk was added to the mixture and the mixture was divided into three portions. The first portion of the mixture was not heated, the second portion of the mixture was forewarmed to 87.5°C (190°F) for five minutes and the third portion of the mixture was forewarmed to 93.5°C (200°F) for ten minutes. This was done to compare the effect of forewarming treatment.

Each mixture was concentrated by evaporative

condensation at 50°C and 28 inches of vacuum until a TS content of 18% was attained. Partially hydrogenated soybean oil (m.p. 92°F) was added and agitated. Two-stage homogenization (2000/500 psi) was performed. The resulting fluid-base product was cooled to 22°C (70°F) and stored at 4°C (40°F) for subsequent analysis.

Analytical Procedures

Determination of Total Calcium

Ten milliliters of milk were placed in a 100 ml volumetric flask and diluted with 20 ml distilled water. Two milliliters of 1N hydrochloric acid were added and the sample allowed to stand for 10 minutes, after which 2.5 ml of 0.5 N sodium hydroxide were added. the acid dissolves the collodial calcium salts and disperses the casein on the acid side of its isoelectric point.

Addition of alkali brings the pH to 4.0 whereupon the casein is precipitated and the calcium remains in solution. The contents of the flask were made to volume, and thoroughly mixed. The precipitate was filtered off; leaving a water clear filtrate. Ten ml of the filtrate was passed through an anion exchange column, followed by two 10 ml portions of distilled water to rinse the column. The entire effluent was collected.

To determine total calcium to 30 ml of ion exchanged solution, 1 to 2 ml of 1.5 N sodium hydroxide was added to bring the pH above 10 as determined with universal indicator

paper. Then 1 scoop (0.2 gram) of prepared calcium indicator was added. The solution was titrated with standardized enthylenediamine tetraacetate solution to a purple color that does not change on addition of another drop of titrant.

Ionic Calcium Determination

One end of the dialysis membrane (approximately 10 cm length) was twisted and a small knot was tied and then filled with 15 ml of imitation evaporated milk. The membrane was closed with a small knot and tied. Cheese cloth was wrapped and placed into a 50 ml centrifuge tube and centrifuge for 15 minutes at approximately 5000 rpm (See Figure 2). To approximately one milliliter of centrifugal ultrafiltrate, 3-4 ml of distilled water was added. One milliliter of 1.5 N sodium hydroxide and 0.1 gram of the prepared calcium indicator were added, and the solution was titrated with ethylenediamine tetraacetate solution to a purple color that did not change on addition of another drop of titrant. The titer was converted to calcium concentration.

Alcohol Tests

Two ml of imitation evaporated milk samples were mixed with 65%, 70%, and 75% alcohol and checked for coagulation. For most accurate results, the addition should be made rapidly.

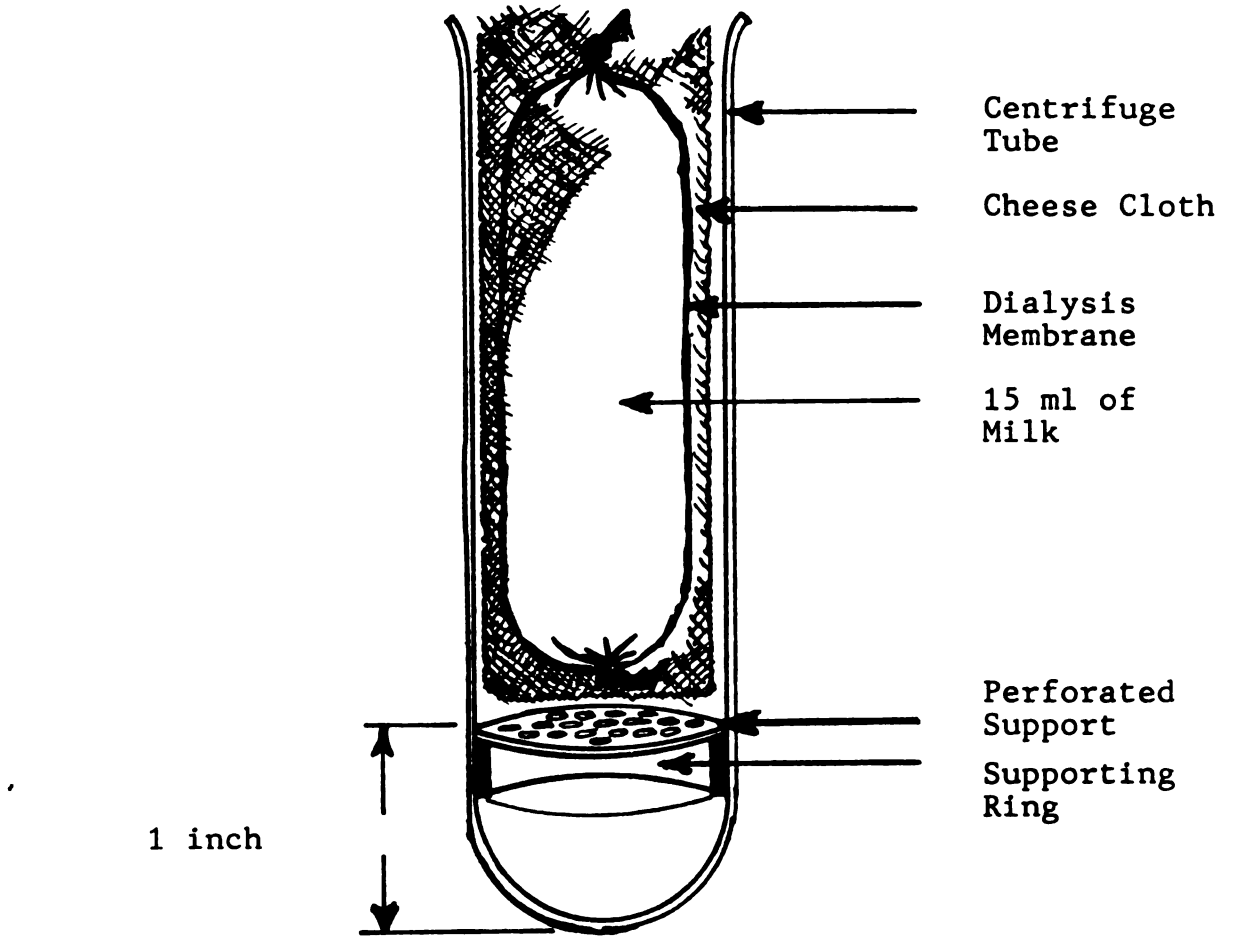


Figure 2. Device used to collect ultrafiltrate for ionic calcium determination.

To determine the effect of 0.25 M Na-citrate solution on the stability of milk to alcohol, different concentrations of 0.25 M Na-citrate were added to 2 ml of imitation evaporated milk.

To determine what influence the salt-balance in milk has on its stability to alcohol, varying quantities of 0.25 M $CaCl_2$ solution were added to 2 ml of imitation evaporated milk.

To determine the amount of 0.25 M Na-citrate bound to calcium ions, 0.375 ml of 0.25 $CaCl_2$ solution, which made the alcohol test distinctly positive, was added to 15 ml of imitation evaporated milk. One and one-half milliliters of Na-citrate were added to the direct-formulation specimen and 1.875 ml of Na-citrate to the fluid-base specimen. These concentrations of Na-citrate prevented the coagulation encountered in the previous test. Then, ionic calcium was determined.

Salt Test

To determine the proper amount of the stabilizing salt (Na_2HPO_4) to add, a solution containing 10 grams of dry salt dissolved of the 10% disodium phosphate solution were added to 5 ml portions of imitation evaporated milk in sealed tubes. The milk tubes were submerged in the oil bath for sterilization at 118°C (245°F) for 15 minutes. After the sterilization process, color, viscosity, and coagulation were evaluated. Viscosity was assessed by measuring the

flow out time from a 3 ml pipette. A stop watch was used to monitor the time.

The coagulation time was evaluated as follows. Different amounts of 10% Na_2HPO_4 solution and distilled water were added to 5 ml of imitation evaporated milk. Milk tubes were submerged in the oil bath which had been heated to 132°C (270°F). Coagulation time (minutes) corresponded to the appearance of coagulated particles.

Similarly, the influence of varying amounts of 0.25 M $CaCl_2$ on the coagulation time of the evaporated milk specimens was monitored.

Evaluation of Forewarming Treatment

To determine the effect of forewarming on the heat stability, samples were taken from imitation evaporated milk manufactured by the direct-formulation and fluid-base methods. The first group of samples was not heated. The second group of samples was heated to 87.5°C (190°F) for five minutes. Remaining samples were heated to 93.5°C (200°F) for ten minutes. Following the forewarming treatment, the coagulation time at 132°C (270°F) was determined.

Browning of Imitation Evaporated Milk

To investigate the effect of selected substances in preventing the discoloration of imitation evaporated milk, different concentrations of 10% ascorbic acid solution were added to 10 ml of imitation evaporated milk. Distilled

water was added to eliminate the dilution factor. Also, various amounts of a sodium hexametaphosphate solution were added in the same manner. The color was subjectively compared to that of commercially-processed, filled evaporated milk.

To determine the effect of pH on browning of imitation evaporated milk, the pH was adjusted to different levels by addition of various amounts of M/10 HCL solution and M/4 NaOH solution to 5 ml of imitation evaporated milk. The color of the sterilized sample was compared subjectively with the control sample.

To determine the effect of pH on browning of imitation evaporated milk as a result of the addition of 10% sodium hexametaphosphate solution and 10% disodium phosphate solution, various concentrations were added to 5 ml of imitation evaporated milk. The color was monitored as before.

To determine the effect of ionic calcium on discoloration of imitation evaporated milk, different concentrations of M/4 $CaCl_2$ solution were added to 5 ml of imitation evaporated milk. The color was monitored as before.

Evaluation of Homogenization

After sterilizing and cooling, slides were prepared from both types of imitation evaporated milk. From each product and without diluting, a sample sufficient to cover the area under the slipcover was taken. The slipcover was pressed slightly to achieve a thin layer. A 10 x lens

was used to examine the field. the oil immersion lens was employed to enlarge the field 100 times for making photomicrographs. Similarly, slides from both samples were prepared at the time of coagulation at 270°F.

Sensory Evaluation Procedure

Ten participants were asked to judge the samples on a 1 to 5 scale as compared with a commercial product. Six of the ten participants were considered dairy product experts. The evaluation was done in the environment of the research laboratory. Figure 3 represents a copy of the evaluation form used.

Check the samples and select one of the following numbers:

1. Very Poor 2. Poor 3. Fair 4. Good 5. Excellent

Sample	Color	Visual texture (body)	Flavor	Mouth feel (smooth, coarse)	Odor

Figure 3. Sensory Evaluation Form.

RESULTS AND DISCUSSION

About 3 liters of imitation evaporated milk were manufactured by both the direct-formulation and the fluid-base procedures.

Constituents acceptable for the formulation of direct-formulation product included 50% sweet whey and 30% sweet cream buttermilk. For the fluid-base method, 20% sweet cream buttermilk and 80% sweet whey were employed. The proportions were selected based on: a) the lowest contents of sweet cream buttermilk and b) the highest contents of sweet whey which were acceptable on the basis of flavor, mouth feel and texture.

Following the production of imitation evaporated milk, numerous experiments were performed to compare this new product with normal evaporated milk and for quality improvement.

The Effect and Control of Calcium as It Relates to Heat Stability of Imitation Evaporated Milk

Prediction of Heat Stability with the Alcohol Test

Alcohol test furnished direct evidence of instability of evaporated milk toward heat treatment. Alcohol exerts

denaturation and dehydration action on the protein system of milk, precipitating calcium caseinate at critical concentrations.

The imitation milks manufactured by both methods were stable to 70% alcohol. Therefore the milk samples should be stable to heat treatment. This test is not sufficiently sensitive to show the heat stability of fluid milk samples, but is capable of detecting abnormal milk.

Milk salts are of importance and to determine the effect of these salts on the alcohol stability of the imitation milks, various quantities of 0.25 M $CaCl_2$ solution were added (See Table 4 and 5). For evaporated milk prepared by direct-formulation method, the addition of 0.02 ml of 0.25 M $CaCl_2$ solution, and 0.01 ml to the second batch sample, caused coagulation, whereas the fluid-base imitation milk was coagulated by the addition of 0.01 ml. The lower amount of added $CaCl_2$ which caused coagulation in the second batch specimen may be ascribed to the higher concentration of indigenous ionic calcium in the sample.

The concentration of ionic calcium required to effect coagulation was found to be 0.22 mg per 2 ml (11 mg%) of the first batch sample and 0.11 mg per 2 mg (5.5 mg%) for the second batch sample of direct-formulation product. For the fluid-base product it was 0.11 mg (5.5 mg%) of ionic calcium. The results illustrate that a slight increase in calcium content will cause a positive reaction to the alcohol test. Presumably, calcium-caseinate-phosphate complex is sensitive to a change

Table 4. Effect of $CaCl_2$ solution on the alcohol test (Direct-formulation product)[a]

H_2O ml	0.1[c]	0.095	0.09	0.08	0.07	0.06	0.04	0.03	0.02	0.01	0
0.25 M $CaCl_2$ ml	0	0.005[b]	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	.1
70%[d]	-	-	$\bar{+}$	+	+	+	+	+	+	+	+
75%	-	-	+	+	+	+	+	+	+	+	+

[a]Two trials

[b]Different concentrations of 0.25 M $CaCl_2$ were added to 2 ml of milk

[c]Different amounts of H_2O to eliminate the dilution factor

[d]The strength of alcohol

Table 5. Effect of $CaCl_2$ solution on the alcohol test (Fluid-base product)[a]

H_2O ml	0.1[c]	0.095	0.09	0.08	0.07	0.06	0.04	0.03	0.02	0.01	0
0.25 M $CaCl_2$ ml	0	0.005[b]	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	.1
70%[d]	-	-	+	+	+	+	+	+	+	+	+
75%	-	-	+	+	+	+	+	+	+	+	+

[a]Two trials

[b]Different concentrations of 0.25 M $CaCl_2$ were added to 2 ml of milk

[c]Different amounts of H_2O to eliminate the dilution factor

[d]The strength of alcohol

in calcium activity. Destabilizing this complex causes aggregation of the casein particle.

The addition of Na-citrate to imitation evaporated milk did not cause coagulation and the alcohol test was negative. Citrate counteracts the action of calcium by decreasing the concentration of ionic calcium.

The Binding of Ionic Calcium by Na-citrate

From the results of previous tests, it was noted that a slight increase in calcium caused coagulation whereas the addition of citrate caused negative alcohol tests.

Data in Table 6 show that 0.05 ml of 0.25 M $CaCl_2$ which rendered the alcohol test distinctly positive and caused coagulation in direct-formulation product was prevented by the addition of 0.2 ml of 0.25 M Na-citrate. The concentration of Na-citrate which prevented the coagulation was found to be 14.6 mg per 0.5 mg of ionic calcium.

The addition of 0.25 ml of 0.25 M Na-citrate to 2 ml of fluid-base product prevented the coagulation caused by 0.05 ml of 0.25 M $CaCl_2$ (See Table 7), indicating that 18.25 mg of Na-citrate prevented the coagulation caused by 0.5 mg of ionic calcium.

To determine the concentration of ionic calcium bound to citrate, 0.375 ml of 0.25 M $CaCl_2$ was added to 15 ml of milk which made the alcohol test distinctly positive. To prevent the coagulation caused by ionic calcium, Na-citrate was added in concentration expected to counteract the action

Table 6. The effect of salt-balance on the alcohol test (Direct formulation product)[a]

0.25 M $CaCl_2$ ml	0.05[b]	0.05	0.05	0.05	0.05
0.25 M Na-citrate ml	0.10	0.15	0.20	0.25	0.30
70%[c]	+	+	-	-	-
75%	+	+	-	-	-

[a]Two trials.

[b]Different concentration of 0.25 M $CaCl_2$ and 0.25 M Na-citrate was added to 2 ml of milk.

[c]The stength of alcohol

Table 7. The effect of salt-balance on the alcohol test (Fluid-base product)[a]

0.25 M $CaCl_2$ ml	0.05[b]	0.05	0.05	0.05	0.05
0.25 M Na-citrate ml	0.10	0.15	0.20	0.25	0.30
70%[c]	+	+	+	-	-
75%	+	+	+	-	-

[a]Two trials

[b]Different concentrations of 0.25 M $CaCl_2$ and 0.25 M Na-citrate were added by 2 ml of milk

[c]The strength of alcohol

of ionic calcium. Data in Table 8 show that of the 10.75 mg of ionic calcium in direct-formulation product, 7.5 mg was determined as Ca^{++}, indicating that 3.25 mg of ionic calcium was bound to citrate. For the second batch specimen, 3.35 mg of ionic calcium was bound to citrate.

In the fluid-base product, of the 12.75 mg of ionic calcium 9.2 mg was determined as Ca^{++}, thus 3.55 mg of ionic calcium was bound to citrate and for the second batch 3.15 mg of ionic calcium was bound to citrate. The concentration of Na-citrate, which bound ionic calcium in direct-formulation product, 33.69 mg of sodium citrate per mg of ionic calcium for the first batch and 32.68 mg for the second batch. For the fluid-base product 36.70 mg of Na-citrate per mg of ionic calcium was required for the first batch and 41.36 mg of Na-citrate per mg of ionic calcium for the second batch.

The above described experiments indicate that salts have an important influence on alcohol stability. The effect of calcium, which cause a positive alcohol test, can be counteracted by the addition of citrate. The concentration of sodium citrate required to prevent coagulation was different for each milk sample.

Prediction and Control of Heat Stability with the Stabilizing Salt Test

Sommer and Hart (1926) stated that heat stability was maximized at an optimum salt-balance. When this optimum salt-balance disturbed, evaporated milk was less heat stable.

Table 8. The concentration of ionic calcium bound to citrate[a]

Product	0.25 M $CaCl_2$ ml added	0.25 M Na-Citrate ml	Ca++ Mg/100 ml	Ca++ Mg added	Ca++ determined
Direct-formulation product	0.375[b]	1.5	7[c] 9	3.75	7.5[d] 9.4
Fluid-base product	0.375	1.875	9 12	3.75	9.2 12.6

[a]Two trials.

[b]The concentration of 0.25 M $CaCl_2$ which caused coagulation distinctly from the previous test added to 15 ml of milk.

[c]The amount of ionic calcium before any addition.

[d]The amount of ionic calcium after the addition of $CaCl_2$ sol. and Na-citrate sol.

To determine the proper amount of stabilizer, disodium phosphate was added to imitation evaporated milks in different concentrations (See Table 9). The first sample represents the direct-formulation product without any salt addition. The second represents the same milk in dilution form to compensate for the dilution factor. The dilution rate was the same in all the milk samples.

Data in Table 9 show that there was no coagulation in any of the samples, but by increasing the addition of 10% disodium phosphate the color became darker in the sterilized product. Color development was minimal for the control sample and was only slightly darker than the color of commercially-processed, filled evaporated milk. Addition of 0.10 ml and 0.15 ml of the phosphate solution caused increased color development. The sample to which 0.2 ml of 10% $NaHPO_4$ had been added developed the darkest color.

In the United States, the addition of stabilizing salt to the extent of 0.1 percent by weight to evaporated milk has been legalized and is equivalent to the sample containing 0.005 ml of 10% Na_2HPO_4 in this experiment. Additionally, the viscosity was increased by increasing the concentration of disodium phosophate. Even though the viscosity was increased, it approximated commercial evaporated milk which showed a 27.5 sec. flow time at 24°C (75°F). The direct-formulation product to which 0.005 ml and 0.01 ml of 10% Na_2HPO_4 had been added had

Table 9. The effect of disodium phosphate on direct formulation product [a]

H_2O ml	0	0.2	0.195	0.19	0.12	0.10	0.05	0
10% $Na_2HP\Theta_4$ ml	0	0	0.005[b]	0.01	0.08	0.10	0.15	0.2
Coagulation	---	---	---	---	---	---	---	---
Color[c]	+++	+++	+++	+++	+++	++++	++++	+++++
Viscosity[d] (sec)	27.8	27.6	27.75	27.75	27.9	28	28.15	30

[a]The average of two trials.

[b]Different concentration of 10% Na_2HPO_4 added to 5 ml of milk and sterilized at 245°F/15 min.

[c]Color was compared visually with commercially-processed filled evaporated milk (++)

[d]Viscosity was measured by comparison with commercially-processed filled evaporated milk at 75°F (27.5 sec.)

a viscosity very close to commercially-processed, filled evaporated milk.

Data in Table 10 indicate that none of the samples showed coagulation. Color was increased by increasing the quality of Na_2HPO_4 solution. For samples ranging from no addition to 0.01 ml of 10% Na_2HPO_4 stabilizer, the color was slightly darker than that of commercial evaporated milk. The addition of 0.08 ml, 0.10 ml and 0.15 ml of 10% Na_2HPO_4 yielded essentially identical color but were darker than the commercial specimen. The highest concentration of added disodium phosphate (0.2 ml) yielded the darkest color.

There was no noticable difference in viscosity between fluid-base and the direct-formulation products. However, the fluid-base product was somewhat higher. This behavior was ascribed to a slight increase in total solids or, perhaps, to an increase in the caseinate-phosphate particles. The fluid-base product has total solids of 26.53% compared to the direct-formulation product which contained 26.26% total solids. Thus, the principle problem encountered was the slight increase in brown color.

Data in Table 11 show the effect of disodium phosphate on the coagulation time of the fluid-base product. Samples to which disodium phosphate solution had not been added were coagulated in 8 min., 50 sec., whereas the coagulation time of all other samples exceeded 15 minutes. By increasing the concentration of the stabilizer to 0.2 ml,

Table 10. The effect of disodium phosphate on fluid-base product [a]

H_2O ml	0	0.2	0.195	0.19	0.12	0.10	0.05	0
10% Na_2HPO_4 ml	0	0	0.005[b]	0.01	0.08	0.10	0.15	0.2
Coagulation	---	---	---	---	---	---	---	---
Color[c]	+++	+++	+++	+++	++++	++++	++++	++++
Viscosity[d]	2.8	27.5	27.8	28.1	28.4	28.5	29.5	29.9

[a]The average of two trials.

[b]Different concentration of 10% Na_2HPO_4 added to 5 ml of milk and sterilized at 245°F/15 min.

[c]Color was compared visually with commercially-processed filled evaporated milk (++)

[d]Viscosity was measured by comparison with commercially-processed filled evaporated milk at 75°F (27.5 sec)

Table 11. The effect of additional varying amounts of disodium phosphate upon the coagulation time of fluid-base product[a]

H_2O ml	Na_2HPO_4 ml	Coagulation time min.	sec.
0.2	0	8	50
		(less than 15 min.)	
0.15	0.05	4	0
0.1	0.1	6	50
0.05	0.15	10	25
0	0.2	14	50

[a]The average of two trials.

[b]Different concentrations of 10% disodium phosphate were added to 5 ml of milk and sterilized at 270°F/15 minutes.

coagulation time was increased. For the direct-formulation product there was no difference in the coagulation behavior except that the coagulation time was longer than that for the fluid-base product (See Table 12). There was a two minute difference for the direct-formulation product in the lowest concentration of 10% Na_2HPO_4 (0.05 ml), which is equivalent to a 5 mg addition of stabilizer. Addition of 0.2 ml (20 mg) of stabilizer salt increased the coagulation time to 35 min., 50 sec. minutes and was longer than that for the fluid-base product by 6.0 minutes.

Therefore, in both types of imitation evaporated milks, optimum addition of disodium phosphate had the effect of stabilizing them against coagulation by sterilization.

Data in Table 13 show the effect of $CaCl_2$ on coagulation time of the fluid-base product. The coagulation time was decreased by increasing additions of 0.25 M $CaCl_2$ solution. For the first sample, to which no $CaCl_2$ was added, the coagulation time was 7 minutes. The addition of 0.005 ml of 0.25 M $CaCl_2$ (equivalent to 0.05 mg of $CaCl_2$) decreased the coagulation time by one minute. The highest addition of 0.25 M $CaCl_2$ (0.1 ml; equivalent to 1.10 mg of $CaCl_2$) decreased coagulation time to 2 min., 50 sec. As shown in Table 14, the addition of 0.25 M $CaCl_2$ to the direct-formulation product decreased the coagulation time. The highest concentration (0.1 ml; equivalent to 1.10 mg of $CaCl_2$) decreased the coagulation

Table 12. The effect of additional varying amounts of disodium phosphate upon the coagulation time of direct-formulation product[a]

H_2O ml	10% Na_2HOP_4 ml	Coagulation time min.	sec.
0.2	0	10 (less than 15 min.)	30
0.15	0.05	6	0
0.1	0.1	9	0
0.05	0.15	13	25
0	0.2	20	50

[a]The average of two trials.

[b]Different concentrations of 10% disodium phosphate were added to 5 ml of milk and sterilized at 270°F/15 min.

Table 13. The effect of $CaCl_2$ upon the coagulation time of fluid-base product[a]

H_2O ml	0.25 M $CaCl_2$ ml	Coagulation time min.	sec.
0.1	0	7	0
0.095	0.005	6	0
0.09	0.01	4	0
0.05	0.05	3	50
0	0.1	2	50

[a]The average of two trials.

[b]Different concentrations of .25 M $CaCl_2$ were added to 5 ml of milk and sterilized at 270°F/15 min.

Table 14. The effect of $CaCl_2$ upon the coagulation time of direct-formulation product[a]

H_2O ml	0.25 M $CaCl_2$ ml	Coagulation time min.	sec.
0.1	0	8	0
0.095	0.005	7	0
0.09	0.01	5	50
0.05	0.05	5	0
0	0.1	3	50

[a]The average of two trials.

[b]Different concentrations of 0.25 M $CaCl_2$ were added to 5 ml of milk and sterilized at 270°F/15 minutes.

time to 3 min., 50 sec. At the same concentration of $CaCl_2$, the direct-formulation product exhibited a longer coagulation time than the fluid-base product. Thus, the latter product possess a lower heat stability.

Casein exists as complex particles or micelles containing citrate, inorganic phosphate and calcium. Many problems associated with heat-treated dairy products depend on the behavior of this system. The caseinate particles are very sensitive to ionic calcium which causes coagulation. Whereas citrate and phosphate exert an opposite action to that of calcium because they decrease the effect of calcium concentration.

It would be expected that the concentration of ionic calcium and phosphate in milk would be decreased by heat treatment because calcium phosphate is less soluble at high temperatures (Jenness and Patton, 1959C). From the result obtained with the salt test, one observes that the heat stability was decreased by increasing the concentration of total milk solids. This behavior is attributed to the increase in destabilizing ions (i.e. Ca^{++}). Furthermore, it was shown that an increase in heat treatment or calcium ions decreased the heat stability of the concentrated milk. Increased heat stability of the caseinate system is achieved not only by the addition of phosphate or citrate salt. Some evaporated milk is stabilized by the addition of calcium and destabilized by the addition of citrate or phosphate (Sommer and Hart, 1926). This atypical behavior is

attributed to a distortion in the salt balance of milk. If this phenomenon is due to an excess of phosphate or citrate, it can be prevented by adding the proper amount of calcium chloride or by an increase in acidity. This procedure changes secondary phosphate to primary phosphate which have a little or no effect on salt balance (Hunziker, 1949). On the other hand, if heat instability is due to an excess of calcium, appropriate amounts of disodium phosphate or sodium citrate will assist in preventing heat coagulation. Therefore an excess of either citrate, phosphate or calcium can cause coagulation. Thus, a salt test is needed to find the type and amount of salt to be used.

Forewarming Effect on the Heat Stability of Imitation Evaporated Milk

Forewarming is one of the most important steps in the manufacture of evaporated milk from the heat stability point of view. Data in Table 15 show that for the direct-formulation product there was a difference in coagulation time. Compared with the product forewarmed to 93.5°C (200°F) for 10 minutes, there were 4 min., 25 sec. less for coagulation time for the product sterilzed without a forewarming treatment, and 2 min., 45 sec. less for the product which forewarmed to 87.5°C (190°F) for 5 minutes. For the fluid-base product, there were 4 min., 10 sec. in coagulation time for the product without forewarming treatments, and one min., 85 sec. for the product which

Table 15. The influence of forewarming treatment on heat stability of imitation evaporated milks

Product	Forewarming		Coagulation time at 270°F	
	Product Temperature	Time (min)	min.	sec.
Direct-formulation product	Without forewarming		5	30
	190	5	7[a]	10
	200	10	9	55
Fluid-base product	Without forewarming		4	0
	190	5	6	25
	200	10	8	1-

[a]The average of two trials.

preheated to 87.5°C (190°F) for five minutes.

Comparing the results in Table 15 with those in Table 11 and 12, one observes that by diluting the sample with 4% water the heat coagulation time was increased. The fluid-base product increased in coagulation time by 40 sec., whereas for the direct-formulation product it was 35 sec. When imitation evaporated milk is not forewarmed, or when a low temperature preheat treatment is used, it will coagulate more readily when sterilized.

Sommer (1923) explained that the albumin content of milk has an effect upon the coagulation. Since albumin is precipitated by forewarming, the heat stability of evaporated milk is increased by this process. Additionally, the forewarming process decreased heat coagulation by precipitating some of the soluble calcium as calcium phosphate.

Forewarming improves the heat stability and viscosity and can be a factor in color development and flavor of evaporated milk. In general, temperatures from 93.5°C (200°F) to the boiling point for 5 to 10 minutes are employed in the manufacture of evaporated milk. Time and temperature depend on the seasonal factor, the concentration of evaporated milk, and the method of forewarming.

The Effect of Selected Substances, pH and $CaCl_2$ Solution on the Development of Brown Discoloration

The prolonged heat treatment of evaporated milk, as in the sterilization process, caused an increased discoloration in the finished product. Stalberg and Radaeva (1966)

studied this problem and recommended using selected substances to minimize or prevent this discoloration.

Addition of 0.01 ml of 10% ascorbic acid solution to 10 ml of direct-formulation product gave a color similar to that of commercially-processed, filled evaporated milk (See Table 16). This is equal to 10 mg of ascorbic acid per 100 ml of evaporated milk.

For the fluid-base product the addition of 0.015 ml, 0.02 ml and 0.025 ml of 10% ascorbic acid gave a color closer to that of filled evaporated milk. Thus, fluid-base product requires a larger addition of ascorbic acid than direct-formulation product. This behavior may be ascribed to a slight increase in the lactose content of the fluid-base product. Addition of 15-25 mg % of ascorbic acid may help to reduce the brown color in the fluid-base products.

Evaporated milk exhibits a darker color than whole milk. Addition of more than 15 mg of ascorbic acid to 100 ml of direct-formulation product and 25 mg to 100 ml of fluid-base product produced a whiter product than the normal color of evaporated milk. On the other hand, the addition of less than 10 mg of ascorbic acid to 100 ml of the direct-formulation product and 15 mg of ascorbic acid to 100 ml of the fluid-base intensified the brown color.

Data in Table 17 show that the addition of sodium hexametaphosphate (10-20 mg/100 ml of evaporated milk) eliminated the browning in the direct-formulation product, whereas 0.015-0.02 ml of 10% sodium hexametaphosphate (15-20

Table 16. The effect of asorbic acid on the browning of imitation evaporated milks [a]

H_2O ml	0.03	0.025	0.02	0.015	0.01	0.005	0
10% Ascorbic acid ml	0	0.005[b]	0.01	0.015	0.02	0.025	0.03
Direct formulation product	++++[c]	++++	+++	+++	++	++	++
Fluid-base product	++++	++++	++++	+++	+++	+++	++

[a]Two trials.

[b]Different concentration of 10% ascorbic acid were added to 10 ml of milk.

[c]Color was compared visually with commercially-processed filled evaporated milk (+++).

Table 17. The effect of sodium hexametaphosphate on the browning of imitation evaporated milks[a]

H_2O ml	0.03	0.025	0.02	0.015	0.01	0.005	0
10% sodium hexametaphosphate ml	0	0.005[b]	0.01	0.015	0.02	0.025	0.03
Direct formulation product	++++[c]	++++	+++	+++	+++	++	++
Fluid-base product	+++++	+++++	++++	+++	+++	++	++

[a]Two trials

[b]Different concentrations of 10% sodium hexametaphate were added to 10 ml of milk

[c]Color was compared visually with commercially-processed filled evaporated milk (+++).

mg/100 ml of evaporated milk) prevented the brown color in the fluid-base product. Less than 10 mg/100 ml caused discoloration and more than 20 mg/100 ml for both types of milk yield a whiter color than commercially-processed, filled evaporated milk.

Stalberg and Radaeva (1966) found that the addition of 0.01 percent of vitamin A, 0.15 percent of glucose oxidase, 0.1 percent of ascorbic acid and 0.15 percent of sodium hexametaphosphate to the sweetened condensed milk inhibited the formation of brown color. They also found that the amino-sugar reaction proceeded at a slower rate when compared with control samples. Comparing the results in Table 16 and 17 with the results of Stalberg and Radaeva (1966), demonstrate that there is similarity for the amount of ascorbic acid (10-15 mg) which was added to 100 ml of direct-formulation product. For fluid-base product, the amount of ascorbic acid was 15 mg/100 ml of evaporated milk which was higher than the level recommended by Stalberg and Radaeva. However, for sodium hexametaphosphate, 10 mg/100 ml of direct-formulation product, was less than the amount used by Stalberg and Radeva. For the fluid-base product, both results were the same; 15 mg/100 ml of evaporated milk.

In general the following conclusions may be drawn. 10 mg of ascorbic acid or 10 mg of sodium hexametaphosphate per 100 ml of direct-formulation product is effective in preventing the borwn color. For the fluid-base product, 15 mg of ascorbic acid or 15 mg of sodium hexametaphosphate

per 100 ml of milk effectively inhibited discoloration.

Data in Table 18 show the effect of pH on the browning of imitation evaporated milk. All samples for both types of milk exhibited brown color. At higher pH levels (7.0 7.2), discoloration increased in both types of imitation evaporated milk. Within the pH range of 6.60-6.70, the color was slightly darker than commercially-processed, filled evaporated milk. Addition of 15 mg of sodium hexaphosphate per 100 ml of milk did not produce a change in the pH (i.e. 6.70) of imitation evaporated milk, whereas the addition of 10 mg of disodium phosphate per 100 ml of milk caused an increase in pH to 6.74. Presumably, this increase in pH was a contributing factor in color formation.

Data in Table 19 show the effect of added $CaCl_2$ solution on the browning of imitation evaporated milks. The addition of 0.25 M $CaCl_2$ to imitation evaporated milks did not promote discoloration. There was no difference in color with or without addition of $CaCl_2$. Thus, calcium is not a factor effecting browning in imitation evaporated milk.

Certainly, the time and temperature of sterilization are important factors which contribute significantly to the formation of brown color. Thus, evaporated milk should be cooled immediately after the sterilization process. Otherwise milk will be exposed to excessive heat which will increase the formation of brown color.

Table 18. Effect of pH on the browning of imitation evaporated milks [a]

pH	Direct-formulation product	Fluid-base product
	Color[c]	
6.40[b]	++++	++++
6.50	++++	++++
6.60	++++	++++
6.70	++++	++++
7.00	+++++	+++++
7.20	+++++	+++++

[a]The average of two trials.

[b]pH was adjusted by addition of M/10 HCl and M/10 NaOH to 5 ml of milk and sterilized at 245°C for 15 minutes.

[c]Color was compared visually with commercially-processed filled evaporated milk (+++).

Table 19. Effect of $CaCl_2$ on the browning of imitation evaporated milks [a]

H_{20}	0	0.095			
.25 M $CaCl_2$	0	.005[b]			
pH	6.70	6.70	6.70	6.71[c]/6.72[d]	6.72/6.72
Direct-formulation product color	++++	++++[e]	++++	++++	++++
Fluid-base product color	++++	++++	++++	++++	++++

[a]The average of two trials.

[b]Different concentration of 0.25 M $CaCl_2$ were added to 5 ml of milk and sterilized at 245°C/15 min.

[c]pH of direct formulation product.

[d]pH of fluid-base product.

[e]Color was compared visually with commercially-processed evaporated milk (+++).

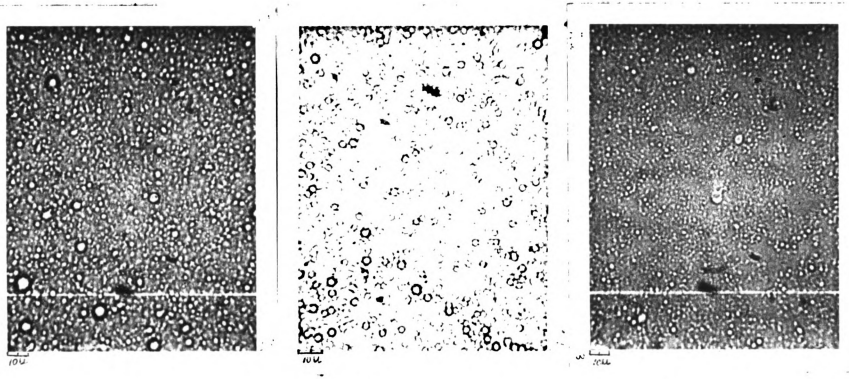
The Effect of Homogenization on the Emulsion of Imitation Evaporated Milk

An emulsion consists of two immiscible liquid phases. One is a dispersed phase and the other is a dispersing medium. The dispersed phase is known as the globular phase while the liquid surrounding the globules is known as the continuous phase (Clayton, 1935).

Milk is an emulsion of the oil/water type in which the oil phase consists of fat globules and the water phase is the milk plasma. The process of reducing the globules to a small and approximately equal diameter is called homogenization. By increasing the number of globules and decreasing their size, the stability of an emulsion will increase. As a result, globular separation will be prevented and a uniform emulsion system will be obtained.

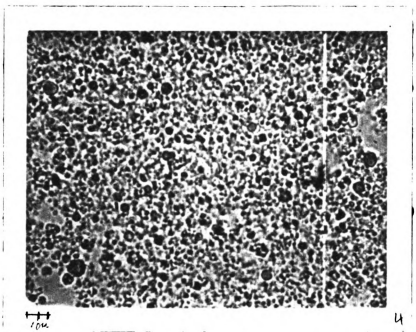
The size of fat globules in the fluid-base product was 3-4 μ, whereas in the direct-formulation product fat globules size were 2-3 μ (See Figure 4a and b). The size of fat globules of commercially-processed, evaporated milk was about 2 μ (See Figure 4c). One observes that the emulsion system of the direct-formulation product approximated that of commercially-processed, evaporated milk. Thus, there was no obvious tendency for the fat globules in imitation evaporated milk to form clusters or fat separation.

The effect of heat treatment on the emulsion system is shown in Figure 5 a, b. In both products, the emulsion system was disturbed (larger fat globules) and the caseinate phosphate micelles aggregated.

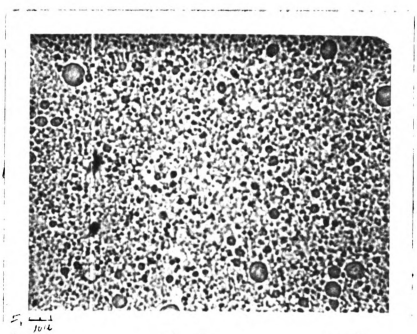


a b c

Figure 4. Photomicrographs of a) fluid-base product; b) direct formulation product, and c) commercially processed evaporated milk (100x magnification)



a



b

Figure 5. Photomicrographs of heat coagulated samples of a) direct formulation product (10 min. at 270°F) and b) fluid-base product (8 min. at 270°F) (100x. magnification)

Sensory Evaluation of Imitation Evaporated Milk

Sensory evaluation is an important part of the processing and development of new milk products. The method employed to evaluate the imitation milks developed in the study consisted of a performance survey in which there were ten participants. This number of participants was too low for extended statistical analysis but large enough to provide a "working" opinion about the products which were produced. Data in Table 20 show the results of this evaluation. By using the analysis of variance there was no significant difference between any of the comparisons at 95% level. The color in all samples was acceptable. For the fluid-base product, samples from 2-4 were similar to each other. The addition of sodium hexametaphosphate to 15 mg/100 milk (sample no. 4) increased the acceptance of the color, flavor, mouth feel, and odor over the commercially-processed, filled evaporated milk.

For direct-formulation product, samples from 5 to 7 were less acceptable in flavor and body. Compared to the commercially-processed, filled evaporated milk, the color, mouth feel, and odor were good.

In general the fluid-base method would be better for the manufacturing of imitation evaporated milk that the direct-formulation method. However, the direct-formulation method produced a product possessing better heat stability and a lighter color when sodium hexametaphosphate or ascorbic acid were not added. However, the defects encountered

Table 20. Sensory evaluation of imitation evaporated milks[a]

Sample	Color	Visual texture (body)	Flavor	Mouth feeling (smooth, coarse)	odor
1	4.4[b]	4.8	3.8	4.3	4.0
2	4.2	4.3	3.5	4.8	3.8
3	4.7	4.5	3.8	4.3	3.8
4	4.6	4.6	4.4	4.6	4.0
5	4.3	4.1	3.3	4.2	3.8
6	4.3	4.2	3.5	4.2	3.8
7	4.1	4.3	3.7	3.5	4.0

1. Commercially processed filled evaporated milk.
2. Fluid-base product without addition of sodium hexametaphosphate.
3. Fluid-base product with addition of 7.5 mg/100 sodium hexametaphosphate.
4. Fluid-base product with 15 mg/100 sodium hexametaphosphate.
5. Direct formulation product without addition of hexametaphosphate.
6. Direct formulation product with 7.5 mg/100 sodium hexametaphosphate.
7. Direct fromulation product with 1.5 mg/100 sodium hexametaphosphate.

[a]By using the analysis of variance there was no significant difference between any of the comparisons at 95% level.

[b]The mean values.

in the fluid-base product can be lessened by the addition of stabilizing salts to prevent coagulation and sodium hexametaphosphate or ascorbic acid to reduce the brown color.

Data in Table 21 show the properties of imitation evaporated milk produced by both methods compared to those of commercially-processed, evaporated milk and filled, commercially-processed evaporated milk.

As indicated, the total solids in fluid-base and direct formulation products were higher than that of commercially-processed, evaporated milks. The viscosity of the imitation evaporated milk was less than that of the commercially-processed, filled evaporated milk. This property may be due to the addition of carrageenan and disodium phosphate to the commercially-processed, filled evaporated milk. Only sodium hexametaphosphate was added to the imitation evaporated milks.

Ionic calcium as a major factor in the heat coagulation of evaporated milk was less in imitation evaporated milk than in the commercially-processed milks and this may increase the heat stability of imitation type of product.

Experimental Imitation Evaporated Milk - Commercial Trials

Imitation evaporated milk was manufactured under commercial conditions, using soybean oil, isoelectric casein, water, and demineralized whey solids as ingredients. By decreasing the amount of demineralization whey solids, there was an increase in ionic calcium and in viscosity (See Table 22).

Table 21. Properties of imitation evaporated and commercially processed evaporated milks

Property	Fluid-base imitation product	Direct formulation product	Commercially processed filled evaporated milk	Commercially processed evaporated milk
TS%	26.53	26.26	25.98	25.81
Total calcium mg/100 ml	55	35	83	85
ionic calcium mg/100 ml	8	6	11	16
Viscosity 3 ml/75° Sec	28	28.8	32	27.5

Table 22. Selected properties of experimental imitation evaporated milk -- Commercial Trials

Property	1st trial[a] 7/7	2nd trial[b] 8/18	3rd trial[b] stabilizer[c] 10/114	3rd trial[b] no stabilizer 10/14
TS%	25.51	26.10	29.17	29.56
Total Calcium (mg/100)	41	48	48	51
Ionic Calcium (mg/100)	5	13.50	11	19
Viscosity 3 ml/75°F sec	18	86.5	139	180

[a]Casein (2.7#) was converted in water with sodium hydroxide at 120°F. Soy oil (7.9#) was added and homogenized at 140°F (150/2,500). 15% demineralized whey solids were added and homogenized at 500 psi, cooled, sterilized. No stabilizer salts were used.

[b]The same as a except that 12.95% demineralized whey solids and 6# of casein were used.

[c]The same as b except that stabilizer was added.

The addition of stabilizing salts to sample from the third trial decreased the ionic calcium, so that the viscosity of that product was less than that of the same batch but without any additional stabilizer.

The amount of demineralized whey solids in the second and third trials were similar. However, the viscosities were different. This increase in apparent viscosity was attributed to the effects of the higher activity of calcium ions. One indication of this is that the addition of stabilizing salts decreased the amount of ionic calcium, and thus decreased the viscosity. Although the second trial sample had higher amounts of ionic calcium than that of the third trial sample with added stabilizer, its viscosity was less. This may be ascribed to the increase in total solids in the third trial.

All of the experimental samples exhibited some degree of browning, but compared to the trial with deionized (lower calcium) whey solids, there was a noticable improvement. Deionized whey (sodium zeolite) increased the browning color, viscosity and salty flavor.

Data in Table 23 show that the viscosity was decreased by increasing the amount of ionic calcium in sample No. 8 of the fifth trial series. Also its viscosity was very high. Possibly, the calcium-casein combination was not at its optimum level.

The increase in total solids from the fourth to the fifth trial was regarded as the cause for the increase

Table 23. Selected properties of experimental imitation evaporated milk Commercial Trials

	4th trial*				5th trial*				
	0	1	2	3	4	5	6	7	8
	mg/100 ml ionic calcium added								
Property	0	7.73	15.46	23.19	30.92	38.65	46.38	54.11	61.84
TS%	27.9	27.9	27.9	27.9	31	31	31	31	31
Total calcium (mg/100)	16	21.5	26	30	35	41	48	52	55
Ionic Calcium (mg/100)	3.5	6.5	10.5	16.5	18	22	26	31	36
Viscosity	83	57	54	51	78	73	69.5	61	92

*Casein (3.9#) was converted with H_2O, Calgon and NaoH. Oil (3.9#) was added, heated to 155°F, homogenized at (500/2500). Demineralized whey (6.75#) was added, heated to 155° and homogenized at 500, cooled, and ionic calcium was added in the form of $CaCl_2$ solution in different concentrations.

in viscosity. Calgon (hexametaphosphate) was added to the fourth and fifth trials, but without effecting the tendency to discolor. In evaporated milk, heat treatment is the most important factor effecting the browning reaction and the rate of formation brown pigmentation.

Total solids content should be the same as the legal standard (25.9%) because increasing the total solids increases the viscosity and the potential for development of color.

Forewarming is an important step in the manufacture of evaporated milk, and one observes that in this study none of the milk samples were forewarmed. In addition to that, the use of 12.95% demineralized whey solids increases lactose content, and thus increases the potential for the browning reaction to occur. Therefore, using 10% or less of mineralized whey or sweet whey and 0.15% Calgon or ascorbic acid may help in reducing the formation of color.

Dissolving casein with KOH and NaOH (4:1) will help in reducing the salty flavor. The addition of whey and calcium or appropriate stabilizer salts before homogenization might also give a better emulsion system and improved viscosity.

CONCLUSION

The stability of imitation evaporated milk manufactured by the direct-formulation method and the fluid-base evaporation method were found to be affected by the addition of calcium, phosphate and citrate ions.

Forewarming increased the heat coagulation time for products produced by both methods. The heat coagulation time of the direct-formulation product was greater than that of the fluid-base product. The evaporative concentration process employed to produce the fluid-base product enhanced the flavor, body and mouth feel of the sterilized product.

BIBLIOGRAPHY

BIBLIOGRAPHY

Alyar, K.R. (1969) Artifical milk as basis for research. New Zealand J. Dairy Tech. 4(1): 11-13.

Ayer, S.H. and Johnson, W.T. (1915) The alcohol test in relation to milk. U.S. Dep. of Ag. Bull. 202: 1-34.

Bell, R.W., Curran, H.R. and Evans, F.R. (1944) Effects of temperature and time of sterilization upon properties of evaporated milk. J. Dairy Sci. 27: 913-919.

Bell, R.W. and Webb, B.H. (1943) Relationship between high temperature forewarming and the color and heat stability of evaporated milk of different solids content. J. Dairy Sci. 26: 579-585.

Benton, A.G. and Albery H.G. (1926) Studies on the stability of evaporated milk during sterilization with reference to the hydrogen in concentration, alcohol test, and addition of scientific buffers. J. Biol. Chem. 68: 251-263.

Clayton, W. Theory of Emulsion and Their Technical Treatment. Published by Blakiston's Son & Co., Inc. Philadelphia, 3rd Ed. p. 2.

Dahlberg, A.O. and Garner, H.S. (1921) The alcohol test as a means of determining the quality of milk for condenseries. U.S. Dep. of Ag. Bull. 1944: 1-13.

DeMan, J.M. and Batra, S.C. (1964) Effect of certain salts on the stability of skim milk as determined by rennet coagulation time and alcohol test. J. Dairy Sci. 47: 954-957.

Dellamonica, E.S., Cusler, J.H., and Zittle, C.A. (1958) Effect of calcium chloride and heat on solutions of mixtures of B-lactoglobulin and casein. J. Dairy Sci. 41: 465-471.

Deysher, E.F., Webb, B.H., and Holm, G.E. (1929) The relations of temperature and time of forewarming of milk to the heat stability of its evaporated product. J. Dairy Sci. 12: 80-89.

DeJongh, M. (1978) Effect of solids not fat, fat, and homogenization pressure on the heat stability of recommended evaporated milk. New Zealand J. Dairy Sci. Tech. (13) p. 242.

deWit, J.N. (1981) Structure and functional behavior of whey. Neth. Milk Dairy J. 35: 47-64.

Evenhuis, N. and DeVries, Th.R. (1957a) The condition of calcium phosphate in milk. Neth. Milk Dairy J . 11(2): 111-121.

Evenhuis, N. and DeVries, Th. R. (1957b) The condition of calcium phosphate in milk. Neth. Milk Dairy J. 11: 213-224.

Evenhuis, N. (1957) The heat stability of milk. Neth. Milk Dairy J. 11: 225-243.

Griffin, A.T., Hickey, M.W. and Chandler, G. (1976) The significance of preheat and pH adjustment in the manufacture of recombined evaporated milk. Aust. J. Dairy Technol. 31(4): 134-137.

Holm, G.E., Webb, B.H. and Deysher, E.F. (1932) The heat coagulation of milk. J. Dairy Sci. 15: 331-343.

Horne, D.S. and Parker, T.G. (1981) Factors affecting the ethanol stability of bovine milk. J. Dairy Res. 48: 273-284.

Hunziker, O.F. (1949a) Condensed Milk and Milk Powder. Published by the author, La Grange, Illinois. 7th Ed. p. 276.

Hunziker, O.F. (1949b) Condensed Milk and Milk Powder. Published by the author, La Grange, Illinois. 7th Ed. p. 225.

Hunziker, O.F. (1949c) Condensed Milk and Milk Powder. Published by the author, LaGrange, Illinois. 7th Ed. p. 291.

Jenness, R. and Patton, S. (1959a) Principles of Dairy Chemistry. Robert E. Krieger Publishing Company, Huntington, N.Y. 2nd Ed. p. 347.

Jenness, R. and Patton, S. (1959b) Principles of Dairy Chemistry. Robert E. Krieger Publishing Company, Huntington, N.Y. 2nd Ed. p. 349.

Jenness, R. and Patton, S. (1959c) Principles of Dairy Chemistry. Robert E. Krieger Publishing, Huntington, N.Y. 2nd Ed. p. 330.

Jenness, R. (1953) Titration of calcium and magnesium in milk and milk fractions with ethylenediamine tetraacetate. Anal. Chem. 25: 966-969.

Kieseker, F.G. (1982) Recombined evaporated milk. Internat. Dairy Fed. Bull Document 142: 79-88.

Lampert, L.M. (1975) Modern Dairy Products. Chemistry Publishing Company, Inc., N.Y. 3rd Ed. p. 416.

Maxcy, R.B. and Sommer, H.H. (1954) Fat separation in evaporated milk. J. Dairy Sci. 37: 1061-1070.

Millory, T.H. (1915) The reaction and calcium content of milk as factor in the coagulation process. Biochem. J. 9: 215-228.

Newstead, D.F. and Baucke, A.G. (1983) Heat stability of recombined evaporated milk and reconstituted concentrated skim milk: effect of temperature and time of preheating. New Zealand J. Dairy Sci. Tech. 18: 1-11.

Newstead, D.F., Conaghan, E.F., and Sanderson, W.B. (1976) Effect of whey protein concentration on the heat stability of evaporated milk. New Zealand J. Dairy Sci. Tech. 11: 223-230.

Newstead, D.F., and Conaghan, E.F. (1979) Studies on the induction of heat stability in evaporated milk by preheating. J. Dairy Res. 46: 387-391.

Pearce, R.J. (1979) Heat stability in concentrated and non concentrated milks, the effect of area and B-lactoglobulin levels and the influence of preheating. J. Dairy Res. 46: 385-386.

Rogers, L.A., Deysher, E.F. and Evans, F.R. (1921) The relation of acidity to the coagulation temperature of evaporated milk. J. Dairy Sci. 4: 294-309.

Rose, D. (1961a) Variations in the heat and composition of milk from individual cows during lactation. J. Dairy Sci. 44: 430-441.

Rose, D. (1961b) Factors affecting the pH sensitivity of the heat stability of milk from individual cows. J. Dairy Sci. 44: 1405-1413.

Rose, D. (1962) Factors affecting the heat stability of milk. J. Dairy Sci. 45: 1305-1311.

Seckles, L. and Smeet, W. (1948) Instability of milk due to an increase of calcium ions. Dairy Sci. Abstr. 9(3): 243.

Sommer, H.H. and Hart, E.B. (1919) The heat coagulation of milk. J. Biol. Chem. 40: 137-151.

Sommer, H.H. and Hart, E.B. (1922) The heat coagulation of milk. J. Dairy Sci. 5: 525-543.

Sommer, H.H. and Binney, T.H. (1923) A study of the factors that influence the coagulation of milk in the alcohol test. J. Dairy Sci. 6: 176-197.

Sommer, H.H. (1923) The heat coagulation of milk. World's Dairy Congr. 2: 1241-1248.

Sommer, H.H. and Hart E.B. (1926) Heat coagulation of milk. Univ. Wis. Agr. Exp. Station Res. Bull. 67: 1-47.

Stalberg, S. and Radaeva, I. (1966) Effect of varoius substances inhibiting melanoidino - formation in sweetened condensed milk. Internat. Dairy Congr. 17: 153-157.

Sweetsur, A.W. and Muir, D.D. (1980) The use of permitted additives and heat treatment to optimize the heat stability of skim milk and concentrated skim milk. J. Soc. Dairy Tech. 33(3): 101-105.

Sweetsur, A.W. and Muir, D.D. (1982) Manipulation of the heat stability of homogenized concentrated milk. J. Soc. Dairy Tech. 35(4): 126-132.

Webb, B.H. and Holm, G.R. (1930) Color of evaporated milk. J. Dairy Sci. 13: 25-39.

Webb, B.H. (1935) Fundamentals of Dairy Science. Reinhold Publishing Corporation, N.Y. 2nd Ed. p. 208.

Webb, B.H. and Bell, R.W. (1942) The effect of high temperature short time forewarming of milk upon the heat stability of its evaporated product. J. Dairy Sci. 25: 301-311.

White, J.C. and Davis, D.T. (1958) The relation between the chemical composition of milk and the stability of caseinate complex. J. Dairy Res. 25: 256-266.

Zittle, C.A., Dellamonica, E.S., Ruddand, R.K. and Cluster, J.H. (1957) The binding of calcium ions by B-lactoglobulin both before and after aggregation by heating in the presence of calcium ions. J. Amer. Chem. Soc. 79: 4661-4665.

Zittle, C.A. and Pepper, L. (1958) Influence of hydrogen andand calcium ion concentrations, temperature and other factors on the rate of aggregation of casein. J. Dairy Sci. 41: 1671-1682.

Zittle, C. (1969) Influence of heat on K-casein: Effect of α_s casein and concentration of calcium chloride and sodium chloride. J. Dairy Sci. 52: 1356-1358.