PROMOTION OF BROWNING IN THE DEVELOPMENT OF NEW DAIRY PRODUCTS

A Thesis
Presented to
the Faculty of the Department of Food Science and Biotechnology
Massey University

In Partial Fulfilment
of the Requirements for the Degree
Master of Food Technology in Food Processing

by
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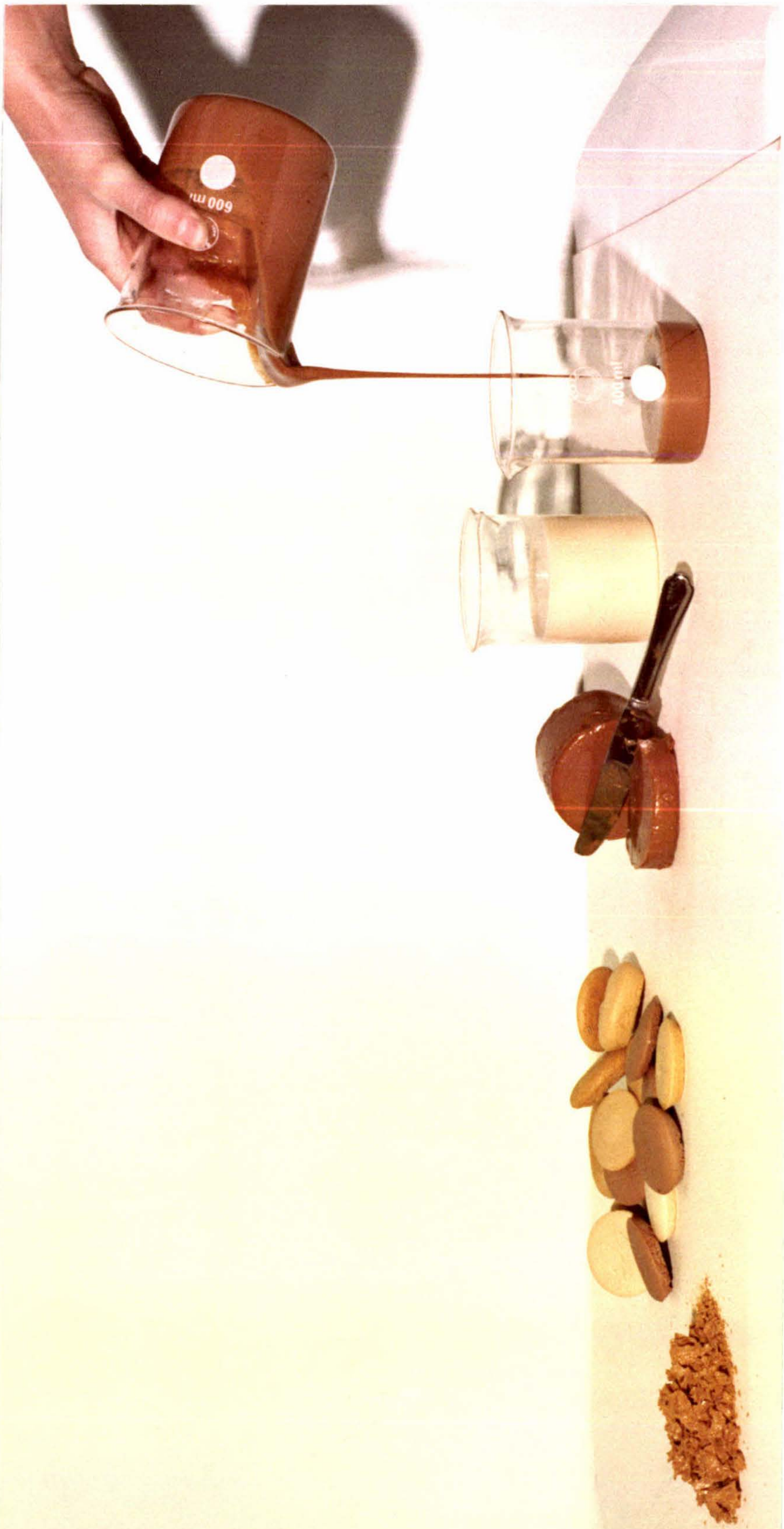
July 1967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"It is not enough to know; we must turn what we know to account. It is not enough to will; we must do."

- Goethe

ACKNOWLEDGEMENTS

The author wishes to thank the supervising committee of Mr. H. A. L. Morris (Convenor), Dr. E. L. Richards, and Dr. R. M. Dolby. Sincere appreciation and gratitude go to Mr. H. A. L. Morris for his encouragement, and particularly for his keen interest in this study. His practical experience, willingness to take part in lengthy discussions, and help in the planning and presentation of this thesis has proved to be invaluable.

Thanks are due to the Dairy Production and Marketing Board and the Sanitarium Health Food Company for financial assistance.

Special thanks to Miss D. Scott for the excellent photography and printing of the graphs and photographs, and also to Miss C. Mitchell for her hand in the photographs, studio work, and fixing of the graphs and photographs.

For much fruitful help and discussion, the author is indebted to the willingness of Mr. J. G. Clarke, Dr. W. B. Sanderson, and Mr. D. Box, of the New Zealand Dairy Research Institute.

To the untiring help and patience of his sister, Miss M. Ward, in the preparation and typing of this thesis the author is gratefully indebted for the final presentation. The author also wishes to thank his family and close friends for their encouragement, and for their help in so many ways to make this work an enjoyable experience.

The assistance and interest of numerous other people who have contributed in many ways is also much appreciated and has made the work on this thesis that much more interesting.

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INTRODUCTION

One readily demonstratable effect resulting from the prolonged heat treatment of milk is browning. A form of non-enzymic browning due to interaction of aldoses with free amino-groups occurs in many foods, and hence this reaction is of broad significance in the food field; e.g., dry milk products (29), processed potatoes (95), dried fruit (102), dried whole eggs (73), dried meat (99), and liquid and concentrated milk products (33,83). The significance of browning in food technology has two aspects - the desirable and the undesirable.

In many areas of the world today people are undernourished, malnourished, and even starved. At the same time in other parts of the world, food is abundant to the point of substantial excess. Although many factors contribute to this unbalance, food spoilage is an important consideration. Some excess food can be processed and stored in a practical manner involving little or no deterioration, but some of it faces spoilage despite man's preventive efforts. One vexing problem of food spoilage is browning which may affect many food products. These include dried food such as milk, eggs, fruits, fruit juices, meat, fish and vegetables (12); canned milk, fruit, and vegetables; and other foods such as molasses. Loss of palatability and nutritive value as well as undesirable changes in physical properties frequently attend the browning of food to varying degrees of intensity, depending on the stage to which the reaction has progressed. This is the undesirable aspect of browning.

On the other hand, the Maillard reaction can make a positive contribution to food technology by producing desirable colours, flavours and aromas in many foods such as ready-to-serve cereals, toffees, roasted coffee, malted barley, and baked goods (65). Toasting, baking, roasting, and frying are processes aimed at intentionally browning the food. Although there is some loss of amino acids when these flavours are produced, the loss is not usually of much importance and is accepted as a price worth paying. The Maillard reaction can be exploited for particular purposes by the addition of reducing agents to the food. For example, the inclusion of milk powder in a loaf of bread permits more even toasting at a lower temperature because of the presence of lactose. Another example is the production of chicken and meat-like flavours by heating amino acids with pentose sugars and aldehydes. The distinctive caramel and butterscotch flavours derived from dairy products result from the browning of milk or milk components. Thus, it is clear that browning has two aspects, both of which concern the acceptability of man's food.

It is the latter aspect which is of principal interest in the present work. By promoting browning in milk solids to varying degrees of intensity, a range of palatable caramel flavours may be obtained. It is clear that dairy-caramel flavours are appetizing by the fact that caramelized milk products are very popular, and are eaten extensively in South America, India, and Europe. Traditional products produced domestically include 'Dulce de leche' (Argentina, Uruguay), 'Manyar blanco' (Chile), and 'Khoa' (India). In Argentina, 2,800 tons of 'Dulce de leche' are commercially produced per annum; 98% of this production is consumed internally. Clearly then, many people enjoy dairy-caramel flavours when purposely produced. With the realization that a potential market is already present, the purpose of this thesis is to explore the possibility of diversifying New Zealand dairy products by the promoted caramelization of milk solids.

A review of previous research into the browning reaction in milk showed that much work has been done and copious literature exists, but most of this neglects the beneficial effects of non-enzymic browning in milk and concentrates on the deteriorative effects. Consequently, methods of measuring browning mainly involve measurements of the reactants and early intermediates as a basis for inhibiting the early stages of browning. As a result of this bias in previous research, the first task of this study was to develop a method of measuring promoted browning ("caramelization") in milk. The method finally chosen was the reflectance measurement of colour.

A reliable method of measuring promoted browning made possible a study of the factors affecting promoted browning, and caramel flavour development, in sweetened condensed milk. The study was restricted to browning in "liquid" systems as the factors affecting browning in "dry" milk powder have been well documented (65,83). In this context, there were two principal areas of interest with regard to browning and associated changes in milk systems. One is practical and concerns the manipulation of process and product variables such as temperature, time, pH, and moisture content, to obtain a controlled amount of browning. The other is fundamental and concerns making the knowledge of milk and its behaviour as complete as possible.

Without incorporation into palatable food structures and textures any flavour is of little value as food. Hence, the remainder of this thesis is an exploration of the possibilities of incorporating dairy caramel flavours into conventional food textures, structures, and types which are of proven palatability. A survey of present food forms marketed, and a consideration of recent trends in food marketing suggests that the following product types are of proven consumer acceptance and worthy of further study and development.

1. Sweet caramelized spread for use in the same way as jams; i.e., spread, pie filling, cakes, etc.
2. Porous wafer or biscuit type of product - perhaps for use as a high protein supplement in a form which the consumer is familiar with.

3. Concentrated dairy caramel flavour in powder or liquid concentrate form for general food flavouring.
4. Confections - sweets, toffees, milk caramel, hokey-pokey, etc. (The production of caramel confections is well documented and was not studied further.)

With an aim of developing these general product types a fundamental study was undertaken to define the factors affecting flavour, colour, and texture of browned milk solids.

PART A

(SECTIONS I, II, III)

BASIC STUDIES

ON

THE BROWNING OF MILK SOLIDS

SECTION I

A REVIEW

OF

PREVIOUS RESEARCH

INTO

THE BROWNING OF DAIRY PRODUCTS

I. INTRODUCTION

In the scope of the present work, there are two principal areas of interest with regard to browning and associated changes in milk. One is practical, and concerns the manipulation of process and product variables such as temperature, time, moisture content, to obtain a controlled amount of browning and caramel flavour. The other is fundamental, and concerns making the knowledge of milk and its behaviour as complete as possible. This review summarizes previous knowledge in the field of the browning of dairy products and forms the basis for the direction of further research into the promoted caramelization of sweetened condensed milk and similar dairy products.

Fundamentally, there appear to be three main types of browning in food systems (55):-

1. Caramelization or non-amino browning of sugars.
2. Amino-sugar or Maillard-type browning.
3. Oxidative browning.

Caramelization browning may be defined as the 'heat decomposition' of sugars as a function of pH and buffers in the absence of amino compounds. Caramelization requires a relatively high order of activational energy. On the other hand, Maillard-type browning requires a relatively low order of energy for its initiation and exhibits autocatalytic qualities once it has started. It may be defined as that browning which results from the interaction of amino compounds (proteins, amino acids etc.) with reducing sugars. This is by far the most important type of browning in the food field and is the type which prevails in milk and its products. Oxidative browning, with which we are not directly concerned here, is typified by the colour change that occurs when the surface of fruits or vegetables is bruised.

II. REACTANTS AND MECHANISM

A. Reactants

Much of the difficulty and confusion resulting from studies of browning in heated milk is due to the dynamic state of the delicately balanced biochemical system; i.e., the completion of one step is not essential to the initiation of the next, and many chemical reactions are proceeding at once. Also, while amino groups may disappear in the primary stage, they may reappear or regenerate in the manner of a true catalyst.

In his thorough review of browning in milk products, Patton (83) concludes that the literature clearly indicates that the two principal reactants in the browning of milk systems are lactose and casein. Neither casein nor lactose brown readily when heated alone but they do so when heated together (83,46).

Considerable evidence supports Maillard-type browning in milk. The independence of browning on oxygen level (83,49), and the acknowledged importance of casein in the discolouration, discount the possibility of oxidative browning or pure sugar caramelization browning. Evidence from three distinctly different areas of study point to the *E-amino groups of lysine (in casein) as key reactants:-

1. Autoclaved systems containing casein and a reducing sugar consistently show the greatest amino losses in lysine (36,68).

2. Lea and Hannan (67) have demonstrated that in the "dry" state glucose reacts with the free amino groups of casein in a 1:1 ratio, that these amino groups are made up almost entirely of E-amino groups of lysine, and that the complex so formed browns readily under suitable conditions of temperature and humidity. Other basic amino acids are involved secondarily in the reaction (68,69).

3. Patton (81,82,85) has noted that the decomposition of lactose in

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* E = ϵ ,epsilon

heated milk and in casein solutions appears to be base catalysed. The free amino groups of casein are the logical catalysts in this instance.

Phosphates and the milk buffer system are of secondary, if any, importance in the browning of milk products (83,86) compared with the primary reactants - lactose and casein.

B. Mechanism

The chemistry of browning in foods is highly complex. In an effort to unravel the problem, model systems have been used by many investigators. In place of the complex media presented by foods, simple, aqueous solutions of a sugar, usually glucose, and various amino compounds, particularly amino acids, have been employed to study the reaction types responsible for browning. These scattered disclosures of reaction types are capable of an orderly arrangement and a perspective view of the entire group of chemical reactions known as browning may be drawn (50). The findings from these simplified systems are very comprehensive in contrast to the limited findings of milk. Those interested in the basic chemistry of browning should consult the reviews of Hodge (50), Danehy and Pigman (31), Reynolds (90,91), and Burton and McWeeney (22). Browning of milk and its products has been reviewed by Patton (83). Indications are that browning in milk closely parallels the pattern which occurs in model systems, although the complete mechanism is as yet far from elucidated.

Between the established fact that casein and lactose are the primary reactants and that a brown product is a resultant of the reaction, there lies an area of chemistry that is largely unknown. The initial reaction, at least in the dry state, between glucose and casein involves a 1:1 reaction of the glucose with the E-amino group of lysine (67). Such a 1:1 reaction between these components has not been demonstrated in an aqueous system; presumably due

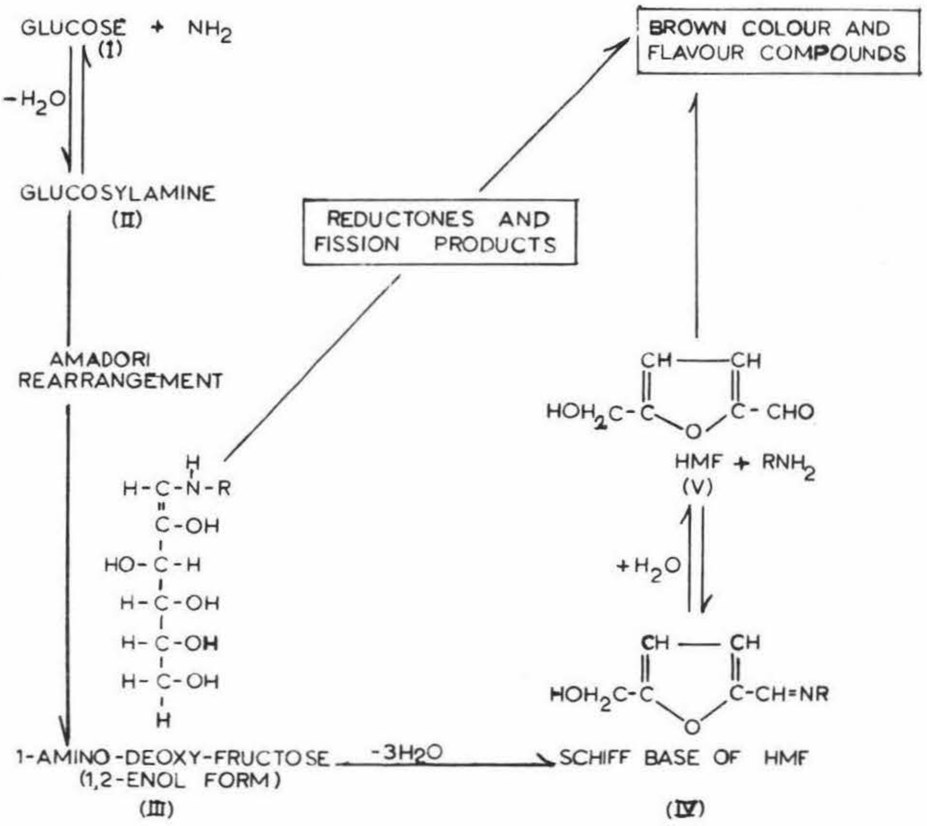


FIG. 1. Scheme of Maillard-type browning reactions involving glucose and amino compound (40, 41, 50, 51, 83, 92). Lactose and galactose will follow the same scheme (1, 84) with hydrolysis of the lactulose disaccharide linkage as an additional step between III and IV.

to the instability of the addition product under such conditions (55). In addition to the amino groups of lysine, the other basic amino acids, arginine and histidine may be involved secondarily (83,69).

The precise nature of the interaction between the lactose and amino groups of lysine has not been established. Richards (93) has shown that for lactose-casein and skim-milk in the "dry" state during storage, there is initially a close relationship between the formation of 1-amino-1-deoxy-2-ketoses and a decrease in free amino-nitrogen. This conforms with an Amadori rearrangement of an initially formed lactose-protein complex. Change in colour is rapid only after there has been a rapid formation of 1-amino-1-deoxy-2-ketoses and a corresponding decrease in free amino-nitrogen. This conforms with browning being due to the breakdown of the Amadori rearrangement complex.

The reaction scheme in Figure 1 has been established as representative of the early reactions between reducing sugars and amino compounds. This integrated scheme was proposed by Gottschalk and Partridge (41), and substantiated by Hodge and Rist (51), and Richards (92,93). The scheme is believed to be applicable in explaining the early reactions in natural sugar amine systems (50,92). Adachi (1) has identified fractions representative of II and III in evaporated milk and non-fat dry milk. Potter and Patton (87A) have identified 5-hydroxymethylfurfural (HMF) (V) in evaporated milk. Whether the principal route of pigment formation is by reductone and fission products or by HMF formation, is not clear. A recent review by Reynolds (90,91) quotes the work of Anet (8,9,10) in support of reductone and fission products being the main route, while Hodge (50) emphasizes the HMF route. However, all these studies have been on model systems and the complex reaction in milk beyond the formation of compound III has not been elucidated.

It is pertinent to note that browning in milk is a catalytic process (83) and that amino compounds catalyse the Amadori rearrangement, and possibly the subsequent degradation, fragmentation, and condensation. Therefore, one might strongly suspect that browning in heated milk involves catalytic decomposition of lactose by the E-amino groups of lysine (in casein). This may help to explain the inconsistent relationship between lactose disappearance, or destruction, and the loss of amino groups that has been observed in heated milk (83).

Much work has been done on concentrated and dry products because of their susceptibility to browning (Lea et al, 44,45,49,63,65,67,69,72). The basic mechanism demonstrated in dry systems has been demonstrated in liquid systems except that there is a more dynamic and progressive formation of melanoidins in liquid systems.

Patton (83) introduces the concept of surface catalysis and adsorption by the milk proteins. This is supported by the fact that about one third of the lactose-casein complex is stable to further heating after 20mins/122°C (83). Lea and Hannan (67) have provided further experimental evidence in support of catalysis in a model system of casein and glucose. Under favourable conditions, and in the presence of excess sugar, glucose continues to disappear from the system after the reaction with amino groups has virtually ceased. This extra glucose, comparable in amount to that combined with amino groups, is found to be 'bound' to the protein, but the nature of the union with the protein has yet to be established with certainty (67). Alternative possibilities are:-

1. A chemical reaction between glucose and reactive groups in the protein other than free amino groups.
2. Caramelization of glucose, catalysed in some way by the protein and followed by adsorption of the caramelized product on to the casein.

Similar reactions may be responsible for the strong binding of the degraded lactose by the protein.

In essence, the phenomenon appears to be a catalysis, by the amino groups of casein, of the decomposition of lactose. Decomposition of the lactose involves dehydration, fragmentation and condensation reactions, leading to the formation of brown pigment, and many associated changes.

C. Brown Pigment

The most important manifestation of the complex and poorly understood chemistry of browning is the pigment. Binding of the pigment by milk proteins and its absence from solution in milk serum is characteristic (83). Kass and Palmer (59) have viewed the association of the pigment with protein as a result of an adsorption process. However, the pigment cannot be removed from the protein without destroying it. This suggests that, at least in part, the binding is chemical rather than purely physical (83). This difficulty excludes any analysis of C:N ratio or other properties of the pigmented polymer.

III. PHENOMENA ASSOCIATED WITH BROWNING

The progressive decomposition of a reducing sugar in the presence of a protein is accompanied by many changes, only one of which is browning. Most of the changes are considered deleterious, and may include any of the following (65):-

1. development of a brown discolouration ranging from a pale cream or biscuit shade to nearly black;
2. production of stale "caramelized" or bitter odours or flavours;
3. loss of solubility of protein leading to a deterioration in texture and a failure of dried foods to reconstitute properly with water;
4. a reduction of pH and the production of carbon dioxide and water;
5. enhanced reducing properties;

6. an increased tendency to froth and foam;
7. the development of the property of fluorescing in ultra-violet light; and finally,
8. a loss of nutritive value of the protein resulting from a reduced availability of certain of the essential amino acids and a destruction of ascorbic acid and some of the B-vitamins when present.

In some heat processed foods and in most of the stored products (e.g., milk powder) in which changes of this type occur, the effects on flavour and colour, and sometimes on texture, solubility or nutritive value, are undesirable and much effort is made to avoid them. On the other hand, non-enzymic browning reactions produce desirable colours, aromas and flavours in many cooked and processed foods where they contribute variety and appetising quality to the diet. It has been known for a long time that amino-aldehyde reactions contribute to the desirable aromas and flavours of many baked, roasted, fried or toasted foods, but a knowledge of the mechanisms and compounds involved still remains rather scanty. One of the most obvious results of incorporating skim milk powder in bread is the production of a loaf with better toasting quality. Similarly, intentional "caramelization" of sweetened condensed milk yields a palatable product. The technological importance of some of the associated reactions of browning to the development of a desirable caramel flavour in dairy products is now discussed.

A. Compound Formation

A substantial number of compounds, which are largely lactose fragments, have been revealed to result from the prolonged high temperature treatment of milk (55). Many of these compounds such as butyric, propionic, acetic, formic, lactic, and pyruvic acid as well as acetaldehyde and acetol, are highly flavoured compounds which undoubtedly contribute, in part, to the caramel flavour of heated milk.

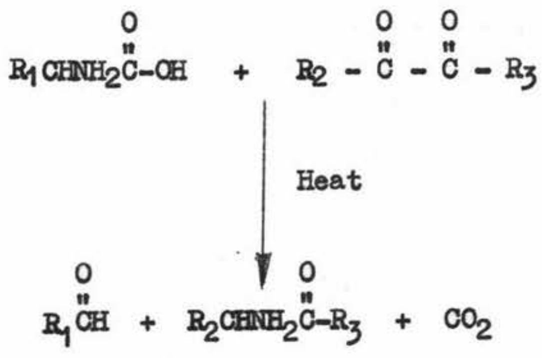
B. Reducing Substances

Heated and dried milks contain a complex reducing system involving sulphydryl compounds, ascorbic acid, and substances associated with the browning reaction (83). Although the reductone-like reducing substances are formed during browning, their structures are not known. Their presence as a result of browning is the basis for the acid ferricyanide method of measuring the rate of browning (25,26).

The presence of these reducing substances would probably eliminate or minimize the incidence of oxidised flavours in "caramelized" milk products.

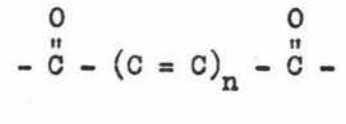
C. Strecker Degradation

The best known mechanism by which highly odorous compounds can arise from amino-sugar interaction is the so-called "Strecker degradation". This reaction is of demonstrated significance in simplified browning systems, but there is little direct evidence of it occurring in milk (50,97). In essence, it accomplishes the conversion of an amino acid, by deamination and decarboxylation, to an aldehyde of less than one carbon when the amino acid is heated with certain types of dicarbonyls; it may be represented as follows:-



$$R_1CHNH_2\overset{O}{\overset{\|}{C}}\text{-}OH + R_2 - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - R_3 \xrightarrow{\text{Heat}} R_1\overset{O}{\overset{\|}{C}}H + R_2CHNH_2\overset{O}{\overset{\|}{C}}\text{-}R_3 + CO_2$$

As shown, the reaction requires a dicarbonyl compound conforming to the following type of structure in which n may be zero or an integer (98):-



$$-\overset{O}{\overset{\|}{C}}-(C=C)_n-\overset{O}{\overset{\|}{C}}-$$

Sugar fragments such as methylglyoxal and pyruvic acid, which have been identified in milk, fulfil these structural requirements.

The sensitivity of the palate in detecting some of the volatile flavour substances (e.g., aldehydes), produced in this reaction, is extremely great (70). Hence, from a practical standpoint, this reaction may be important in converting non-odorous amino acids into flavourful aldehydes which have extremely low taste thresholds. In addition to producing volatile aroma constituents, which may contribute, in part, to the desirable flavour of caramelized sweetened condensed milk, the browning reaction can probably also contribute bitter tasting non-volatile products of high molecular weight (70).

D. Loss of Nutritive Value

While the interested reader should consult the exhaustive review of Kon and Henry (61), Patton's (83) brief summary makes clear that lowered nutritional and biological value is a distinct possibility in food products which have undergone a noticeable degree of browning. This is of real importance in the present work where browning is promoted because it yields a desirable caramel flavour. However, with the lowering price of amino acids and increased nutritional knowledge this problem may be overcome by supplementation and complementation with other foods. Food acceptance is of primary importance, and nutritive value can be adjusted as a matter of secondary importance.

E. Loss of Protein Solubility

During the earlier stages of the interaction between casein and lactose, the rapid combination of lactose with the protein free amino-groups, which consist mainly of the E-amino groups of the lysine residues, predominates over other reactions; the ratio of amino-groups destroyed to lactose bound is practically 1:1 (67,93,49,69). The protein-lactose complex at this stage of the reaction is still colourless and soluble, and the formation of the complex corresponds to an increase in acid ferricyanide reducing power (65,49,63). Subsequently, progressively more carbohydrate becomes attached to the protein than can be accounted for by combination with free amino groups, and other reactive side chains, including those of arginine and histidine and probably also of tyrosine and methionine, become involved (67,68,69). The protein complex at this stage has become brown in colour and insoluble over a wide pH range (69).

The situation, after the initial phase of the reaction, is obviously complex, with the possibility of protein groups reacting (69):-

1. directly with glucose;
2. by cross-linking with carbohydrate already attached to the amino groups of the protein; or
3. with reactive decomposition products of glucose.

A catalysed "caramelization" of the sugar, followed by adsorption on the protein is also possible. Henry et al (49) proposed the theory that the accompanying insolubility is a result of an induced denaturation of the protein molecule, or degradation of the protein-sugar complex by secondary reactions between the now adjacent protein molecules and carbohydrate chains.

The effect of sugars on the development of insolubility of the protein is complex and has not been fully elucidated (63). Lea (63) suggests that at least two mechanisms are involved. The potential aldehyde group of reducing sugars combining with free amino-groups tends to destabilize the protein and produce insolubility. It is not clear whether this is achieved by acceleration of the normal process of denaturation, (itself far from completely understood), or is the result of a bridging or other chemical action involving the sugar molecule and reactive groups in the protein. Glucose shows this type of reaction predominantly and its effect is definitely harmful (63).

In addition to this action, disaccharides when present in relatively high concentration, show a retarding effect on the development of insolubility. Lactose appears to be even more effective than sucrose in combating glucose-induced insolubility, probably as a result of successful competition with glucose for the amino-groups of the protein, but in the absence of added glucose, lactose is less beneficial than the inert sucrose, presumably because of the harmful effect of its own aldehyde group (63). In general, sucrose has a protective effect on the protein and tends to prevent insolubility when present in high concentrations (63).

IV. CARAMELIZED FLAVOUR

Flavour is one of the most important practical considerations with any food commodity. The changes of flavour in milk products upon heating are largely responsible for the acceptance or rejection of the product by the consumer. A concomitant of the browning of milk is caramelized flavour. Often it is objectional and coincident to faulty processing or product deterioration, but in the present study development of this distinctive flavour is promoted purposely. At present there is no clear or simple explanation of its origin, but rather it appears to be the result of several possible reactions.

As heat treatment of milk intensifies beyond 75°C, volatile sulphide evolution declines and cooked flavour slowly gives way to caramelized flavour (83,55). There appears to be no cause and effect relationship between these two flavours at this time and the chemical nature or origin of caramelized flavour is unknown (55). In general it is indicated that the degree of caramelized flavour is correlated positively with the degree of browning and related changes (83). Hence, a measurement of colour in a given system is also an indirect measure of flavour development. Patton (83,55) proposed a tentative definition of caramelized flavour, by listing four components:-

1. caramel or malty, resulting from sugar decomposition and Strecker degradation of amino acids;
2. stewed meat, arising from methionine decomposition and the presence of H_2S;
3. hydrolytic rancidity caused by fat hydrolysis; and
4. coconut-like, resulting from the formation of a lactone in the milk fat.

The importance of fat in imparting flavour is uncertain as skim milk powder will yeild caramel flavour of a type. It is known that casein is directly involved, and is essential to this flavour development, and Patton (84) has discussed the possibility of δ-decalactone and ketones being an integral part of the caramel flavour in whole milk. There is no question that chemistry is bound to play an important role in the science of flavour and odour, as volatile organic compounds provide a basis for stimulation of the flavour and odour receptors. However, it is not known just what compounds are responsible for the integrated flavour response known as milk caramel flavour, nor have the compounds been identified which are responsible for the bitter flavour often associated with caramel flavour development.

V. FACTORS AFFECTING THE RATE OF THE BROWNING REACTION

From studies on the glucose-casein system (66), milk (82,19), and milk powder (49), a general picture of the qualitative effect of process and product variables may be deduced. In a system where the concentrations of casein and lactose are approximately constant, the principal variables affecting the rate of browning are: (1) moisture, (2) temperature, (3) pH, (4) reducing sugar, and (5) ions. The qualitative effect of these variables is now discussed briefly. A more detailed discussion of the theories associated with the effect of these variables appears later in SECTION III.

A. Moisture Content or Water Activity

A striking thing about the reaction is that progress is not rapid in dry solid (65,66). The peak is actually at about 65 - 70% RH corresponding to a moisture content of 13%. In the very dry solid or in aqueous solution the reaction is very slow (55,65,66). The explanation of this is not very clear. Although Lea (66) proposed quite a plausible theory, more research is required to determine if this is in fact an adsorption effect or whether water is required to be present for browning to take place.

B. Temperature

Over the range of 0 - 90°C the reaction conforms to the Arrhenius equation (66); i.e., the plot of the logarithm of the rate of browning versus the reciprocal of the absolute temperature is a straight line.

C. pH

The rate of the reaction increases approximately linearly with increasing alkalinity from low values at pH 3 up to high values at pH 8.

Above pH 8 rate measurement is difficult because of its rapidity (66,65,82,19). The reaction is very dependent on pH and acid-base catalysis (83). Mohammad et al (77) found browning is accelerated by increased alkalinity. Barnes and Kaufman (12) found the rate of browning is doubled at pH 6 as compared with pH 4.

D. Sugar

The reactivity of the carbohydrates in browning parallels the general reactivity of the carbohydrate compounds (12,65). The aldopentoses react more rapidly or at a lower temperature than the di-, tri-, or polysaccharides. Carbohydrates having the necessary free aldehyde group naturally react more rapidly than those sugars (e.g., sucrose) that have to be hydrolysed, or otherwise have to be broken down, to release this group. The effects of combinations of pentoses, glucose, and disaccharides on solubility and colour changes is poorly understood.

E. Ions

The effect of citrate, phosphate, and calcium ions have been investigated by Burton (20). The effect of these ions on browning acts mainly through a change in pH.

VI. SALIENT FEATURES OF PREVIOUS WORK

From the review of previous research into the browning of dairy products, several salient features of the reaction are apparent:-

1. Much work has been done and copious literature exists on non-enzymic browning, but much of this neglects the beneficial effects of reactions of this type and concentrates on the deteriorative aspects. Research has been mainly limited to the factors influencing the undesirable occurrence of browning in "dry" milk powder, sterilized and evaporated milks. As a result, research has centred on the earlier stages of the reaction as a basis for preventing the occurrence of browning. Little work has been done on promoted browning, or "caramelization" in dairy products.
2. The primary reaction in milk has been shown to be an amino-sugar or Maillard-type browning involving lactose and the E-amino groups of lysine (in casein) as key reactants.
3. Browning in foods is highly complex and much of the present knowledge of the chemistry of browning has been gained from a study of model systems. Indications are that browning in milk closely parallels the pattern disclosed by model systems. However, between the established fact that casein and lactose are the primary reactants and that a brown product is a resultant of the reaction, there lies an area of chemistry that is largely unknown. The initial reaction in the "dry" state involves a 1:1 reaction of lactose with the E-amino groups of lysine to form the aldosylamine. Following this reaction there is a close relationship between the formation of 1-amino-1-deoxy-2-ketoses and a corresponding decrease in free amino-nitrogen. This Amadori rearrangement compound is believed to undergo dehydration fragmentation and condensation to

yield brown polymers and flavour compounds, with an accompanying loss in solubility.

4. Browning in milk appears to be a catalysis of the Amadori rearrangement by amino compounds (of casein), followed by an adsorption of the polymerized lactose fragments (brown pigment) by the casein molecules.

5. The most important phenomena of practical significance associated with browning are:-
   - i) compound formation responsible for the brown pigment and caramel flavour.
   - ii) loss of nutritive value.
   - iii) loss of solubility of the protein to a varying extent, depending on the type of sugars present.
   - iv) increased tendency to froth and foam.

6. Caramelized flavour is a concomitant of the browning reaction and the degree of "caramelization" is correlated positively with the degree of browning and related changes. Often the flavour is objectionable and coincident to faulty processing; e.g., milk powder, but in the case of sweetened condensed milk the promoted caramel flavour has consumer appeal.

7. The principal factors affecting the rate of browning in milk products are:-
   - i) Moisture content
   - ii) Temperature
   - iii) pH
   - iv) Type of sugar

8. As very little research has been reported on promoted browning in dairy products, there is a wide scope for investigation into promoted browning, and associated flavour and texture changes, in products such as sweetened condensed milk.

SECTION II

DEVELOPMENT of a METHOD

FOR

MEASURING THE DEGREE

OF

PROMOTED BROWNING IN A DAIRY PRODUCT SYSTEM

Basic to a fundamental study of browning in condensed milk systems, is a precise and accurate method of measuring the degree of browning. Methods for the estimation of browning are well documented. However, as most research has been done on the chemistry of browning in the earlier stages of the reaction, the methods available are mainly based on a chemical analysis of the reactants and earlier intermediates of the reaction. The most important methods for the measurement of the progress of the reaction are reviewed with an aim to finding the method most suitable for measuring advanced browning, or promoted browning, in concentrated milk systems.

I. CHEMICAL METHODS

A. Literature Review

In the study of the various systems, both wet and dry, a number of different methods have been made to determine the progress of the reaction. The most important chemical methods used are discussed below.

1. Measurement of Free-Amino Groups

a) The monometric method of Van Slyke (105), which measures the nitrogen evolved on reaction of a free-amino group with nitrous acid, has long been known as a rapid and sensitive method for the estimation of amino acids. Lea (64) demonstrated that with adequate precautions, Van Slyke determinations of the free amino-nitrogen content of casein, fresh and deteriorated milk protein, yield quite reproducible results. This method was used widely by Henry et al (49), Lea (66), and Richards (90), in their studies of the early stages of the reaction between the free-amino group of casein and lactose.

b) The formol titration has been used extensively for measurement of free amino-nitrogen in highly heated milks, but with questionable success as results showing both increase and decrease have been reported (83). The reasons for this are not clear. Increase in free amino-nitrogen by hydrolysis on heating and the probability that the amino groups of casein are still basic after reaction with glucose are two probable explanations (49,83). The first would probably apply to the Van Slyke method (64). Another cause of difficulty is the possibility of regeneration of amino groups in the dynamic medium (83). The Van Slyke method is considered to give a more useful picture of free amino-nitrogen changes in dry powder (49).

c) The Method of Carpenter (23) for estimation of free E-amino groups of lysine has been used in studies on loss of available lysine (90). This method is fairly long and it does not appear to offer any advantages for the present work.

2. Lactose Determination

The other primary reactant in the Maillard-browning reaction of milk, is lactose and other minor reducing sugars. Hence, lactose disappearance is an obvious possibility for measuring the progress of milk browning. Determination of lactose by several different methods has not been found to be entirely satisfactory (35). With methods based on the reducing power of lactose, the reducing substances formed in milk by heating interfere. It is also possible that some products of the lactose-casein interaction interfere with the polarimetric determination of lactose (62).

a) The Method of Fearon (37) for reducing disaccharides, as modified by Howitz (54), has been suggested as a possible method for the determination of lactose in milk (85). Results for the standard curve were highly reproducible and the method appears to be quite simple if interfering compounds can be removed.

b) Another method which is inconvenient in a number of respects is the chromatographic method of Honer and Tuckey (53). This is the most accurate method.

c) Henry et al (49) used the method of Somogyi (101) for the estimation of the combined sugar. The copper reagent is known to oxidise sugars fairly selectively. The milk was first dialysed and the sugar remaining in the undialysable fraction was estimated. If the dialysis was replaced by precipitation and washing as in the ferricyanide (26) method, the methods would be fairly similar as both measure the reducing power of the insoluble fraction of milk.

d) Larsen and Gould (62) showed that the picric acid method as developed by Dehn and Hartman (32) and modified by Bierman and Doan (13) was comparable with the copper reduction method described in A.O.A.C. (11).

e) An indirect method of measuring combined sugar is the measurement of the increase in undialyseable fraction as applied by Henry et al (49) in their study of changes in milk powder during storage.

Similar methods as those outlined above were used by Lea et al (67) for the measurement of glucose in casein-glucose systems. While precise, accurate measurements for the determination of changes in free amino-nitrogen and combined lactose are available in the literature, their main value is in following the earlier stages of the browning reaction in milk. For the present work, a method of following the more advanced stages of browning is required. The chemical methods available are now discussed.

3. Reducing Value

It is generally known that reducing groups, which may consist of sulphydryl groups derived from protein denaturation and as yet partially identified compounds resulting from the browning reaction, are produced in the heat treatment of milk. Studies of Chapman and McFarlane (24) and Crowe et al (30) have shown that the amount of reduced ferricyanide increased with increasing heat treatment of the milk. Choi et al (26) modified the method of Chapman and McFarlane (24) for whole milk to the acid precipitated protein curd. The method is quite sensitive to light and heat treatments. This method does give a more general indication of the degree of browning, but appears to be most useful during the earlier stages of browning (90).

4. 5-Hydroxymethylfurfural (HMF)

Keeney and Basette (60) presented a quantitative method for determining HMF and/or its precursors by spectrophotometric measurement of the 2-thiobarbituric acid (TBA) reaction product. HMF is accepted as being one of the principal reaction products in browning and immediately precedes condensation to brown melanoidin polymers (60). Hence, it is to be expected that the level of HMF is more likely to be correlated to the incidence of brown pigment formation during high levels of browning, than any measurements of earlier intermediates. It was for this reason that this type of measurement was chosen as a chemical method of measuring the rate and degree of browning in concentrated milk systems which had undergone advanced browning.

B. Selection of a Method for Studies on Advanced Browning in Sweetened Condensed Milk

From the literature review on methods of measuring the advanced steps of the browning reaction, measurement of HMF development would appear to be the method most likely to be correlated with incidence of brown pigment and flavour formation. HMF measurement by 1% Resorcinol in concentrated hydrochloric acid has been used in wines by Amerine (7). However, after repeated unsuccessful attempts at adapting this method to sweetened condensed milk, it was concluded that the method was only useful for clear, relatively simple foods. As the method of Keeney and Basette (60) has been shown to be applicable to non-fat dry milk, and whole milk powder, it was decided to use this method to develop a technique of measuring HMF in sweetened condensed milk.

From preliminary experiments it was found that a thiobarbituric acid (TBA) derivative of HMF could readily be obtained from browned sweetened condensed milk. After a few modifications of the original method, a method was adopted which was shown to be both precise and a good indicator of the rate of browning. The method used is described in APPENDIX I and experimental evidence for the precision of the method is given below.

1. Precision of the Method

The precision of the method, when used on sweetened condensed milk, was tested by two experiments.

a) Three samples of sweetened condensed milk were heated simultaneously at 120°C for one hour. The absorbance of the TBA derivative of each sample was then determined by the method described in APPENDIX I. Results are recorded below in Table I, page 26.

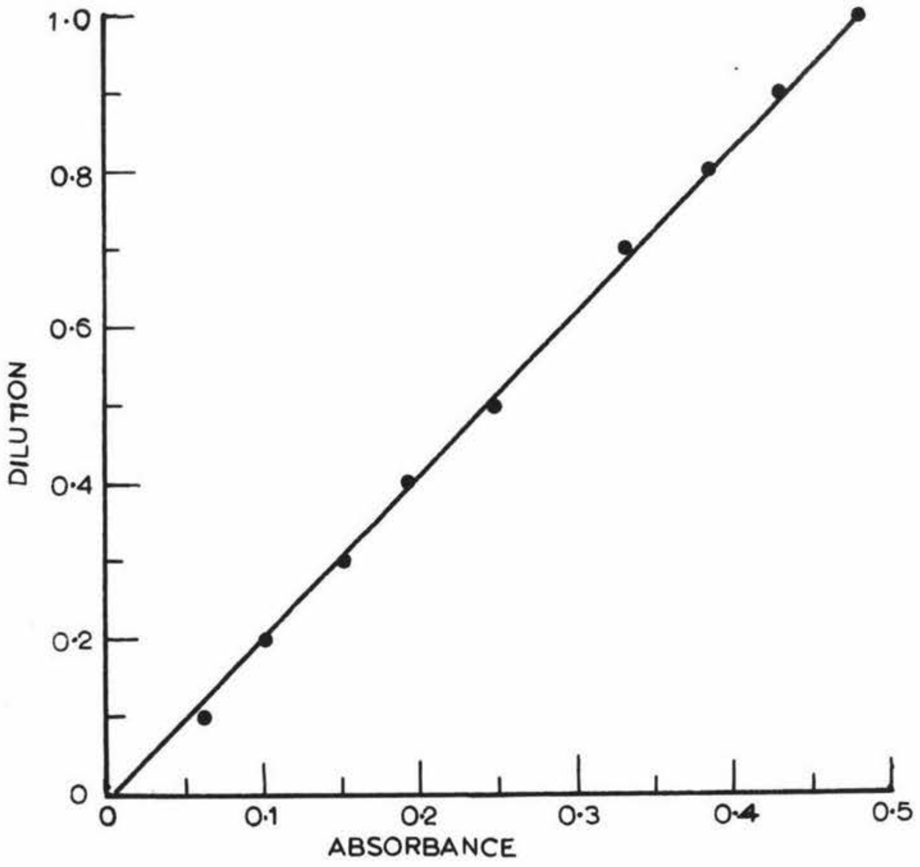


FIG. 2. RELATIONSHIP BETWEEN DILUTION OF BROWNED MILK AND ABSORBANCE OF THE TBA DERIVATIVE.

From Table I it is clear that despite the multiplicity of operations involved in the method, the method is quite reproducible.

TABLE I.

ABSORBANCE OF THE TBA DERIVATIVES OF SWEETENED CONDENSED MILK SAMPLES UNDERGOING THE SAME HEAT TREATMENT OF 120°C FOR ONE HOUR

SAMPLE No.	ABSORBANCE (Duplicate Determination)
1	0.52 ; 0.52
2	0.51 ; 0.52
3	0.52 ; 0.52

---

b) The filtrate from step (2) of the method (APPENDIX I) was taken and serial dilutions of 0.9 to 0.1 at intervals of 0.1 were prepared. The absorbance of the TBA derivative was determined in the usual manner (APPENDIX I), and the results plotted on the graph appearing in Figure 2. On the basis of these results, the method shows considerable accuracy and obviously follows Beer-Lambert's law.

$$\text{i.e., } \underset{\text{(of the TBA derivative)}}{\text{Absorbance}} \propto \underset{\text{(dilution of milk)}}{\text{Concentration of HMF}}$$

Furthermore, the plot of absorbance versus time of heating is linear. This relationship is demonstrated later in Figure 6, on page 35. This substantiates the claim that the Keeney and Basette (60) method of measuring HMF is a good indicator of the progress of the browning reaction during heating and may be used to determine the rate of browning.

2. Discussion of the Method

The method used measures the free HMF in the original sample (60). The method is somewhat arbitrary as the Maillard reaction is so complex and dynamic that any attempt at stoichiometric measurement of a single symptom should be applied with caution. The purpose of this discussion is not to discourage the quantitative application of the HMF test, but merely to point out its limitations, since the test is a measure of early transitory intermediates in the Maillard reaction. Even if the method does measure an early transitory intermediate of the reaction, it would appear to be at least as reliable as the measurement of the initial reactants - free amino-nitrogen groups and/or lactose.

Despite the above limitations of the method, the indirect measurement of HMF by the absorbance of its TBA derivative is directly related to the time of heating (Figure 6, page 35), and it is hence a direct arbitrary measure of the degree of browning and heat treatment.

II. DEVELOPMENT OF A METHOD OF MEASURING PRODUCT COLOUR AS AN INDEX TO THE PROGRESS AND RATE OF THE BROWNING REACTION

A. Literature Review

The browning which occurs when milk is heated is now generally considered to be an example of a general class of condensation reactions between amino acids (E-amino group of lysine in casein) and aldehyde reducing groups (lactose) to form dark coloured pigments as end products (83). It is generally agreed that the brown colouration is so closely associated with the protein that only by rendering the protein itself insoluble can the colour be released into solution for measurement by conventional colorimetric methods.

Several methods for the measurement of the degree of brownness have been suggested and used in investigations of the reaction. Doob, Willmann and Sharp (33) used a method of alkaline extraction to obtain the pigment in clear solution. A more satisfactory way of obtaining the coloured material in solution for colorimetric estimation is the method of trypsin digestion of the protein used by Choi et al (25).

However, methods of colour measurement not involving chemical procedures would be simpler and of more practical value for routine examination and process control. Webb and Holm (108) used the Munsell colour system for work on evaporated milk. The Lovebond Universal Tintometer, using similar principles, was tried by Burton (19) but was found not to be sufficiently sensitive for the measurement of slight colour changes.

Since the colour of an opaque medium is in fact a characteristic spectral distribution of light reflected from it, the spectral distribution of reflectance is a statement of the colour of the medium. This method of colour determination was used by Nelson (78,79) in work on evaporated milk. The preliminary experiments reported by Burton et al (21) showed that the method was equally suitable for use with sterilized milk. Burton (19) used two different instruments, a Beckman spectrophotometer with reflectance attachment, and an EEL reflectance spectrophotometer.

The Beckman spectrophotometer system was suitable for precise work with monochromatic incident light over a wide range of wavelengths. It was not, however, convenient for large numbers of samples where less precise results can be tolerated and some degree of portability in the apparatus is an advantage.

The EEL spectrophotometer was fitted with a series of nine filters with transmission maxima at various points in the visible spectrum. It was therefore not capable of giving continuous data over a wide range of wavelengths. It was, however, simple, portable, and convenient to use, and gave results generally to a suitable degree of accuracy.

B. Development of a Method for the Measurement of Browning - Based on Product Colour

After a few preliminary trials, the EEL spectrophotometer was found to be suitable for studies on advanced browning in sweetened condensed milk and related systems.

The arrangement of the reflectance head of the EEL spectrophotometer is shown in Figure 3, page 30.

The milk was contained in a shallow square container having a depth of at least 1 cm. so that the measurements were not affected by light reflected from the bottom of the container. The milk surface had to be about 2 mm. below the level of the top of the dish to prevent fouling of the bottom of the spectrophotometer. The reflectance obtained was affected by the milk level, so the same volume of milk was placed in the dish at each measurement.

This instrument requires a standard reflecting surface with which the 100% reflectance point at any wavelength can be determined. A block of magnesium carbonate is the accepted standard of reflectance, but it is difficult to maintain in good condition, and a piece of 3/16" while opal glass is more convenient and satisfactory for this type of work.

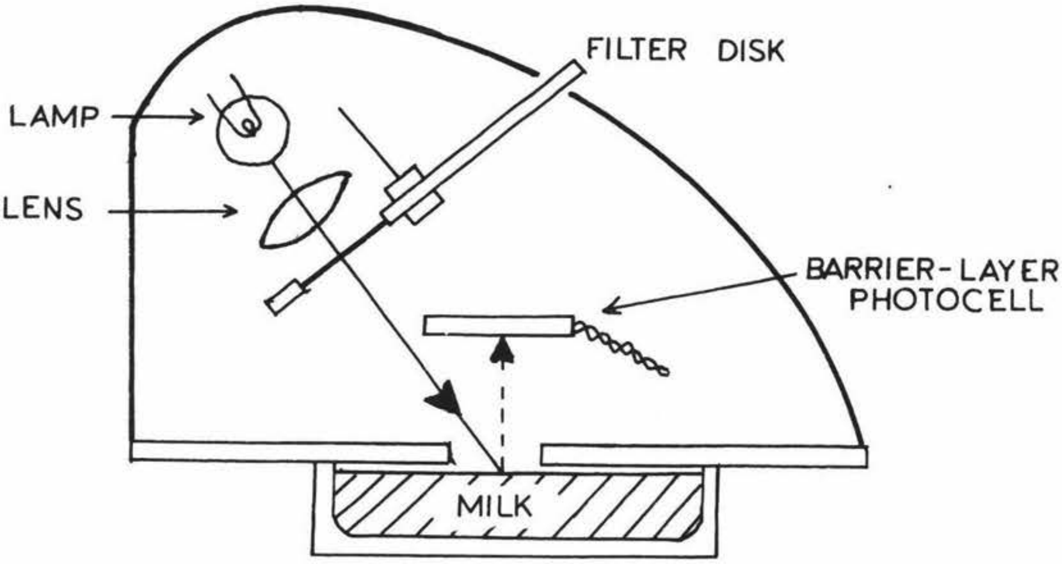


FIG. 3. ARRANGEMENT OF 'EEL' REFLECTANCE HEAD

The reflectances were measured with the EEL spectrophotometer using a No. 601 filter having a peak of transmission in the extreme blue part of the spectrum at 426 millimicrons. While the maximum change in reflectance occurred at 380 millimicrons, the 426 millimicrons filter was used as this was the standard filter, supplied with the equipment, which had the lowest wavelength, and the general trend of results were unaffected when a standard wavelength was used. All results are given relative to the reflectance of opal glass.

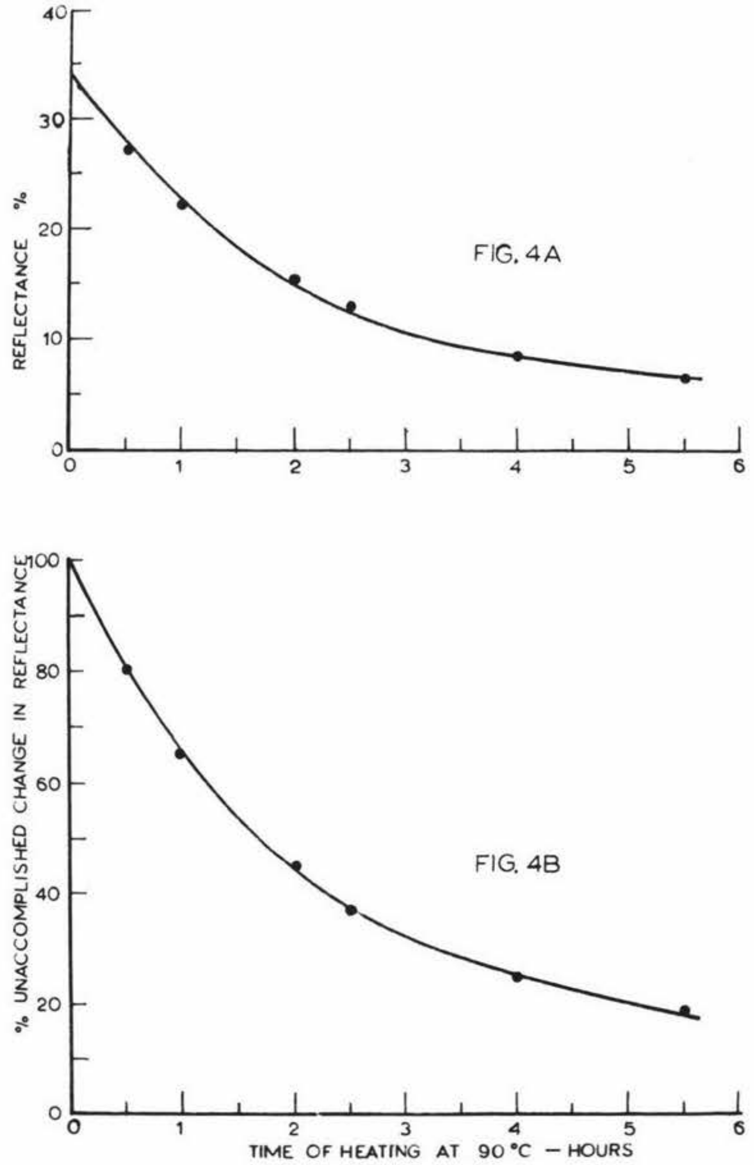


FIG. 4 EXPONENTIAL NATURE OF THE BROWNING REACTION (REFLECTANCE CHANGES).
(SWEETENED CONDENSED MILK SYSTEM)

C. A New Method of Plotting Reflectance Results to Determine the Rate of Browning

A plot of % reflectance versus time of heating appears in Figure 4A. This plot indicates that browning proceeds in such a manner that there is an exponential fall in reflectance with time. On theoretical chemistry grounds this was to be expected (39).

If it is assumed that in the limit as time of heating tends to ∞ the % reflectance tends to 0, then the plot of % reflectance versus time (Figure 4A) may be considered to be a plot of unaccomplished change in % reflectance versus time. If at time = 0, the unaccomplished change is made equal to 100, and all the other values of unaccomplished change at time of heating = T are expressed relative to the unaccomplished change at time = 0, then a plot of % unaccomplished change in reflectance versus time results. This plot appears in Figure 4B and still is apparently of an exponential nature.

The exponential curve (Figure 4B) may be expressed by the general equation:-

$$Y = ae^{KT}$$

where Y = % unaccomplished change in % reflectance

a = constant

e = exponential number

K = constant which depends on the rate of the reaction

T = time (hours)

therefore $\log Y = \log a + KT \log_{10} e$

and $\log Y = \log a + K_r T$

Figure 5, page 33, derived from Figure 4B, verifies that a plot of log Y versus T yields a straight line of slope K_r. The straight line relationship only holds true during the first 2 - 3 hours of browning. The reason for this is discussed later in Section III, Part III-C, page 63. The value of K_r is given by the expression -

$$K_r = \frac{\log Y_2 - \log Y_1}{T_2 - T_1}$$

This value, denoted as K_r, is a measure of the rate of change in reflectance, which is in fact a measure of the rate of browning. Hence, the measurement of % reflectance, by the method described on page 29, during the progress of browning gives a simple reliable method of measuring the rate of browning. Incidentally, the rate of browning measured by this method is directly proportioned to the rate of browning as measured by the chemical determination of HMF. This correlation is discussed later in Part III, page 36.

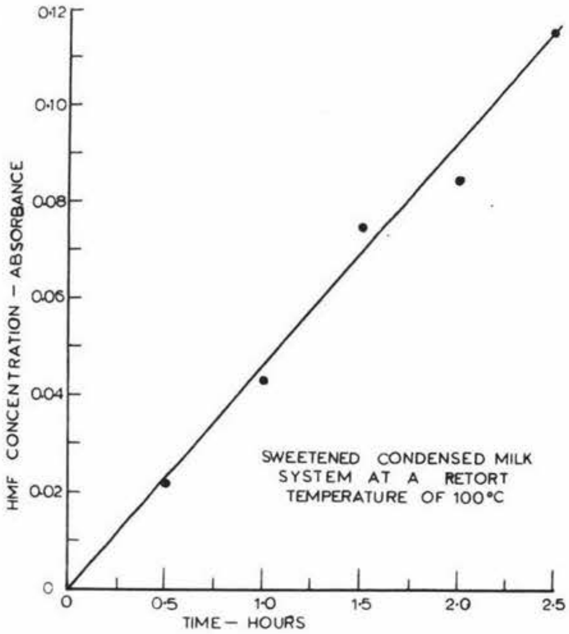


FIG. 6. LINEAR INCREASE IN HMF CONCENTRATION WITH TIME OF HEATING

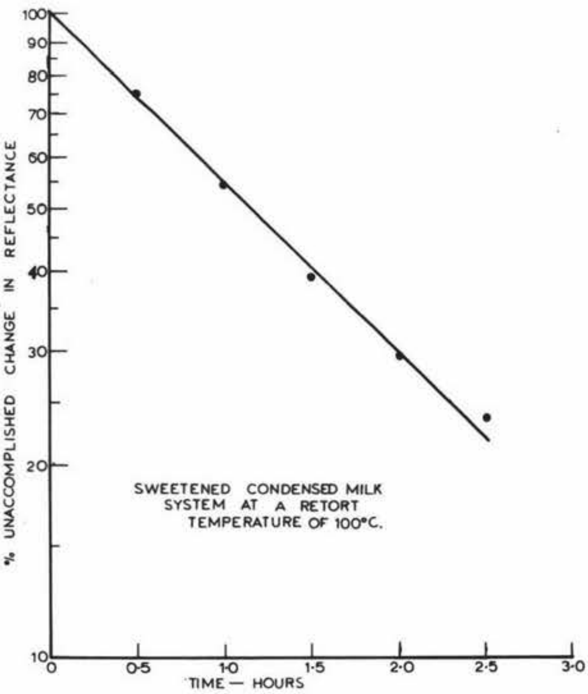


FIG. 7. LOG-LINEAR PLOT OF REFLECTANCE CHANGES DURING HEATING.

III. CORRELATION BETWEEN CHEMICAL (HMF) AND PHYSICAL (REFLECTANCE) METHODS FOR THE MEASUREMENT OF THE RATE OF BROWNING

During the development of the reflectance measurement of browning, and the chemical determination of HMF formation during browning, it was found that both $\log_{10}$ of the % unaccomplished change in reflectance, and the absorbance of the TBA derivative were directly proportional to the time of heating. Hence, it was deduced that both the chemical and the physical method of measuring the rate of browning were directly related. It is the purpose of this section to demonstrate the correlation between the chemical (HMF) and the physical (reflectance) method for measuring the rate of browning.

A. Experimental Method

Cans of commercial sweetened condensed milk were heated at a retort temperature of 100°C. At known time intervals of 0.5, 1.0, 1.5, 2.0, and 2.5 hours, the cans were removed from the retort and cooled rapidly in cold water. The following measurements of the browning reaction were made:-

1. HMF as determined by the TBA method of Keeney and Basette (60) described in APPENDIX I. Results were expressed in terms of absorbance as the concentration of HMF had been previously shown to be directly proportional to the absorbance. (Refer to Figure 2, page 25.)
2. The % reflectance as described in SECTION II, Part II - B and C.

B. Results

Figure 6 summarizes results expressing the increase in HMF concentration of sweetened condensed milk with time of heating at a retort temperature of 100°C.

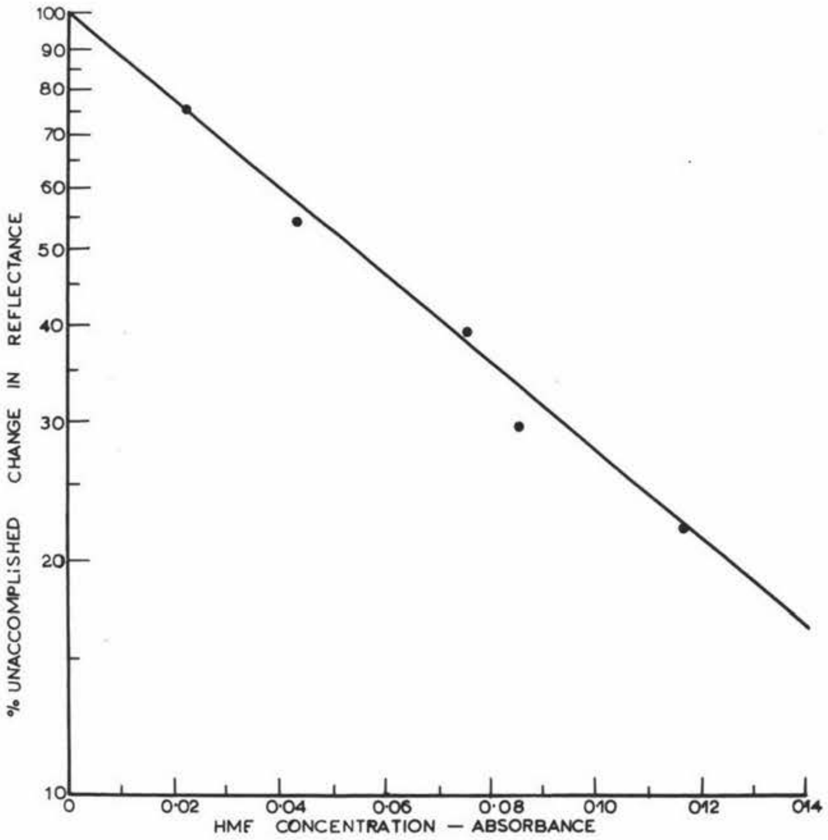


FIG. 8. LINEAR CORRELATION BETWEEN CHEMICAL (HMF) AND PHYSICAL (REFLECTANCE) METHODS OF MEASURING THE RATE OF BROWNING.

Figure 7 summarizes the changes in % unaccomplished change in reflectance of sweetened condensed milk heated at a retort temperature of 100°C. The initial reflectance of the sweetened condensed milk before heating was 34%.

C. Discussion of Results

As both the plot of absorbance versus time (Figure 6, page 35), and log % unaccomplished change in reflectance versus time (Figure 7, page 35), are linear, the plot of log % unaccomplished change in reflectance versus absorbance must also be linear as demonstrated in Figure 8 which is derived from Figures 6 and 7, page 35. Hence, there is a definite proportional correlation between the accepted chemical measurement of the progress of the reaction and the convenient physical measurement of the same reaction.

As described in APPENDIX I, the determination of HMF concentration, (by measuring absorbance of the TBA derivative), is quite a lengthy time-consuming procedure which requires intricate equipment. On the other hand, the reflectance measurement is quick, simple, reliable, and the equipment used is inexpensive and robust. Also there is nothing to suggest that reflectance measurement is less accurate or precise than the HMF method. On the other hand, from Figures 6 and 7, page 35, it would appear, in fact, that the HMF method gives a wider scatter of points than the reflectance method.

The reflectance measurement of colour is also an indirect measurement of caramel flavour as the one is closely associated with the other (83). Therefore, it appears that the reflectance method has obvious advantages for quick routine measurement of the reaction progress in fundamental studies, and in commercial practice. It was for these reasons that this method was used throughout the present studies on browning.

IV. SUMMARY

Before a fundamental study of the factors affecting browning in sweetened condensed milk (and related systems) could be undertaken, a precise and accurate method of measuring the degree of browning had to be either developed or adapted from previous work. A literature review of previously used chemical and physical methods accentuated the fact that most methods had been developed to study the early stages of the browning reaction. Despite this bias in the study of the browning reaction, both a chemical and a physical method of measuring reaction progress were found to be adaptable to studies on promoted browning in milk systems.

1. The chemical determination of 5-hydroxymethylfurfural (HMF) and/or its precursors by spectrophotometric measurement of the 2-thiobarbituric acid (TBA) reaction product, as developed by Keeney and Basette (60), was found to be a good arbitrary measure of the degree of promoted browning.
2. The physical measurement of colour by determining the % reflectance (as compared with an opal glass standard), with an EEL reflectance spectrophotometer, gave a direct measure of one of the prominent associated changes in promoted browning, and was also an indirect measure of flavour development. This method was based on previous work by Burton (19) on evaporated milk.

Further investigation of these two methods of measuring promoted browning in milk systems led to the selection of the physical measurement of colour (reflectance) as the key to further basic and technological studies on browning.

1. A new method of plotting reflectance results to give an arbitrary measure of the rate of browning was developed. This method involved the plotting

of the log % unaccomplished change in reflectance versus time. The slope of this plot gave an arbitrary measure of the rate of browning.

2. Further investigation showed that there was a linear correlation between the chemical (HMF) and physical (reflectance) methods of measuring the rate of browning. This correlation indicated that both methods were measuring the progress of the same overall reaction and further, that either method could be used to measure the rate of browning.
3. The physical measurement of colour (reflectance) was chosen for further studies as it had several advantages when compared with the chemical method.
    - a) Reflectance measures an end product of browning - not a transient intermediate, such as HMF.
    - b) From a comparison of Figure 6 and Figure 7, reflectance measurements appear to be at least as accurate as the chemical (HMF) method.
    - c) Reflectance gives a direct measurement of colour and is hence an indirect measure of flavour development.
    - d) Reflectance measurements are quick, simple, and are equally applicable to quality control of promoted browning in commercial production, as to a study of fundamental aspects of browning.

The physical measurement of colour (reflectance) is used as an index to browning throughout both the basic and technological sections which follow. The slope of the plot of the % unaccomplished change in reflectance versus time is expressed throughout this thesis as K_r - an arbitrary measure of the rate of browning.

SECTION III

A BASIC STUDY

OF

FACTORS INFLUENCING BROWNING

IN

SWEETENED CONDENSED MILK

From the literature review on factors affecting the rate of the browning reaction in glucose-casein, milk, and milk powder systems, it was found that for a system where the concentration of casein and lactose are approximately constant, the principle variables affecting the rate of browning are:-

1. Temperature.
2. Moisture.
3. pH.
4. Type of reducing sugar.

While it is expected that the qualitative effects of these variables on browning in sweetened condensed milk will follow the same pattern as that described in the literature for related systems (82,65,66,19), the author is not aware of any literature describing the quantitative effects. This lack of information made necessary a study of the quantitative effects of temperature, moisture content, pH and sugar on the rate of promoted browning in sweetened condensed milk and closely allied systems. This basic information is essential to controlling promoted browning in milk systems so that the desired caramel flavour is obtained in the most efficient way - with due consideration for desired texture, appearance and process economics.

Although the accent of the present work is on the manipulation of product and process variables to obtain a controlled amount of browning, it is hoped that this work will contribute substantially to making the knowledge of milk and its behaviour more complete. It is with this latter thought in mind that theories and results arising out of these studies are discussed in detail so that the fundamental knowledge of the browning system in milk will become more complete.

I. STUDIES ON THE EFFECT OF TEMPERATURE ON THE DEVELOPMENT OF DAIRY CARAMEL

From early observation, it was obvious that the rate of browning increased with temperature in sweetened condensed milk. Lea and Hannan (66) found that the effect of temperature could be summarized in an Arrhenius plot for the closely related system of casein-glucose, and Burton (19) has demonstrated a similar relationship for browning in milk.

The purpose of the present study was to verify this relationship, and to determine the quantitative effect of temperature on the rate of dairy caramel development in sweetened condensed milk.

A. Experimental Method

Standard commercial sweetened condensed milk of 25% moisture content was placed in test-tubes and heated in a water bath thermostatically controlled at the required temperature $\pm$ 1°C. A steam retort was used for temperatures greater than 100°C. The tubes were taken from the bath at intervals after known times of heating, and cooled rapidly in refrigerated water. A sample was then taken from the tube and the % reflectance determined by the method described in SECTION II, Part II - B, page 29.

B. Results

Results expressing the rate of change of reflectance as affected by time and temperature are summarized in Figure 9. The initial reflectance of sweetened condensed milk before heating was 34% when the No. 601 filter was used. All results are expressed as the % unaccomplished change in reflectance (i.e., as a percentage of 34) versus time. Hence, Figure 9 is, in fact, a plot of log Y versus T, as explained in SECTION II, Part II - C, page 32.

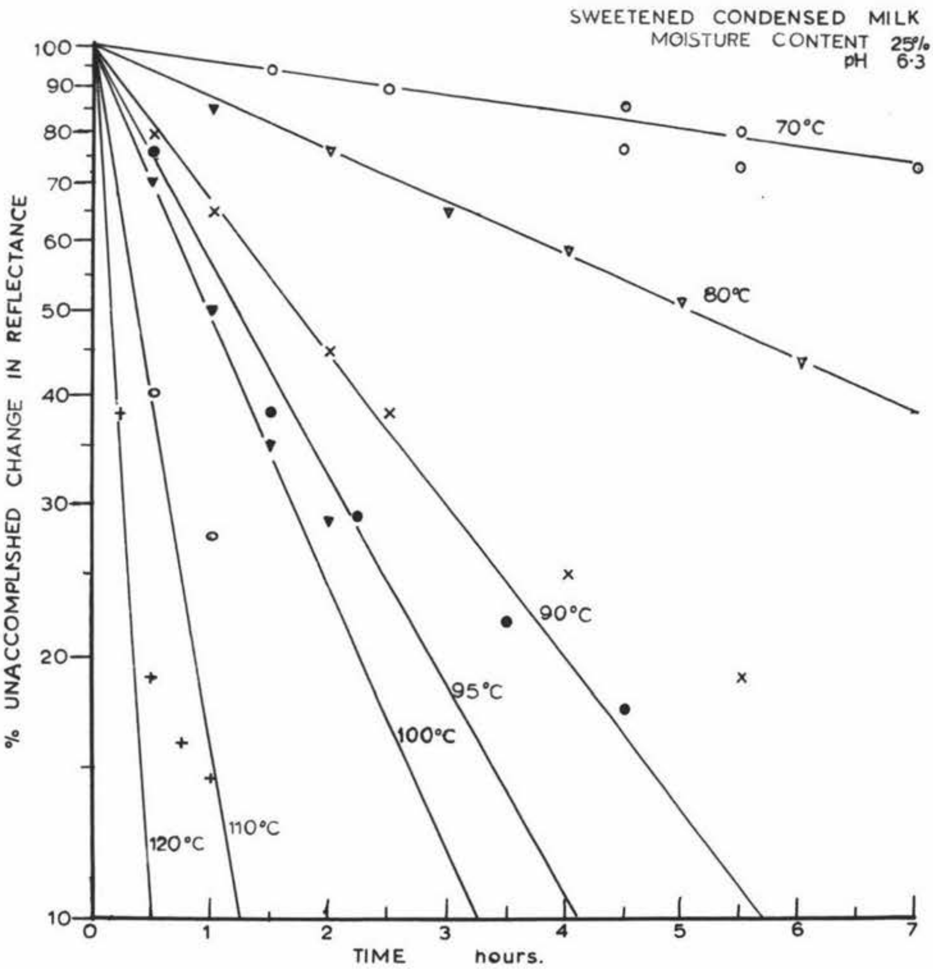


FIG. 9. RATE OF COLOUR (REFLECTANCE) CHANGES.

It is apparent from Figure 9 that the linear relationship, between log % unaccomplished change in reflectance and time, holds well over the earlier section of the curve but that after some time the rate of browning appears to have slowed down. The reason for this is discussed later in SECTION III, Part III - C, page 63.

From the curves in Figure 9, the values of K_r, (the empirical index of browning rate), at various temperatures may be derived to plot the Arrhenius plot of log K_r versus the reciprocal of the absolute temperature. This data appears in Table II, and the Arrhenius plot appears in Figure 10.

TABLE II

DATA DERIVED FROM FIGURE 9 FOR THE ARRHENIUS PLOT IN FIGURE 10

Temperature $^{\circ}C$	Temperature $^{\circ}K$	Reciprocal of absolute temp. $1/^{\circ}K$ or $1/t$	Rate of Browning K_r
70	343	2.92×10^{-3}	0.018
80	353	2.83	0.06
90	363	2.75	0.17
95	368	2.72	0.24
100	373	2.68	0.31
110	383	2.61	0.85
120	393	2.55	2.0

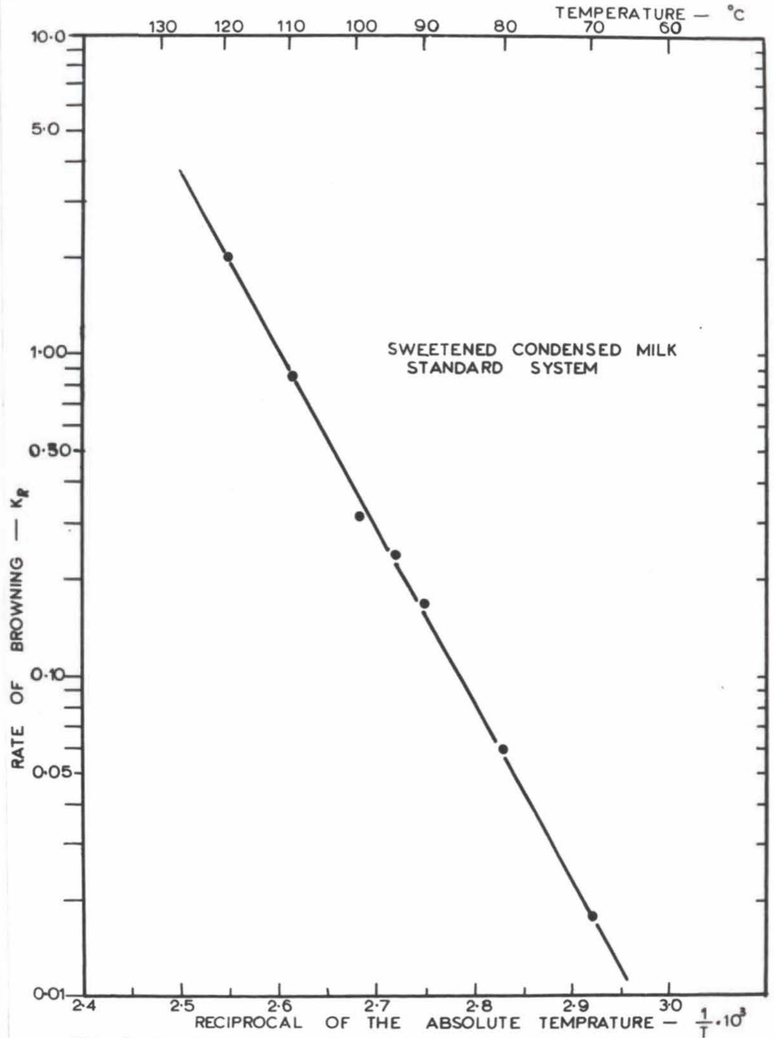


FIG. 10. EFFECT OF TEMPERATURE ON THE RATE OF BROWNING

C. Discussion of Results

On a theoretical basis the plot of log K_r versus $1/{}^{o}K$ was expected to give a straight line according to the Arrhenius equation:-

$$K_r = A\,e^{\frac{-E}{Rt}}$$

where K_r = reaction rate

A = constant

R = gas constant (1.987 cal/mole ^{o}K)

t = ^{o}K or absolute temp.

$$\text{therefore,} \quad \log K_r = \log A - \frac{E}{2.303Rt}$$

Also, over the small range of temperatures (70 to 120°C) which was used, a plot of log K_r versus temperature (°C) is approximately a straight line, and is a more convenient plot in practice. These results from the present study on the effect of temperature on browning agree, in general, with the kinetic studies that have been done on browning in different systems.

Thus Mohammad et al (77) have demonstrated this relationship for a model bovine serum albumin-glucose system, and the same relationship holds for a complex homogeneous system containing amino acids and glucose extracted from cod muscle. Lea and Hannan (66) have demonstrated this relationship in a casein-glucose system and Burton (19) has demonstrated it in milk. In contrast, Lewin (71) showed a non-linear plot over part of the 20-50°C scale for model glucose-histidine systems.

In Figure 9, a reduction in the rate of browning was observed during the latter part of the run; i.e., after browning had occurred to a considerable extent. This phenomenon is thought to be due to:-

1) a reduction in pH caused by a build-up of acid products which retard the rate of browning. This is later shown to occur in fact, and is discussed in SECTION III, Part III - C, page 63.

2) reduced accuracy of reflectance measurements (± 2%) at low reflectance levels which results in large errors in the plotted figure of % unaccomplished change in reflectance.

This problem was overcome by placing less "weight" on the latter points when drawing the curves of Figure 9. Hence, the values of K_r derived from Figure 9 are considered to be a reliable index of the relative rates of browning.

D. Conclusions

It may be concluded from the present work that the Arrhenius plot for sweetened condensed milk yields a straight line relationship. From the slope of Figure 10 an activation energy of -26,000 calories may be deduced. This value agrees favourably with the value of about 29,000 obtained by Lea (66), and later by Burton (19) on evaporated milk systems.

In practice the rate of browning approximately doubles for a 10°C rise in temperature between 100°C and 110°C.

II. STUDY OF THE EFFECT OF MOISTURE CONCENTRATION ON THE RATE OF BROWNING OF SWEETENED CONDENSED MILK

It is well known that in dried foods there is an optimum moisture content, of 10-15%, at which browning is a maximum. At higher or lower moistures the rate of browning decreases. However, most work has been done on the rate of browning of milk powder and other foods in the dry state. Except for the knowledge that browning in liquid systems is favoured by increasing solids concentration (55), little is known of:-

1. the effect of water on browning in liquid systems;
2. the role of water in the browning reaction.

The present study was undertaken in an attempt to fill this lack of knowledge on the effect of water on browning in liquid systems similar to that of sweetened condensed milk. Naturally, at the same time quantitative data was collected on the effect of moisture content on the rate of browning in sweetened condensed milk.

A. Effect of Moisture Concentration on Browning in Sweetened Condensed Milk

1. Experimental Method:-

Standard sweetened condensed milk was taken and diluted to the desired moisture content. Samples were placed in test-tubes and heated in a water bath at $90^{o}C \pm 1^{o}C$. At known time intervals, samples were removed, rapidly cooled, and the % reflectance determined by the method described in SECTION II, Part II - B, page 29.

2. Results:-

Results were plotted as % unaccomplished change in reflectance versus time in the manner described in SECTION II, Part II - C,

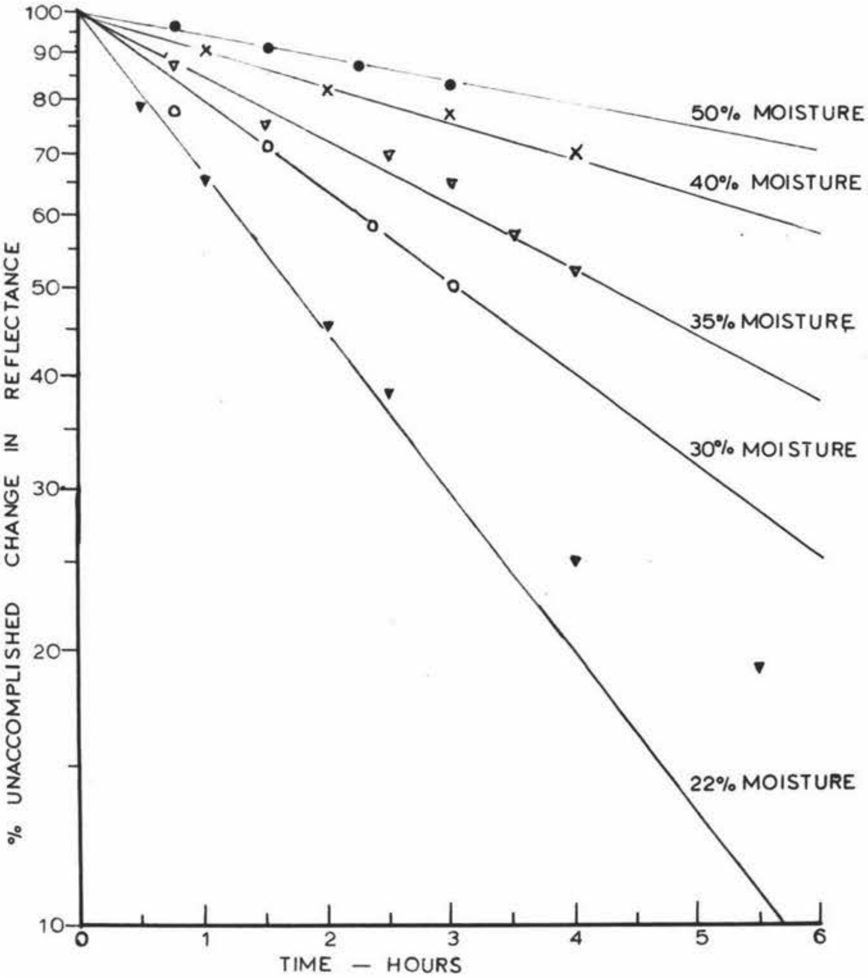


FIG. 11. RATE OF COLOUR (REFLECTANCE) CHANGES
EFFECT OF MOISTURE CONTENT
(SWEETENED CONDENSED MILK AT 90°C)

page 32. This plot of % unaccomplished change in reflectance versus time appears in Figure 11; from it a measure of the rate of browning, K_r, may be derived. The plots in Figure 11 are based upon an initial reflectance of 34% for 22% moisture; 45% for 30% moisture; 40% for 35% moisture; 46% for 40% moisture; and 48% for 50% moisture. The initial reflectance is expressed as 100% unaccomplished change in reflectance in Figure 11.

The relationship between K_r, and moisture content, is shown later in Figure 13, page 54.

B. Effect of Moisture Content on Browning in a Model System Containing Skim Milk Powder

Because of lactose and sucrose crystallization, it was not possible to reduce the moisture of sweetened condensed milk below 20% and yet maintain it in the liquid state. In an attempt to overcome this problem, glycerol was chosen to replace sucrose. The reason for this choice is discussed below.

1. As sucrose is a non-reducing sugar it takes no part in browning and only functions in the capacity of increasing the solids content.
2. There is no evidence that glycerol is involved in browning and hence, it may be used to replace sucrose as an inert diluent to increase the solids content.
3. Glycerol is miscible with water and hence is capable of maintaining a solution of skim milk powder and water in the dispersed, liquid state - even at negligible moisture levels.
4. Lactose is still soluble in glycerol at 90°C although only to the extent of about 5 gm. per 100 gm. of glycerol as compared with 140 gm. per 100 gm. of water at the same temperature (110).

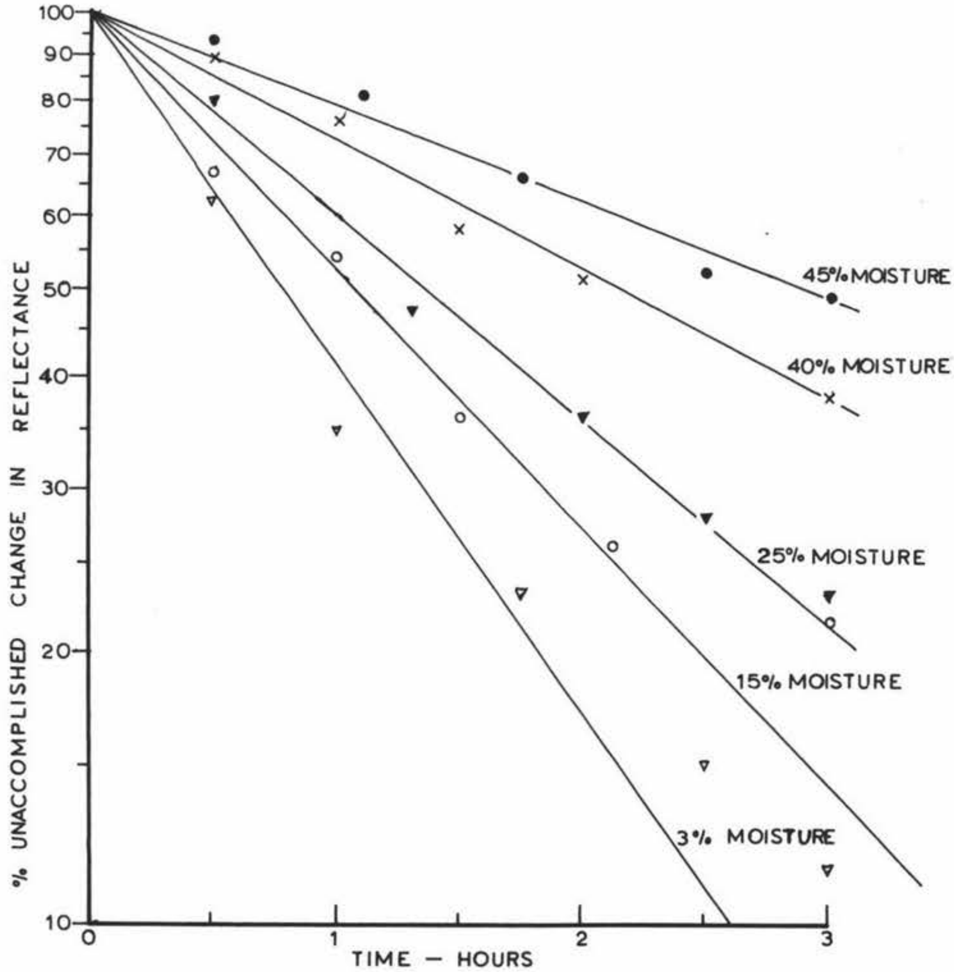


FIG. 12. RATE OF COLOUR (REFLECTANCE) CHANGES
EFFECT OF MOISTURE CONTENT
(GLYCEROL-MILK POWDER SYSTEM AT 90°C)

1. Experimental Method

The solution was made up in a standard manner as follows:-

31% full cream milk powder
69-X% glycerol
X% water

The mixture was vigorously dispersed in a Kenwood Chefette at top speed. Samples were placed in test-tubes and heated in a water bath at 90°C. At known times of heating, samples were removed, rapidly cooled, and the % reflectance determined by the method described in SECTION II, Part II - B, Page 29.

2. Results

Results were plotted as % unaccomplished change in reflectance versus time after the manner described in SECTION II, Part II - C, on page 32. This plot appears in Figure 12 where the % unaccomplished change in reflectance is based upon an initial reflectance of 60% for 3% moisture; 66% for 15% moisture; 55% for 25% moisture; 55% for 40% moisture; and 58% for 45% moisture. The initial reflectance is expressed as 100% unaccomplished change in reflectance in Figure 12.

A measure of the rate of browning, K_r, was derived from the slope of the curves, and the relationship between K_r and moisture content is summarized in Figure 13, on page 54.

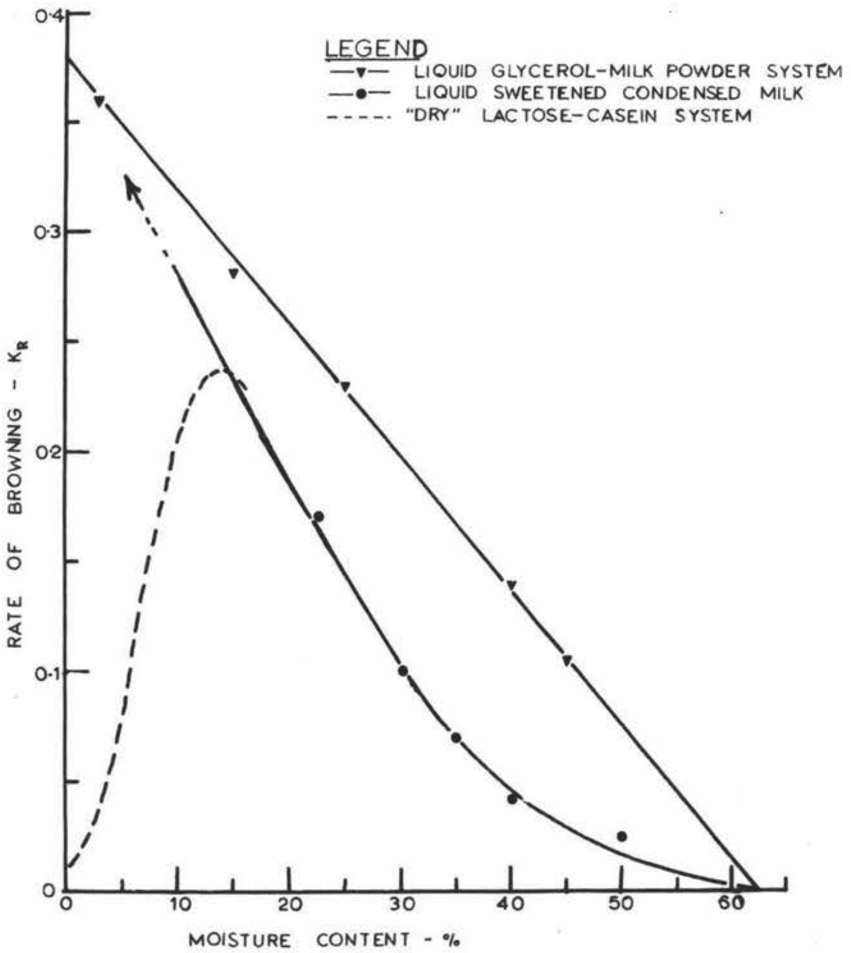


FIG.13. COMPARISON OF THE EFFECT OF MOISTURE ON THE RATE OF BROWNING IN "DRY" AND "LIQUID" MILK SOLID SYSTEMS

C. A Proposed Theory to Explain the Effect of Moisture Concentration on Browning in Liquid Systems - Arising out of the Previous Study of Sweetened Condensed Milk and Glycerol-Milk Powder Systems

Jones (57) stated that "browning in heterogeneous systems is maximal at a low critical moisture level, the exact value of which varies from system to system. In general, systems of carbonyl compounds of high molecular weight are in equilibrium with a higher relative humidity (moisture content) at the point of maximum browning than reaction mixtures with relatively simple compounds". Lea and Hannan (66) studied the effect of water activity on the primary reaction between casein and glucose in the "dry" state - a system quite similar to skim milk powder in which casein and lactose are the principal reactants. The general trend of their results is represented by the dotted lines in Figure 13. They found a sharp maximum rate of browning at about 13-14% moisture or 70% R.H., and a rapid decrease in browning with any increase or decrease in moisture content from this figure. At 0% moisture, the reaction rate would be approximately zero. To explain this phenomenon, they developed the following theory as to the effect of water on the rate of browning:-

The relative humidity at which the reaction rate reaches a maximum corresponds with the end of the approximately linear portion of the adsorption isotherm for casein, above which the curve swings steeply upwards. Bull (17) has suggested, on the basis of the general multilayer adsorption theory of Brunauer et al (15), that this point on the isotherm of proteins represents the completion of a double layer of water molecules between the protein planes, and probably also represents the point at which the exposed polar groups of the protein have become saturated with water. Under these conditions the force of attraction between the protein molecules will be greatly decreased and their capacity for movement and rearrangement increased. Mellon et al (76) concluded that at very low water vapour pressures (0 - 6% R.H.) one molecule of water is probably held between two amino groups. As the water vapour pressure increases, the quantity of water held by the amino groups increases linearly to reach saturation of the hydrogen bonding capacity, (about 2½ molecules per amino group), at 60 - 70% R.H. Above 70%, and particularly above 80% R.H., there is a rapid increase in the water adsorbed on the amino groups, probably by condensation of water on water molecules already bound. A fraction varying from one quarter to one third of the total water held by the protein at various humidities was considered to be associated with the amino groups, but this included none of the water responsible for the phenomenon of hysteresis.

On the basis of these data it was not difficult for Lea et al (66) to account for an increasing rate and extent of the reaction between casein amino groups and glucose with increasing R.H. up to 65 or 70% but it was less easy to understand the marked falling off in reaction rate as the humidity continued to increase beyond this point. It may be that a simple dilution effect was coming into play after sufficient water had been added to bring all the glucose into solution, or that an increasing thickness of aqueous film was tending to keep apart amino and potential aldehyde groups which, while both hydrophilic, had no great affinity for one another as evidenced by their slow and incomplete reaction in aqueous solution. Separate experiments by Lea (66) showed that the rate of reaction at 70% R.H. can be considerably increased by increasing the concentration of glucose. This would seem to militate against the simple solubility theory.

While the above theory appears to be a plausible explanation for the role of water in the browning reaction of proteins (casein) in the solid state, it cannot explain completely the results of the present work which is concerned with browning in the liquid phase.

The results from the present study of sweetened condensed milk and glycerol-milk powder systems, illustrated in Figure 13, show that for the liquid system of glycerol-skim milk powder browning increases linearly with decreasing moisture content to a maximum at 0% moisture. Also, the hypothetical extrapolation of the liquid sweetened condensed milk line suggests that a maximum browning rate would also be reached at 0% moisture if the system could be maintained in the liquid state. Hence, it would appear that the rate of browning is directly related to the moisture content. This suggestion is supported by the statement of Hodge (50) that ketoseamine formation (i.e., the initial reaction between lactose and the E-amino group of lysine in casein) is favoured by low moisture and high pH. Furthermore, many of the postulated intermediate reactions leading to melanoidins evolve water (50,69). These facts indicate that browning as a reaction in a liquid system would be favoured by the absence of water.

So far, this theory of the importance of water explains the increase in browning with reduced moisture content but does not explain the decrease in browning below 70% R.H. (or 13% moisture) in "dry" systems. While the theory of Lea et al (66) may be applicable, it seems likely that the movement of dissolved lactose to the amino groups is so restricted at moistures below this that browning is reduced. That is, browning is not reduced simply by the decrease in water but because of the immobility of lactose, a principal reactant. Hence, if the milk powder is dispersed in an anhydrous system which will dissolve lactose (and thus make it available to react) the observation (Figure 13) of an increasing reaction rate is compatible with the theory that browning is favoured by complete absence of water.

<u>Conclusion</u>:- From the above discussion, it is suggested that a minimum of water, or complete absence of water, maximizes the browning rate as long as lactose is still mobile and made available to react.

D. Changes in Moisture Concentration During Browning of Sweetened Condensed Milk

Lea (69) showed that the average amount of water liberated by glucose in becoming bound to casein was of the order of one molecule of water per glucose residue in the earlier stages of the reaction, although it showed signs of increasing later. Furthermore, many of the postulated intermediate reactions leading to melanoidin formation evolve water (50). In view of these facts, it was decided to investigate the extent of moisture increase, if any, during the "caramelization" of sweetened condensed milk.

A. Experimental Method

Sweetened condensed milk having a moisture content of 22.7% was filled into cans and heated in a retort at 100°C. At known time intervals of 2, 3, 4, 5 and 6 hours, the cans were removed from the retort, cooled, and their moisture content determined by two methods.

1. A sample of 2 gm. was smeared evenly over the bottom of a moisture dish and vacuum dried at 30°C for 48 hours. The % moisture was determined by an accurate measurement of the weight difference, before and after drying.
2. Dean and Stark toluene distillation at 110°C. This method is described in APPENDIX V.

B. Results

Results from the moisture determinations are summarized below in Table III.

TABLE III

THE EXTENT OF CHANGES IN MOISTURE DURING HEATING OF SWEETENED CONDENSED MILK

Time of Heating	Initial Moisture	Moisture after Heating	
		Vacuum	Toluene Distillation
Hours	%	%	%
2	22.7	22.6	22.5
3	22.7	22.8	23.0
4	22.7	22.6	23.0
5	22.7	22.7	22.5
6	22.7	22.8	23.0

C. Discussion of Results

It is clear, from the results recorded in Table III, that there is no significant increase of moisture content indicated by the techniques of measurement employed. The apparent discrepancy between these results and the published results of Lea et al (69) may be due to any one of the following reasons.

1. Lea et al (69) used a "dry" casein-glucose system of low moisture content which is distinct from the liquid system of casein-lactose which exists in sweetened condensed milk.

2. The methods of moisture determination used in the present work were not as accurate as those employed by Lea (69). The vacuum method has an accuracy of ± 0.1% and the toluene distillation method has an accuracy of ± 0.5%. Hence, very small changes in moisture content would not have been detected by these methods.
3. While it appears from the literature that water is liberated during some of the initial reactions of browning (50), it may well disappear again in the secondary and final reaction stages.

D. Conclusion

There is no significant increase in moisture content during the heat "caramelization" of sweetened condensed milk.

III. STUDIES ON THE EFFECT OF pH ON BROWNING IN SWEETENED CONDENSED MILK

The main body of evidence indicates that, in general, Maillard-type reactions increase in rate with increasing pH (e.g., 111,31) and that amino acids do not react in the cationic form, only slightly in the zwitterion form, and fully in the anion form. The rate of formation of ketoseamines increases with pH and is subject to acid-base catalysis (90).

At present there is little doubt as to the way in which pH affects the rate of browning in milk systems. Lea and Hannan (66) have shown that the browning of dry casein-glucose mixtures increases with alkalinity, and Patton (82) has shown a similar relationship for autoclaved separated milk by using the trypsin-digestion method of brownness determination. Using a reflectance method of measurement, Burton (19) obtained a curve very similar to that obtained by Patton (82).

The purpose of this study was to verify the above general trend in sweetened condensed milk, and to determine the average rate of browning over 1 - 2 hours at a temperature of 90°C for an initial pH which varied from pH 5.4 to pH 9.5.

A. Experimental Method

Samples of sweetened condensed milk were adjusted to an initial pH ranging from 5.45 to 9.5 with 1N solium hydroxide or 1N citric acid. The samples were heated in 1" test-tubes in a water bath at 90°C. At known time intervals samples were removed, rapidly cooled, and the % reflectance determined by the method described in SECTION II, Part II - B, page 29.

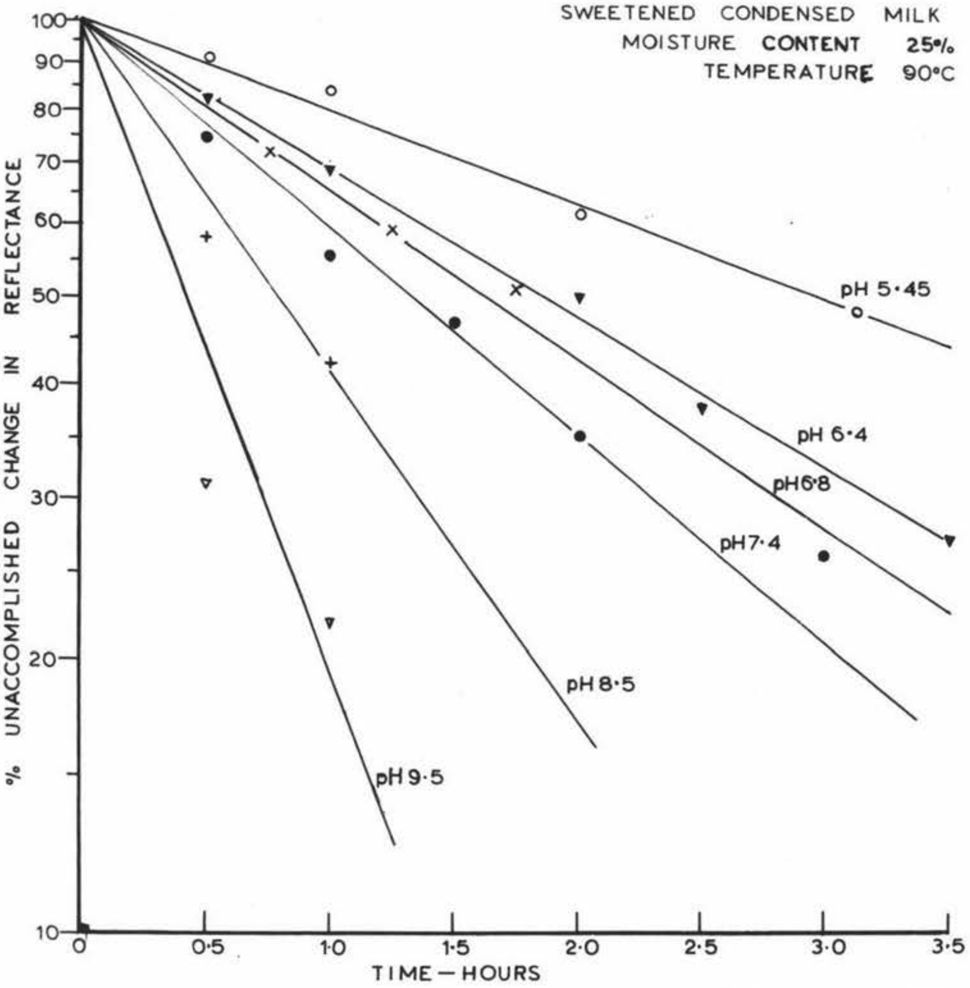


FIG. 14. RATE OF COLOUR (REFLECTANCE) CHANGES EFFECT OF pH

B. Results

Results were plotted as % unaccomplished change in reflectance versus time after the manner described in SECTION II, Part II - C, page 32. These results appear in Figure 14 where the % unaccomplished change in reflectance is based upon an initial reflectance of 44% for pH 5.45; 34% for pH 6.4; 39% for pH 6.8; 34% for pH 7.4; 45% for pH 8.5; and 39% for pH 9.5. The initial reflectance is expressed as 100% unaccomplished change in reflectance in Figure 14.

A measure of the rate of browning, K_r, was derived from the slope of the curves in Figure 14 (see SECTION II, Part II - C, page 32) and the relationship between K_r and pH is expressed in Figure 15 on page 64.

C. Discussion of Results

By comparison of the results of the present work (summarized in Figure 15) with the results of Burton (19) and Patton (82), the rates of browning above pH 7.0 are low as related to the rate at pH 6.4, (natural pH of condensed milk). The reason for this is quite simple. Their (19,82) samples were only heated for short time periods whereas in these experiments the rate was measured over a period of 1 to 2 hours for a particular initial pH. If browning has been allowed to progress to an advanced stage, the formation of acid degradation products of lactose and the loss of the strongly basic amino groups inevitably causes the pH to drop (55,66). Table IV demonstrates that there is a marked drop in pH during the "caramelization" of the sweetened condensed milk system used in the present study. Due to the rapid drop in pH from the initial value, the browning reaction rate decreases. Hence, the average rate determined over 1 - 2 hours must be less than the real rate for the same initial pH determined over a short initial period.

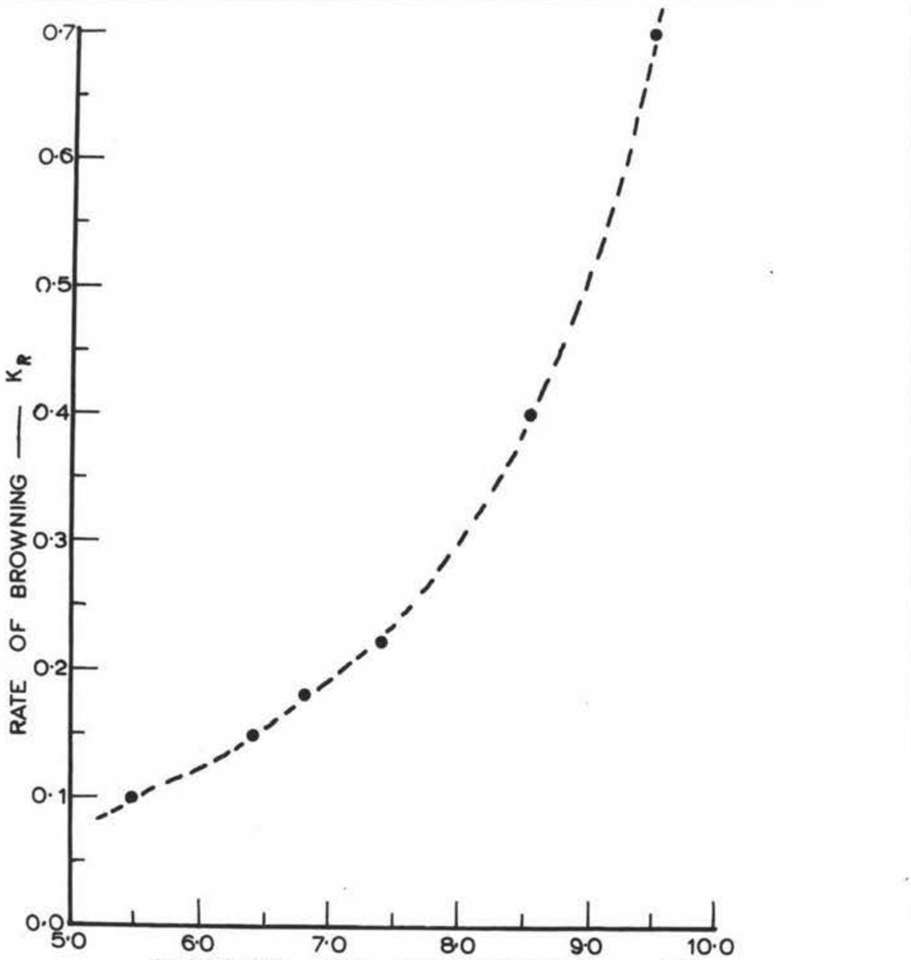


FIG.15. EFFECT OF pH ON THE RATE OF BROWNING
(SWEETENED CONDENSED MILK SYSTEM)

Nonetheless, these data amply demonstrate the importance of pH in the browning of milk during prolonged heating. Normal sweetened condensed milk having a pH of 6.4 to 6.5 falls at a critical point on the curve - relatively minor variations in pH towards greater alkalinity increased colour signficiantly while corresponding changes towards more acid values gave appreciable reduction in colour.

TABLE IV

pH CHANGES OCCURRING IN SWEETENED CONDENSED MILK DURING HEATING

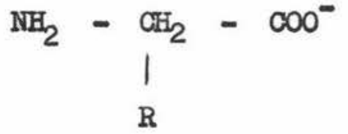
TIME (Hours) Heating @ 90°C		0.0	0.5	1.5	2.0	2.5	3.0
pH:	Batch No. 1	8.3	7.3	6.8	6.7	6.4	6.1
	Batch No. 2	6.4 (Initial pH)	6.3	6.1	6.0	5.8	5.6 (Final pH)

In practice this effect of pH is most likely to be of importance in chemical leavening of milk-solid foams and in the addition of sodium bicarbonate for the manufacture of caramel "hokey-pokey".

D. Conclusions

The rate of browning in sweetened condensed milk increases rapidly with increasing pH up to pH 9.5, and most probably continues to increase with increasing pH beyond this.

These results are in agreement with the findings from studies on model systems which have shown that it is the anion, not the zwitterion, of the amino acid which functions as the catalyst (50).



$$NH_2 - \underset{\displaystyle R}{\underset{|}{CH_2}} - COO^-$$

Anion form of amino acid

The anion form of the E-amino group of lysine (in casein) becomes increasingly dissociated with increasing pH and hence is better able to catalyse the browning reaction.

Although browning is not likely to be controlled in practice by adjusting pH, it is of practical significance where milk solids are heated with alkaline chemical leavening agents.

IV. COMPARISON OF THE EFFECT OF TWO SUGARS ON THE BROWNING REACTION IN CONCENTRATED MILK

A. Effect on the Rate of Browning

In a product such as sweetened condensed milk, or similar sweetened milk product, there are only two sugars which would be of any real commercial use - glucose and sucrose. Lea (63) has shown that glucose is far more rapid than lactose in its reaction with casein. Sucrose is inert and gave no brown discolouration when heated with pure casein. The purpose of this section is to confirm that Lea's conclusions apply to sweetened condensed milk and to determine the quantitative effect of sucrose and glucose on this system.

1. Experimental Method

Two systems were prepared in the following manner:-

a) Standard sweetened condensed milk of composition:
water 25%; sucrose 44%; and milk solids 31%.

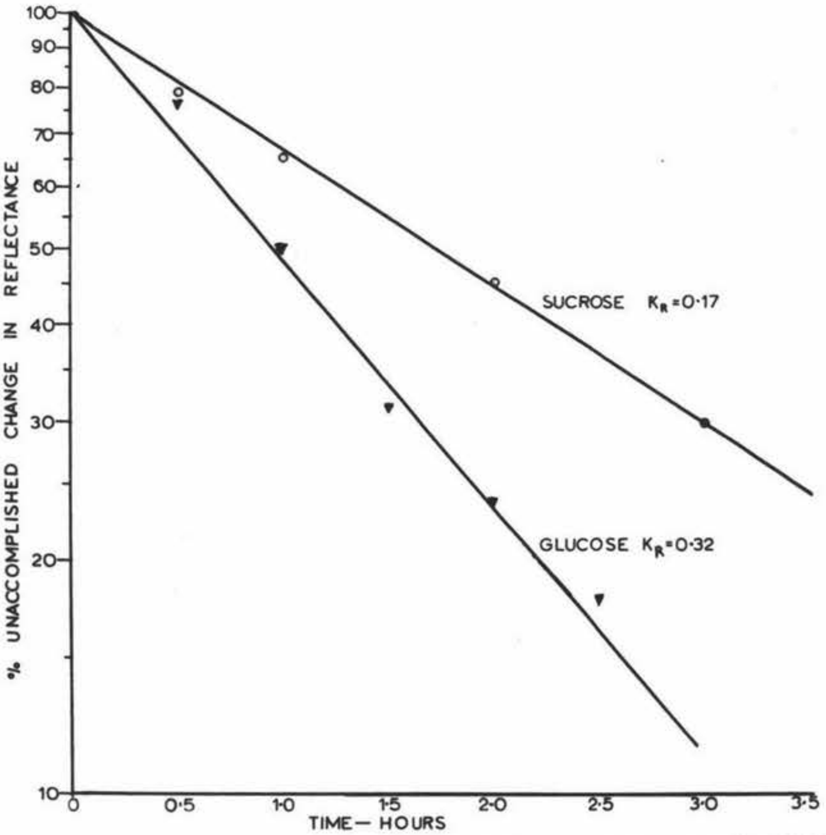


FIG. 16. COMPARISON BETWEEN THE RATES OF BROWNING OF GLUCOSE- AND SUCROSE-SWEETENED CONDENSED MILKS.

b) Sweetened condensed milk with pure glucose completely replacing the sucrose. Hence, the composition was water 25%; glucose 44%; and milk solids 31%.

Samples of both systems were placed in test-tubes and heated in a water bath at 90°C. At known time intervals, samples were removed, rapidly cooled, and the % reflectance determined by the method described in SECTION II, Part II - B, page 29.

2. Results

Results were plotted as % unaccomplished change in reflectance versus time after the manner described in SECTION II, Part II - C, page 32. These results appear in Figure 16 where the % unaccomplished change in reflectance is based upon an initial reflectance of 34% for the sucrose-sweetened system and 45% for the glucose-sweetened system.

3. Discussion and Conclusions

It is obvious from the results shown in Figure 16 that glucose and whole milk browns about twice as fast as sucrose and whole milk. This conclusion is in general agreement with the work of Lea (63).

Although glucose-sweetened condensed milk browns more rapidly than sucrose-sweetened condensed milk, the resultant caramelized product has a pronounced "malty" off-flavour which is slightly bitter. This off-flavour is quite unpalatable and it is produced even when only small amounts of glucose are substituted for sucrose. The cause of the off-flavour is not known but it is probably due to the fact that the fragmentation products resulting from glucose-casein "caramelization" are quite different from the fragmentation products of lactose-casein "caramelization". The nature of the various fragmentation and/or condensation products responsible for the various flavours is not known.

B. Rate of Solubility Decrease

Lea (63) has demonstrated in the casein-lactose system that glucose increased the loss of solubility of the protein while sucrose appears to protect the protein from insolubility - even during severe browning. The decrease in solubility of sweetened condensed milk upon browning is now compared, using glucose and sucrose as the sweetening agent.

1. Experimental Method

Two mixtures were prepared as follows:-

a) Standard sweetened condensed milk of composition:
44% sucrose; 31% milk solids; 25% water.

b) Sweetened condensed milk with glucose syrup replacing the 44% sucrose.

Samples were heated at 100°C in 301 x 409 cans for known periods and the solubility index determined according to the method described in APPENDIX II.

2. Results

Table V compares the results of the solubility index determinations. A high solubility index denotes high insolubility.

TABLE V

COMPARISON OF THE SOLUBILITY CHANGES IN SUCROSE - AND GLUCOSE-SWEETENED CONDENSED MILKS

Time of Heating at 100°C Hours	Solubility of Glucose Sample mls. of sediment	Solubility of Sucrose Sample mls. of sediment
0	0.8	0.10
1	1.1	0.2
2	2.0	0.25
3	3.0	0.3
4	4.0	0.5
5	5.0	0.8

3. Discussion and Conclusions

In agreement with the work of Lea (63), glucose promotes insolubility and sucrose inhibits insolubility of the protein during browning. This fact could be of real practical significance with respect to nutritive value and where dilution of the caramel to a soluble drink may be desired.

V. SUMMARY OF FACTORS INFLUENCING BROWNING IN SWEETENED CONDENSED MILK

The reflectance determination of colour (SECTION II, Part II - B and C, pages 29-34) was used for all studies on the factors affecting the rate of browning in sweetened condensed milk. While the accent of this section has been on obtaining basic knowledge on the effect of product and process variables on the rate of browning, results are discussed fully in the hope that the knowledge of the browning reaction in milk may become more complete. The salient conclusions are now summarized.

A. Temperature

At constant moisture and initial pH, there is a linear relationship for the Arrhenius plot of the rate, K_r, versus reciprocal of the absolute temperature. There is a temperature coefficient of 2.3 between $100^{\circ}C$ and $110^{\circ}C$.

B. Moisture Concentration

Evidence suggests that a minimum or complete absence of water maximises browning in a liquid milk solids system, provided that lactose is still soluble and available to react. The rate of browning in sweetened condensed milk doubled if the moisture content was reduced from 30% to 20%.

There is no significant increase in moisture content during the "caramelization" of sweetened condensed milk.

C. pH

The rate of browning in sweetened condensed milk increases rapidly with increasing pH from pH 5.4 to pH 9.5, and most probably continues to increase with increasing pH beyond this.

Although the pH falls during browning to a neutral pH of about 6.0, an initial pH of greater than 7.5 causes permanent damage to the flavour of the caramelized product.

D. Comparison of Sucrose and Glucose

Sucrose is inert in the browning reaction of lactose and casein. Substitution of sucrose with glucose results in a doubling of the rate of browning. Although the addition of glucose accelerates browning, its use in practice is not possible, due to the bitter end products and byproducts resulting from its reaction with casein.

Glucose promotes insolubility and sucrose inhibits insolubility of the protein during browning.

PART B

(SECTIONS IV, V, VI)

DEVELOPMENT OF NEW PRODUCTS

BY

PROMOTING BROWNING IN MILK SOLIDS

INTRODUCTION

It is well known that caramelized milk products are a very popular food eaten extensively in South America, India and Europe. On the basis of these facts, investigation of the possibility of converting commercially available milk products to caramelized forms would be a timely step towards diversifying New Zealand dairy products. Such caramelized dairy products have export possibilities as well as some potential on the home market.

Ideas for the type of caramelized product to develop arise from an appraisal of the way in which this type of product is used traditionally, and by studying the eating habits and trends of the consumer market for which the product is intended. It is from such a study that the following product types were suggested for further study and development:-

1. Sweet caramelized spread, for use in the same way as jams; i.e., spread, piefillings, cakes, etc.
2. Wafer or biscuit type of product - perhaps for use as high protein supplement in a form with which the consumer is familiar.
3. Concentrated dairy caramel flavour in the form of a powder or liquid concentrate, for addition to drinks, dilution to topping, general food flavouring of such products as ice-cream.
4. Confections - the production of caramel confections is well documented and was not studied further.

With these general types of product as a basis, it was decided to undertake a fundamental study of the factors affecting flavour, colour, and texture of selected commercially available milk products with an aim to achieving the above product types.

SECTION IV

STUDIES ON THE DEVELOPMENT

OF A

SWEETENED CARAMELIZED DAIRY SPREAD

I. INTRODUCTION

Caramelized milk products are very popular in South America and Europe. Traditional products produced domestically include 'Dulce de leche' (Argentina, Uruguay) and 'Manyar blanco' (Chile). A recipe used domestically is to add 1 Kg. of sugar to 4 litres of milk and a little sodium bicarbonate. The mixture is boiled slowly for 2 hours and constantly stirred. Vanilla flavouring is added to taste. Such a product is used as a spread on bread, as a cake filling or topping, and in the flavouring of bakery goods and ice-cream.

This product is obviously very similar to jam - a product consumed in large amounts throughout the European world. Caramelized dairy spreads are so popular that they are made domestically from sweetened condensed milk in countries where there is an absence of commercial production. In fact, a very acceptable product may be made by heating commercial sweetened condensed milk for 2 hours at 100°C. Consequently a readily available commercial sweetened condensed milk was used in the present study.

Although the method of product preparation is traditionally well established, it was considered that a study of the fundamental factors affecting flavour and texture would be essential to a successful commercial application of these variables to produce an acceptable product. With this thought in mind the basic theory of texture and caramel flavour development in sweetened condensed milk is fully discussed. From an understanding of the basis of texture and flavour development, methods of measuring changes in them may be developed. From measurements of texture, and flavour changes, an understanding of the effects, and technological significance, of product and processing variables is made possible.

It is by manipulation of product and process variables that the desired product flavour and texture is obtained. Possible commercial production methods and their effect on product characteristics and quality may be discussed on the basis of a basic understanding of the effect of product and process variables.

II. FLAVOUR DEVELOPMENT

A. Theory

The development of this distinctive dairy caramel flavour is an important consideration in the acceptance or rejection of the product. Although the chemical nature or origin of the flavour is unknown, its development is a concomitant of the browning of milk and, furthermore, the degree of caramelized flavour is correlated positively with degree of browning and related changes (83). It follows from this that a measurement of colour development is an approximate measure of flavour development. It is believed that the caramel flavour is a result of the end products and/or by-products of the browning reaction initiated by the condensation reaction of the E-amino group of lysine (in casein) with lactose, or other reducing sugar present (see SECTION I for detailed discussion). Hence, generally the factors affecting browning will similarly affect the flavour development.

1. Factors Affecting Flavour Development

The variables affecting browning and flavour development in sweetened condensed milk are well documented and discussed in SECTION III, page 41. The salient conclusions are summarized again here, but SECTION III should be consulted for a more detailed presentation and discussion of results.

a) Temperature

The rate of browning increases with increasing temperature in accordance with the Arrhenius equation. In practice, the rate of browning increases about 2.3 times for a 10°C rise in temperature between 100°C and 110°C. The higher the temperature, the more readily bitter flavours tend to develop.

b) Time

Flavour intensity increases linearly with time of heating to about 6 hrs./100°C. Beyond this, bitter flavours develop which are masked, to a greater or lesser extent, by the sweetness of the sucrose.

c) Moisture

Rate of flavour development increases rapidly with decreasing moisture content between 50% and 20% moisture.

d) pH

Any increase in pH markedly increases the rate of flavour development. Any decrease in pH markedly reduces the reaction rate.

e) Sugar

Sucrose is inert in caramel flavour development but provides the essential sweet background flavour. Replacement of sucrose with invert sugar or glucose results in a sickly sweet product. The presence of glucose causes rapid browning which is not accompanied by a pure caramel flavour, but gives rise to bitter compounds which are quite unpalatable.

f) Fat

Fat imparts a smooth rich flavour which is absent in sweetened condensed skim milk. Hence, this product is of necessity a full cream product.

2. Measurement of Flavour Development

As caramel flavour development is directly related to browning in sweetened condensed milk, colour measurement of the degree of browning would be an indirect measure of flavour development. The modified reflectance method of Burton (SECTION II, Part II - B, page 29) appears to be quite suitable for this purpose. Hence, reflectance measurement is a useful method of comparing the flavour intensity developed in samples of different time-temperature treatments.

While the objective method described above would be of real benefit in routine quality control, its usefulness may be further improved by relating reflectance measurements to a subjective flavour assessment score. Subjective assessment is very important - only by this method can the full-bodied caramel flavour of full cream sweetened condensed milk be readily distinguished from the inferior flavour of caramelized sweetened condensed skim milk.

B. Technological Applications

From the basic theoretical study (in SECTION III) of the factors affecting flavour development, the significance and manipulation of these factors to obtain an acceptable caramelized sweetened condensed milk product, on the commercial scale, may be discussed.

1. Temperature

While browning would be more rapid at high temperatures, this is not the only consideration in choosing the temperature for production. At processing temperatures above 100°C, the following factors must be considered:-

ADVANTAGES	DISADVANTAGES
1. Shorter processing time	1. Possibility of bitter compound development
2. Greater throughput per capacity of heating equipment	2. Expensive pressure processing equipment
3. Smaller factory floor space required for a given capacity	3. Less tolerance on any variation in the time of heating

A consideration of these factors suggests that atmospheric steaming (100°C) is the most suitable method of heating for small to medium scale production.

2. Time of Heating

The time required will depend on the temperature used. From subjective assessment, a flavour development equivalent to a processing of 2 hours at 100°C was considered to give a product of optimum flavour. However, it is expected that the intensity of caramel flavour considered as optimum will vary from person to person. The optimum flavour for marketing must be determined by consumer tests.

A problem arises when it is necessary to brown to a very intense caramel flavour for use as a flavouring or other special uses. While a good caramel flavour may be intensified by browning for 5 - 6 hours at 100°C, beyond this heat treatment bitter flavours tend to develop. Table VI tabulates the heat treatments which may be tolerated before there is an incidence of bitter off-flavours.

The reflectance corresponding to this bitter flavour development varies from less than 4% up to 6%.

TABLE VI

TIME TEMPERATURE REQUIREMENTS FOR THE DEVELOPMENT OF BITTERNESS

Temperature	Time of Heating Required to Develop Bitterness (Hours)
100°C	7
110°C	$2\frac{1}{2}$
120°C	1

3. pH

As the principal objective of this study is to promote browning, the addition of sodium bicarbonate, or other agent to increase the pH, would be desirable. Table VII demonstrates the flexability allowed in adjusting the pH as an aid to increase browning rate.

TABLE VII

EFFECT OF INITIAL pH ON THE FLAVOUR OF CARAMELIZED SWEETENED CONDENSED MILK

Initial pH	Final pH after heating for 3 hours at 100°C	Flavour Score
6.4	5.6	Good
7.0	5.8	Good
7.5	6.0	Good
8.0	6.0	Slight off-flavour
8.3	6.1	Marked ammoniacal off-flavour

It is obvious from Table VII that the pH should not be increased beyond about pH 7.5, as beyond this, changes occur in the protein which have undesirable effects on flavour and texture. It is pertinent to note that the final pH of the caramelized product is neutral despite a high initial pH before browning.

4. Moisture

While a decrease in moisture increases the rate of flavour development, it has more important disadvantages.

a) The less water, the greater the product costs and the greater the probability of lactose crystallization.

b) If the moisture content is reduced much below 25% the excellent spreadability and smooth texture of the product rapidly deteriorates.

Subjective assessment indicates that the optimum moisture for an acceptable product is 25 - 30%.

5. Sugar

While glucose syrup and invert syrup increase browning, they cause unacceptable changes in flavour and texture. For this reason their use in the making of the caramel spread is not recommended.

Sucrose provides an essential background flavour to the dairy caramels. Levels of 30 - 40% are recommended for caramel spread manufacture.

6. Fat

As fat is an integral part of flavour development, it is recommended that full cream milk (at least 26% milk solids as fat) solids be used.

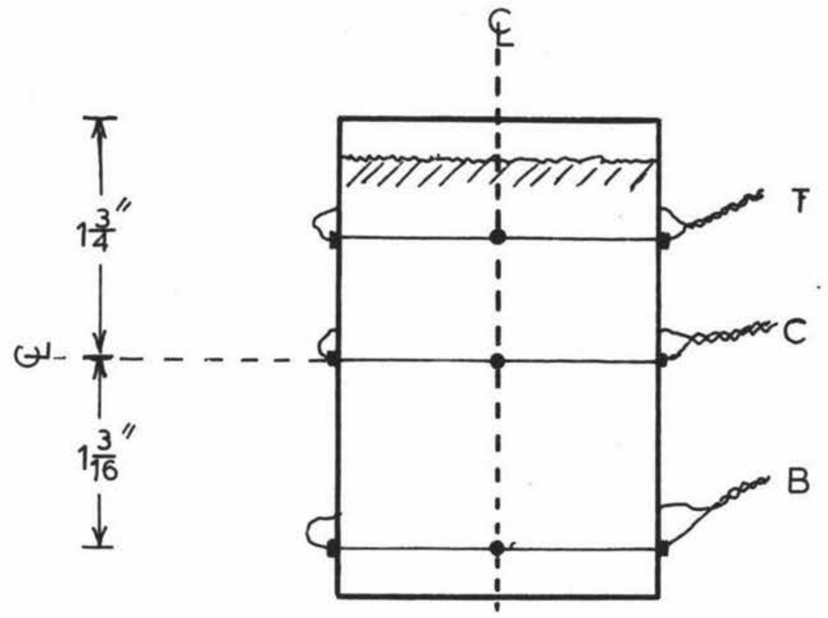


FIG. 17 PLACEMENT OF THERMOCOUPLES IN A 301 x 409 CAN

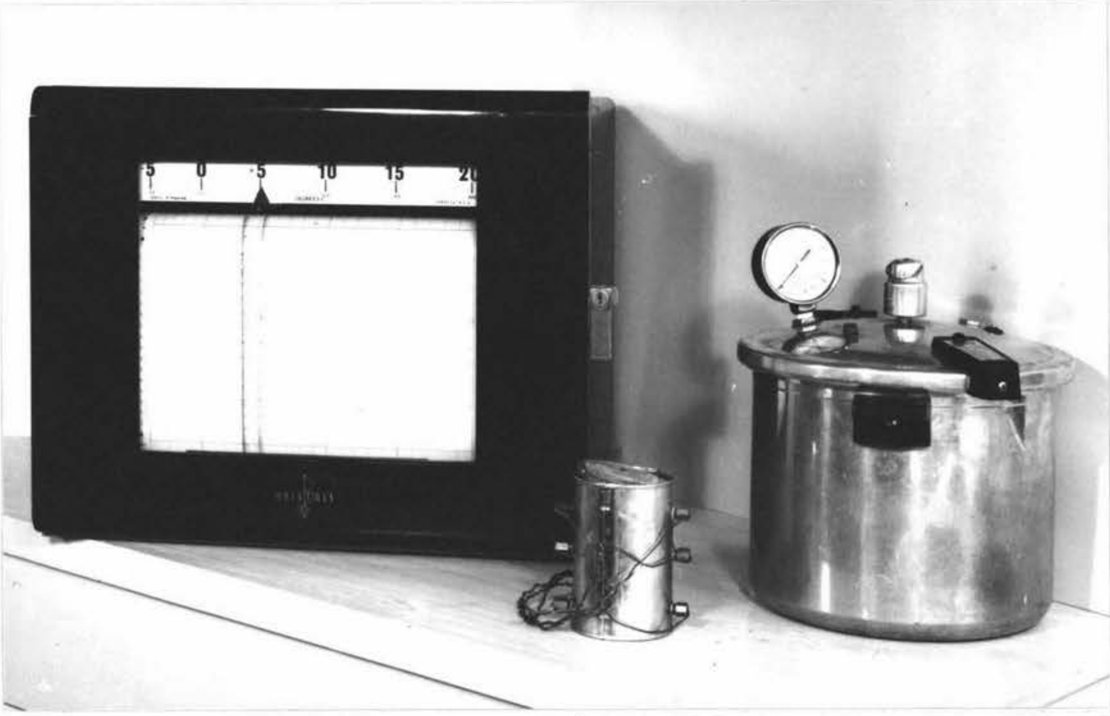


FIGURE 18. The 'BRISTOL' recorder, 301 x 409 can fitted with thermocouples, and retort which were used for heat penetration studies on sweetened condensed milk.

III. TEXTURE DEVELOPMENT

A. Theoretical Study

1. Studies Leading to a Postulated Theory for the Mechanism of Gelation in Heated Sweetened Condensed Milk

It was apparent from visual inspection that the texture of sweetened condensed milk changed, on heating at 100°C for 2 hours, from the viscous flow texture characteristic of fresh sweetened condensed milk to a smooth, spreadable gel texture. It would have appeared at first glance that the mechanism was very similar to the sugar-pectin gelation of most jams. However, while sugar-pectin gels only occur on cooling after heating, the sweetened condensed milk system had already gelled when the can was opened immediately after heating for 2 hours at 100°C.

If there is a large change in texture from a viscous liquid to a gel within a can of sweetened condensed milk, it logically follows that there will be some change in the rate of heating of the can. To determine the temperature at which this change in texture occurred, heat penetration data was obtained by the method described below. The significance of the results obtained are discussed with reference to the literature and a postulated theory is presented to explain the cause of the thickening or gelation.

a) Experimental Method

A 301 x 409 can was fitted with thermocouples positioned as shown in Figure 17. The can was then filled with sweetened condensed milk and sealed. The thermocouples were connected to a 'BRISTOL' temperature recorder which recorded the T, C and B temperatures as well as the steam temperature within the pressure cooker (retort). The can, fitted with thermocouples, was then heated at the desired

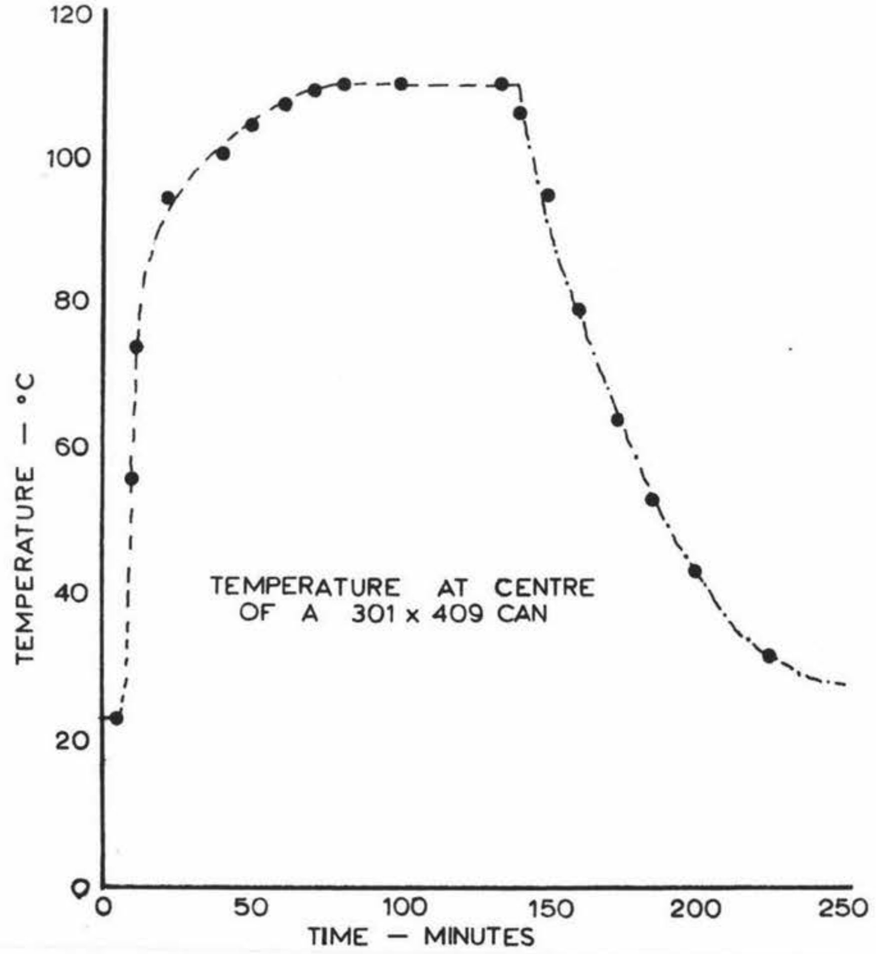


FIG.19. HEATING AND COOLING CURVE FOR CANNED SWEETENED CONDENSED MILK

retort temperature. A continuous record of the changing temperatures within the can was kept by the 'BRISTOL' recorder. Figure 18 portrays the type of equipment used.

b) Plotting of Results

The curve in Figure 19 typifies the shape of the heating and cooling curves obtained when temperature is plotted as a function of time on rectangular co-ordinate paper.

A conventional plot of time-temperature heat penetration data on semilogarithmic graph paper yields a straight line described by two parameters fh and j (56). The majority of heating curves when conventionally plotted yield a straight line which may be described by the equation

$$\log (RT - T) = - {}^{t}/_{fh} + \log j\,(RT - IT)$$

Where the come-up-time of the retort is very rapid (1 - 3 minutes), j tends to 1.0, and the equation now becomes (56) -

$$\log \frac{RT - T}{RT - IT} = - {}^{t}/_{fh}$$

where RT = Retort temperature

IT = Initial product temperature in the can

T = product temperature in the can at time t

t = time of heating of the can

fh = heating rate

For a given "run" at constant retort temperature, RT - IT is constant. Hence, by plotting the conventional plot of

$$\log RT - T \quad \text{vs.} \quad t$$

the heating rate within the can, fh, is simply derived by determining the slope of the curve.

While the majority of cooling curves, when plotted on semilogarithmic paper, can be represented by a straight line, there are products which have a heating or cooling curve where the initially straight line abruptly changes slope or "breaks". Such a curve requires two straight lines to represent these data and is called a broken heating curve. Such curves are illustrated in Figures 20, 21, and 22, on pages 87, 88, and 89. Broken heating curves are usually due to the nature or consistency of the product. For instance, in "cream style" corn the heating rate, fh, is initially quite rapid due to a predominance of convection heating. After the gelation temperature of the starch has been reached, a gel forms and the slower conduction heating results. A similar change in texture is believed to be the cause of the broken heating curve of sweetened condensed milk.

c) Discussion of Results

A conventional plot of time-temperature heat penetration data appears in Figures 20, 21, and 22, for the retort temperatures of 100°C, 110°C, 120°C. The obvious broken heating curve represents a sudden change in the heating rate of the can contents. Under the steady state conditions of heating that prevailed, this sudden change in the rate of heating could only be caused by a change in state of the can contents, with a resultant change in thermal conductivity or mode of heating. Such a change in state is most probably due to the gelation of the viscous liquid. Before the break in the curve, convection heating predominated

SECTION IV

STUDIES ON THE DEVELOPMENT

OF A

SWEETENED CARAMELIZED DAIRY SPREAD

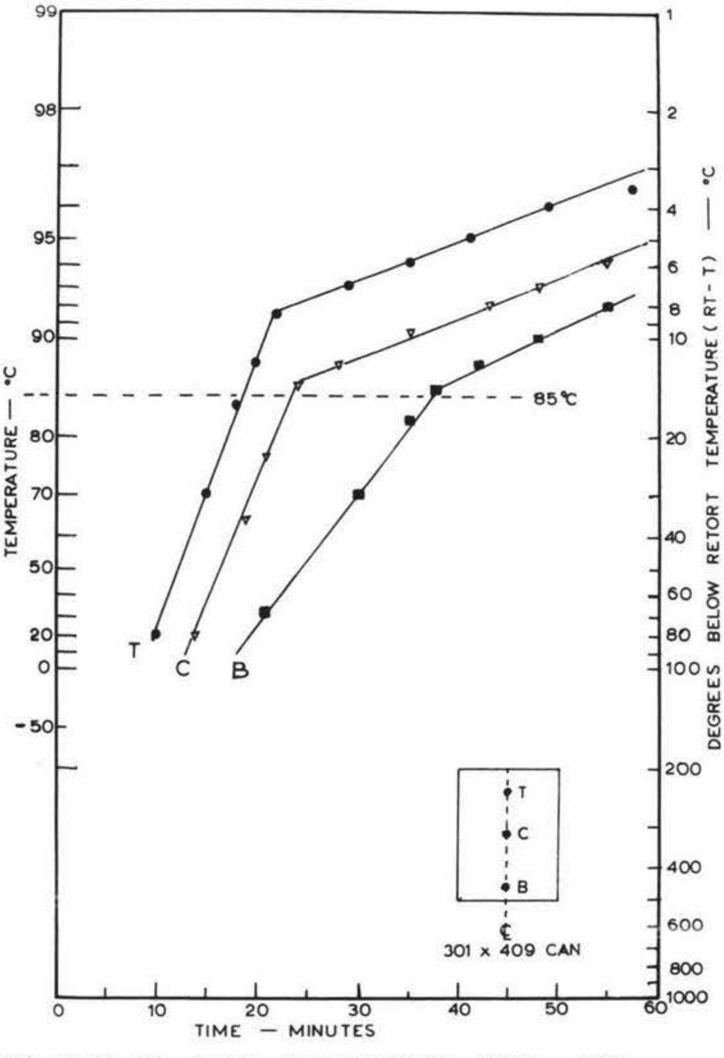


FIG. 20. PLOT OF HEAT PENETRATION DATA FOR SWEETENED CONDENSED MILK RETORTED AT 100°C

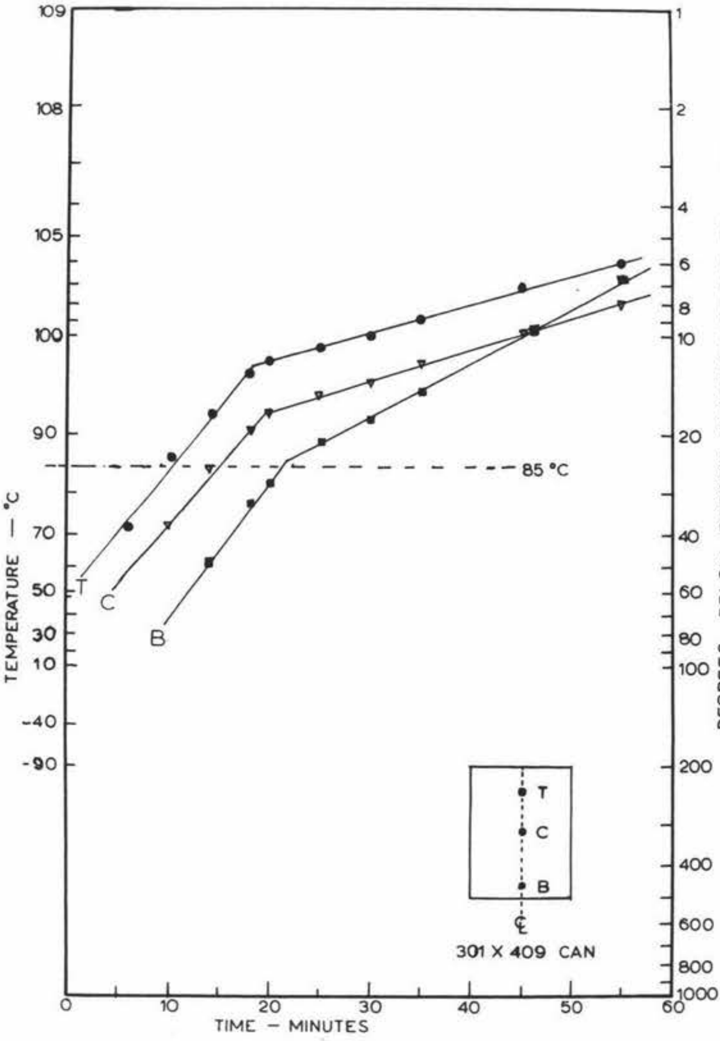


FIG. 21. PLOT OF HEAT PENETRATION DATA FOR SWEETENED CONDENSED MILK RETORTED AT 110°C

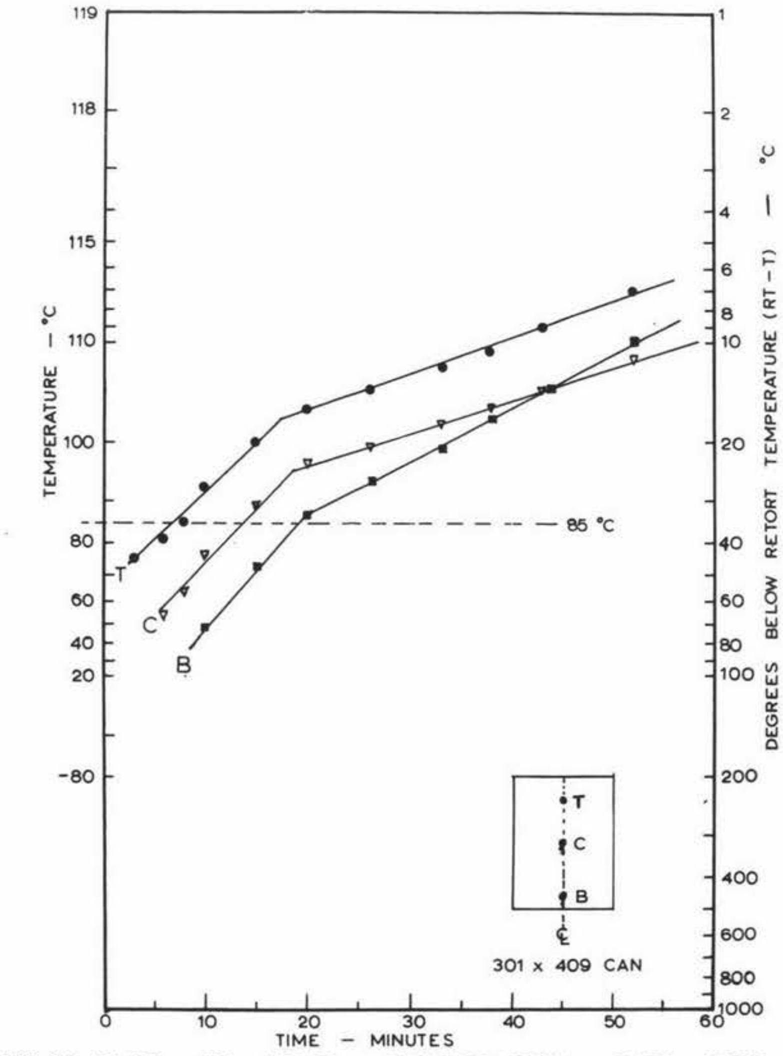
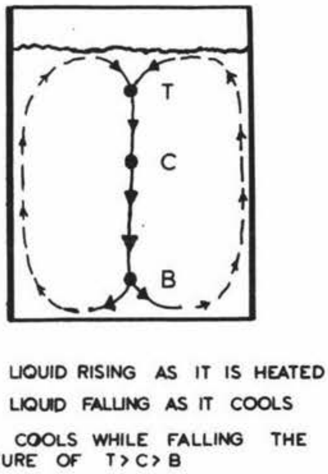


FIG. 22. PLOT OF HEAT PENETRATION DATA FOR SWEETENED CONDENSED MILK RETORTED AT 120 °C

as $T > C > B$. This indicates that the typical convection circulation of a viscous liquid was occurring. Refer to Figure 23.



AS THE LIQUID COOLS WHILE FALLING THE TEMPERATURE OF $T > C > B$

FIG.23. CLASSICAL CONVECTION CIRCULATION OF A LIQUID WITHIN A HEATED CAN

After the break in the curve, conduction heating predominated as:-

1. heating rate, fh, was markedly reduced;
2. both T & $B > C$, indicating that convection circulation of the liquid had ceased.

Furthermore, the change in state occurs rapidly as is indicated by:-

1. the sharp break in the curve;
2. visual appraisal of the change in consistency (from a viscous to a gel texture) of the sweetened condensed milk after opening cans immediately prior to, and after the change in state indicated by the heating curve.

Figures 20, 21, and 22, show that the change in state occurred at varying times of heating, depending on the retort temperature, but in all cases a product temperature of 85°C was reached before the change in

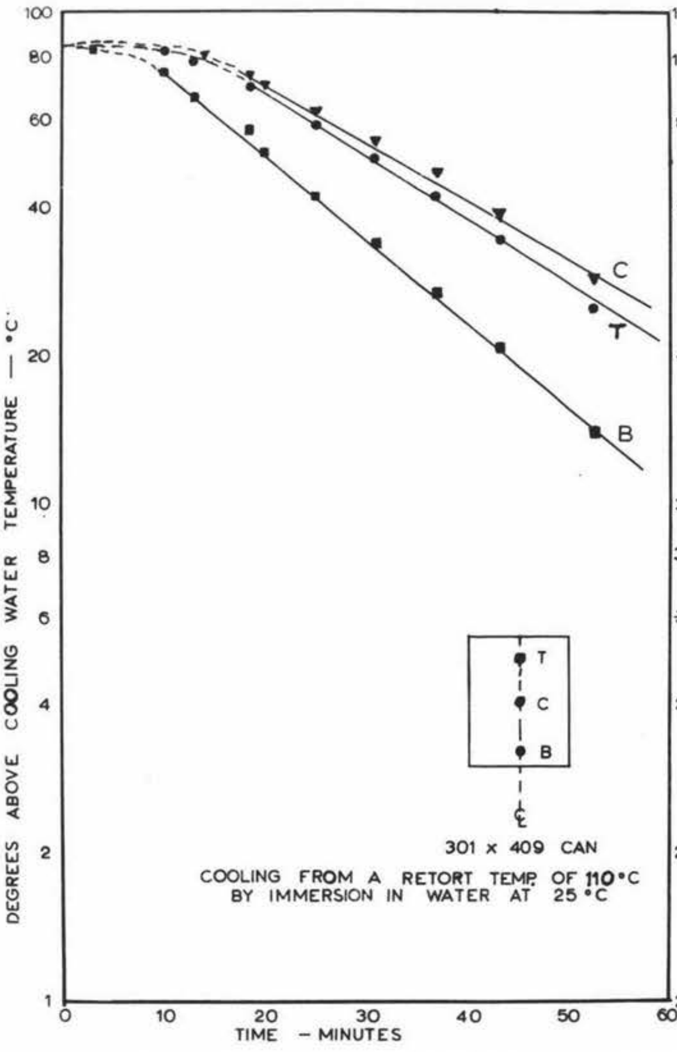


FIG. 24. CONVENTIONAL PLOT OF COOLING DATA FOR SWEETENED CONDENSED MILK

state occurred. From this it was concluded that when the product has been heated to at least 85°C, gelation occurred, and any further heating occurred at a slower rate by simple heat conduction through the can and product.

No change in state occurred during cooling as indicated by the unbroken cooling curve; see Figure 24.

d) Postulated Theory of the Cause of Gelation

On the basis of this experimental evidence, a tentative explanation of the gelation of heated sweetened condensed milk is possible. The above evidence supports the theory that at 85°C/20 mins., κ-casein and β-lactoglobulin interact completely to give a complex of lower electrophoretic mobility, which may be due to an increase in molecular size or change in molecular configuration (48). It is suggested here that this complex formation, as manifested in sweetened condensed milk, is the major cause of the marked change in consistency from a liquid to a gel texture. Complete knowledge of what happens to the protein molecule during gelation and the part that acids, salts, and sugars have in this process, is lacking (74). Coagulation of casein is ruled out as it takes 12 hours at 100°C for denaturation to occur (107). The complexing of the κ-casein and the β-lactoglobulin could quite likely form a three dimensional network. Sucrose and water could fill the intervening spaces and thus impart the observed plastic consistency to the gel structure.

2. Measurement of Gel Texture

On the basis of the classification system for food texture pro-

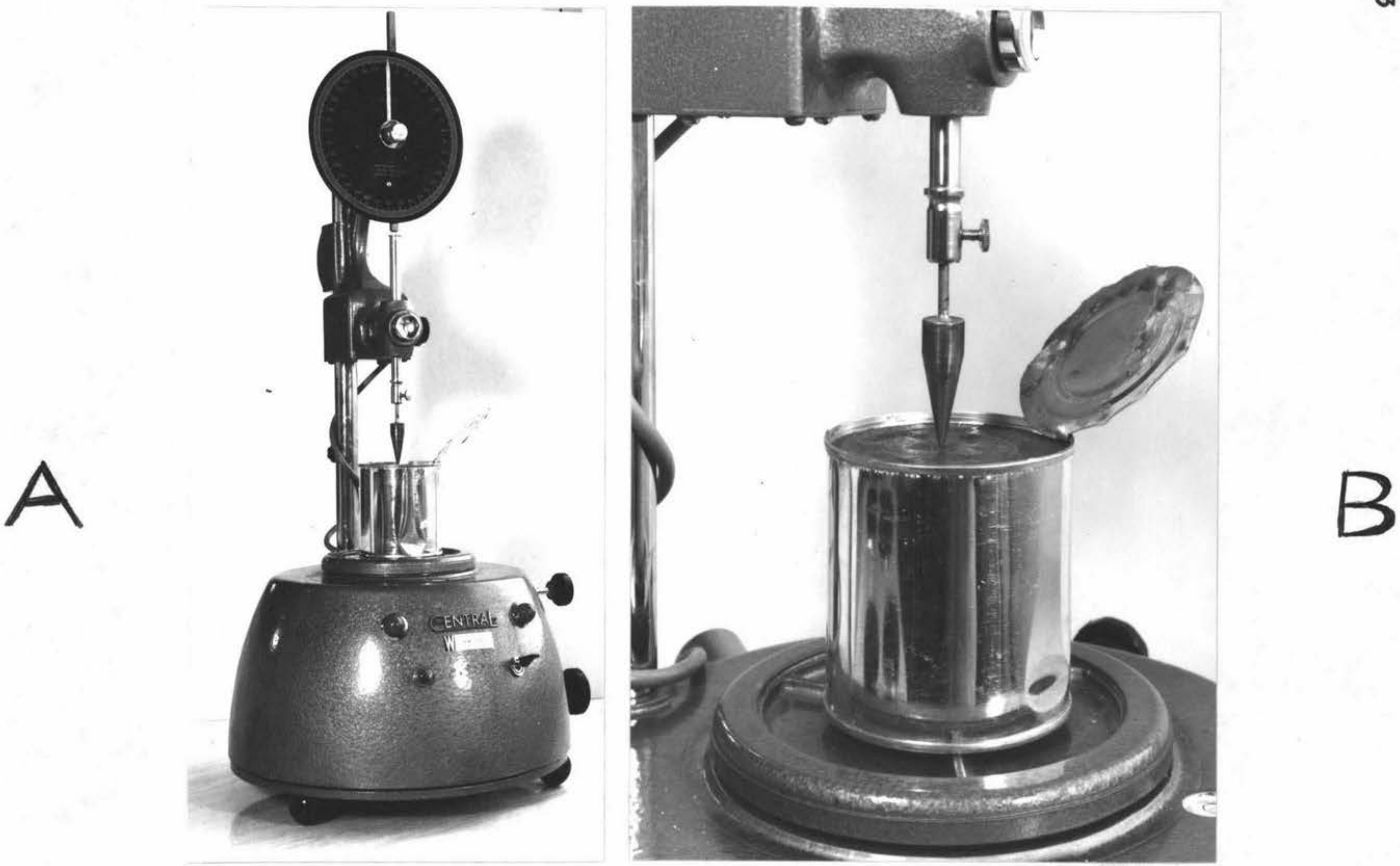


FIGURE 25. 'CENTRAL' penetrometer model used for the determination of the gel strength of caramelized sweetened condensed milk. Both the complete unit (left) and a closer view of the type of plunger used (right) are shown.

posed by Matz (75), the caramelized sweetened condensed milk is a gel; i.e., the predominant influence on texture is a two phase colloidal system with a high degree of interface between a continuous, or at least intermeshed, system of solid material holding an aqueous phase which may also be continuous or finely dispersed. A certain degree of structural rigidity is contributed by the extended skeleton of the protein continuous phase so that the system as a whole possesses many properties of a solid; e.g., rigidity, and elastic response to applied distorting surfaces.

It is these properties of the gel which are the key to an objective measurement of gel properties. A detailed review of methods for determining jelly properties can be found in Joseph and Baier (58). For the system under discussion, the most convenient method appears to be the measurement of the resistance offered by the gel to penetration by plunger, probe, or paddle. An empirical method of measurement based on this principle is described below.

a) Equipment

Equipment used was the commercially available 'CENTRAL' penepeneter model shown in Figure 25 A and B. The plunger used was a custom-made stainless steel cone of dimensions shown in Figure 26, page 95.

b) Preparation of Sample and Method of Operating Equipment

i) A sample of the spread to be tested was equilibrated at 30°C.

ii) The surface of the sample was then scraped until a fresh surface was exposed.

iii) The plunger was fitted to the 'CENTRAL' machine; and then allowed to just come in contact with the surface of the gel.

iv) Button at left (Figure 25 A) was then pressed, allowing the plunger

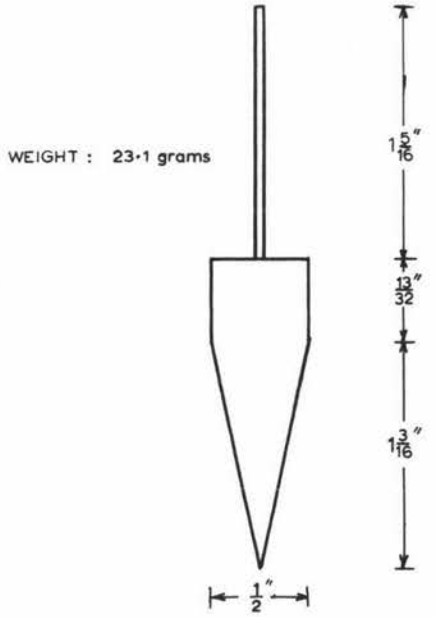


FIG. 26. DIMENSIONS OF THE CONE-SHAPED PLUNGER FITTING FOR THE "CENTRAL" PENETROMETER

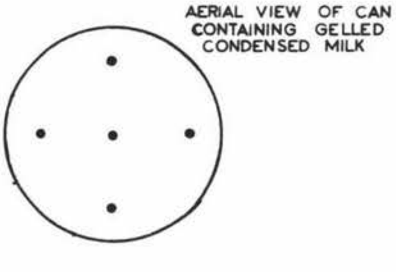


FIG. 27. DISTRIBUTION OF THE POINTS AT WHICH THE PENETROMETER READINGS WERE DETERMINED

to fall freely under gravity for an automatically determined time of 5 seconds.

v) The objective index of texture was then obtained by turning the pointer until its attached rod just came into contact with the top of the plunger attachment. Readings were obtained by reading directly from the scale of the penetration depth.

vi) This procedure was repeated until five measurements were obtained at different points on the gel surface, according to the pattern shown in Figure 27. The measurement had to be taken at least ½" from the side of the can to prevent the side of the can from interfering with the measurement.

vii) The mean of the five readings was taken. Any given reading must not vary more than ± 15 units from the mean if the reading is to be accepted as a valid index of the texture of the bulk spread.

c) Test of the Method

Cans of sweetened condensed milk were heated for known time intervals and the gel strength determined by the penetrometer method described above.

Results of time of heating versus penetrometer reading are plotted in Figure 28, page 97.

It is apparent from this graph that no appreciable gelation occurs until 40 mins./100°C. At this point, a marked "Knee" occurs in the curve and the rate of gelation falls off at about 3 hours/100°C, whereupon little further increase in rigidity of the gel occurs. The "knee" in the curve coincides with a completion of the change in state of the can contents as indicated by the heat penetration curve. Refer to Figure 20, page 87.

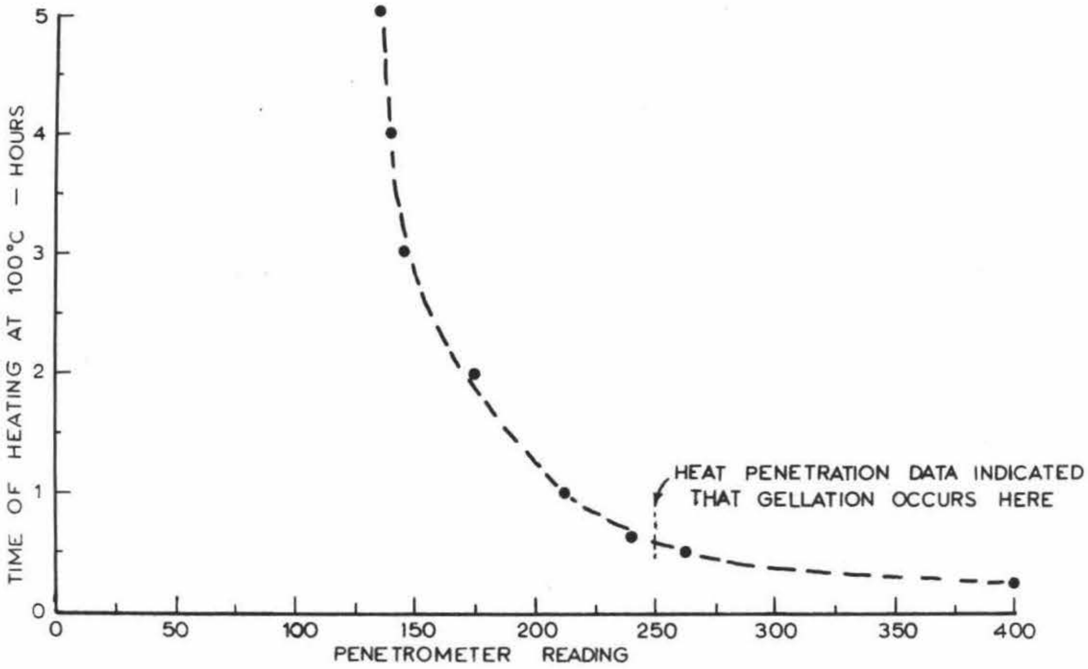


FIG.28. CHANGES IN GEL STRENGTH (P.R.) OF SWEETENED CONDENSED MILK RETORTED AT 100°C IN A 301 x 409 CAN

Table VIII shows that the objective measurement of gelation is also correlated with subjective assessment of spreadability.

TABLE VIII

RELATIONSHIP BETWEEN OBJECTIVE AND SUBJECTIVE ASSESSMENT OF SPREADABILITY

Penetrometer Reading	Subjective Spreadability Assessment
>200	too thin
160-200	good
<160	too thick

d) Conclusions

It may be considered that this method:-

i) does measure the change in state occurring during heating;

ii) provides an objective measure of spreadability.

3. Factors Affecting Gel Structure Development

From a knowledge of the factors affecting the formation and nature of the gel, the product and process variables may be manipulated to yield the desired texture. It was for this reason that the effect of several variables was studied.

a) Time-temperature

At a given temperature, the rigidity of the gel texture increases with time of heating (Figure 28) until a stage is reached where the gel becomes too rigid for convenient spreading. Subjective assessment indicated that the time required to reach this "too thick" or "too rigid" stage decreases with increasing temperature of heating.

b) Aeration

Aeration during gel formation disrupted the gel structure, and yielded a grainy, viscous texture which had a penetrometer reading of >600.

Aeration before gel formation resulted in a semi-porous frothy texture which increased in density towards the bottom of the can; i.e., a non-uniform product resulted which was considered to be unsuitable for a a consumer market.

c) Agitation

Agitation during gel formation is most probably the cause of the effect observed when the product is aerated. A grainy, viscous liquid results which tends to be free flowing; i.e., it has lost its gel properties. This is presumably due to a continuous breakdown of the gel structure as it forms.

d) Sugar

The adverse effect of glucose and invert sugar on caramel flavour development made any further study on the effect of these sugars on gel texture of academic interest only.

e) Solids Concentration

Table IX demonstrates that, for a standard process time, with increasing moisture content there is a decrease in gel strength.

e) Fat

Fat was an integral part of the smooth texture, and hence, full cream milk was used.

TABLE IX

THE EFFECT OF MOISTURE CONTENT ON GEL STRENGTH OF SWEETENED CONDENSED MILK AFTER 2 HOURS HEATING / 100°C

Moisture Content %	Gel Strength (Penetrometer Reading)
25	150 - 160
30	200
35	240
40	>600

B. Technological Applications

From the basic study of the theory and factors affecting gel formation, the manipulation of process variables to obtain the desired texture may be discussed.

1. Time - temperature

The optimum time of heating at any given temperature should be such as to give a product of Penetrometer Reading 160 - 200. This was the P.R. found to correspond to the optimum texture as evaluated subjectively. At 100°C this degree of gelation is accomplished by 2 hours heating.

2. Agitation

Even with gentle stirring, the gel structure, typical of sweetened condensed milk heated in the can, is broken, and a grainy, lumpy, texture results. To eliminate the grainy, lumpy appearance, the product may be homogenized to a thick, viscous, free-flowing dairy caramel syrup. A gel texture is completely absent in this type of product and its use as a spread is limited. However, it may be used as a free-flowing caramel concentrate for use in jam spreads, toppings, ice-cream flavouring, etc.

3. Fat

Full cream milk is a necessity if the smooth spread characteristics of the gel is to be maintained.

4. Moisture Content

Any reduction in moisture content of either the gelled product or the viscous liquid form (produced by agitation during heating) would increase the problem of "graining" or crystallization of lactose. Hence, a moisture content below 25% is to be avoided in practice.

Increasing the moisture content decreases the strength of the gel. A moisture content of 25 - 30% yields an optimum gel texture of Penetrometer Reading 160 - 200 after 2 hours heating at 100°C.

IV. POSSIBLE COMMERCIAL PRODUCTION METHODS

Having discussed the factors affecting the laboratory production of a dairy caramel spread having acceptable flavour and texture, it is now possible to discuss and compare possible commercial production methods. Whatever the method used, the aim is to develop an acceptable caramel flavour by heating sweetened condensed milk to the equivalent heat treatment of 2 hours at 100°C. Although flavour development is an important consideration, attention must also be given to the effect of the production method on the texture of the finished product. In heating any food product, there are two possible methods (56).

1. Heating the food in the container; and
2. heating the food in a heat exchanger prior to filling the product into the container.

In the present discussion, the food is sweetened condensed milk and the purpose of heating it is primarily to develop caramel flavour, and secondarily a gel texture. An important result of the heating process is pasteurization of the milk. The high solids content (75%) prevents the growth of spoilage bacteria not destroyed by pasteurization treatment. Any moulds or yeasts which may grow at this level of solids are quickly destroyed at the temperatures of 90 - 100°C used to caramelize the sweetened condensed milk.

The suitability of two methods of heating (to develop flavour and texture) are now discussed on the basis of previous studies on the effects of product and process variables.

A. Caramelization in the Packaging Container

Basically this method entails filling sweetened condensed milk into the container to be used for marketing - either a can or glass container. The can is then given the heat treatment necessary to yield the desired caramel flavour. Heating of food products in containers is, in general, a slow and inefficient process compared with heating in a heat exchanger. However, the problems encountered in manipulating some types of foods such as asparagus or pickles, and the inability to pump other types of food products through heat exchangers due to their physical consistency, are reasons why most foods are sterilized in the container after packaging. In the case of sweetened condensed milk, any agitation during heating disrupts or prevents gel formation and the unique gel texture, which is excellent for a spread, is destroyed. The only way to evenly heat such a product without agitation is in the can. The heat treatment and other factors required to uniformly develop optimum flavour and texture in the can contents is now discussed.

1. Effect on Flavour

Table X expresses the nature of % reflectance changes of sweetened condensed milk retorted in a 214 x 301 can at 100°C.

TABLE X

REFLECTANCE CHANGES OF SWEETENED CONDENSED MILK RETORTED AT 100°C IN A 214 x 301 CAN

Time of Heating @ 100°C Hours	% Reflectance Using "EEL" Filter No. 601
0	34
1	20
2	11
3	9
4	7
5	6

Subjective assessment indicated that from 2 to 3 hours heating at 100°C yielded the optimum dairy caramel flavour. This may be objectively specified as a % reflectance of 9 to 11 when using "EEL" Filter No. 601. The relationship between time of heating and optimum caramel flavour development for can sizes other than the one listed could be readily determined.

Uniformity of heat treatment throughout the can is very necessary if a uniform product is to obtained. Fortunately cans as large as the 301 x 409 showed a remarkable uniformity of browning throughout the can after 3 hours of heating at 100°C. A slight variation in browning occurred from centre (light) to the outside (darker) of the can when a higher retort temperature of 120°C was used. The explanation of these observations is as follows.

a) At a retort temperature of 100°C the product slowly heated by convection to 85 - 95°C before gelation occurred. After gelation, conduction heating predominated and the product near the outside of the can quickly reached 100°C. However, since the difference between the centre temperature and the can wall temperature was comparatively small for the last 2 hours of the 3-hour heating cycle, there was no more than 1% difference in % reflectance between the product at the wall, and the product at the centre, of the can. Such a small difference in % reflectance was not visible visually.

b) At a retort temperature of 120°C, the product reached 85°C more rapidly, and convection heating stopped before the can contents had a uniform temperature distribution. Hence, at the advent of conduction heating, the product nearest the wall rapidly reached about 120°C while the centre product was only at 100°C. From Figure 10, page 46, it is apparent that browning occurred seven times as fast at 120°C, as compared with 100°C. As this differential in the rate of browning persisted for 20 minutes of a 60-minute processing cycle (Figure 22, page 89) it was not surprising that there was a visual variation in colour from the outside to the centre of the can. This problem of non-uniform browning throughout the can will increase with:-

i) increasing can size

ii) increasing retort temperature

This means that for small can sizes up to 301 x 409, there is little problem of uneven browning even at a retort temperature of 120°C. However, for large cans, the temperature of the centre will lag well behind the wall temperature. This problem could be minimized by slowly heating to 85°C by convection heating so that the whole can contents are uniformly heated to 85 - 95°C. Hence, at the advent of conduction heating, after gelation, there is little temperature difference between the centre and wall of the can if the retort temperature is as low as 100°C (or slightly less). At the start of conduction heating, the walls are at 100°C while the centre is at about 90°C and this differential is reduced to an insignificant 5°C within a few minutes. This technique of using a low retort temperature could possibly be used to uniformly brown sweetened condensed milk in an A10 can for use as a caterers pack.

While the A10 can must be heated at 100°C the smaller cans may be retorted at higher temperatures. A comparison of the rates of browning at various temperatures appears on Figure 10, page 46. However, there is no real substitute for processing trials which determine the time required at a given retort temperature to achieve optimum caramel development; i.e., 9 - 11% reflectance.

2. Effect on Texture

The gel texture which results when sweetened condensed milk is "caramelized" is an important factor in the popularity and acceptance of the product as a spread. This phenomena of gelation is also a very important consideration in processing so that the can contents are evenly heated (i.e., caramelized). At the advent of gelation, convection heating ceases and the slower conduction heating results. It is this change from convection to conduction heating which is largely responsible for the previous consideration of non-uniform browning throughout the can.

It is now well established that the product must be heated to 85°C before gelation will occur. The relationship between increasing gel strength and time of heating in a 214 x 301 can at a retort temperature of 100°C has been well documented in Figure 28, page 97. Subjective assessment of spreadability on bread, indicated that a Penetrometer Reading (P.R.) of 160 to 200 corresponded to optimum spreadability. From Figure 28, it is apparent that this texture is obtained by 2 - 3 hours retorting at 100°C in the 214 x 301 can. This time of heating fortunately corresponds with a concurrent optimum flavour development. Two to three hours heating in the larger 301 x 409 can at 100°C also yields a product of optimum flavour and texture.

The relationship between time of heating and texture for other can sizes could be readily determined by similar techniques to that described on page 96.

To summarize, this method of dairy caramel production has been well documented by present studies using a laboratory scale retort.

Furthermore, this method of production has been shown to yield a product of good texture and flavour by retorting at 100°C for 2 hours in a 301 x 214 or 301 x 409 can. As the recommended retort temperature is only 100°C, either glass or metal containers could be used. A screw-top glass container is recommended for marketing as the product surface dried out and crystallized into a hard cake when a can was opened and left to stand for a few days.

B. Caramelization Before Packaging

It is much easier to heat a food product that can be pumped through a heat exchanger than to heat it after it has been sealed in a container. Under a given set of conditions the rate of heating a product depends upon the distance the heat has to flow (rate of heat flow varies inversely with the square of the thickness) and the degree of agitation or mixing. In heat exchangers, the distance heat must flow is small, and the rate of fluid flow of both the heating medium and product are as high as economical pumping will permit, since short heat flow distances and high velocities produce the highest heat transfer rates. The chief limiting factor is that the product must be of such consistency that it can be pumped through the heat exchanger. Common types of heat exchangers are:-

1. The tubular heat exchanger (round or flattened tubes are used and the product normally flows through the tubes and the heating medium surrounds the tubes).
2. Plate heat exchangers - a series of plates are built up with appropriate openings and gaskets so that the heating medium is on one side of the plate and the product is on the other side.

3. Scraped-surface heat exchangers are in reality large diameter tubular heat exchangers in which there is a mechanical scraping device to help agitate the product and keep the product next to the wall continuously scraped away from the wall and mixed with the remainder of the product. Scraped surface heat exchangers have very large heat transfer coefficients. They are mainly used for difficult materials which are very viscous and tend to foul other types of heat exchangers (56).

   Another type of scraped surface heat exchanger which has a smaller heat transfer coefficient is a steam-jacketed pan fitted with a double action stirrer.

Sweetened condensed milk is a viscous food which may be pumped at room temperature. However, it tends to gel when heated to temperatures greater than 85°C. This gelled form of sweetened condensed milk tends to cling to the side of the pipe when it is pumped through the pipe under viscous (Newtonian) flow. Hence the product tends to "burn-on" to the side of the pipe, reduce the heat transfer, and thus cause uneven heating of the product. Because of this property of heated sweetened condensed milk, the only type of heat exchanger suitable for efficiently heating the product is a scraped-surface heat exchanger.

Initial experiments to determine the effect of continual agitation during heating were conducted in a stainless steel beaker fitted with a motor-driven low speed scraping agitator. Fat or boiling water was used as the external heating medium for the beaker. These experiments indicated that the product prepared by this method differed widely in textural characteristics from the product prepared by heating in the can. The changes in flavour and texture as a result of heating the product in a scraped-surface heat exchanger are now discussed.

1. Effect on Flavour

The time-temperature effect of heat on flavour development is well documented in the basic studies of SECTION III, page 43. The most desirable flavour was obtained by heating for 2 to 3 hours at 100°C. This corresponds to an objective index of 9 - 12% reflectance. The time required to achieve the same flavour at higher temperatures may be derived from Figure 10, page 46; and Figure 9, page 44. Generally, there is no difference in flavour produced by this method when compared with the flavour resulting from heating in the can.

2. Effect on Texture

One of the most important physical factors affecting gel texture formation is stirring or agitation. As previously discussed on page 99, even gentle agitation of sweetened condensed milk during heating either prevents the gel texture from forming or breaks up any gel that does form. The result is a caramelized product having a grainy, lumpy appearance. As such a product is unacceptable, it was homogenized to yield a thick, viscous liquid which flowed freely. While such a product is unsuitable as a caramel spread it may well be used as a dairy caramel concentrate for flavouring purposes. The free-flowing nature of such a product facilitates handling by pumps and easy filling into any type of container which can be pasteurized. This type of production has the advantages of bulk processing and packaging. Packaging in any container such as glass, metal or films is possible so long as the packaging material can tolerate being filled at pasteurizing temperatures.

Left: Typical gel products obtained from heating sweetened condensed milk (far left) in the can for 1, 2, 3, 4, and 5 hours at 100°C.

Right: Viscous liquid formed by heating sweetened condensed milk in bulk (with stirring) for 3 hours at 100°C.

FIGURE 29. The two basic caramel products - gel spread and viscous liquid.

C. Possible Commercial Product Types

The product (formed by heating standard sweetened condensed milk in the can) has a texture and flavour which makes an excellent spread. There is a host of possibilities of varying and improving the flavour of such a product. Some of the possibilities which have been explored, are discussed below.

1. Vanilla at low levels of 0.1 - 0.2% adds a pleasing background flavour which enhances the basic dairy caramel flavour.
2. Spices such as cinnamon, mace, and cloves, at low concentrates may appeal to some palates.
3. There are numerous possibilities of modifying the flavour by adding fruit pulp (jam) or flavouring essences.

The thick viscous dairy caramel base formed by heating in bulk, is not ideally suited for use as a spread. This type of product could be flavoured in any of the methods described above. The addition of jam or similar additive would thicken the product to a spread consistency. The caramel base could be used as jam in cake fillings, ice-cream flavouring, and cake toppings. The basic caramel flavour could be favourably incorporated into many desserts.

Figure 29, page 110, demonstrates the basic characteristic product types discussed in this section. It is from these basic product types that a host of variations in flavour and texture is possible. Hence, this allows some latitude in developing a "tailor-made" product to comply with given market specifications.

V. STUDIES ON THE CHANGES OCCURRING DURING STORAGE OF CARAMELIZED SWEETENED CONDENSED MILK

A. Introduction

The successful marketing of any food product depends on the customer receiving the product in the same condition that it passed factory quality control standards. To determine the changes occurring in the product during storage and transit, the product must undergo storage trials. These storage trials are a crucial part of the final steps in developing a new product for marketing, and the product must not be marketed until its behaviour under expected storage conditions has been evaluated. Consequently the next logical step in the study of caramelized sweetened condensed milk was to investigate the changes which occurred in the product during storage.

Early observations indicated that caramelized sweetened condensed milk (3 hours/100°C) developed large lactose crystals after 10 week storage at ambient temperatures (about 20°C). Although these crystals could be readily "crunched" between the teeth they detracted from the pleasant smooth gel texture, characteristic of the freshly prepared product. The cause of this crystallization is believed to be explained by the following facts.

1. During the manufacture of sweetened condensed milk, the supersaturated solution of lactose formed is seeded with crushed lactose crystals. The seeding precipitates the crystallization of the supersaturated solution of lactose into numerous microscopic crystals which are unable to be detected by the sensory organs of the mouth (i.e., crystal size is less than 50 microns). This is the reason for the apparent absence of lactose crystals when commercial sweetened condensed milk is tasted.

2. When the sweetened condensed milk is heated from about 20°C to 100°C for the purpose of caramelizing it, the solubility of lactose increases from 20 gm. per 100 gm. of water to 160 gm. per 100 gm. of water (110). This marked increase in solubility results in a redissolving of the microscopic lactose crystals.

3. Upon cooling of the caramelized condensed milk, the solution (gel) again becomes supersaturated with lactose as the solubility is reduced from 160 gm./100 gm. water to 20 gm./100 gm. water. At the first opportunity this lactose crystallizes. Crystallization may be precipitated by factors such as:-
    a) seeding (heterogeneous nucleation)
    b) homogeneous nucleation due to the critical supersolubility limit being reached
    c) heterogeneous nucleation by minute inclusions

    In the case of slow cooling of a supersaturated solution, homogeneous nucleation occurs and a few nuclei form. Subsequently, these few crystals grow as lactose precipitates from the supersaturated solution. In the final stages of growth these crystals become large enough to be a very important factor affecting the textural changes occurring during storage.

Lowe (74) has reviewed the factors affecting sugar crystallization in super-saturated solutions. The principal factors which could be altered to inhibit the formation of large crystals are:-

1. Temperature of storage. Low temperatures increase supersaturation and favour crystallization.
2. Mixture of sugars. Crystallization of a mixture of sugars is slower

than that of a single sugar.

3. Concentration of sugar.

These factors are capable of manipulation in an attempt to control crystallization of caramelized sweetened condensed milk which has been processed in the can.

Dairy caramel produced in bulk by heating before canning shows no large crystals. The possibility of agitation during crystallization and the practice of seeding ensure that only microscopic crystals form. Hence the problem resolves itself into a study of the possibilities of preventing the formation of large lactose crystals in dairy caramel formed by heating in the can.

B. Experimental Method

To overcome the problem of lactose crystallization in sweetened condensed milk heated in the can, some of the standard methods of inhibiting crystallization used by confectionary manufacturers were tried. The methods used were:-

1. adjustment of the solids concentration.
2. partial substitution of the sucrose solids with other sugars such as invert sugar and glucose.
3. temperature of storage.

To determine the practical feasibility of these methods, the following experiments were conducted.

1. Samples

Three groups of samples were prepared as described below:

a) Solids Concentration

Samples of commercial sweetened condensed milk (75% solids) were diluted to the desired solids concentrations of: 75% (standard or control), 70%, 65%, and 60%. Samples were filled into cans, labelled, and retorted for 3 hours at 100°C.

b) Substitution of Sucrose with Glucose

Commercial sweetened condensed milk is composed of 25% moisture, 31% milk solids, and 44% added "sugar solids" which is usually in the form of sucrose. Glucose syrup was added to commercial sweetened condensed milk in such a way that the 44% "sugar solids" was made up by the desired ratio of glucose:sucrose. Both the milk solids concentration (31%) and moisture concentration (25%) were unaltered.

TABLE XI

PROPORTION OF GLUCOSE:SUCROSE IN THE 44% "SUGAR SOLIDS" OF SWEETENED CONDENSED MILK STORAGE TRIAL SAMPLES

Sample No.	Parts of GLUCOSE	Parts of SUCROSE
1 (control)	0	10
2	1	9
3	2	8
4	3	7
5	4	6
6	5	5
7	6	4

Table XI shows the range of samples that were prepared having a glucose:sucrose ratio ranging from 0:10 to 6:4. Samples were canned, labelled, and retorted for 3 hours at 100°C.

c) Substitution of Sucrose with Invert Sugar

Invert syrup was added to commercial sweetened condensed milk in such a way that the 44% "sugar solids" of sweetened condensed milk was made up by the desired ratio of invert sugar : sucrose. Both the milk solids concentration (31%) and moisture concentration (25%) of standard sweetened condensed milk were unaltered. Table XII shows that a range of samples were prepared having an invert sugar : sucrose ratio ranging from 0:10 to 6:4.

TABLE XII

PROPORTION OF INVERT SUGAR : SUCROSE IN THE 44% "SUGAR SOLIDS" OF SWEETENED CONDENSED MILK STORAGE TRIAL SAMPLES

Sample No.	Parts of INVERT SUGAR	Parts of SUCROSE
1 (control)	0	10
2	1	9
3	2	8
4	3	7
5	4	6
6	5	5

Samples were canned, labelled, and retorted for 3 hours at 100°C.

2. Storage Conditions

The three groups of samples, (prepared as described above), were stored at $5^{\circ}C$ for 12 weeks. The low storage temperature of $5^{\circ}C$ was chosen as it was thought that this would increase the supersaturation of the sugars (decrease solubility), and hence accentuate the problem of crystallization.

During the same period of 12 weeks, control samples of standard sweetened condensed milk heated for 3 hours at $100^{\circ}C$ were stored at $5^{\circ}C$; ambient (approx. $20^{\circ}C$); $37^{\circ}C$; and $45^{\circ}C$.

3. Methods Used for Examining The Samples

At the termination of the 12 weeks storage, the sample cans were opened and the following types of measurements taken.

1. Subjective assessment of the degree of crystallization
2. Subjective assessment of flavour
3. Subjective and/or objective assessment of colour
4. Penetrometer readings on some of the samples having varying moisture contents.

C. Observations on the Condition of Samples After Storage

1. Effect of Storage Temperature

This discussion is based on observations of the condition of caramelized standard sweetened condensed milk (3 hours/$100^{\circ}C$) after storage for 12 weeks at $5^{\circ}C$, ambient ($20^{\circ}C$), $37^{\circ}C$ and $45^{\circ}C$. Results expressed in Table XIII show that the samples stored at $5^{\circ}C$, $37^{\circ}C$, and $45^{\circ}C$ exhibit less severe crystallization than the sample stored at ambient - in fact, the $5^{\circ}C$ sample showed very little crystallization and was quite acceptable. As the temperature control of the $5^{\circ}C$, $37^{\circ}C$, and $45^{\circ}C$ storage environments was quite accurate, it is considered that the fluctuating temperatures of the ambient environment is the cause of the formation of the larger crystals in the sample stored at ambient temperatures.

TABLE XIII

EFFECT OF STORAGE TEMPERATURE ON THE INCIDENCE OF CRYSTALLIZATION AND ON CHANGES IN COLOUR OF CARAMELIZED SWEETENED CONDENSED MILK

	Storage Temperature	Incidence of Lactose Crystals	Changes in Colour
1.	5°C	few macroscopic crystals - product is of acceptable quality	No change in colour
2.	20°C	large number of very large macroscopic crystals - unacceptable product quality	No change in colour
3.	37°C	a few large crystals but not as bad as in 2. - acceptable quality	Slight darkening in colour
4.	45°C	a few large crystals but not as bad as in 2. - acceptable quality	Marked darkening in colour

Table XIII also shows that at the higher storage temperatures (37°C, 45°C) there is a marked increase in intensity of "caramelization" during storage. This is accompanied by an increased intensity of caramel flavour. Such colour and flavour changes are important factors when considering the possibility of marketing and storing the product under tropical conditions.

2. Effect of Solids Concentration

The following observations are based on the condition of sweetened condensed milk samples, (having solids contents of 75%, 65%, and 60% -(see Part V - B, 1, (a), page 114), after 12 weeks storage at 5°C. Table XIV compares the effect of solids concentration on three main properties of the product - colour, gel strength, incidence of large lactose crystals.

1. Reducing the solids concentration has little effect on crystallization until the solids is reduced to as low as 60%. Although the sample having only 60% solids had not crystallized, this system failed to form a gel with good spread characteristics. These results demonstrate that reducing the solids concentration is not a practically feasible method of producing a quality spread free from crystallization during storage.
2. The colour was unaltered during storage, but there is the usual increase in browning with increased solids concentration. This effect is described more fully in SECTION III, Part II - A, page 49.
3. There is a decrease in Penetrometer Reading (increase in gel strength) with increasing solids concentration. This effect has been discussed on page 99.

TABLE XIV

EFFECT OF SOLIDS CONCENTRATION ON THE FINAL QUALITY OF DAIRY CARAMEL AFTER 12 WEEKS STORAGE AT 5°C

Solids Concentration	Incidence of Lactose Crystals	Penetrometer Reading	Colour
75% (control)	few macroscopic crystals - product is of acceptable quality	150 - 160	↓ Decreasing Degree of Brownness
70%	" "	200	
65%	" "	240	
60%	no crystals present	> 600	

3. Partial Substitution of Sucrose with Invert Sugar and Glucose

In all the samples tested (Refer Part V - B, 1 (b) & (c), pages 115,116) there was no improvement in the incidence of lactose crystals compared with the standard sweetened condensed milk control. Even with small additions of glucose or invert sugar there was a pronounced off-flavour. This flavour resembled a "malty" flavour rather than the characteristic caramel flavour, and tended to have a "sickly-sweet" taste which was quite unacceptable. This off-flavour effect is discussed more fully in SECTION III, Part IV - A, 3.

D. Discussion and Conclusion

From the storage trial results it is clear that the main defect occurring in caramelized sweetened condensed milk during storage is the formation of large lactose crystals. In an attempt to eliminate this crystallization several variables were studied and it was concluded that:-

1. Substitution of sucrose with invert sugar or glucose did not decrease the incidence of large crystals. Moreover, the resultant flavour is quite undesirable if the sweetened condensed milk contains even small quantities of invert sugar or glucose.
2. Decreasing the solids concentration to 65% did not help. A solids concentration of 60% eliminated crystallization, but this solids concentration was too low for the characteristic gel formation to occur. Also the microbiological stability of sweetened condensed milk having only 60% solids is doubtful.
3. High (45°C) or low (5°C) storage temperatures do not promote crystallization.
4. Fluctuating storage temperatures appear to be the main cause of crystallization. As this is unavoidable in practice the only solution at present appears to be a control of product turnover. Some crystals may form at ambient temperatures after 8 - 12 weeks.

High temperature storage (37°C and 45°C) causes further browning in the product which results in an appreciable increase in intensity of the caramel flavour. This problem would have to be considered when determining the optimum process times for dairy caramel intended for marketing in the tropics.

VI. SUMMARY

This section describes the development of a dairy caramel which was very similar in flavour and texture to the indigenous caramelized dairy products of South America and India. From a basic study of the cause of the characteristic flavour and texture, methods of measuring changes in these characteristics were developed. Further study of the integrated effect of product and process variables, production methods, and storage on the final product quality, led to the conclusions and recommendations summarized in Table XV.

TABLE XV

PRINCIPAL FACTORS OF IMPORTANCE
IN DAIRY CARAMEL MANUFACTURE

A. PRODUCT VARIABLES

1. pH

Initial pH before heating may be adjusted to as high as pH 7.5 without flavour or texture changes. pH adjustment is not recommended.

2. Moisture Content

Optimum product moisture is 25 - 30%. Above 30% gel texture becomes very weak. Below 25% lactose crystallization during storage becomes a serious problem.

3. Sugar

Sucrose provides essential background flavour - 30-40% is the recommended concentration. Glucose and invert sugar substitution of sucrose has no advantages and a bitter flavour results. Hence, this practice is not recommended.

4. Fat

Fat is an integral part of the smooth texture and flavour of the product. Thus, the dairy caramel is of necessity a full cream milk product; i.e., 8% fat or 26% of the milk solids.

B. PROCESS VARIABLES

1. Time-temperature

Equivalent time-temperature heat treatments ranging from 1 hour/100°C to 6 hours/100°C will produce palatable products. Heat treatments equivalent to 7 hours/100°C, or more, produce a bitter flavour. Recommended optimum is 2 hours/100°C.

2. Agitation during Heating

Agitation during heating disrupts the gel texture and makes possible two basic types of products.

i) No agitation - gelled spread

ii) With agitation - viscous flowing caramel base.

C. PRODUCTION METHODS

There is basically two types of methods:

i) Heating in packaging container - no agitation during heating.

ii) Heating in bulk by heat exchanger prior to packaging - agitation during heating which disrupts any gel formed.

D. PRODUCT TYPES

1. Two basic types of product, depending on whether agitation

occurred during heating.

i) gelled spread type (No agitation)
ii) viscous flowing caramel (With agitation)

2. To these two basic forms of dairy caramel may be added spices, essences, jam, etc., to form a large range of products to comply with diverse market requirements.

E. STORAGE STABILITY

1. The main problem is the formation of large lactose crystals. No known method of control and some crystals may form at ambient temperatures after 8 - 12 weeks.

2. Tropical storage (37°C) causes further browning and increases the intensity of caramel flavour. Overcome by adjustments in process time-temperature.

SECTION V

STUDIES ON THE DEVELOPMENT

OF

A POROUS WAFER FROM MILK SOLIDS

I. INTRODUCTION

Foams include those foods in which small bubbles of gas constitute a major portion of the volume. These products consist of a discontinuous phase of gases (usually those of air) and a continuous solid phase which supports and maintains the structure.

Many commercially important foods rely on a foam structure for consumer acceptance. Some of the most important types of foods included in this category are meringues, mousses, souffles, whipped toppings such as whipped cream, "fluff" desserts or chiffon, marshmallow, and leavened bakery products. Leavened bakery products are probably more important economically than all the others combined. Products in this group range in texture from the soft heavy texture of bread and light spongy texture of sponge cakes, to the crisp short texture of biscuits having little entrained gas and low moisture.

New foods which have made an impact on the consumer market frequently feature a porous or foam texture. A large group of breakfast cereals, including puffed rice, puffed wheat, etc., have a porous structure. Foam structures figure prominently in many snack foods and confections; for example, hokey-pokey, "Cheez-pops", popped corn, dessert biscuits, honey-combed chocolate.

It is apparent that there are many foods having a foam texture which are familiar to, and accepted by the consumer. Hence, in an attempt to diversify the use of milk solids, it appears that the development of a porous milk solids wafer has considerable potential in the light of present consumer trends. To develop such a texture from milk solids, the problem resolves itself into a basic study of the factors affecting the foaming of milk solids concentrates, followed by a study of possible methods of stabilizing this structure.

II. THEORETICAL BACKGROUND DISCUSSION

A. Bubble Mechanics

Fundamental to the development of a porous structure having maximum stability is a basic knowledge of bubble mechanics. Handleman et al (43) have provided an excellent discussion of bubble mechanics in cake batters while the texts of Bikerman (14) and Adamson (3) furnish a more general treatment of the subject. Most of the following analysis is derived from these three sources.

For a single submerged bubble in an ideal thick-walled foam:-

$$F_1 = \pi r^2 P, \qquad (1)$$

$$F_2 = 2\pi r \gamma, \qquad (2)$$

$$F_3 = 4/3 \pi r^3 g (\rho_2 - \rho_1), \text{ and} \qquad (3)$$

$$F_4 = 6\pi r \eta \sigma \qquad (4)$$

In these expressions:-

F_1 = force tending to expand the bubble;

F_2 = force tending to contract the bubble;

F_3 = buoyant force tending to make the bubble rise;

F_4 = frictional force exerted against a spherical body moving in a viscous fluid (Stokes' law);

r = radius of bubble;

P = pressure of gas in bubble in excess of the hydrostatic pressure;

γ = surface tension at the gas-liquid interface;

g = gravitational constant;

ρ_1 = density of gas in bubble;

ρ_2 = density of liquid in foam;

η = Newtonian viscosity;

σ = rate at which the sphere moves in the fluid.

Equating the expression for F_1 and F_2 and solving for P, it can be shown that, for a bubble in equilibrium (3),

$$P = \frac{2\gamma}{r} \qquad (5)$$

From equation 5, it is apparent that, as bubbles become extremely small, their internal pressures become exorbitantly large, so that spontaneous nucleation of bubbles in a continuous fluid is extremely unlikely. One proof of this statement is based on equation 5. The dissolved gas of the solution, being in equilibrium with a gas at pressure P, would lose gas to a bubble in which the partial pressure of the gas is less than P and would take up gas from bubbles in which the partial pressure is more than P. Therefore, it is clear that bubbles can only grow when $2\gamma/r$ is less than P. The surface tension remaining the same, P becomes less likely to be reached as r becomes smaller. Thus, for infinitely small values of r, only infinitely large values of P will permit the formation of bubbles.

This difficulty in creating a foam is overcome by injection of gas through small orifices from outside sources, chemical or steam leavening, and by mechanical agitation. In the latter case, bubbles are drawn into the material by the paddle and are trapped on the surface as the plastic material folds in upon itself to form cavities. These bubbles then provide the majority of sites for collecting leavening gas and/or water vapour as they are evolved. If the number of nucleating sites is few, then individual cells will tend to be large and the foam structure will be open-grained. Conversely, with a large number of sites available to be inflated, the cells will be small and the grain fine or close. In viscous systems undergoing agitation by any method, the bubbles in the centre of the mass tend to become subdivided and approach a more uniform size. In a system at rest, large bubbles tend to increase in size at the expense of the smaller bubbles. Also, leavening gas is expelled into bubbles of low pressure; that is, large bubbles. This conclusion follows from the equation quoted previously, $2\gamma/r = P$, which shows that higher pressures are present in smaller bubbles. Hence, the more uniform the bubbles are, the more stable the foam will be.

If the expressions for F_3 and F_4 are equated and the expression solved for v, it is found that the terminal rising velocity of a bubble is -

$$v = 2 g r^2 (\rho_2 - \rho_1) / 9 \eta \qquad (6)$$

Equation 6 shows that, in a liquid of given viscosity, the rate of rise of a bubble due to its buoyancy is proportional to the square of the bubble radius and is inversely proportional to the viscosity. These relationships show that a foam composed of small bubbles suspended in a viscous Newtonian fluid would be more stable with respect to buoyancy-induced segregation than a foam composed of larger bubbles in a less viscous Newtonian fluid.

During the drying of a milk solids foam, rapidly rising bubbles cause loss of volume and "layering"; i.e., a gradient in wafer texture, varying from tight at the bottom to open at the top of the wafer. Fewer bubbles should reach sufficient size to rise out of the batter during baking (or drying) when the number in which the leavening gas or steam collects is large, than in the case where only a few bubbles are available to serve as nuclei. This is assumed, because, if only a few sites receive all the gas, these sites must each attain a relatively larger size. An increase in viscosity should also reduce volume loss by increasing the critical size which a bubble must attain to rise rapidly. Yield values of a non-Newtonian liquid should have the same effect of stopping bubble movement as very high viscosities.

Foams are spontaneously destroyed by collapse and drainage. Collapse results from rupture of the bubbles at the surface or elsewhere, with consolidation of gas spaces or loss of gas to the atmosphere. Collapse generally causes the remaining bubble walls to become thicker. Drainage is the thinning of the bubble walls resulting from the outflow of fluid under the influence of gravity or suction. Suction effect at the periphery of the film (Plateau's Border) (3) due to the high curvature of the film, has a more pronounced effect than gravity which results in a pronounced thinning adjacent to the concave edge of the foam film. These thin portions of the film situated between thicker patches are unstable and rise in the film until they reach a stable position in a portion of the film the same thickness - so drainage continues. Suction increases with increasing diameter.

Summary of Bubble Mechanics

1. Systems of uniform bubble size are more stable than those having a wide range in bubble sizes. In systems with uniform bubbles, the system having the smallest bubbles will tend to be more stable. The stability has been empirically estimated to be inversely proportional either to the diameter of the bubbles or to the square of their diameter.
2. Increased viscosity, or the presence of a yield strength in the foam liquid increases stability. Although many phenomena with conflicting effects result from temperature changes in foams, these systems are usually more stable at the lower temperatures due to the increased viscosity.
3. Substances which affect interfacial tension can exert pronounced effects on foam structure, but the gross results of these changes are difficult to predict. Generally, decreased interfacial tension makes the formation of a foam easier;

   i.e., $P = \frac{2\gamma}{r}$

   but need not improve foam stability.

B. Foam Preparation

Preparation methods for food foams always involve two stages; an aerating step in which a liquid of relatively low viscosity is filled with bubbles by whipping, by injection of gas, or by evolution of dissolved gas; and a fixing phase which gives the product sufficient rigidity to withstand handling and transportation (75). The aerating stage can usually be subdivided into two phenomena which often overlap or even occur more or less simultaneously. These are the introduction into the fluid of bubbles having widely varying dimensions, and a reduction process in which these bubbles are subdivided until they reach a smaller and more nearly uniform size. In whipping, the two stages overlap but in chemical leavening the second phase occurs separately, if at all.

The fixing phase involves a firming or hardening of the continuous phase as a result either of denaturation of the protein component, or of a hardening due to drying or cooling of a plastic mass. During the drying of a milk foam, denaturation may occur by thermal treatment and/or surface energy absorption. However, the principle factor in stabilizing the foam would appear to be simply the drying of the continuous phase to a rigid framework.

With these basic steps for the formation of a stable foam briefly defined, a study was undertaken to apply these steps to the development of a porous milk solids structure. The study was divided into two broad fields:-

1. Methods of, and factors affecting the incorporation of air into a stable milk solids concentrate foam.
2. Methods of, and factors affecting the drying of this stable foam to a solid porous structure.

III. STUDIES ON METHODS OF, AND FACTORS AFFECTING AERATION OF MILK SOLIDS SOLUTIONS

A. Methods of Aeration

As discussed previously, the first step in foam formation is aeration. Aeration may be accomplished by any one of the following ways:-

1. Whipping and/or injection of gas.
2. Chemical leavening.
3. Thermal liberation of moisture vapour.
4. Vacuum liberation of moisture vapour and expansion of entrapped gases.

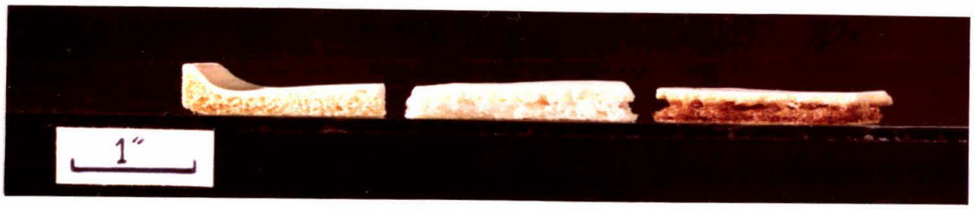
Experiments were undertaken to determine the practicability, and relative advantages of each of these methods. A review of the results and conclusions from these experiments follows.

1. Whipping and/or Injection of Gas (Air)

This is one of the most commonly used aerating methods in both commercial and domestic use. It is particularly used in whipping of confections such as marshmallow, meringues, etc., and of course the method by which whipped cream and egg foams are obtained. Whipping of concentrated (45% solids) skim milk solution in a Kenwood Chefette indicated that this method was particularly suitable for this system. Aeration by injection of air or beating under pressure is a further possibility but it was not pursued in the present study.

2. Chemical Leavening

This is a commonly used method for cake, bread and biscuits. Extensive experiments were conducted on the use of leavening agents



Typical structures obtained from the oven drying of 45% skim milk powder solutions (0.2% Edifas B) using the following levels of leavening agents:-

A. 0.4% ammonium bicarbonate.

B. Control - 45% skim milk powder solution with 0.2% Edifas B and no leavening agent added.

C. 0.3% sodium bicarbonate and 0.6% glucono-δ-lactone.

D. 0.16% sodium bicarbonate and 0.3% tartaric acid.

E. 0.67% sodium bicarbonate and 1.0% tartaric acid.

FIGURE 30. Effect of chemical leavening agents (pH) on the final texture of oven dried (hot air) skim milk powder foams.

as an aid to increasing the aeration of the milk foam during drying. A 45% skim milk foam was formed by beating at top speed in the Kenwood Chefette for 2 - 3 minutes and a known amount of leavening agent and 0.2% Edifas B added. The foam was then poured on trays at a loading of 1.2 lb./ft^2 and dried in a 200°F oven. While the foams containing only 45% skim milk and Edifas B remained stable throughout drying, no foams containing any leavening agent were stable to any appreciable extent. The exact reason for this is not clear but the following factors may be significant:-

i) Upon heating, the leavening gases are liberated and the previously formed bubbles expand. During this expansion there is a balance of forces between expansion and contraction at any instant of time. However, as more gas is liberated and expansion increases, the bubble becomes so large, and the walls so thin that the resisting or contracting force approaches zero and the bubble "explodes". This is not likely to be the case as the very little expansion caused by 0.16% sodium bicarbonate ($NaHCO_3$) still results in partial foam collapse (Figure 30 D).

ii) It is possible that the liberated gases which expand the structure may escape before the bubble walls are sufficiently stabilized and hence the contraction forces cause collapse as the expansion forces decrease. The fact that slow leavening throughout drying with glucone-δ-lactone and $NaHCO_3$ did not improve stability appears to militate against this theory. The effect of glucone-δ-lactone and $NaHCO_3$ on texture is demonstrated in Figure 30 C.

iii) A more plausible theory is that the alkali leavening agents such as $NaHCO_3$ and ammonium bicarbonate (NH_4HCO_3) cause a type of peptisation of the surface active milk proteins during heating. Figure 30 E shows the coarse gelatinized foam which resulted when only 0.67% $NaHCO_3$ was used. If denaturation of the protein is obvious at this level, it is quite possible that even small amounts of alkali could cause denaturation of the surface active proteins. This theory is substantiated by the fact that foaming of 45% skim milk powder is markedly inhibited by raising the pH above 6.4 - 6.5. Refer to page 153.

By comparing the control sample (Figure 30 B) with the other textures formed by adding leavening agents, it was apparent that all the leavening agents tried were unsuccessful. It was concluded from these studies that chemical leavening was an unsuccessful method of aerating milk-solid foams.

3. Thermal Liberation of Moisture Vapour

This method of obtaining a porous structure is used in popped-corn, puffed gels, etc. To obtain any significant volume of increase of the wafer by thermal expansion of dissolved gases and liberation of steam, temperatures in excess of 250°F are required. However, at this temperature the browning was extremely rapid, and as heat and moisture transfer through the foam film was slow, the foam structure formed at temperatures greater than 250°F had not dried sufficiently to be stable before the foam surface had become dark brown or charred.

Hence, at present this method of aeration must be discarded as being impracticable.

4. Vacuum Expansion

It is known that dissolved and entrapped gas will expand under vacuum according to Boyle's Law (39). If the vacuum is sufficiently low, the vapour pressure of the moisture in the food exceeds the pressure in the vacuum chamber. When this occurs the food moisture flashes off into any entrapped gas vesicles or forms bubbles of water vapour - the liquid food puffs and forms an expanded honey-combed structure. For a food at a temperature of $50^{\circ}C$, simple vacuum expansion occurs at a pressure of 760 mm. of Hg. down to 93 mm. of Hg.; below 93 mm. of Hg. moisture vapour flashes off, (i.e., liquid boils), and "vacuum-puffing" of the liquid occurs. In general, vacuum-puffing may be defined as the formation of a highly expanded sponge-like structure of dried material from a liquid concentrate, under conditions of high vacuum and low temperature.

While vacuum expansion has not been used to obtain a porous biscuit (or wafer) as such, vacuum-puffing is widely used to obtain a porous, soluble powder from liquid concentrates. Copley et al (28) have reviewed the early developments in vacuum drying of fruit and vegetable powder and the work of Morgan et al (38,47) demonstrates the modern application of vacuum puffing in the form of Foam-Mat and Micro-flake drying. Foam-Mat drying has recently been successfully applied to the drying of milk (100).

Laboratory trials indicated that a 45% skim milk concentrate, with or without Edifas B as stabilizer, could be successfully puffed to four times the original volume and dried without foam collapse. This process was <u>not</u> "vacuum-puffing" as previously defined. At all times the vacuum chamber pressure was higher than the moisture vapour pressure of the liquid concentrate and hence expansion was almost wholly due to expansion of dissolved and entrapped gases.

This method was investigated further and a detailed discussion of its successful application appears in SECTION V, Part IV - B, page 167.

B. Factors Affecting Aeration

1. Introduction and Literature Review

Fundamental to the development of a porous structure was the ability to incorporate air into the milk solids. Initial experiments with sweetened condensed milk indicated that, despite the use of a wide variety of foaming agents, foaming (by whipping) to a foam density less than 90 gm./100 ml. was not possible. A foam structure was achieved by vacuum-puffing.

This difficulty in foaming sweetened condensed milk led to a study of the parameters affecting the foaming of "made-up" concentrated skim milk powder solutions. Whipping at atmospheric pressure was used as the aerating method because this method of aeration was more sensitive than the vacuum method to successful foaming and drying.

The following parameters were studied:-

1. Heat treatment of the powder
2. Milk solids concentration
3. Temperature of foaming
4. Fat content
5. pH
6. Addition of other solids; e.g., sucrose
7. Foaming agent
8. Stabilizing agent

Holden et al (52) found that very little information has been gathered concerning milk concentrate foams and not much has been learned about any dairy product from the standpoint of determining how foaming is affected by physical properties. Other workers (34,96) using a variety of foam tests, have investigated relationships existing between the foaming properties of dairy products and the various protein fractions, fat levels, and minor chemical constituents encountered in these products. Most of these investigations have been carried out on either unconcentrated fluid milk or water solutions containing specific milk constituents near the levels in which they appear in fluid milk. The effects of physical properties on foams have also been studied. However, these studies have been confined in most cases to detergent-water solutions (18), which are not complicated by the great profusion of chemical constituents found in dairy products.

Pure liquids do not foam, nor does the formation of a stable foam depend on a low surface tension since many pure liquids possess this property. Broadly speaking, a good foaming agent must be adsorbed at the air-water interface and it must have a structure that endows the layer with certain mechanical properties (16). Foams are formed by mechanical means, and in order to avoid rupture of the films by local stresses during formation it is necessary that, (a) a stretching of the film should rapidly increase the surface tension and a contraction should rapidly lower it, or (b) that the film should possess some of the properties of an elastic or plastic solid. The first factor appears to predominate during the formation of soap foams, and the second during the formation of many protein foams. The maintenance of the foam involves additional factors, and foaming power and foam stability do not always go hand in hand.

The surface properties of protein foams were investigated by Ramsden (88) in 1903, and later work has amply confirmed his original conclusions. He found that solutions of proteins showed a superficial resistance to shear that could only be attributed to a solid coating or a highly viscous and coherent coating on the surface. By purely mechanical means, it was possible to sweep up these coatings into visible aggregates which were usually permanently insoluble; e.g., egg-albumin. Coagulation is caused by adsorption, denaturation, and aggregation of the protein at freshly made surfaces.

It is now known (2,4) that molecules of globular protein (e.g., lactalbumin) become unfolded when they enter an air-water interface, presumably by means of the resident asymetric forces, and that, in consequence, the thickness of the adsorbed protein layer is approximately that of a single polypeptide chain lying with its long axis parallel to the surface. When a few molecules are placed on the surface, a coherent surface layer results. These surfaces or films are better characterized by surface elasticity than by surface tension. The marked stability of many protein foams is attributable to the fact that the films behave as elastic or plastic solids. The mechanical strength may also be reinforced by the tendency of proteins to form polymolecular surface layers. Talmud (103) relates the maximum foam stability to the concentration that allows for maximal hydration at the interface. At the optimum concentration the protein molecules are orientated, inclining at a certain angle to the surface and interlacing with each other to form a kind of gel structure or a film with the highest tensile strength. El-Rafey (34) discussed the stability of protein foams by a consideration of micellar size, solubility, orientation, and degree of hydration.

Even though the experiments presented in this section were undertaken to gain information for direct application to foaming of milk solids for drying to a crisp, porous structure, any information obtained about milk concentrate foams should be applicable to other dairy operations where foaming of a milk concentrate is encountered. In fact, the information could also assist, at least qualitatively, in understanding the properties of foams formed from any proteinaceous material of high viscosity.

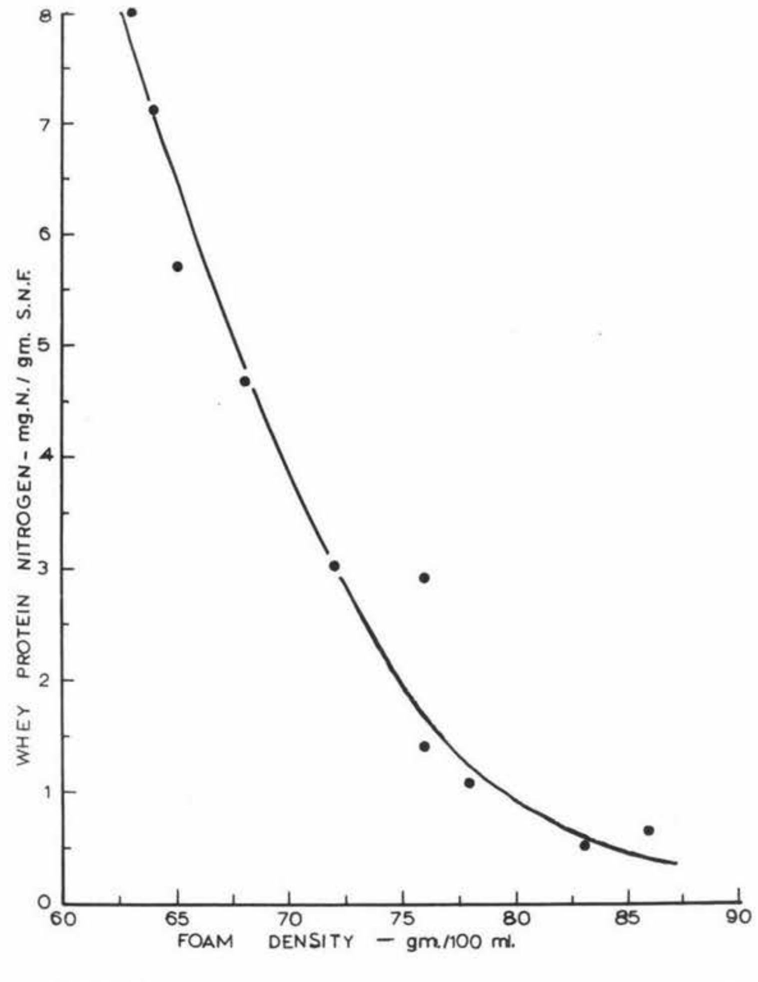


FIG.31. EFFECT OF HEAT TREATMENT OF MILK POWDER ON THE FOAMING ABILITY OF ITS SOLUTION.

2. Experimental Studies

a) Effect of Whey Protein Nitrogen (W.P.N.) or Heat Treatment of the Skim Milk Powder on the Foaming Ability of its Solution

During early preliminary experiments it was found that evaporated skim milk (46% total solids) taken from a triple effect evaporator, prior to preheating for drying, yielded a foam of density 57 gm./100 ml. In contrast, a sample of milk powder (having a W.P.N. of 3.0) when made up to a 45% solids solution yielded a foam of density 76 gm./100 ml. This large difference in foaming ability was thought to be due to the denaturation of important surface active constituents (34) during the preheating and drying of the milk powder.

It was with this thought in mind that a study was undertaken to determine the effect of heat treatment of the powder on the foaming ability of its solution.

i) Method

Samples of skim milk powders which had undergone a range of heat treatments were collected and their W.P.N. determined as an index to the degree of heat treatment (6). A 135 gm. sample of powder was reconstituted in 165 gm. of water (28 - 30°C) by beating at speed 1 in a Kenwood Chefette until the powder dissolved, followed by foaming at speed 3 (top speed) for half a minute. Within one minute the foam density was measured by the method described in APPENDIX III.

ii) Results

Results are summarized in Table XVI on page 142, and further amplified in Figure 31.

iii) Discussion of Results

From Figure 31 there is apparent a definite relationship of increasing foam density with increasing heat treatment (decreasing W.P.N.). Hence, the original supposition that the cause of the large difference in foam density between 46% T.S. evaporated skim milk and reconstituted powder solution would appear to be correct.

TABLE XVI

EFFECT OF HEAT TREATMENT (W.P.N.) ON THE FOAM DENSITY OF WHIPPED 45% MILK SOLIDS SOLUTIONS

Sample No.	W.P.N. mg. N./gm. S.N.F.	Foam Density gm./100 ml.
1	0.48	83
2	0.66	86
3	1.1	78
4	1.4	76
5	1.5	76
6	2.9	76
7	3.0	72
8	1.5 - 5.99	71
9	4.65	68
10	5.7	65
11	7.11	64
12	8.0	63
13	6.0	64

iv) Conclusion

As the foam density is directly dependent on the W.P.N. of the milk powder used, a powder having a W.P.N. of at least 4.5 mg. N./gm. S.N.F. is necessary to yield a foam of minimum density for drying to a porous structure.

b) Effect of Milk Solids Concentration on the Foaming of Skim Milk Powder Solutions

Preliminary experiments indicated that milk solids concentration was an important factor affecting foam density, and particularly foam stability. The effect of milk solids concentration in the range 30 - 55% is discussed below and the optimum solids concentration for minimum foam density and maximum foam stability determined.

i) Method

A sample of powder having a W.P.N.of 5.7 mg. N./gm. S.N.F. was dissolved in the required amount of water and then foamed at a temperature of 25 - 30°C. Speed 1 of a Kenwood Chefette was used until the powder was dissolved, followed by foaming at speed 3 (top speed) for half a minute. The foam density and stability was determined by the method described in APPENDIX III.

ii) Results

Results are recorded in Table XVII and Figure 32.

iii) Discussion of Results

From Figure 32, there is evident two definite relationships.

1. There is a sharp minimum foam density at 45% milk solids.
2. Foam stability increases rapidly with increasing % of milk solids between 40% and 50% milk solids.

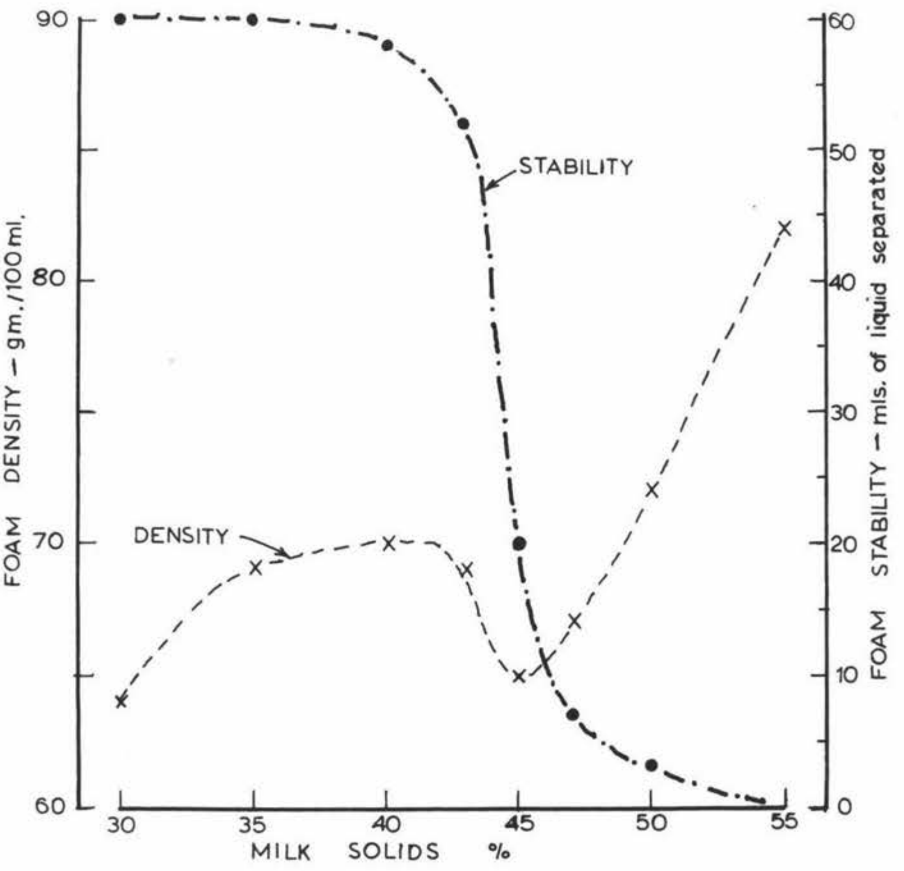


FIG.32. EFFECT OF MILK SOLIDS CONCENTRATION ON THE FOAMING PROPERTIES OF SKIM MILK POWDER SOLUTIONS

A detailed explanation of these results is not possible due to the paucity of information available. However, it is suggested that the viscosity effect may provide a possible explanation. With increasing milk solids concentration, the fluid viscosity increases. This viscosity increase readily explains the increasing foam stability with increasing concentration but does not obviously explain the sharp maximum in foam density at 45% solids concentration. It is probable that with increasing viscosity the foaming ability increases to an optimum, but any further increase in viscosity makes foam formation increasingly difficult. It appears that 45 - 46% solids concentration corresponds to such an optimum viscosity.

TABLE XVII

DATA ON THE EFFECT OF MILK SOLIDS CONCENTRATION TO THE FOAM DENSITY AND STABILITY OF MILK POWDER SOLUTIONS

Solids Content %	Foam Density gm./100 ml.	Stability mls. of liquid separated
30	64	60
35	69	60
40	70	58
43	69	52
45	65	20
47	67	5
50	72	3
55	82	1

NOTE: A low figure for stability; e.g., 1 ml. of liquid separated, indicates a foam of high stability and vice versa.

iv) Conclusions

A milk solids concentration of 45% corresponds to a foam of minimum foam density and good stability. With the use of a suitable stabilizing agent, the problem of stability would not be great between 40% and 50% solids. In drying, the greater the initial concentration, the shorter the drying time. Hence, the maximum foamable concentration would be used in practice. Fortunately, 45% solids not only foams well, but is sufficiently concentrated for drying.

c) Effect of Temperature on the Foaming of a Solution of 45% Skim Milk Powder

i) Method

A sample of powder having a W.P.N. of 5.7 was made up to a 45% solids solution and adjusted to the required temperature. The solution was then foamed in the same manner as in the previous experiments (page 143). The foam density and the stability after 3 hours was measured (APPENDIX III).

ii) Results

In Table XVIII are recorded the results for the effect of temperature on the foam density and foam stability of 45% skim milk powder solutions after whipping under standard conditions. Figure 33 portrays the effect of temperature on the foam density of a 45% solution of milk powder having a W.P.N. of 5.7 mg. N./gm. S.N.F.

iii) Discussion of Results

From Figure 33 and Table XVIII it is apparent that with increasing temperatures from 28°C - 65°C there is an increase in foam density and a decrease in foam stability.

Holden et al (52) have reported a minimum in the tendency of whole milk concentrate to foam (i.e., maximum foam density) in the region of 70°F (21°C). Rogers (94) has similarly reported a minimum in the tendency of unconcentrated whole milk to foam at temperatures between 68 - 86°F (20 - 30°C). El-Rafey and Richardson (34) also found a minimum in their foam parameter, (half volume time), in the region about 70°F followed by an increase in foaming with increasing temperature to 55°C.

TABLE XVIII

DATA ON THE EFFECT OF TEMPERATURE ON THE FOAM DENSITY AND STABILITY OF A SOLUTION OF 45% SKIM MILK POWDER

Temperature °C	Foam Density gm./100 ml.	Stability mls. of liquid separated
25	64	12
28	65	12
46	72	20
56	79	30
65	82	40

In apparent contrast with these results of previous workers, the present results indicate that for the foaming of reconstituted skim milk powder solutions, foaming ability and stability decreases with increasing temperature. This apparent anomality may be explained as follows:-

1. The systems described in the literature are for whole milk containing a large % of solids in the form of fat. This fat is responsible for the minimum foaming in the 20 - 30°C range. (34).

The system used in this study was reconstituted skim milk powder solution with very little fat present and hence the effect of fat is reduced, if not covered by other factors which have a greater effect on foaming.

2. El-Rafey (35) concluded from his studies with undenatured milk protein systems, that the foaming properties of skim milk are due to the presence of calcium caseinate, lactalbumin and milk fat. They concluded that calcium caseinate was the foaming substance of milk at low temperatures while lactalbumin is the substance contributing to the foam at temperatures above the melting point of milk fat.

In the system used for the present experiments the whey protein (i.e., lactalbumin) has been denatured to a greater or lesser extent during the drying of the skim milk powder, as is indicated by the reduced Whey Protein Nitrogen value. At the same time the calcium caseinate would be denatured during drying also. As the whey protein has lost much of its foaming ability, due to denaturation, the foaming characteristics of the reconstituted skim milk powder solution is most probably characterized by the remaining major foaming protein - partially denatured sodium caseinate.

El-Rafey (34) has shown that solutions of partially denatured caseinate prepared by the Van Slyke and Baker (106) or Cohn and Hendry (27) methods yielded foams which increased in density and decreased in stability as the temperature increased from 5°C to 55°C. The greater the extent of denaturation, the poorer the stability of the foam. This agrees with the conclusion of Section 2 (a), page 141.

It is believed that the foregoing discussion explains why the partially denatured protein system used in these experiments yielded foams which increased in density and decreased in stability as the foaming temperature increased. In this case the effect of temperature most likely acted through viscosity changes in the milk concentrate.

iv) Conclusions

The lower the temperature, the lower the foam density and the better the foam stability. However, as the foam was to be subsequently dried, foaming at room temperature (20 - 30°C was used to obtain the best foams for further drying.

d) Effect of Fat Content on the Foaming Ability of 45% Skim Milk Powder Solutions

Full cream milk powder yielded foams having very high foam densities of 80 - 100 gm./100 ml., while the skim milk powder foams had a foam density of 65 - 70 gm./100 ml. Hence, it is apparent that fat content is a major factor in the ability of a reconstituted milk powder system to foam. The actual effect of fat content on foaming at room temperature is demonstrated below.

i) Method

Skim milk powder (W.P.N. of 5.7 mg. N./gm. S.N.F.) was dissolved in water at 28 - 30°C until a 45% solution of milk powder was obtained. The powder was dissolved by beating at speed 1 in a Kenwood Chefette. The desired amount of butter fat was added and the mixture was then foamed by beating at speed 3 for half a minute in the Kenwood Chefette. The foam density and foam stability were then determined by the method described in APPENDIX III.

ii) Results

Results are tabulated in Table XIX.

TABLE XIX

EFFECT OF BUTTER FAT ON THE FOAM DENSITY AND STABILITY OF A 45% SKIM MILK POWDER SOLUTION

Fat Content %	Foam Density gm./100 ml.	Stability mls. of liquid separated
0	65	20
0.3	70	30
1.0	74	40
4.0	80	50

iii) Discussion

These results agree with the work of El-Rafey (35). He has clearly demonstrated that the presence of any fat, in model milk constituent systems, has a depressant effect upon foaming. He also showed that this effect increased with increasing fat content.

iv) Conclusions

As any fat present has a depressant effect on foaming, it was decided that skim milk powder should be used and that no fat be added when preparing the solutions for foaming and subsequent drying to a porous wafer.

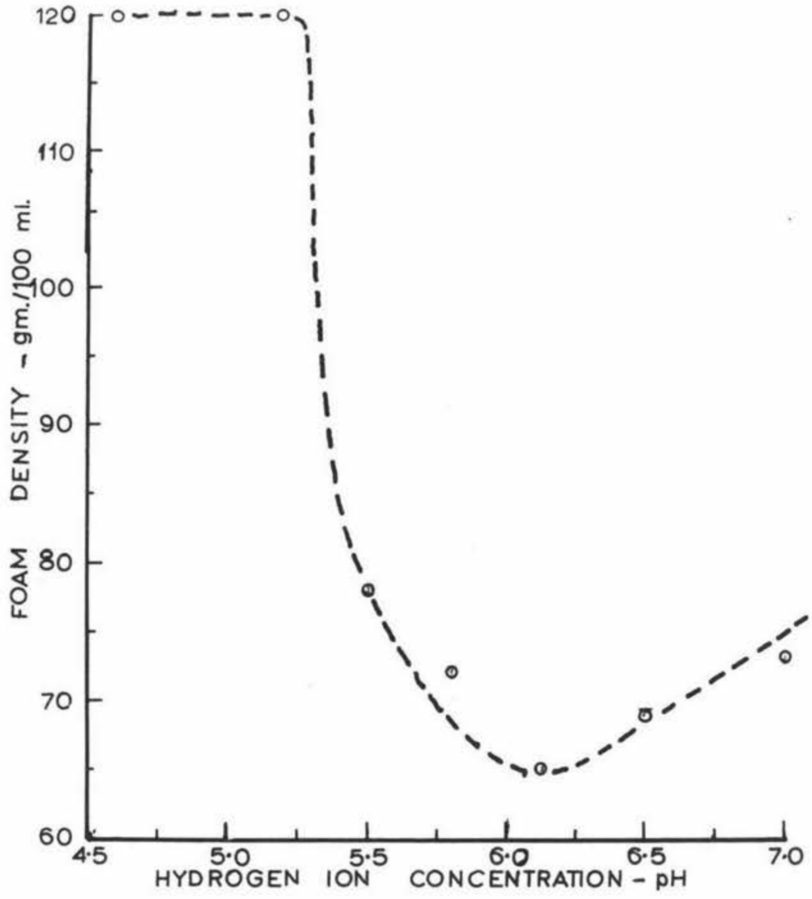


FIG.34. EFFECT OF HYDROGEN ION CONCENTRATION ON THF FOAMING OF A SOLUTION OF 45% SKIM MILK POWDER

e) Effect of pH on the Foaming of 45% Skim Milk Powder Solutions

It has previously been stated (on page 139) that the formation and stability of protein foams is dependent on micellar size, solubility, orientation, and degree of hydration of the protein at the air-water interface (34). Hence, it is expected that slight changes in the charge of the polar groups could radically alter the ability of the protein to form an elastic coherent film. pH will affect the charge of the polar groups and thus alter the foaming characteristics of the milk.

i) Method

A standard 45% skim milk powder solution (W.P.N. of 5.7 mg. N./gm. S.N.F.) was prepared in the Kenwood Chefette, and adjusted to the desired pH with 1N citric acid or 1N sodium hydroxide. The solution was then foamed by beating at speed 3 (top speed) for half a minute and the foam density determined (Refer to APPENDIX III).

ii) Results

Results are plotted as pH versus foam density in Figure 34.

iii) Discussion of Results

It is apparent from Figure 34 that any change in the natural pH of the skim milk concentrate causes a change in the nature of the protein film which decreases the foamability. The exact nature of this change in the protein, and whether other physical characteristics such as viscosity are affected also, is not known.

iv) Conclusion

The natural pH (6.2) of the skim milk concentrate is the optimum for foaming.

f) Effect of Other Solids on the Foaming Properties of 45% Skim Milk Powder Solutions

It was anticipated that, in the formulation of a solution for foaming and drying to a porous wafer, other ingredients, such as sweeteners, would have to be added for flavouring. It was with this thought in mind that the following experiments were undertaken to determine the quantitative and qualitative effect of added sucrose and invert sugar on the foam density and stability.

i) Method

Skim milk powder (W.P.N. of 5.7) was used to make a solution having a composition of 45% milk solids; 55-X% water; and X% sugar. The solution was foamed at 28 - 30°C according to the standard procedure and the foam density and stability determined (Refer to APPENDIX III).

ii) Results

In Table XX are recorded the results for the effect of added invert sugar and sucrose on the foaming properties of a 45% skim milk powder solution.

iii) Discussion and Conclusion

It is apparent that any added sugar increases foam density and stability. The effect could possibly by due to an increase in viscosity beyond the optimum for foaming. (Refer to Part III - A, 2 (b), page 143). Invert sugar has less effect than sucrose. Also, because of its greater sweetness its use would be preferred in the formulation of a wafer having a minimum foam density.

TABLE XX

EFFECT OF ADDED INVERT SUGAR AND SUCROSE ON THE FOAM DENSITY AND STABILITY OF A 45% SKIM MILK POWDER SOLUTION

	% Sucrose	Foam Density gm./100 ml.	Stability - 3 Hours
1.	0	65	12
2.	5	71	6
3.	10	75	3
4.	15	81	1
	% Invert Sugar (75% Solids)		
1.	0	65	12
2.	5	68	7
3.	10	71	3
4.	15	77	1

g) Effect of Foaming Agents on the Foaming Properties of 45% Skim Milk Powder Solutions

Although milk contains its own foaming agents it was thought that the foam obtained from the reconstituted milk solution could be improved by the addition of commercially available foaming agents. To check this, commercially available foaming agents were obtained and tested under standard conditions.

i) Method

A 45% skim milk powder (W.P.N. of 5.7) solution was foamed at 28 - 30°C with the addition of known amounts of foaming agent. Foam density and stability were measured. (Refer to APPENDIX III.)

ii) Results

Results are summarized below in Table XXI.

TABLE XXI

EFFECT OF ADDED COMMERCIAL FOAMING AGENTS ON THE FOAMING PROPERTIES OF 45% SKIM MILK POWDER SOLUTIONS

Foaming Agent	% Foaming Agent Added	Foam Density gm./100 mls.	Stability mls. liquid separated
45% S.M.P. Standard	0.0	65	12
Hyfoama	0.5	65	12
	1.0	62	6
	1.5	63	2
	2.0	62	1
Lactalbumin	1.0	66	5
	2.0	69	2
Sodium Caseinate	1.0	67	5
	2.0	71	3
Edifas A	1.0	71	10
	2.0	82	-

iii) Discussion

The only foaming agent which improved the foam density at this temperature was Hyfoama - even this improvement was very slight. Hyfoama is a special multipurpose foaming agent made by controlled hydrolysis of casein.

iv) Conclusion

Milk contains sufficient of its own surface active agents to yield a near minimum foam density. The addition of commercially available foaming agents resulted in insignificant changes in foam density and only slight changes in stability. Hence, the cost of addition is not warranted.

h) Effect of Stabilizing Agent on the Foaming Properties of 45% Skim Milk Powder Solutions

While the milk solids system is capable of yielding a foam of near minimum foam density, without the addition of foaming agents, there is scope for improving the stability. The 45% milk solids foam suffered extensive collapse at the temperatures of 80°C to 100°C required for drying the foam. In an attempt to develop a foam of minimum density and yet sufficiently stable to withstand drying at 100°C, the commercially available stabilizing agents - Edifas B and Alginate - were tested.

i) Method

To a 45% skim milk powder (W.P.N. = 5.7) solution was added the desired amount of commercial stabilizing agent. The mixture was foamed at a temperature of 28 - 30°C by beating for half a minute at speed 3 in the Kenwood Chefette. Foam density and stability were measured by the methods described in APPENDIX III.

ii) Results

Results are summarized in Table XXII.

TABLE XXII

EFFECT OF EDIFAS B AND ALGINATE STABILIZING AGENTS ON THE FOAMING PROPERTIES OF 45% SKIM MILK POWDER SOLUTION

Type of Stabilizer	% Stabilizer	Foam Density	Stability ml. liquid separated
1. Edifas B	0.0	65	12
	0.17	64	0
	0.33	66	0
	0.50	71	0
2. Alginate	0.0	65	12
	0.22	66	7
	0.37	68	10

iii) Discussion of Results

While Alginate makes no significant improvement in foam density or stability, the addition of 0.2% Edifas B causes a slight decrease in foam density and completely stabilizes the foam. An oven drying test at 100°C on the foam, verified that 0.2% Edifas B imparted a rigidity to the foam which enabled complete drying with little collapse of the foam. It is pertinent to note that Edifas B is a commercial preparation of carboxymethyl cellulose.

iv) Conclusions

Edifas B is not only suitable, but necessary for complete stability during drying of the foam at temperatures greater than 80°C.

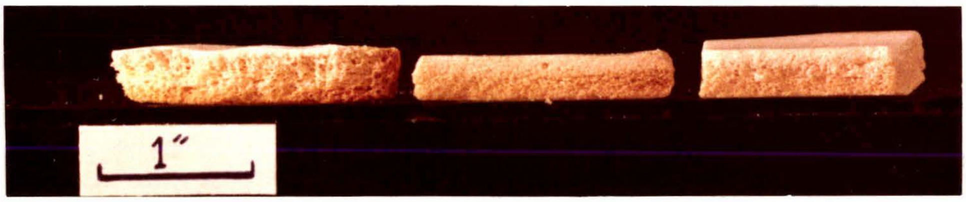
3. Conclusions

From the foregoing basic studies of the factors affecting foaming and stability of aerated concentrated skim milk solutions, conclusions may be drawn as to the optimum manipulation of these variables to obtain a stable foam for drying.

From a review of the data, the following variables are specified to obtain the optimum foam for drying.

1. W.P.N.; as high as possible and at least >4.5
2. Solids Concentration: 46% milk solids
3. Temperature: 25 - 30°C
4. Fat content: nil, or as little as possible
5. pH: leave at natural pH
6. Other solids: as little as possible
7. Foaming agents: none necessary
8. Stabilizing agent: 0.2% Edifas B

These specifications are very necessary for successful oven drying of the milk foam. Although foam formation and drying in vacuum of full cream milk concentrates may be successful if variables such as vacuum-temperature cycle are carefully controlled, the above specifications should yield a more stable system which would make the vacuum-temperature cycle less critical.



A B C

To a 45% solution of skim milk powder was added:-

A. 0.2% Edifas B (uneven browning).
B. 17% invert sugar (even browning).
C. 17% sucrose (slight variation in browning).

FIGURE 35. Typical foam structures obtained from oven drying a foamed 45% skim milk powder concentrate (0.2% Edifas B).

IV. METHOD OF DRYING TO A SOLID FOAM

The stable foam (developed in the previous section) needs to be dried to yield a crisp porous wafer. Of all the techniques available, only two methods were chosen for further study.

1. Oven or hot air drying
2. Vacuum foam drying

The characteristics, and operational variables, of these two methods were studied and the results are reported below.

A. Oven or Hot Air Drying

1. Method of Drying and Characteristics of the Dried Foam

To accomplish hot air drying on the laboratory scale a thermostatically controlled electrical oven was used. The concentrated milk solids foam (by whipping) was spread on a tray at a loading of 1 lb/ft^2 and at a temperature of 30°C. The loaded tray was then dried in the oven at a temperature of 100°C until the foam structure had become brittle; i.e., about 2 - 4% moisture.

A foam prepared according to the specifications listed on page 159 and dried by the method described above, yielded a foam of texture shown in Figure 35. From this photograph, it is apparent that a dense, fine foam with a solid impermeable upper layer is the result. A variation of brown colour from dark brown at the bottom to pale brown or white at the top is also apparent. A very important characteristic of the foam dried in such a manner is that little variation is possible in foam structure, due to:-

a) any increase in oven temperature to cause steam leavening, accentuates the uneven browning of the foam.

b) There is a very definite limit to the minimum foam density which may be obtained by whipping.

2. Factors Affecting Drying and Characteristics of the Dried Foam

It is by manipulation of operational and product variables that a range of foam structures and characteristics may be obtained while still minimizing the drying time. Some of these variables are now discussed.

a) Oven Temperature

While increased oven temperature might be expected to increase the drying rate, the temperature cannot exceed 100°C if a marked difference in brown colour between the bottom and top of the wafer is to be avoided.

A possible explanation of this problem is discussed below.

1. The top of the foam collapses and forms a condensed impermeable layer, and all moisture vapour must pass from the bottom of the foam through this layer.
2. After a short period of time the top layer dries out to below 10% moisture, and less as drying progresses. At this low moisture content, browning is very slow (66) - even at 100°C.
3. Meanwhile the underlayers approach oven temperature (100°C), and as the moisture content is reduced a long period of drying occurs between 25% and 14% moisture content. This moisture content corresponds to the optimum for browning. Therefore at the end of the drying cycle browning has progressed more near the bottom of the foam than the top.

This problem also precludes the possibility of forming a lighter foam by steam leavening at temperatures in excess of 100°C.

b) Loading

The greater the tray loading (or thickness of foam) which must be dried, the longer becomes the drying time (104). Experiments showed that the problem of uneven browning of the wafer became greater as the loading was increased. Both the increase in drying time and the problem of uneven browning is most probably associated with the increased resistance of the structure to the escape of moisture vapour. These factors place an economic limit on the thickness of wafer which may be dried; i.e., the thinner the wafer that is acceptable, the better the economics of production.

c) Effect of the Foam Density of the Initial Liquid Concentrate on the Texture and Density of the Dried Foam

Milk-solid foams were prepared from three milk powder samples by whipping a 45% solution of the powders. The foam density before and after drying was determined and the results are summarized in Table XXIII.

TABLE XXIII

DATA FOR THE EFFECT OF INITIAL FOAM DENSITY
ON THE DENSITY OF THE DRIED WAFER

Milk Powder Sample No.	Density of Foamed Concentrate (45% solids)	Density of Dried Wafer gm./ml.
1	6.7	.33
2	8.5	.42
3	10.1	.50

These results are also plotted later in Figure 38, page 171. From the plot for a vacuum chamber pressure of 760 mm. of Hg. (i.e., oven drying at atmospheric pressure) it is clear that the density of the dried wafer is directly proportional to the foam density of the milk solids concentrate prior to drying.

It may be concluded that, within definite limits, the density of the dried wafer may be varied (from 0.33 gm./ml. to 0.5 gm./ml.) by manipulating the foam density of the milk solids concentrate.

d) Addition of Sweetener

Any addition of sweetener during whipping increased the density of the foam before and after drying. However, the sweetener is necessary to make the wafer palatable. Sucrose and invert sugar were used. Sucrose yielded a sweeter wafer of increased density. Invert syrup increased the browning and caramel flavour intensity while less was required than sucrose to achieve the same sweetness. Addition of invert sugar also yielded a more evenly browned product of lower density than the addition of sucrose. Refer to Figure 35, page 160.

e) Browning Before Drying

To overcome the uneven browning in the wafer it was thought that either browning before drying, or addition of a dairy caramel concentrate to the foam would minimize this problem. This possibility was investigated but was found to be unsatisfactory for the following reasons.

1. Any browning or heat treatment of all the milk proteins reduced foaming ability and increased foam density to an unacceptable level.

2. Addition of a concentrated caramel flavour (of the desired intensity) to unbrowned skim milk powder solution also increased foam density to an unacceptable extent.

3. To achieve even browning the oven temperature must be reduced to below 80°C. This temperature drop causes the drying time to increase from $5\frac{1}{2}$ hours (at 100°C) to 7 hours (at 80°C).

From Figure 35, page 160, it would appear that the addition of invert syrup yields the most evenly browned wafer. The invert sugar also imparts an acceptable flavour.

FIGURE 36. Typical foam structures obtained by evolution of water-vapour from a deaerated concentrate (bottom), and by expansion of entrained gas of low solubility (top).

B. Vacuum Foam Drying

1. Method of Drying and Characteristics of Dried Foam

While vacuum of itself will develop a foam structure by evolution of water-vapour from a deaerated concentrate, the structure thus formed is characterized by large, non-uniform bubbles and a preponderance of unpuffed intercellular material. (Refer to Figure 36.) This texture was unacceptably coarse in appearance and mouth-feel. The foam structure formed by expansion of entrained gas of low solubility (e.g., air) is characterized by small, uniform bubbles and a minimum of unexpanded intercellular material (Figure 36). The latter texture is obviously the more desirable. (100). Hence, the skim milk concentrate was prepared according to the specifications of page 159, and whipped as for oven drying.

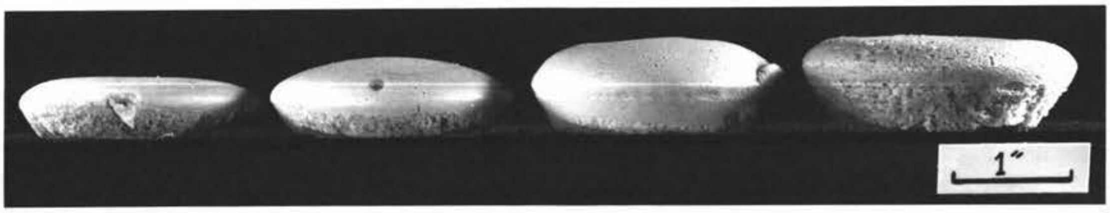
The whipped foam was loaded onto trays at the desired loading and at a temperature of 30°C. The foam was then dried at 80°C under vacuum. The vacuum could be adjusted to yield the desired foam density. The effect of vacuum is fully discussed below. However, in any vacuum small uniform bubbles were formed, the size of which varied with the vacuum. As in the case of oven drying, there was a solid impermeable skin formed on the upper surface of the wafer.

2. Factors Affecting Drying and Characteristics of the Dried Foam

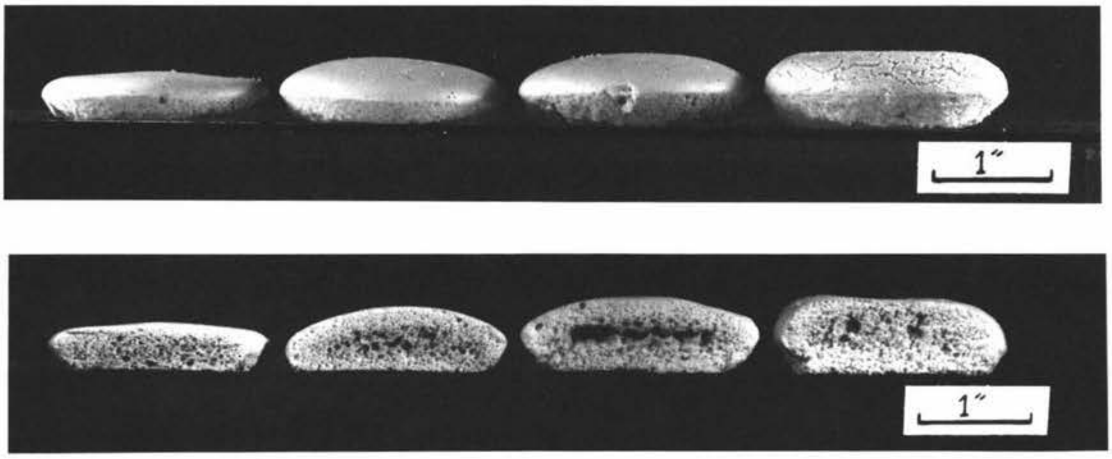
It is by manipulating temperature, vacuum, tray loading, and the addition of flavouring agents that a range of textures and flavours are possible. Hence, from the wide range of flavoured structures so produced, a wafer may be chosen to comply with given market requirements.

a) Temperature

As in the case of oven drying, high temperatures resulted in



Size of wafers formed by vacuum foam drying the aerated milk concentrate (tray loading of 9 gm./in.^{2}) at chamber pressures of 500, 360, 240, and 110 mm. of Hg.



Size and texture of wafers formed by vacuum foam drying the aerated milk concentrate (tray loading of 7 gm./in.^{2}) at chamber pressures of 500, 360, 240, and 110 mm. of Hg.

FIGURE 37. Effect of vacuum on the volume and texture of the vacuum foam dried wafer.

uneven browning of the product. A temperature of 85°C to 90°C gave a good drying rate without unevenly browning the product.

b) Vacuum

It is well known that dissolved and entrained gas will expand under vacuum according to Boyle's Law. Hence, it is to be expected that the volume of a given weight of original foam will increase with increasing vacuum. Figure 37 illustrates the effect of vacuum on both volume and texture of the wafer. These samples were prepared by beating 200 gm. of 45% skim milk powder solution with 200 gm. of caramel concentrate (Composition: 33% skim milk powder, 40% sucrose, 20% water - heated for 3 hours at 100°C). The resultant aerated concentrate had a foam density of about 80 gm./100 ml. The foamed concentrate was loaded onto small pans at a tray loading of 7 gm./in.^{2} and then dried at the desired vacuum with an oven temperature of 80°C.

Figure 37 demonstrates that a whole range of foam textures may be obtained by adjusting the vacuum. This is of real advantage in the marketing of such a product which often has to be 'tailor-made' to suit the market requirements.

It is also apparent from Figure 37 that as the vacuum is increased there is an increasing tendency for the centre of the wafer to collapse. This problem is mainly one of vacuum control. The chamber pressures of 500 mm. of Hg. and 360 mm. of Hg. were quite easy to control and maintain, but the lower pressures of 240 mm. of Hg. and 110 mm. of Hg. were difficult to control in the laboratory vacuum oven. This is the reason for the partial collapse of the samples dried at low oven pressures (Refer to Figure 37 C). This collapse is believed to be due to the following series of events.

1. During the early stages of the drying cycle, the vacuum slowly increases due to the decreased water vapour load. As the outer layers dry first, they will be "set" to a solid structure at a lower vacuum than will the inner layers of the wafer. It may be possible to eliminate this effect by good control of commercial vacuum units, but on the laboratory vacuum oven (used for these experiments) any fine adjustment of the vacuum caused a significant drop in vacuum with a resultant partial collapse of any undried foam.

2. If, (in the process of controlling the vacuum), there is a significant drop in vacuum, the wet centre of the wafer recedes from the dry "crust" and partially collapses. This means that the wet centre becomes partially deaerated and any further increase in vacuum will not fully restore the collapsed foam. Hence, the hollow centres of foams dried at higher vacuum.

This problem is minimized, or eliminated, if the vacuum is very carefully controlled and any significant drop in vacuum is prevented. Control is much easier at pressures higher than 360 mm. of Hg.

c) Effect of Foam Density of the Initial Liquid Concentrate on the Texture and Density of the Dried Foam

Samples of 45% skim milk powder foamed solutions were prepared with foam densities ranging from 0.7 gm./ml. to 1.0 gm./ml. The foams were dried at pressures of 500 mm. of Hg. and 240 mm. of Hg. in a vacuum

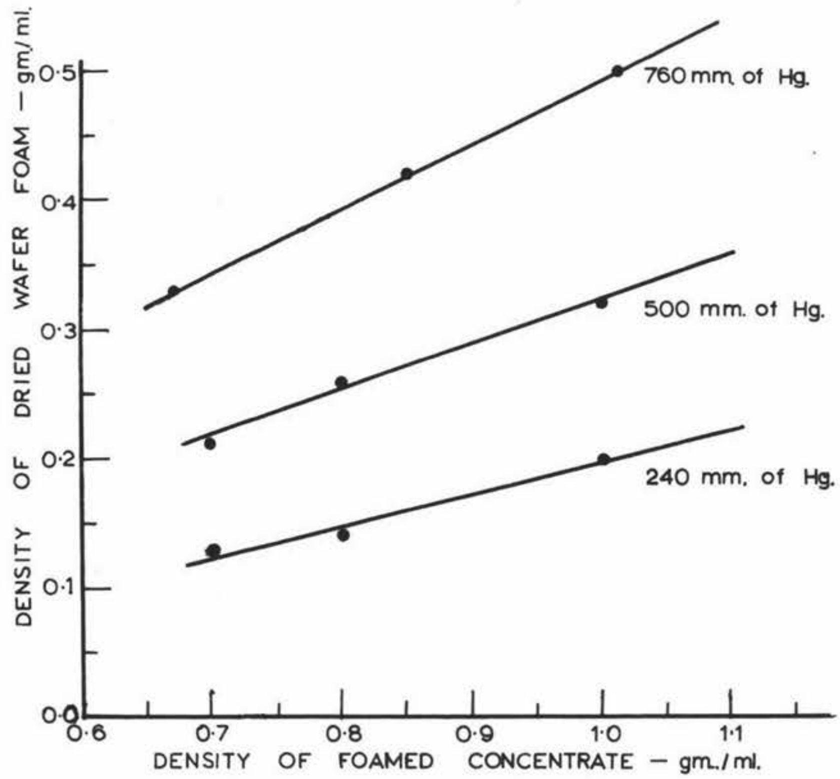


FIG. 38. EFFECT OF INITIAL FOAM DENSITY ON THE DENSITY OF THE DRIED WAFER (AFTER DRYING AT VACUUM CHAMBER PRESSURES OF) 760, 500, and 240 Mm. of Hg.

chamber. The foam density before and after drying was determined and the results are summarized in Table XXIV.

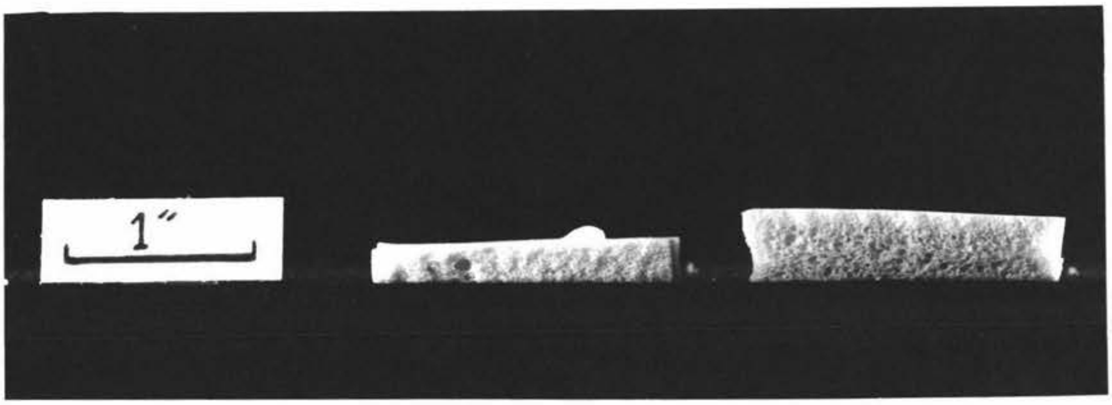
TABLE XXIV

DATA FOR THE EFFECT OF INITIAL FOAM DENSITY ON THE DENSITY OF THE VACUUM-DRIED WAFER

Sample No.	Density of Foamed Concentrate. gm./ml.	Density of Wafer Dried at 500 mm. of Hg. gm./ml.	Density of Wafer Dried at 240 mm. of Hg. gm./ml.
1	0.7	0.21	0.13
2	0.8	0.26	0.14
3	1.0	0.32	0.20

These results are also plotted in Figure 38 where it is clear that, for both atmospheric and vacuum drying, the density of the dried wafer is directly proportional to the foam density of the milk solids concentrate prior to drying. Figure 38 demonstrates the wide range of wafer densities (and textures) which are possible by controlling both the initial foam density of the milk concentrate and the vacuum used for drying.

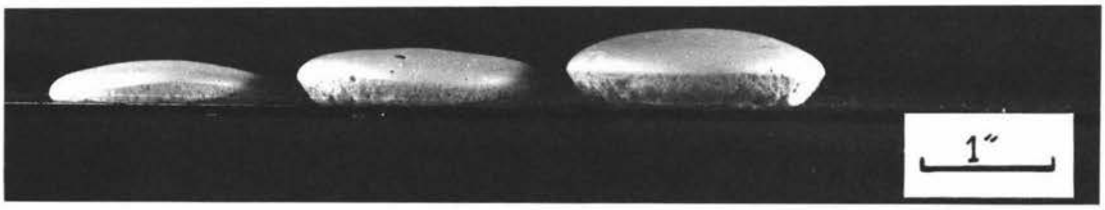
Figure 39, page 173 shows the large difference in texture between a foam density of 0.7 gm./ml. dried at a vacuum chamber pressure of 500 mm. of Hg to yield a wafer density of 0.13 gm./ml., and a foam density of 1.0 gm./ml. dried at the same vacuum to yield a wafer of density 0.20 gm./ml. Figure 39 demonstrates that, for a given vacuum, the lower the initial density of the foamed concentrate, the more porous will be the texture of



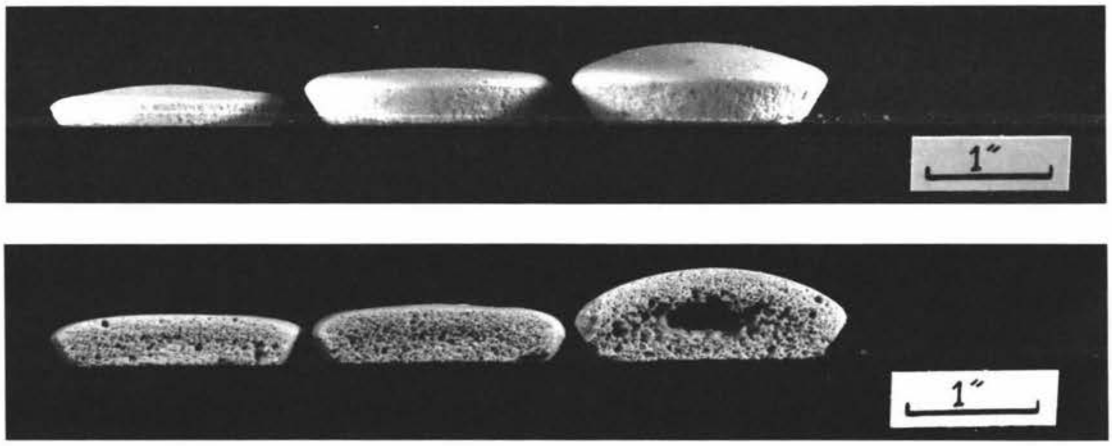
Left: wafer of density 0.20 gm./ml. resulting from the drying of a foamed concentrate of density 1.0 gm./ml. in a vacuum chamber pressure of 500 mm. of Hg.

Right: wafer of density 0.13 gm./ml. resulting from the drying of a foamed concentrate of density 0.7 gm./ml. in a vacuum chamber pressure of 500 mm. of Hg.

FIGURE 39. Effect of foam density of the 45% skim milk concentrate on the texture and density of the dried foam.



Size of wafers formed by vacuum foam drying the aerated concentrate at a chamber pressure of 360 mm. of Hg. and tray loadings of 5, 7, and 9 gm./in.^{2}.



Size and texture of wafers formed by vacuum foam drying the aerated concentrate at a chamber pressure of 240 mm. of Hg. and tray loadings of 5, 7, and 9 gm./in.^{2}.

FIGURE 40. Effect of tray loading on the volume and texture of the vacuum foam dried wafer.

the wafer when dried.

These results are for studies on skim milk concentrates only; foaming of full cream milk concentrates was not studied in detail.

d) Tray Loading

Increased tray loading markedly increased the drying time and consequently increased the cost of vacuum drying. Figure 40 shows that the size of the dried wafer is approximately proportional to the tray loading.

Figure 40 also shows that the texture varies with tray loading. There are two principal changes in texture with increased tray loading.

1. With increased loading, the pore size increases. This is believed to be due to a slow increase in the vacuum throughout the drying cycle. This means that foam layers which dry, or "set" first, will have a smaller pore size than those which dry at the latter part of the drying cycle.
2. A more obvious effect of increased tray loading is the difficulty of preventing foam collapse in the wet centre. The greater the loading, the longer the drying time, and hence, the greater the chance of vacuum changes causing collapse of the large volume of wet foam encased in the dried crust.

e) Browning Before Drying

Vacuum drying at temperatures below 80°C resulted in very little browning. Hence, the product must, of necessity, be browned before drying to develop the dairy caramel flavour. A satisfactory procedure was to foam a mixture of 200 gm. of 45% skim milk powder solution and 200 gm. of dairy caramel concentrate (sweetened condensed milk heated for 4 hours at 100°C). The resultant foam could readily be vacuum-dried to a palatable wafer.

V. POSSIBLE COMMERCIAL ASPECTS OF THIS WAFER TYPE OF PRODUCT

This major section of the work has traced the basic and technological studies undertaken to develop the porous milk-solids wafer or biscuit. All work has been carried out on a small scale with laboratory-sized equipment, and hence, there will likely be problems in scaling up these well-defined laboratory operations to commercial equipment. No attempt is made here to outline commercial detail. However, it is possible to comment and make suggestions on the basis of these laboratory studies.

A. Texture

The most outstanding feature of the milk wafer is its texture. SECTION V, Part IV, has discussed and illustrated the wide range of textures which are possible. The principal variables which may be controlled to produce a product of the desired texture are:-

1. Foam density of the 45% milk concentrate prior to drying.
2. Vacuum at which the wafer is dried.
3. Tray loading.

It is by manipulation of these variables that a whole range of product textures are possible with densities ranging from less than 0.1 gm./ml. for a foam dried at a pressure of 110 mm. of Hg., to 0.5 gm./ml. for a foam dried at atmospheric pressure. (Refer to Figure 38, page 171.)

The texture can be best described as crisp and crunchy to the bite with a smooth "melting" mouthfeel. The only undesirable textural characteristic is the tendency for the milk solids to cling to the teeth and palate. This problem was overcome to some extent by the addition of sucrose.

B. Flavour

As in the case of the caramelized dairy spread, there are hosts of possibilities of varying and improving the flavour of the wafer. Some of the successful possibilities explored are enumerated below.

1. Vanilla at low levels of 0.1 - 0.2% adds a pleasing background flavour which enhances the caramel flavour. The intensity of the caramel flavour may be adjusted by controlling the amount and intensity of the caramel concentrate added to the milk concentrate foam before drying.
2. Spices such as ginger, cinnamon, cloves, etc., at low concentrations may appeal to some palates.
3. Sugar is a necessary part of the flavour. Either invert sugar, glucose, or sucrose may be used as sweeteners - less invert sugar or glucose being necessary for a given level of sweetness.
4. There is also the possibility of developing a wide range of flavours by use of the wide range of commercially available natural and synthetic flavouring essences.

C. Use of Full Cream Milk Solids

Just as the presence of milk fat enhances the flavour and texture of the caramelized dairy spreads developed in SECTION IV, so its presence also enhances the flavour and mouthfeel of the porous wafer. It is true that, for all the studies of foam drying discussed here, skim milk solids were used - in fact, the use of skim milk foams was essential to maintain a stable porous structure throughout oven (hot air) drying. However, in the case of vacuum drying, a foam structure may be developed and maintained by careful control of the vacuum during drying. Thus, vacuum drying enables a full cream milk concentrate to be foamed and dried to a porous wafer. Preliminary investigation of this possibility indicated that sweetened condensed whole milk could be successfully vacuum dried to a porous wafer. It was impossible to foam and dry this product at atmospheric pressure without forming a collapsed hygroscopic mass.

While the foaming and vacuum-drying of whole milk concentrates to a porous wafer was not studied further, it is clear that this is a definite product possibility. The wafer product formed from whole milk concentrates has an improved flavour and texture compared with the product formed from skim milk concentrates. The undesirable tendency of the milk solids to cling to the mouth is substantially decreased by the presence of milk fat and sucrose.

D. Packaging and Storage

Time did not permit either a study of packaging materials and techniques or a study of the effect of various storage conditions on the quality of the product. The purpose of this study was principally to suggest and develop new product possibilities. The specific details of production and packaging were unable to be studied in the time available. There are, however, a few product characteristics which would dictate, to a large extent, the nature of packaging required to minimize the physical and chemical damage occurring during handling and storage.

1. The hygroscopicity of dry milk solids and sugar would necessitate the use of a packaging material having high moisture barrier properties.
2. The wafer foam structures are quite robust and can withstand considerable mechanical shock. Hence, it would seem that the standard commercial techniques of packing baked biscuits would be applicable.
3. While it is certain that a packaging material having a low moisture permeability is required, the importance of excluding oxygen has not been determined. The rate of autocatalytic oxidation will most probably be quite low, or inhibited, due to the presence of reducing substances formed as a result of the non-enzymic browning reaction.

There is no substitute for proper packaging and storage trials before any attempt is made to produce or market the product on a commercial scale.

VI. SUMMARY

New foods appearing on the consumer market frequently feature a palatable porous, or foam, texture. Hence, in an attempt to diversify the use of milk solids a study was undertaken to develop a porous wafer from milk solids. This involved two steps:-

1. Aeration of the milk solids concentrate.
2. Stabilization and drying of the foamed concentrate to a solid porous milk wafer.

Aeration of milk concentrates could be accomplished by either whipping or vacuum expansion of entrained gas.

A. Specifications For a Stable Foamed Milk Concentrate

A basic study of the factors affecting the foaming and stability of aerated concentrated skim milk solutions enabled specification of the variables necessary to form a stable foam which could be oven dried to a porous structure.

1. Whey Protein Nitrogen (of milk powder) : as high as possible and at least >4.5
2. Solids Concentration : 45% skim milk solids
3. Temperature : 25 - 30°C
4. Fat Content : NIL, or as little as possible
5. pH : leave at natural pH
6. Other solids; e.g., sucrose : use as little as possible
7. Foaming agents : none necessary
8. Stabilizing agent : 0.2% Edifas B

While these specifications are necessary for successful atmospheric oven drying of the milk foam, vacuum drying may be successfully applied to full cream milk concentrates if the variables such as vacuum-temperature cycle are carefully applied.

B. Drying of the Specified Milk Concentrate Foam

The foam prepared according to the above specifications was successfully oven or vacuum dried and a study was undertaken of the factors affecting drying and the characteristics of the dried foam. A wide range of textures were possible by controlling:-

1. Foam density of the 45% milk concentrate prior to drying.
2. Vacuum at which the wafer is dried.
3. Tray loading.

C. Commercial Aspects of the Wafer

As in the case of the caramelized dairy spread (SECTION IV), there is a host of possibilities for improving the flavour of such a product. The wide range of textures which may be developed by controlling the method of drying, together with the large choice of wafer flavours, make the development of a commercial product very flexible. That is, the wafer texture and flavour may, to a large degree, be 'tailor-made' to comply with specific market specifications.

A full cream wafer may be made by vacuum drying under carefully controlled conditions. While some full cream wafers were made, the details of the variables affecting their production were not studied.

In the absence of storage trials, it is suggested that these wafers could be packed in the same way as baked biscuits. A packaging material which is impermeable to moisture vapour would be a necessity.

SECTION VI

STUDIES ON THE DEVELOPMENT

OF

A CONCENTRATED CARAMEL FLAVOUR BASE

I. INTRODUCTION

As the milk caramel flavour is very palatable, another form in which it could be marketed is a concentrated liquid or flavoured powder. In such a form the concentrate could readily be dissolved or diluted for use as a flavouring agent in drinks, desserts, confections and biscuits.

Many common flavours are marketed in the liquid concentrate or powdered form; e.g., vanilla, malt, strawberry, etc. It is possible that the distinctive, desirable flavour of milk caramel in a concentrated, readily dilutable form, could find a market along with these types of products. Also, a caramel powder could be added to water to give a beverage of 20% solids. Such a product could form part of light-weight rations of high energy food for use by trampers, campers, and the armed services. With these thoughts in mind, the possibility of producing either a liquid concentrate or caramel flavoured powder was investigated.

II. LIQUID CONCENTRATE

The development of a suitable caramel base for flavouring milk was developed during World War II by Webb and Huffnagel (109). They found that the best caramel flavour was developed when a milk and sugar mixture was concentrated by boiling in an open kettle by methods similar to those used by caramel manufacturers. The formula for the base finally developed by them is given in Table XXV. Factors affecting the formulation of this caramel concentrate are discussed in the literature (109).

Initially, the caramel base was developed to flavour sterilized milks (109). A 1:6 dilution of caramel base with milk yielded a caramel milk which possessed an attractive flavour when served either hot or cold. While the caramel flavour is most suited to milk products, there is undoubtedly use for such a caramel concentrate in the flavouring of other types of foods. As a suitable caramel concentrate had already been developed, further work was not pursued in this area of study except for the observation that sweetened condensed milk heated for 3 hours at 100°C yielded a very soluble, attractively flavoured, milk caramel concentrate. The caramel flavour was intensified, (without any occurrence of bitterness) by heating to 100°C for 6 hours. Suffice to say here that a liquid caramel concentrate is a practical possibility with a potential market.

TABLE XXV

FORMULA FOR CARAMEL FLAVOUR BASE

Ingredients	Weight of Ingredient lbs.	Weights of Components Fat lbs.	SNF lbs.	T.S. lbs.
Cream (30% fat)	33.3	10	2.1	12.1
Condensed skim milk (30% solids)	15.0	-	4.5	4.5
Corn syrup	45.0	-	-	36.0
Sucrose	14.3	-	-	14.3
Salt	0.7	-	-	0.7
TOTAL	108.3	10	6.6	67.6

Heat the complete mixture with stirring to 160°C, and homogenize at 2,500 lbs. pressure. Cook in a candy kettle with double action stirrer to 238°F, cool slightly and add $8\frac{1}{4}$ lbs. of water and vanilla flavouring to suit the taste. Stir well and pour into a suitable receiver. Approximately 84 pounds of base containing 20% water will be recovered.

III. POWDERED CARAMEL FLAVOUR

A readily soluble powder has several economic and practical advantages when compared with a liquid concentrate. The principal advantages are:-

1. Ease of reconstitution and dilution.
2. While cost of production may be higher, packaging and storage is cheaper due to the greater concentration of solids.
3. Cheaper and easier transport by the user; e.g., troops, hikers.

Hence, the development of a milk caramel flavour in a suitable powdered form is an important market possibility. With this aim in mind, two methods of obtaining a caramel powder were explored:-

1. Heating of dry milk powder.
2. Heating of milk concentrate, followed by vacuum drying.

A. Heating of Dry Milk Powder

Wright (112) has clearly shown that at 13 - 14% moisture where browning is a maximum, only 0.5 seconds heating at 100°C is required to induce 50% insolubility of the milk solids. Even at 50°C, where the browning is extremely slow, only one hour is required for 70% insolubility to occur. Wright (112) presents evidence which indicates that this insolubility induced by liquid or moist heating is due to denaturation of the milk proteins, and particularly of casein. There is every reason to believe that the production of an insoluble form of protein during the process of milk drying is identical in nature to the ordinary heat coagulation of a protein, such as occurs, for instance, in the manufacture of evaporated milk. It is unlikely that browning has a great influence on this denaturation process which is almost complete in 87% milk solids after 1 hour heating at 50°C - a heat treatment during which little browning would have taken place.

It is obvious from the above discussion of the literature that any heating of milk powder, reconstituted or dry, will result in denaturation and insolubility long before there is appreciable "caramelization". This conclusion is supported by the many futile attempts of producing a soluble "caramelized" milk powder. Both whole milk powder and skim milk powder at a range of moisture contents, with or without the protecting influence of sucrose on protein solubility, were heat "caramelized". But in every case where appreciable "caramelization" occurred the milk protein became completely insoluble. After a consideration of such experimental results and the available literature, any further attempt at producing a caramel powder by heating dry milk powder appeared to be futile.

B. Heating of Milk Concentrate Followed by Vacuum Drying

During previous studies on sweetened condensed milk it was observed that even after 6 hours heating at 100°C or 1 hour at 120°C the resultant caramelized sweetened condensed milk had a solubility index as low as 0.7 - 0.8 ml. The excellent solubility of this caramel concentrate hints that if the soluble concentrate was dried under mild conditions the desired soluble dairy caramel powder would result.

"Vacuum-puff" drying at 70°C and a pressure of 4 mm. of Hg. was selected as a mild method of drying. To obtain a range of dairy caramel concentrates for drying, samples of sweetened condensed milk were heated for 1 hour at 100°C and 6 hours at 100°C. The concentrates were then vacuum dried and the solubility index of the powders determined by the method described in APPENDIX II. Results are recorded in Table XXVI which shows that both the low heat (1 hour/100°C) and high heat (6 hours/100°C) samples showed no increase in solubility index (i.e., decreased solubility) during drying.

TABLE XXVI

EFFECT OF DRYING ON THE SOLUBILITY OF DAIRY CARAMEL CONCENTRATE

Heat Treatment of Caramel	Solubility Index Before Drying	Solubility Index After Drying
1 hour at 100°C	0.1 - 0.3	0.2 - 0.3
6 hours at 100°C	0.7 - 0.8	0.7 - 0.8

Furthermore, the crushed caramel powder readily dissolved in water to give a pleasant tasting caramel drink. Because of its excellent solubility, the powder would also be suitable for use as a general flavour concentrate.

<u>NOTE</u>: Both the liquid concentrate and the caramel powder studied and discussed in this section, are, of necessity, full cream milk products. The milk fat is an integral part of these caramel flavours.

SECTION VII

SUGGESTIONS

FOR

FURTHER STUDY

The studies described in this thesis are very broad in scope and touch on several fields of investigation. As a consequence of this scope, it clearly was not possible to study every phase of the work in great depth or detail. Arising from these studies on promoted "caramelization" and texture development in milk solids, were several questions which required further study. It is the purpose of this section to outline some of the limitations of the present work, and to suggest fields of further study which would contribute in a practical way towards food technology generally, and specifically make the knowledge of milk more complete.

I. BASIC STUDIES OF PROMOTED BROWNING IN MILK SOLIDS

1. It is true that both the development of brown colour and caramelized flavour are closely associated reactions of the non-enzymic browning reaction in milk. In general, it is indicated that the degree of caramelized flavour is correlated positively with the degree of browning and related changes (83). This is easily verified subjectively by the observation that as the brown colour of sweetened condensed milk becomes darker, so does the intensity of the dairy caramel flavour increase. The question arises, however, as to how closely colour (as measured by reflectance) and flavour are correlated. This could best be determined by carefully controlled taste panel correlations of caramel flavour intensity with the objective measurement of colour (reflectance).

2. Patton (55,83) has proposed a tentative definition of caramelized flavour by listing four components (Refer to page 14). It is known that casein is directly involved and is essential to flavour development. Patton (84) has discussed the possibility of several aromatic compounds being an

integral part of the caramel flavour in whole milk. However, it is still not known what components are responsible for the integrated caramel flavour response known as milk caramel flavour. The paucity of information in this field still leaves the following questions unanswered:-

a) What compounds are responsible for caramel flavour? - could they be blended artificially to give a synthetic dairy caramel flavour?

b) What are the bitter compounds formed in advanced browning? Are these bitter compounds associated with the bitter by-products of glucose-casein "caramelization"? Could caramel flavour be intensified without the formation of bitterness?

3. The study of the effect of moisture concentration on the rate of browning in sweetened condensed milk (SECTION III, Part II, page 49) has injected new ideas into the concept of the browning model at low moisture contents. The theoretical discussion on pages 55 - 57 concluded that in "liquid" systems browning was favoured by a minimum, or complete absence, of water provided that the lactose (or reducing sugar) was soluble and available to react. While it is possible that the model proposed by Lea and Hannan (66,67) could well apply to the reaction between proteins and reducing sugars in the "dry" state, evidence suggests that a different model is applicable to the "liquid" system. There still remains the question:-

> Is the role of moisture in the dry systems of Lea (66,67) one of adsorption and attraction between protein molecules or does water function merely as a solvent for lactose?

Present evidence suggests the latter to be the case - browning being favoured by a complete absence of water so long as lactose is dissolved in a suitable solvent which makes it available to react. More study of model "liquid" and "dry" protein-reducing sugar systems is needed to determine which view is more likely to be correct.

4. The present study of the effect of glucose and sucrose on the rate of solubility decrease during browning in sweetened condensed milk (SECTION III, Part IV - B, page 69) has added little to the observations of Lea and Hannan (63) on the reaction between milk protein and reducing sugar (glucose) in the "dry" state. They (63) observed that the combining of the potential aldehyde group of reducing sugars with the free amino-groups tends to destabilize the protein and produce insolubility. The mechanism of producing insolubility is far from completely understood. Glucose shows a definitely harmful effect on solubility while disaccharides (e.g., sucrose) when present in relatively high concentrations, show a retarding effect on insolubility whether aldose or not. Similar effects of the same sugars occur in dried egg systems.

   A further study of the mechanism of sucrose protection from insolubility, would undoubtedly elucidate much of the mechanism of denaturation. While the protecting effect of sucrose on protein insolubility is of real technological importance, a study of the protein chemistry involved is beyond the scope of the present study.

II. QUESTIONS ARISING OUT OF THE STUDIES ON THE DEVELOPMENT OF A CARAMELIZED DAIRY SPREAD

1. While a good deal is known about the mechanism and factors responsible for the flavour of caramelized sweetened condensed milk, knowledge of the gel texture (formed during heating of sweetened condensed milk) is very meagre.

A comparison of the heat penetration studies with existing knowledge on the heat reactions of milk proteins suggests that the gel texture is a result of an interaction between κ-casein and β-lactoglobulin. While it is quite likely that the complex formed by this interaction could form a three-dimensional gel network, the present evidence is purely circumstantial.

Further study is needed to determine if κ-casein and β-lactoglobulin, are, in fact, the proteins responsible for the gel network. Also, the role of sugar, moisture, fat, and ions in the formation of the gel is unknown. There is a paucity of reported work on this gel formation and its study would be a significant contribution towards making the knowledge of milk and its behaviour more complete.

2. Possible commercial production techniques of producing the caramelized spread have been discussed in SECTION IV, Part IV, page 102. This discussion has been based completely on laboratory-scale trials and a knowledge of the commercial handling of similar food products. Pilot plant trials would be required to determine the relative advantages of the possible production techniques before such a product could be manufactured commercially. While the broad types of equipment have been described and suggested, the details of handling, filling, etc., remain to be determined.

3. The range of possible commercial product types has been suggested (SECTION IV, Part IV - C, page 111) and the recommended control of product and process variables to yield an optimum dairy caramel flavour has been summarized in Table XV, page 122. These recommendations are based purely on the subjective assessment of flavour and texture by the experimentor, and it is obvious that consumer preferences will vary from that of the

experimentor. Hence, a consumer survey or market needs and preferences would be an essential step in the final stages of developing a product for a given market.

4. Storage trials of sweetened condensed milk "caramelized" in the can (SECTION IV, Part V, page 112) indicated that the most serious change occurring during storage was the formation of macroscopic crystals. The normal methods of inhibiting the formation of these large crystals proved unsuccessful or impracticable (Refer to Part V - D, page 120). One possibility would appear to be the removal of most of the lactose from the sweetened condensed milk prior to "caramelization" in the can. It is suggested that this could be done by promoting the formation of large lactose crystals in sweetened condensed milk and then removing them by centrifugal screening. Studies on the feasability of such a technique may supply the answer to this important practical problem.

III. QUESTIONS ARISING OUT OF STUDIES ON THE DEVELOPMENT OF A POROUS WAFER FROM MILK SOLIDS

1. Foam Formation and Drying

The specification of product variables to obtain an optimum foam has been very empirical. While El-Rafey (34,35) has made a detailed study of factors affecting foaming in milk, there is a paucity of information on foaming in concentrated milk systems. The present study (SECTION V, Part III - B, page 132) has defined the qualitative effects of several variables on the foam stability and density of concentrated milk powder solutions. However, much work remains to be done in determining the quantitative effects of these variables on the surface active proteins of concentrated milk systems. The present study has concentrated on studying "made-up" concentrated solutions from a supply of milk powder having uniform quality, but indications are that concentrated fresh milk may behave in quite a different manner.

2. The present study has been restricted to the study of factors affecting the porous wafer structure formed by drying foams of "made-up" concentrated skim milk powder. A few experiments with concentrated fresh milk indicated that porous wafers formed from it had different textural and mouthfeel characteristics. This is most probably due to the solubility of such a wafer - wafers formed from "made-up" concentrated skim milk powder solutions are quite insoluble. Obviously much work remains to be done on the relative advantages of using "made-up" milk powder solutions or concentrated fresh milk.

3. SECTION V, Part IV, page 161, has described the possibility of developing a wide range of flavours and textures which should be capable of slight modification to comply with a given market specification. The present study in this field has been limited and a greater study of the effect of additives on bubble and pore formation is required.

4. A brief study of vacuum drying of sweetened condensed milk indicated that full cream milk concentrates could be successfully vacuum dried to a porous wafer. Hence, it is quite possible to develop a whole range of porous wafers having a range of desirable fat contents - depending on consumer preferences. To achieve this a further study would have to be undertaken to determine the manipulation of process variables to achieve the desired texture.

5. The possibility of achieving a wide range of wafer textures and flavours has been outlined. From this range, a product may be selected to meet specific market requirements. The purpose of this study was to develop and demonstrate the range possible, and only a consumer survey could answer the question as to which wafer was the most desirable.

APPENDIX

I. DETERMINATION OF 5-HYDROXYMETHYLFURFURAL (HMF) BY SPECTROPHOTOMETRIC MEASUREMENT OF THE 2-THIOBARBITURIC ACID (TBA) REACTION PRODUCT

Notes:-

This method was originally developed by Keeney and Basette (60) and has been successfully used by Richards (93) for his quantitative study on browning in "dry" skim milk and lactose-casein systems. The method was found to be directly applicable as a chemical measurement of the rate of browning in sweetened condensed milk. The standard method used in the present study is basically the Keeney and Basette method (60), except for a few minor modifications in the method of obtaining the TBA extract.

Method:-

1. 20 gm. of caramelized sweetened condensed milk was dissolved in 180 ml. of water by beating for 2 mins. at top speed in a Kenwood Chefette.
2. The resultant solution was centrifuged at 2000 RPM in a centrifuge of 19½ "head diameter" (distance between inside bottoms of opposite cups measured through the centre of rotation of the centrifuge, while the cups are horizontally extended). The supernatant was then decanted and filtered through Whatman No.1 filter paper.
3. 10 ml. of filtrate was pipetted into a 50 ml. test tube.
4. 10 ml. of 40% trichloroacetic acid solution (40 gm. TCA diluted to 100 ml. with water) was added to the filtrate from a burette.
5. The contents of the tube were mixed well and filtered through Whatman No.42 filter paper.
6. 4.0 ml. of filtrate was pipetted into a test tube and 1.0 ml. of

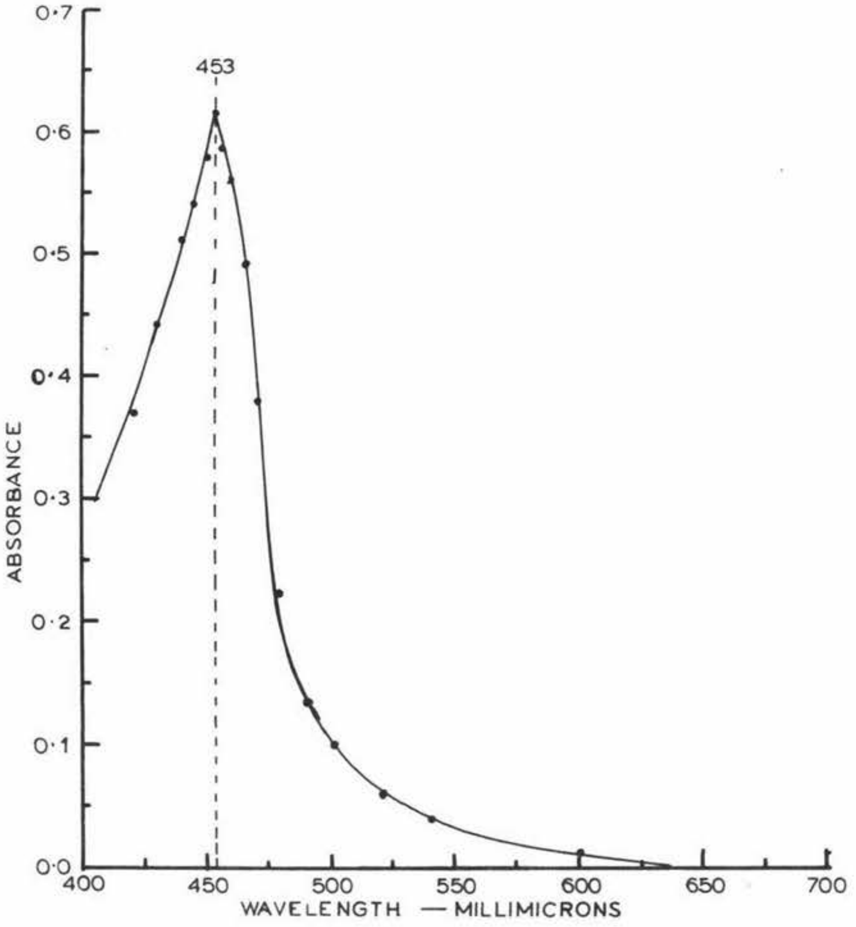


FIG.41. ABSORPTION SPECTRUM OF THE TBA DERIVATIVE OF SWEETENED CONDENSED MILK

0.05 N TBA added. (0.72 gm. 2-thiobarbituric acid in 100 ml., solution prepared by warming slightly and cooling to 25°C before use.)

7. The tube was then placed in a 40°C water bath for 30 - 40 minutes.
8. The tube was then removed from the bath and rapidly cooled to room temperature (20°C) before measuring the absorbance at 453 millimicrons.

   (The absorption spectrum of the TBA derivative of sweetened condensed milk, obtained by the above method, is shown in Figure 41. The peak absorbance is at 453 millimicrons.)
9. The optical density of the solution was measured against a blank prepared in the same way as the sample except that 10 ml. of water is substituted for the 10 ml. of milk extract in step (3).

II. DETERMINATION OF SOLUBILITY INDEX

Notes:-

This is an adaptation of the method outlined by the American Dry Milk Institute, Inc. Bulletin 916. (5).

Procedure:-

1. To 200 ml. of water at 60 - 70°F add a sample containing 20 gm. of skim milk solids; i.e., a sample of 13 gm. for full cream milk powder. For sweetened condensed milk, a sample of 60 gm. was used.
2. Add 3 drops of an antifoam (optional)
3. Disperse the mixture in a Kenwood Chefette at speed 1 for exactly 90 seconds.
4. Allow the sample to stand for a period not to exceed 15 minutes. Mix the sample thoroughly and fill a conical graduated centri-

fuge to the 50 ml. mark with liquid.

5. Centrifuge the tube for 10 minutes at 1000 RPM in a centrifuge of "head diameter" 19½ inches.

   (The "head diameter" is the distance between the inside bottoms of opposite cups measured through the centre of rotation of the centrifuge while the cups are horizontally extended.)

6. Immediately siphon off the supernatant liquid to within 5 ml. of the surface of the sediment level, using care not to disturb the sediment layer.

7. Add about 25 ml. distilled water at 60 - 70°F and shake the tube gently to disperse the sediment, dislodging it if necessary with a wire.

8. Fill the tube to the 50 ml. mark with distilled water at 60 - 70°F.

9. Again centrifuge at 1000 RPM for 10 minutes.

10. Hold the tube in a vertical position with the upper level of the sediment on a level with the eye and report the millilitres of sediment in the tube to the nearest graduated scale division. The sediment is easily distinguished when the tube is held between the eye and a strong source of light.

III. MEASUREMENT OF FOAM CHARACTERISTICS

The two basic parameters of a foam are its volume, or foam density, and its stability. Simple techniques of measuring these two parameters are described below.

A. Foam Density

Foam density was measured simply by pouring 100 ml. of foam into an

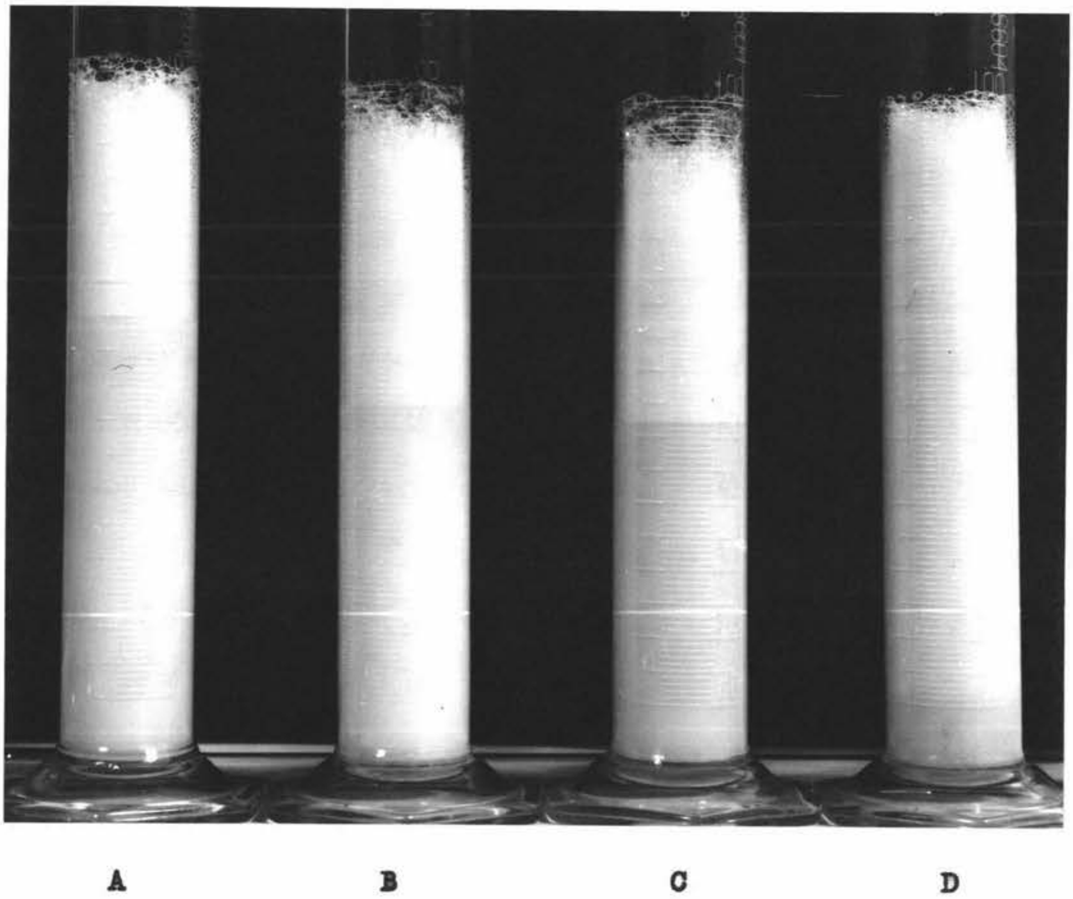


FIGURE 42. Demonstration of the difference between an unstable foam (A, B, and C with 65, 54, and 52 mls. of liquid separated) and a stable foam (D, with only 10 mls. of liquid separated).

100 ml. measuring cylinder and determining the weight of this volume of foam. Foam density is hence expressed as gm./ml. of foam, or gm./ml.

B. Foam Stability

Several methods have been described for measuring foam stability, some of which depend on the measurement of half-volume time, rate of collapse, and rate of drainage to the bottom (3). In the present work a simple measure of drainage of liquid to the bottom of the foam was found to correlate well with the stability of the foam to oven and vacuum drying.

The method simply consists of allowing 100 ml. of foam (from foam density measurement) to stand at room temperature for 3 hours in an 100 ml. measuring cylinder. After 3 hours, the volume of liquid separated at the bottom of the foam was recorded as mls. of liquid separated.

Figure 42 demonstrates the simplicity of this measurement. Samples A, B, and C are unstable foams of 25 - 40% milk solids solutions. The instability of these foams is evident by the high drainage of 54 - 65 mls. of separated liquid, and the collapse of the upper foam layers. Collapse and drainage is complete in these samples after 6 hours.

Sample C is a 50% milk solids solution showing very little collapse or drainage. Hence, it is obvious that this is a very stable foam.

Note:-

The greater the mls. of liquid separated in 3 hours, the less is the foam stability, and vice versa.

IV. MEASUREMENT OF WAFER (DRIED FOAM) DENSITY

The density of the dried foam was simply measured by taking a known weight of foam and measuring its volume by volume displacement of rape seed. The density is then expressed as gm./ml.

V. TOLUENE DISTILLATION DETERMINATION OF MOISTURE CONTENT

This was determined by the standard method described by the American Dry Milk Institute, Inc., 1954. Standard Methods of Analysis. Bull. No.911, page 18.

BIBLIOGRAPHY

Ref. No.

1. ADACHI, S. 1956. New amino-acid glycosides isolated from tryptic hydrolysates of milk products. Nature 177, 976.

2. ADAM, N. K. 1949. The Physics and Chemistry of Surfaces, 3rd. Ed. Oxford Clarendon Press.

3. ADAMSON, A. W. 1960. Physical Chemistry of Surfaces. Interscience Publishers, New York.

4. ALEXANDER, A. E., and JOHNSON, P. 1949. Colloid science. Oxford University Press.

5. AMERICAN DRY MILK INSTITUTE, INC. 1954. Standard Methods of Analysis. Bull. No.911.

6. AMERICAN DRY MILK INSTITUTE, INC. Standards for Grades of Dry Milks including Methods of Analysis, "Determination of undenatured whey protein nitrogen in nonfat dry milk".

7. AMERINE, M. A. 1948. Hydroxymethyl furfural in Californian wines. Food Res. 13, 264.

8. ANET, E. F. L. J. 1959. Chemistry of non-enzymic browning, VII. Crystalline di-D-fructose-glycine and some related compounds. Aust. J. of Chem. 12, 280.

9. ANET, E. F. L. J. 1960. Degradation of carbohydrates. I. Isolation of 3-deoxyhexosones. Aust. J. of Chem. 13, 396.

10. ANET, E. F. L. J. 1961. Degradation of carbohydrates. II. The action of acid and alkali on 3-deoxyhexosones. Aust. J. of Chem. 14, 295.

11. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. 1945. Official and Tentative Methods of Analysis, 5th Ed. Pp. 309, 570-572.

12. BARNES, H. M., and KAUFMAN, C. W. 1947. Industrial aspects of the browning reaction. Ind. Eng. Chem. 39, 1167.

13. BIERMAN, H. R., and DOAN, F. J. 1924. A colorimetric picric acid method for the determination of lactose. J. Dairy Sci. 7, 381.

14. BIKERMAN, J. J. 1953. Foams: Theory and Industrial Applications. Reinhald Publishing Corp, New York.

15. BRUNAUER, S., EMMET, P. H., and TELLER, E. 1938. Adsorption of Gases in multimolecular layers. J. Am. Chem. Soc. 60, 309.

Ref. No.

16. BROOKS, J., and TAYLOR, D. J. 1955. Eggs and Egg Products. D.S.I.R., Food Investigation Special Report No.6, HMSO, London.

17. BULL, H. 1944. Adsorption of water vapour by proteins. J. Am. Chem. Soc. 66, 1499.

18. BURICK, E. J. 1950. The rate of surface tension lowering and its role in foaming. J. Colloid Sci. 5, 421.

19. BURTON, H. 1954. Colour changes in heated and unheated milk. I. The browning of milk on heating. J. Dairy Res. 21, 194.

20. BURTON, H. 1955. Colour changes in heated and unheated milk. III. The effect of variation in milk composition on the whitening and browning of separated milk on heating. J. Dairy Res. 22, 82.

21. BURTON, H., ADAM, D. N., THIEL, C. C., GRINSTEAD, E., and CLEGG, L. F. L. 1953. Some investigations into the batch process of milk sterilization. J. Soc. Dairy Tech. 6, 98.

22. BURTON, H., and McWEENEY, D. J. 1964. Non-enzymic browning: routes to the production of melanoidins from aldoses and amino-compounds. Chem. Ind. i, 462, 1964.

23. CARPENTER, K. J. 1960. The estimation of available lysine in animal-protein foods. Biochem. J. 77, 604.

24. CHAPMAN, R. A., and McFARLANE, W. D. 1945. A colorimetric method for the estimation of reducing groups in milk powders. Can. J. Res. 23B, 91.

25. CHOI, R. P., KONCUS, A. F., O'MALLEY, C. M., and FAIRBANKS, B. W. 1949. A proposed method for the determination of colour of dry products of milk. J. Dairy Sci. 32, 580.

26. CHOI, R. P., KONCUS, A. F., CHERREY, G., and REMALEY, R. J. 1953. Determination of protein reducing value of milk as an indication of the presence of nonfat dry milk solids. J. Milk and Food Tech. 16, 241.

27. COHN, E. J., and HENDRY, J. L. 1926. Organic Synthesis. 10, 16. Wiley and Sons, Inc., New York.

28. COPLEY, M. J., KAUFMAN, V. F., and RASMUSSEN, C. L. 1956. Recent developments in fruit and vegetable powder technology. Food Tech. 10, No.12, 589.

29. COULTER, S. T., JENNESS, R., and GEDDES, W. F. 1951. Physical and chemical aspects of the production, storage and utility of dry milk milk products. Adv. Food Res. 3, 45.

30. CROWE, J. K., JENNESS, R., and COULTER, S. T. 1948. The reducing capacity of milk and milk products as measured by a modified ferricyanide method. J. Dairy Sci. 31, 595.

Ref. No.

31. DANEHY, F. P., and PIGMAN, W. W. 1951. Reactions between sugars and nitrogenous compounds and their relationship to certain food problems. Adv. Food Res. 3, 241.

32. DEHN, W. M., and HARTMAN, F. A. 1914. The picric colorimetric method for the estimation of carbohydrates. J. Am. Chem. Soc. 36, 403.

33. DOOB, H., Jr., WILLMAN, A., and SHARP, P. F. 1942. Influence of moisture on browning of dried whey and skim milk. Ind. Eng. Chem. 34, 1460.

34. EL-RAFEY, M. S., and RICHARDSON, G. A. 1944. The role of surface-active constituents involved in the foaming of milk and certain milk products. I. Milk proteins. J. Dairy Sci. 27, 1.

35. EL-RAFEY, M. S., and RICHARDSON, G. A. 1944. The role of surface-active constituents involved in the foaming of milk and certain milk products. III. Whey, skimmed milk, and their counterparts. J. Dairy Sci. 27, 19.

36. EVANS, R. J., and BUTTS, H. A. 1951. The inactivation of basic amino acids and tryptothan. Food Res. 16, 415.

37. FEARON, W. R. 1942. The detection of lactose and maltose by means of methylamine. Analyst 67, 130.

38. GINNETTE, L. F., GRAHAM, R. R., MIERS, J. C., and MORGAN, A. I., Jr. 1963. Tomato powder for Foam-Mat drying. Food Tech. 17, No.6, 133.

39. GLASSTONE, S., and LEWIS, D. 1960. Elements of Physical Chemistry. Macmillan and Co. Ltd., London.

40. GOTTSCHALK, A. 1952. Some biochemically relevant properties of N-substituted fructoseamines derived from N-glucosylamino acids and N-arylglucosylamines. Biochem. J. 52, 455.

41. GOTTSCHALK, A., and PARTRIDGE, S. M. 1950. Interaction between simple sugars and amino acids. Nature 165, 684.

42. GOULD, I. A. 1951. Compounds formed by the heat treatment of milk. Milk Plant Monthly. 40, (2), 44.

43. HANDLEMAN, A. R., CONN, J. F., and LYONS, J. W. 1961. Bubble mechanics in thick foams and their effects on cake quality. Cereal Chem. 38, 294.

44. HANNAN, R. S., and LEA, C. H. 1951. Reactions between glucose and the terminal amino group of lysine. Nature 168, 744.

45. HANNAN, R. S., and LEA, C. H. 1952. Studies of the reaction between proteins and reducing sugars in the "dry" state. VI. The reactivity of the terminal amino groups of lysine and model systems. Biochim. et Biophys. Acta 9, 293.

Ref. No.

46. HARLAND, H. A., JENNESS, R., and COULTER, S. T. 1947. Changes produced in milk on heating. J. Dairy Sci. 30, 526.

47. HART, M. R., GRAHAM, R. P., GINNETTE, L. F., and MORGAN, A. I., Jr. 1963. Foams for Foam-Mat drying. Food Tech. 17, No.10, 90.

48. HARTMAN, G. H., Jr., and SWANSON, A. M. 1965. Changes in mixtures of whey proteins and κ-casein due to heat treatments. J. Dairy Sci. 48, 1161.

49. HENRY, K. M., KON, S. K., LEA, C. H., and WHITE, J. C. D. 1948. Deterioration on storage of dried milk. J. Dairy Res. 15, 293.

50. HODGE, J. E. 1953. Chemistry of browning reactions in model systems. J. Agr. Food Chem. 1, 928.

51. HODGE, J. E., and RIST, C. E. 1953. The Amadori rearrangement under new conditions and its significance in non-enzymic browning reactions. J. Am. Chem. Soc. 75, 316.

52. HOLDEN, T. F., ACETO, N. C., and SCHOPPET, E. F. 1964. Effects of viscosity and temperature on the foaming characteristics of concentrated whole milk. J. Dairy Sci. 47, 359.

53. HONER, C. J., and TUCKEY, S. L. 1953. A method for determination of lactose in milk by paper chromatography. J. Dairy Sci. 36, 1233.

54. HOWITZ, M. G., DAVIDSON, H. M., HOWARD, F. D., and REITH, F. J. 1951. Determination of lactose in biological materials. Anal. Chem. 23, 375.

55. JENNESS, R., and PATTON, S. 1959. Principles of Dairy Chemistry, Pp 348. John Wiley & Sons, Inc. New York.

56. JOSLYN, M. A., and HEID, J. L. 1963. Food Processing Operations, 2, 424. Avi Publishing Co. Inc., Westport, Conn.

57. JONES, N. R. 1957. Non-enzymic Browning Reactions in Foods. Torry Research Station, Memoir No. 8, Aberdeen Food Investigation Organisation, D.S.I.R., HMSO, London.

58. JOSEPH, G. H., and BAIER, W. E. 1949. Methods of determining the firmness and setting time of pectin test jellies. Food Tech. 3, 18.

59. KASS, J. P., and PALMER, L. S. 1940. Browning of autoclaved milk, chemical factors involved. Ind. Eng. Chem. 32, 1360.

60. KEENEY, S. K., and BASETTE, R. 1959. Detection of intermediate compounds in the early stages of browning reaction in milk products. J. Dairy Sci. 42, 945.

61. KON, S. K., and HENRY, K. M. 1949. Nutritive value of milk and milk products. J. Dairy Res. 16, 68.

Ref. No.

62. LARSEN, P. B., and GOULD, I. A. 1951. A comparative study of three methods of determining the heat destruction of lactose in milk with special reference to the picric acid colorimetric procedure. J. Dairy Sci. 34, 16.

63. LEA, C. H. 1948. The reaction between protein and reducing sugar in the "dry" state. J. Dairy Res. 15, 369.

64. LEA, C. H. 1948. Determination of the free amino-nitrogen of casein and of fresh and deteriorated milk protein by the Van Slyke method. J. Dairy Res. 15, 364.

65. LEA, C. H. 1950. The role of amino-acids in the deterioration of food: the browning reaction. Chemistry and Industry, Pp 155, 1950.

66. LEA, C. H., and HANNAN, R. S. 1949. Studies on the reaction between proteins and reducing sugars in the "dry" state. I. The effect of activity of water, of pH, and of temperature on the primary reaction between casein and glucose. Biochim. et Biophys. Acta 3, 313.

67. LEA, C. H., and HANNAN, R. S. 1950. Studies on the reaction between proteins and reducing sugars in the "dry" state. II. Further observations on the formation of the casein-glucose complex. Biochim. et Biophys. Acta 4, 518.

68. LEA, C. H., and HANNAN, R. S. 1950. Studies on the reaction between proteins and reducing sugars in the "dry" state. III. Nature of protein groups reacting. Biochim. et Biophys. Acta 5, 433.

69. LEA, C. H., HANNAN, R. S., and RHODES, D. N. 1951. Studies on the reaction between proteins and reducing sugars in the "dry" state. IV. Decomposition of the amino-sugar complex and the reaction of acetylated casein with glucose. Biochim. et Biophys. Acta 7, 366.

70. LEA, C. H. 1965. The advantages of non-enzymic browning reactions in food processing and storage. Food Manufacture 1965. No.2, 1.

71. LEWIN, S. 1956. Studies on the reaction of amino and imino compounds with sugars: the reaction of histidine with glucose. J. Biochem. 63, 14.

72. LEWIS, V. M., and LEA, C. H. 1950. A note on the relative rates of reaction of several reducing sugars and sugar derivatives with casein. Biochim. et Biophys. Acta 4, 532, 1950.

73. LIGHTBODY, H. D., and FEROLD, H. L. 1948. Biochemical factors influencing the shelf life of dried whole eggs and means of their control. Adv. Food Res. 1, 149.

74. LOWE, R. 1959. Experimental Cookery from the Chemical and Physical Standpoint. 4th Ed. John Wiley & Sons, Inc., New York.

Ref. No.

75. MATZ, S. A. 1962. Food Texture. Avi Publishing Co. Inc., Westport, Conn.

76. MELLON, E. F., KORN, A. H., and HOOVER, S. R. 1947. Water absorption of proteins. I. The effect of free amino groups in casein. J. Am. Chem. Soc. 69, 827.

77. MOHAMMAD, A. H., FRAENKEL-CONRAT, and OLCOTT, H. S. 1949. The browning reactions of proteins with glucose. Arch. Biochem. 24, 157.

78. NELSON, V. 1948. The spectrophotometric determination of the colour of milk. J. Dairy Sci. 31, 409.

79. NELSON, V. 1948. The colour of evaporated milk with respect to time and temperature of processing. J. Dairy Sci. 31, 415.

80. OSBORNE, T. B., VAN SLYKE, D. D., LEAVENWORTH, C. S., and VINOGARD, M. 1912. Some products of hydrolysis of gliadin, lactalbumin, and the protein of rice kernel. J. Biol. Chem. 12, 275.

81. PATTON, S. 1950. Studies of heated milk. III. Mode of formation of certain furan compounds. J. Dairy Sci. 33, 904.

82. PATTON, S. 1952. Studies of heated milk. IV. Observations on browning. J. Dairy Sci. 35, 1053.

83. PATTON, S. 1955. Browning in milk: a review. J. Dairy Sci. 38, 457.

84. PATTON, S. 1958. Review of organic chemical effects of heat on milk. J. Agr. Food Chem. 6, 132.

85. PATTON, S., and FLIPSE, R. J. 1953. Studies of heated milk. V. The reaction of lactose with milk protein as shown by lactose-1-C^{14}. J. Dairy Sci. 36, 766.

86. PATTON, S., and JOSEPHSON, D. V. 1949. Observations on the application of the nitroprusside test to heated milk. J. Dairy Sci. 32, 398.

87. POTTER, R. D., and PATTON, S. 1951. Unpublished data, 1951, quoted in J. Dairy Sci. 38, 457, (1955).

87A. POTTER, R. D., and PATTON, S. 1956. Evidence of maltol and hydroxymethylfurfural in evaporated milk as shown by paper chromatography. J. Dairy Sci. 39, 978.

88. RAMSDEN, W. 1903. Proc. Royal Soc. 72, 56.

89. RAMSEY, R. J., TRACEY, P. H., and RUEHE, H. A. 1933. The use of corn sugar in the manufacture of sweetened condensed milk. J. Dairy Sci. 16, 17.

Ref. No.

90. REYNOLDS, T. M. 1963. Chemistry of non-enzymic browning. I. The reaction between aldoses and amines. Adv. Food Res. 12, 1.

91. REYNOLDS, T. M. 1965. Chemistry of non-enzymic browning. II. Adv. Food Res. 14, 167.

92. RICHARDS, E. L. 1956. Non-enzymic browning: the reaction between D-glucose and glycine in the "dry" state. Biochemical J. 64, (4), 639.

93. RICHARDS, E. L. 1963. A quantitative study of changes in dried skim-milk and lactose-casein in the "dry" state during storage. J. Dairy Res. 30,223.

94. ROGERS, L. A. 1928. Fundamentals of Dairy Science, Pp 171-174. Chemical Catalogue Co., New York.

95. ROSS, A. F. 1948. Deterioration of processed potatoes. Adv. Food Res. 1, 257.

96. SANMANN, F. P., and RUEHE, H. A. 1930. Some factors influencing the volume of foam on milk. J. Dairy Sci. 13, 48.

97. SCHONBERG, A., and MOUBASHER, R. 1952. The Strecker degradation of α-amino acids. Chem. Revs. 50, 261.

98. SCHONBERG, A., MOUBASHER, R., and MOSTOFA, A. 1948. Degradation of α-amino acids to aldehydes and ketones by interaction with carbonyl compounds. J. Chem. Soc. 176, (1948).

99. SHARP, J. G. 1957. Deterioration of dehydrated meat during storage. II. Effect of pH and temperature on browning changes in dehydrated extracts. J. Sci. Food Agr. 8, 21.

100. SINNAMON, H. I., ACETO, N. C., ESKEY, R. K., and SCHOPPET, E. F. 1957. Dry whole milk. I. A new physical form. J. Dairy Sci. 40, 1036.

101. SOMOGYI, M. 1945. A new reagent for the determination of sugars. J. Biol. Chem. 160, 61.

102. STADTMAN, E. R. 1948. Non-enzymic browning in fruit products. Adv. Food Res. 1, 325.

103. TALMUD, D., and SUCHOWOLSKAJA, S. Z. 1931. Phys. Chem. 154, 277.

104. VAN ARSDEL, W. B. 1963. Food Dehydration, Volume I. Avi Publishing Company, Inc., Westport, Conn.

105. VAN SLYKE, D. D. 1913-1914. The hexone bases of casein. J. Biol. Chem. 6, 531.

106. VAN SLYKE, L. L. 1923. The Chemistry of Casein. Proc. World's Dairy Cong. 2, 1145.

Ref. No.

107. WEBB, B. H., and HOLM, G. E. 1930. Colour of evaporated milks. J. Dairy Sci., 13, 25.

108. WEBB, B. H., and HOLM, G. E. 1932. The heat coagulation of milk. II. The influence of various added salts upon the heat stabilities of milks of different concentrations. J. Dairy Sci. 15, 345.

109. WEBB, B. H., and HUFFNAGEL, C. F. 1946. The manufacture of sterilized caramel milk. J. Dairy Sci. 29, 607.

110. WHITTIER, E. O., and WEBB, B. H. 1950. Byproducts from Milk. Reinhold, New York.

111. WOLFROM, M. L., KOLB, D. K., and LANGER, A. W. 1953. Chemical interaction of amino compounds and sugars. VII. pH dependency. J. Am. Chem. Soc. 75, 3471.

112. WRIGHT, N. C. 1933. Factors affecting the stability of milk proteins. I. The effect of heat on the solubility of milk proteins. J. Dairy Res. 4, 122.