MILKFAT - VEGETABLE OIL BLENDS FOR THE MANUFACTURE OF DANISH PASTRY MARGARINE

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PEARL WING MING CHIN

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ERRATA

pg. 32... line 7. Should read "... with 0.2% of Pricat 9900 catalyst (w/w on a nickel basis)."

pg. 32... lines 21 and 24 should read "... Pricat 9908 catalyst (w/w on a nickel basis)..."

SUMMARY

In an attempt to increase the utilization of milkfat in the baking industry, the present study was undertaken to manufacture a margarine containing a large proportion of milkfat which would be suitable for the production of danish pastries.

Initially, a sample of commercial pastry margarine used for manufacture of danish pastries in Japan was purchased. The fatty acid and triacylglycerol compositions were determined by gas liquid chromatography while the melting characteristics were studied using nuclear magnetic resonance spectroscopy and differential ~~scale~~ scanning calorimetry. The analysis showed that the Japanese pastry margarine contained a sufficient proportion of solid fat in the region at which the pastry was rolled (15-20°C) and enough solid fat was retained at the proofing temperatures. In addition, this pastry margarine melted totally at body temperatures.

A series of blends was formulated with melting characteristics similar to that of the Japanese pastry margarine. These blends contained a large proportion of milkfat (60-70%), an oil with a final melting point below 5°C and a fat with a large proportion of high melting triacylglycerols. These latter fats were prepared by hydrogenating cottonseed and palm oil in a pilot scale hydrogenation vessel made at the New Zealand Dairy Research Institute.

A blend containing hydrogenated palm oil : milkfat : sunflower seed oil (20 : 70 : 10) was manufactured into margarine by four different methods. Two processes involved churning cream in a z-blade reworker, the other two involved rapid cooling of the product mix in a scraped surface heat exchanger. From these manufacturing trials, two experimental margarines were selected for use in the danish pastry baking trials. These margarines gave satisfactory danish pastries although they had less flakiness and volume increase than the pastries made from the Japanese pastry margarine. This was probably due to the worksoftening of the experimental margarine which caused the dough layers to stick together and bring about a loss in the flakiness and volume of the pastries.

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NOMENCLATURE

For lipids containing glycerol, the nomenclature suggested by the IUPAC - IUB Commission on Biochemical Nomenclature (Biochem. J. 1967) is used.

Fatty acids are designated by number of carbon atoms : number of double bonds, e.g. 16:0 refers to palmitic or 1-hexadecanoic acid.

Triacylglycerols are designated by the number of acyl carbon atoms, e.g. C_{38} or 38.

A number of abbreviations have been used:

FA	Fatty acid
FFA	Free fatty acid
HMF	High melting fraction
IMF	Intermediate melting fraction
LMF	Low melting fraction
rpm	revolutions per minute
TG	Triacylglycerol

All pressures stated in the text are in absolute pressures.

CHAPTER 1

INTRODUCTION

Legally, butter must contain at least 80% fat (all of which must be pure milkfat) and a maximum of 16% water. As a consequence of these legal restrictions, there has been a reluctance for the dairy industry to blend oils with milkfat since products like this cannot be termed as butter. However, in recent times there has been some interest in the mixing of milkfat and vegetable oils for dairy spreads. An example of this type of product is "Bregott" made from an 80:20 milkfat: oil mix (Anon, 1969) manufactured in Sweden and claimed to have superior spreading properties over normal butter.

The blending of milkfat and oil for reasons other than improving spreadability has not been extensively researched. It would seem advantageous to incorporate milkfat into cake and pastry margarine to enhance the flavour of the end products, although the high cost of milkfat in some countries may prevent this from becoming commercially feasible.

In New Zealand, milkfat is relatively cheap and it may be possible to produce a cake or pastry margarine containing a significant amount of milkfat at a competitive price. This type of product could capture a segment of the commercial baking industry which is at present monopolised by margarine.

1.1 PRODUCTION OF MARGARINE

1.1.1 Oil Processing

Before margarine is produced, crude oils are purified and modified to give fats and oils of desired melting characteristics and acceptable taste. The methods involved are well known and have been reviewed by Swern (1964a, 1982), Vernon Young (1980), Gavin (1981), Harraldson (1983) and Forster *et al*. (1983).

(a) Purification

Purification consists of refining, bleaching and deodorization. Refining is the removal of free fatty acids (FFA), phosphatides or mucilaginous material. Bleaching involves the adsorbtion of unwanted pigments while deodorization removes traces of constituents which give unwanted flavours and odours (Swern, 1964b).

The crude oil is first degummed, a process by which hydratable substances are subjected to water or steam treatment followed by centrifuging while non-hydratable substances are removed by treatment with acid, e.g. phosphoric acid (Harraldson, 1983; Forster et al., 1983).

After degumming, the free fatty acids (FFAs) are neutralized with caustic soda to form a soapstock which is removed from the neutralized oil (Swern, 1964b; Young, 1980). Bleaching involves the adsorbtion of unwanted pigments onto a diatomaceous earth which is then removed from the bleached oil by filtration. The final stage of oil purification is deodorization (Gavin, 1981). This process involves steam stripping of the oil in a batch, semi-continuous or continuous deodorizer to remove residual FFAs, aldehydes and ketones which are responsible for unacceptable oil odours and flavours. The effectiveness of the process depends on a combination of the mixing of steam and oil.

A recent development in the purification of oils has been the introduction of physical refining (Forster et al., 1983). The basis of this process is a high temperature deodorization which removes flavours, odours and FFAs. The crude oil is usually degummed and bleached prior to this high temperature deodorization. The advantage of physical refining is that it can treat oils containing a large percentage of FFA (>8%) and the only effluent problem is 50 ppm or less of fat which remains in the waste water (Young, 1980). However, the process is not as flexible as that involving neutralization with caustic soda and consequently not all types and qualities of oil can be effectively purified by physical refining.

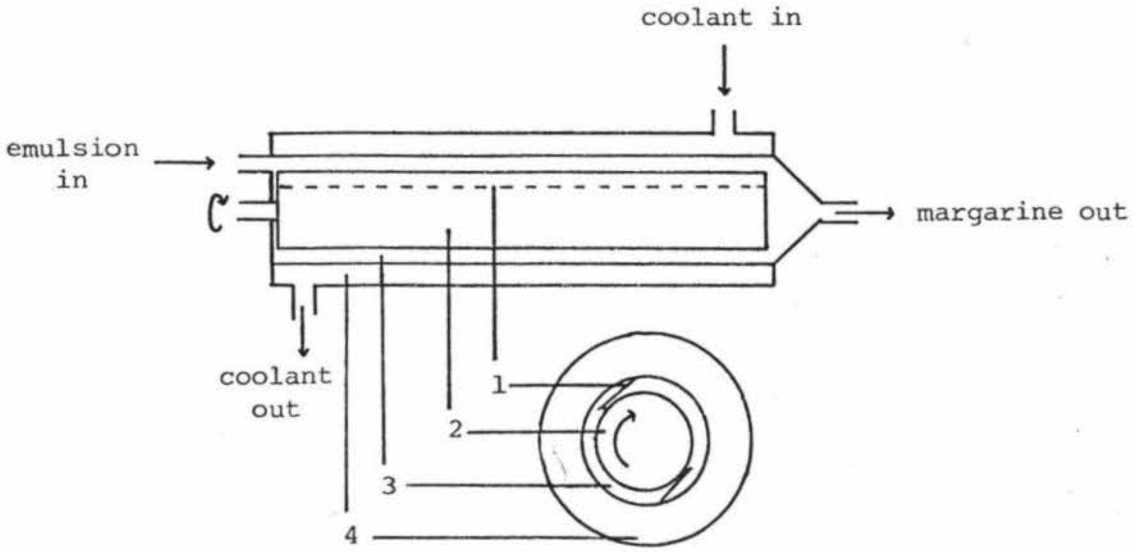

FIGURE 1: Diagram of a scraped surface heat exchanger*

1. blades	3. annular space for emulsion
2. rotor shaft	4. annular space for coolant

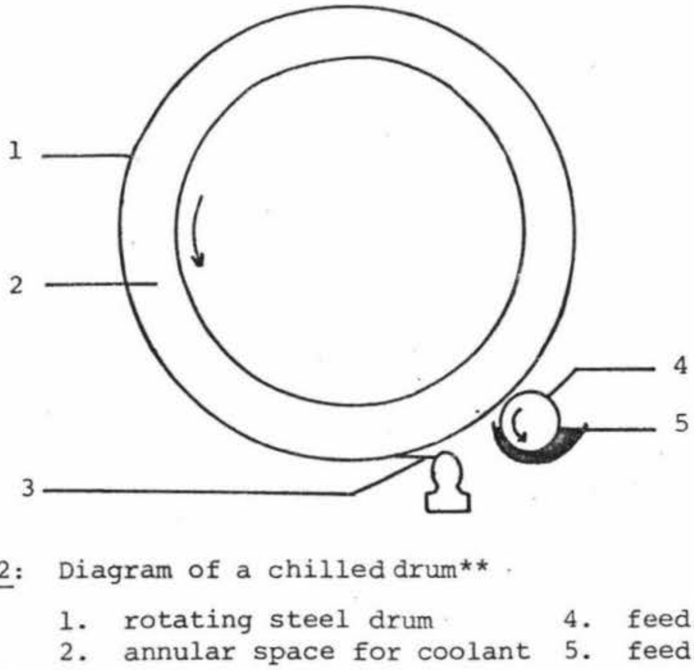

FIGURE 2: Diagram of a chilled drum**

1. rotating steel drum	4. feeding cylinder
2. annular space for coolant	5. feeding trough with liquid emulsion
3. scraper blade	

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* Wiedermann (1978)

** Andersen & Williams (1965b)

1.1.2 Modification Processes of Oil

The uses of edible oils can be extended by modification processes like fractionation, hydrogenation and interesterification (Swern, 1964c; Bernadini *et al.*, 1975, Kreulen, 1976; Hustedt, 1976; Sreenivasan, 1978; Allen, 1981; Hastert, 1981; Young, 1980).

Fractionation is used to separate the constituent triacyglycerols (TGs) of fats and oils into fractions of different melting characteristics. It is carried out commercially by fractional crystallization. The methods currently in use are dry fractional crystallization, *e.g.* Tirtiaux process (Kreulen, 1976), surfactant fractionation, *e.g.* Alfa Laval process (Norris *et al.*, 1971), solvent fractionation, *e.g.* Costruzioni Mecchaniche Bernadini process (Bernadini *et al.*, 1975).

In dry fractional crystallization, the fat is melted and then pumped into vats where crystallization is carried out by controlled cooling and agitation. The crystals which form the high melting fraction (HMF) are then separated from the low melting fraction (LMF) by filtration (Kreulen, 1976).

Fractional crystallization with surfactant works on the same principle as the dry fractionation process but the HMF and LMF are separated by centrifugation after an aqueous surfactant has been added. The surfactant replaces the oil phase on the surface of the crystals so that they form a suspension which can be separated from the LMF by centrifugation (Norris *et al.*, 1971; Young, 1980).

In the case of solvent fractionation, the melted fat is mixed with a solvent like hexane or acetone and then cooled to a predetermined temperature. After crystallization, the fat crystals (HMF) are separated from the solution of LMF and solvent by filtration. Residual oil is removed from the fat crystals by washing with solvent. Both fractions are then evaporated to dryness (Norris *et al.*, 1971).

In dry fractional crystallization, there is difficulty in effectively separating the liquid oil (LMF) from the fat crystals (HMF) with the result that the HMF is contaminated with the LMF. The fractionation process involving surfactant overcomes this problem only to a limited extent (Norris et al., 1971). On the other hand, solvent fractionation can produce large, easily separable crystals at relatively high cooling rates, and the viscosity of the liquid phase is reduced so that separation of the LMF from the fat crystals is more efficient (Swern, 1964b). Furthermore, the contamination of the fat crystals with LMF can be reduced by solvent washing.

Hydrogenation of an oil involves the addition of hydrogen at the double bond in the FA chains of TGs causing a reduction in the number of double bonds. During the reaction a significant proportion of the double bonds also undergo geometrical and positional isomerization. As a result of these two chemical changes, there is an increase in the stability and temperature range in which the fat melts (Hastert, 1981).

The rate and selectivity of the hydrogenation reaction depends on the type of oil, hydrogen pressure, agitation speed and catalyst type and concentration. (Selectivity is defined as the ratio of reaction rates for conversion of linoleic acid to oleic acid over that of oleic to stearic acid.) (Allen, 1981).

Hydrogenation is normally carried out by a batch process in an autoclave containing heating coils and agitator. In operation, the vessel is kept under vacuum while the oil and catalyst are heated to obtain a dry and deaerated oil. When the required temperature is reached, the vacuum is closed and hydrogen is admitted up to the desired pressure. At the end of the reaction, the flow of hydrogen is stopped and the oil is cooled and filtered.

Interesterification is a reaction which changes the distribution of FAs among the TGs of fats or mixtures of fats, using a catalyst such as sodium methoxide. The process can be visualised as a removal of FA at random from a TG, shuffling it among the rest of the FA pool and replacing it at random by another FA. As a consequence of this, the physical properties of the fats are changed (Sreenivasan, 1978).

Interestification can proceed in two ways, random or directed. When random rearrangement is preferred, the fat is heated to 80°C in the presence of a catalyst. At the end of the reaction, the catalyst is inactivated with water. When directed interesterification is required, some of the FAs or their TGs are removed during the course of the reaction. The procedure commonly used is either to continuously distil low molecular weight FAs from the reaction mixture or to carry out the process at such low temperatures that the high melting TGs crystallize out. When this reaction is carried out at low temperatures, sodium methylate or a liquid alloy of sodium-potassium is used as a catalyst (Hustedt, 1976).

1.1.3 Manufacture of Margarine

(a) Formulation of fat blends

Margarine consists of a water in oil emulsion. Dispersed in the continuous oil phase are fat crystals, water droplets and proteins. The rheological properties of margarine are largely determined by the number, type and structure of these fat crystals (Haighton, 1976). Hence, prior to manufacture, fats and oils are blended together in suitable proportions to produce the required crystal structure. For instance, a table margarine may contain a liquid oil blended together with three other fats with melting points of 24°C, 34°C and 44°C (Andersen & Williams, 1965a). Blending and formulation of fats and oils are normally monitored by measuring the solid fat content (SFC) of the fat blend.

It should be noted that the choice of fats and oils is also important. Certain oils, especially those which are stable in the β form tend to produce margarine of a 'sandy' texture (Merker *et al.*, 1958). Hence, oils which are stable in the β' form are required to produce a margarine of a smooth consistency.

(b) Manufacturing processes

In view of the importance of fat crystals, the most critical operation in the manufacture of margarine is the process of forming the desired crystal structure. This is achieved by cooling the mix of melted fat, water and milk powder and then removing the heat released during crystallization. In some cases agitation is carried out simultaneously with cooling.

There are two main processes used in the manufacturing of margarine and they involve the scraped surface heat exchanger (SSHE) and chilled drum (Andersen & Williams, 1965b; Opfer, 1978; Wiedermann, 1978).

The SSHE consists of a steel rotor inside a tube which is cooled externally by refrigerant (Figure 1). The annular space between the rotor and the cooling tube is small to assist rapid cooling. Scraper blades are attached to the rotor and the high rotation speed presses the blades against the tube surface. The mix of melted fat, water and milk powder is pumped into the SSHE where it is chilled rapidly. The super-cooled product is then usually passed through a crystallizer or pinworker where crystallization is allowed to continue (Haighton, 1976). In the case of the pinworker, the mixing action also reduces the extent of the formation of crystal network.

The chilled drum consists of a rotating steel drum with a finely grounded surface. A coolant passes through an annular space in the drum (Figure 2) (Andersen & Williams, 1965b). A thin, uniform layer of emulsion is applied to the surface of the drum by means of a small, rapidly revolving cylinder at the side which rotates in the same direction as the cooling drum. This feeding cylinder dips into a trough containing the liquid emulsion. The thickness of the layer applied to the surface of the chilled drum can be varied by adjusting the distance between the feeding cylinder and the chilled drum. After an almost complete revolution of the drum, the solidified product is scraped off with a blade, held for a period and then passed through a kneading device, e.g. complector.

Normally, this process gives almost complete crystallization of the fat and hence little crystallization after manufacture occurs. The holding and kneading procedures are carried out to reduce the extent of the formation of crystal network (Haighton, 1976).

1.1.4 Analytical Techniques

In the production of margarine many analytical techniques are used throughout the various stages of purification, modification and manufacturing to ensure that the product conforms to the chemical, physical and microbiological specifications.

The principal tests carried out during oil purification determine the levels of free fatty acids (FFAs), oxidation and colour. The determination of FFA involves titration of a sample of oil with sodium hydroxide (AOCS, 1973a; Ca 5A-40). This test is usually performed on the fats and oils before and after refining. Colour is determined by colorimetry, (AOCS, 1973b; Cc 13b-45) and is carried out in conjunction with the bleaching process. After deodorization, which is the final stage of purification, the extent of oxidation is determined by measuring the peroxide value of the product (AOCS, 1973c; Cd 8-53). This is a sensitive test and any change in procedure may produce a variation in the results. In some purification plants, FFA determination is also carried out at this stage.

The principal tests carried out during modification of oils determine the degree of unsaturation, FA composition and proportion of solid fat. For each of the modification processes the proportion of solid fat in the final products can be determined either by dilatometry (AOCS, 1973d; Cd 10-57) or by nuclear magnetic resonance (Bruker Minispec p 20 Booklet, Bruker-Physik AG, Karlsruhe, Germany). In addition, the FA composition of these products can be determined by gas liquid chromatography (Christopherson et al., 1969). Refractive index determinations which measure the degree of unsaturation can be used to monitor the hydrogenation reaction (AOCS, 1973c; Tp 1a-64).

In the case of formulation of fat blends for margarine manufacture, SFC and FA analysis are the more important tests carried out.

After manufacture, the rheological properties of the margarine are assessed. A wide variety of instruments have been used for textural evaluation of margarine. Examples are the sectilometer and penetrometer which have been used for measuring hardness (Kawanari et al., 1981). At present there is no appropriate method for measuring plasticity, and some processors have reported to finger touch methods by a trained panel (Grinsted, 1981). In addition to the assessment of rheological properties, the level of oxidation measured by the peroxide value test and the microbiological quality of the margarine is also determined (Collins & Lyne, 1976).

1.1.5 Types of Margarine

Margarine is widely used nowadays, not just as a spread but also as a frying fat or in cakes and pastries. Different rheological properties are required in each of these types of margarine but, generally, the aim is to obtain a margarine of high stability and suitable consistency.

There are many types of margarine which are used as spreads, the more common ones being the table and soft margarine. Table margarine has a consistency which is suitable for spreading within a wide temperature range. This will vary from country to country and may be higher in the tropics (22-30°C) than in the temperate zone (13-22°C) (Haighton, 1976). On the other hand, soft margarine has to be spreadable when taken out of the refrigerator at 5°C and hence it contains a high proportion of liquid oil (40-70%). Compared to table margarine, it has a much smaller proportion of solid fat at 5-10°C (Grinsted, 1981). Figure 3 shows the melting curves for these three types of margarine (Haighton, 1976).

Fat is used in cakes to improve the texture and to help increase the volume of the cake. For cakes where a highly aerated dough is required, e.g. sponge cakes, the margarine

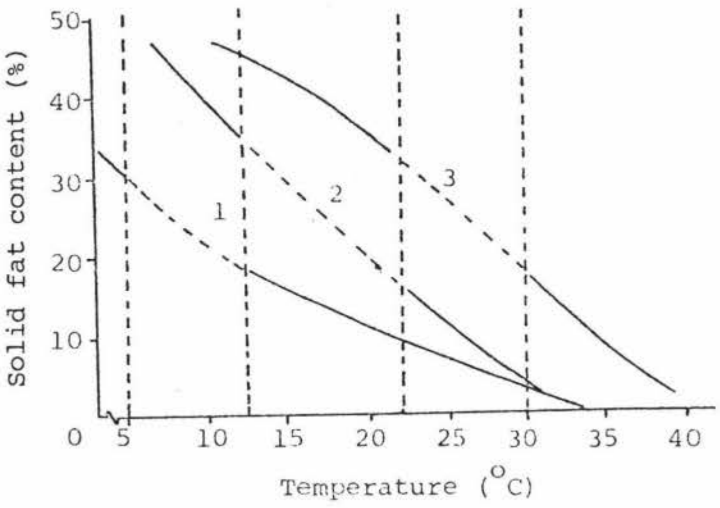

FIGURE 3: Melting curves for soft and table margarines.

1. soft margarine
2. table margarine for the temperature zone
3. table margarine for the tropics

has to be plastic over a fairly wide range of temperature and possess high 'creaming power' (Anderson & Williams, 1965c). Creaming is the incorporation of air into cake dough with the air being principally held in a film of liquid fat locked by a network of crystals. A margarine possessing such qualities will result in the production of small spherical air bubbles of standard size, uniformly scattered throughout the mass (Meara, 1980).

In the case of pastry margarines, especially for the production of flaky pastries, the fat will have to be of plastic consistency and yet be firm enough to maintain the discrete layers of fat and dough at the rolling temperatures (15-20°C) (Baldwin _et al_., 1972). It is also important that a small proportion of fat remains solid during proofing in order to keep the dough layers separate. All fat crystals should also melt at body temperatures, otherwise pastries which give a fatty mouthfeel will be formed.

1.2 PRODUCTION OF BUTTER

Butter is similar to margarine in that it is a water in oil emulsion. It has a continuous phase of liquid oil in which fat crystals, water droplets and curd are dispersed. However, in contrast to margarine, the fat component of butter is milkfat, which has been neither purified nor modified.

1.2.1 Manufacture of Butter

Normally butter is produced by churning cream. Traditionally this was done in a batch churn but nowadays churning is carried out in a continuous buttermaker (Dolby, 1967). In New Zealand, the commercial production of butter is carried out in the following manner:

The cream which is received at the factory is initially neutralized to reduce the level of lactic acid and then pasteurized in a vacreator (Mauri Brothers, NZ). The cream is rapidly cooled in a plate heat exchanger and held overnight. During this holding period, a portion of the fat crystallizes. The cream is then fed into the churning section of the continuous buttermaker where it is rapidly churned to butter granules in a few seconds (Figure 4). The granules and buttermilk enter the separation section where buttermilk is drained through screens and the granules are aggregated into clumps. Subsequently, these clumps are pressed and kneaded together to give a uniform mass of butter.

Several workers have shown that the manner in which cream is cooled prior to churning has an effect on the rheological properties of the product. For example Dolby (1953; 1954) found that when cream was treated by the modified Alnarp method (i.e. cooling of cream to 5°C, holding at 19°C for 2 hr, cooling slowly to churning temperature and holding overnight) the butter had a lower hardness value than that made from cream which was cooled rapidly to churning temperature. This is presumably due to the greater extent of mixed crystal formation in the product made from rapidly cooled cream.

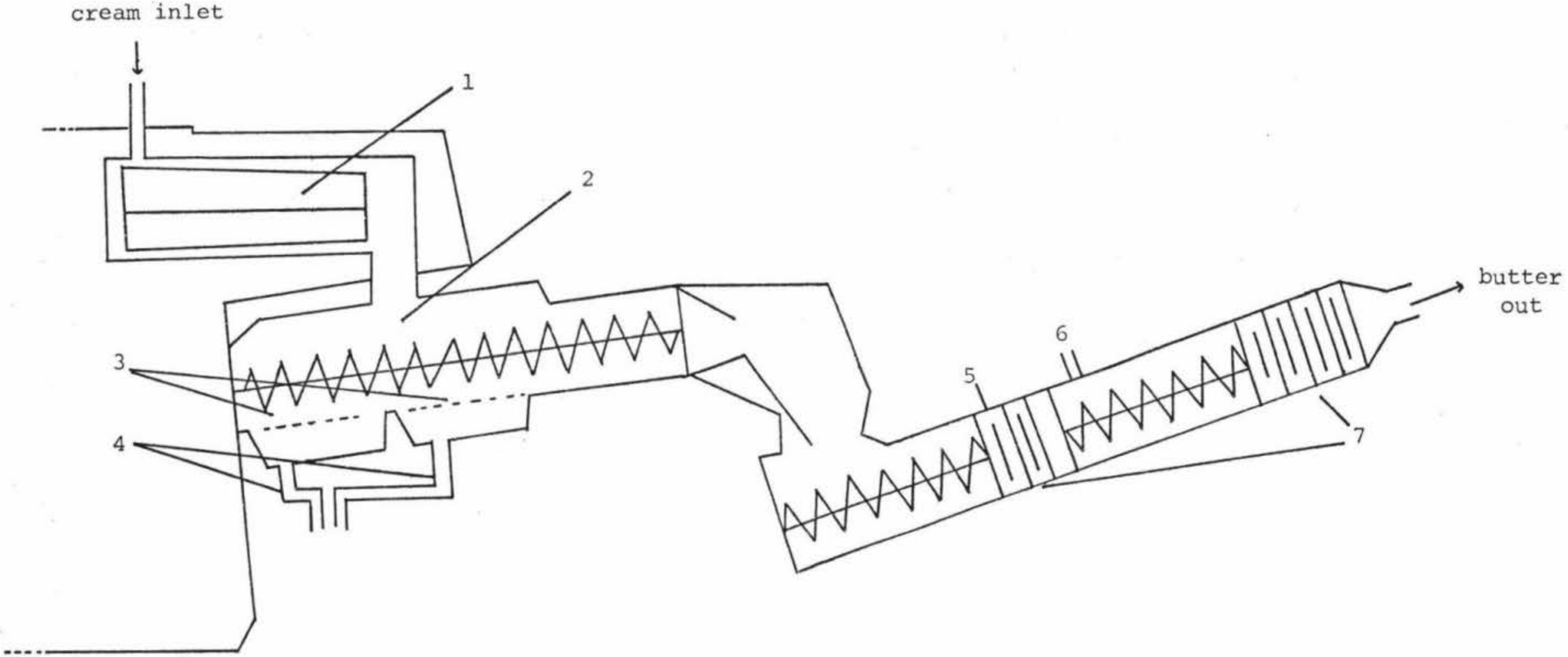

FIGURE 4: Diagram of continuous buttermaker*

1. churning cylinder
2. buttermilk / butter granule separation
3. buttermilk screens
4. buttermilk drain
5. salt injection
6. vacuum section
7. working section

* J C Lochore, NZ Dairy Research Institute, 1981.

An alternative method of making butter is to produce milkfat, prepare a mix of milkfat, water and skim milk powder and pass this mix through a SSHE. Milkfat can be manufactured by increasing the fat content of the cream to 70-80% in a cream concentrator. This is followed by shearing in a clarifixator where the fat globules are completely split. The released fat is then separated from the aqueous serum by centrifugal separation. Any water remaining in the fat phase is removed by heating under vacuum to 104°C (Kaipara Co-op Dairy Co., 1971).

This milkfat can be recombined with water and skim milk powder and then passed through the SSHE in a manner similar to that used in the manufacture of margarine. Butter is made commercially by this process in New Zealand (Hawkey, 1980).

1.2.2 Modification Processes of Milkfat

As noted earlier, butter is produced commercially from milkfat which has not been modified. However, investigations have been carried out into the modification of milkfat to obtain milkfat products which have more desirable properties. de Man (1961) found that interesterification of milkfat resulted in a milkfat with an increased softening point and hardness value. The interesterification was carried out on the dried milkfat at 50°C with 0.2% sodium methylate as catalyst. Experiments carried out by Yoncoskie et al. (1969) on the hydrogenation of milkfat showed an increase in the high melting portion of the fat as hydrogenation increased. Reaction conditions examined included catalyst concentrations which ranged from 0.1 - 1%, temperatures from 90-120°C and hydrogen pressure of 200 - 400 kPa (absolute pressure). Although these processes lead to significant changes in the physical properties of milkfat, they suffer from a disadvantage in that the processing conditions destroy the desirable buttery flavour. This is probably the reason why neither of these processes has been carried through to commercial scale.

An alternative process is the separation of milkfat into portions of different melting ranges by fractional crystallization either from solution in an organic solvent or from the melted fat. This has been developed at the New Zealand Dairy Research Institute to produce spreadable butter (Jebson et al., 1975). In this process, milkfat is mixed with acetone at 30-40°C, the temperature is lowered to 10°C and the mix is held for 1 hr in a crystallizer. The crystal slurry formed is then filtered to obtain fat crystals (HMF) and a filtrate of liquid oil and acetone. The filtrate is then cooled to -15°C, held for 1 hr, and then filtered to give fat crystals (intermediate melting fraction IMF) and a filtrate of liquid oil (LMF) and acetone. Finally, all three fractions are evaporated to dryness. The HMF and LMF are then mixed in suitable proportions to obtain a butter which is spreadable directly from the refrigerator.

1.3 BAKING OF DANISH PASTRIES

Danish pastries are made from a sweet dough which is leavened by yeast. The conventional technique which is known as the roll-in method involves the folding of fat into the developed dough by hand. The process can also be carried out commercially using mechanical pastry breaks (Hayashi, 1975).

The pastry dough is mixed and kneaded in the same manner as most yeast doughs (Sultan, 1969a). Kneading causes the protein chains in the gluten to alter and form linear chains which facilitate cross linkages like hydrogen bonding, disulphide and thiol bonds (Kent et al., 1967). The formation of these linkages produces a strong network of hydrated proteins which is further extended by steam produced from water in the dough during baking. It is essential that this network is maintained until the starch grains have gelatinized otherwise a pastry with poor lift will result. Hence, a high protein flour is required to form such a stable network.

A major proportion of the fat in danish pastries is rolled-in. This roll-in fat has to be of plastic consistency and yet be firm enough to maintain the discrete layers of fat and dough at the rolling temperatures (Baldwin et al., 1972). The presence of large proportions of solid fat will result in a fat which is too hard for rolling. This will cause the dough to tear and flake unevenly. On the other hand, large quantities of liquid oil will cause the fat to lose its firmness during rolling and the dough layers to stick together as well as to the rollers. More dusting flour will be required, thus causing lumpiness. It is also important that a small proportion of fat remains solid during proofing in order to keep the dough layers separate and also to retain the gas and moisture which are formed (Kent et al., 1967). However, the fat should have a melting point lower than body temperature, otherwise the pastries will give an unpleasant fatty mouthfeel. Usually the fats which are rolled by mechanical pastry breaks must be able to withstand a heavier treatment than those rolled by hand.

Traditionally butter was used as a roll-in fat but now margarines with a wider plastic range are more popular. This is because butter has a small plastic range and is difficult to roll-in. Unfortunately, with the use of margarine, the favourable flavour given by butter is lost.

The number of folds and rolls carried out depends on the type of fat used (Sultan, 1969b). Too much rolling can cause the layers to disappear while too little will not produce a flaky pastry. The number of layers in danish pastries may vary from 80 to 300. After the final roll, the pastry is normally held in a refrigerator for up to 24 hr before making up into units. The length of this holding depends largely on the preference of the chef. During refrigeration, the pastry dough should be wrapped in polythene to prevent crustation of the dough. If the temperature of refrigeration is too high, or if the pastry dough is too thick, overfermentation may occur which can result in uneven layering.

Proofing and baking are very important. Improper proofing may tear the dough during baking causing flatness, spreading, greasiness and loss in volume. Danish units should be three quarter proofed. A fully proofed unit may collapse due to the inability of the extended gluten to support the richness of the dough. On baking, the correct temperature must be used and this depends on the size of the units.

The making of danish pastries depend very much on the ability of the chef. If one of the ingredients like the roll-in fat or the flour has qualities which deviate slightly from normal, the chef may be able to alter the conditions to produce a good product.

An alternative technique of making danish pastries is the Scotch method which involves the mixing of particulate fat with dough (Schaible & Jackel, 1968). Although this technique is less labour intensive, it generally does not give the same volume increase as the pastries made by the roll-in methods.

1.4 AIM OF PRESENT WORK

The present study was undertaken to manufacture a margarine containing a large proportion of milkfat. Initially, a sample of margarine used for manufacture of danish pastries in Japan was purchased and analysed. Several fat blends were formulated using hydrogenated oils, milkfat and sunflower seed oil to imitate the melting properties of the Japanese pastry margarine. Subsequently, a suitable fat blend was manufactured into margarines by various methods and then used in the baking trials for danish pastries.

CHAPTER 2

MATERIALS AND METHODS

2.1 CHEMICALS AND SOLVENTS

The chemicals used were supplied either by British Drug House Ltd (Poole, England) or by May & Baker Ltd (Dagenham, England) except for the following:

Silver nitrate supplied by Peking Chemical Works, Peking;

linoleic acid, methyl elaidate, butylated hydroxytoluene (BHT) and standard triacyglycerols were supplied by Sigma Chemical Co., St Louis, MO, USA;

Celite 545 supplied by Fisher Scientific Co., Chemical Manufacturing Co., Fair Law, NJ, USA;

Unichema International Pricat nickel catalysts 9900 and 9908 were supplied by Unichema Chemie GmbH, Steintor 9, 4240 Emmerich, Federal Republic of Germany;

The solvents were supplied by J T Baker Chemical Co., Phillipsburg, NJ, USA, except for the following:

Carbon tetrachloride was supplied by Reidel de Haenag, Seelze, Hannover.

The petroleum spirit (40-50°C) and diethyl ether were distilled before being used.

2.2 MATERIALS

Two batches of danish pastry margarine (Violon EMP 300) were generously provided by Kanegafuchi Chemical Industry Co. Ltd, 2-4, 3-Chome, Nakanoshima, Kita-ku, Osaka, Japan.

20 kg of refined, bleached and deodorized (RBD) palm oil was provided by Kaipara Edible Oils, Private Bag, Auckland.

20 kg of cottonseed oil, and sunflower seed oil (RBD) were

provided by Abels Ltd (P O Box 9573, Newmarket, Auckland, New Zealand).

Two batches of butter were churned from summer cream in a MD12 Contimab Buttermaker at the New Zealand Dairy Research Institute, Palmerston North, New Zealand.

Milkfat was made from summer cream at the New Zealand Dairy Research Institute, Palmerston North, New Zealand.

20 kg of pastry flour was obtained from the Manawatu Flour Mills.

2.3 CHEMICAL ANALYSIS

2.3.1 Determination of Salt, Moisture and Curd

The salt contents of the butter/margarine samples were determined by the International Dairy Federation method (1969). This involves titration of the sample with a standard solution of silver nitrate.

Moisture determinations were carried out by the method stated in the Dairy Division Manual (1982a). This involves evaporating off the moisture from a weighed sample of butter/margarine and reweighing.

Curd determinations were also carried out by the method stated in the Dairy Division Manual (1982b). The sample from the moisture determination is washed with petroleum ether (40-60^{o}C) to remove the fat and weighed. This gives the weight of the curd and salt. This value less the salt content gives the weight of the curd.

2.3.2 Determination of Peroxide Value

Peroxide value determinations were carried out by the method stated in the Dairy Division Manual (1982c). This method, which is based on the procedure of Hills & Thiels (1946) involves the oxidation of ferrous to ferric ions by hydroperoxides in the fat and the subsequent formation of ferric thiocyanate. The amount of ferric thiocyanate formed is determined spectrophotometrically. The weight of fat used in this method varied from 0.02 to 0.5g.

2.3.3 Determination of Alkalinity

The soap contents of fat samples were determined by the method given in the British Standard Institute (1977). This involves titration of the sample with a standard solution of hydrochloric acid.

2.3.4 Determination of Iodine Value

Iodine values (IV) of fat samples were determined by the official method of the American Oil Chemist Society (Cd 1-25) (1973f). The procedure involves the addition of excess iodine to the fat solution, a portion of which is absorbed by the olefinic double bonds in the fat. The excess iodine is titrated against a standard solution of sodium thiosulphate. The iodine used in this mathod was added in the form of iodine monochloride which was prepared according to the method given by Cocks van Rede (1966).

2.3.5 Determination of Refractive Index

The refractive index of all samples was measured at 80°C with a refractometer (Zeiss Opton Nr 123133, Germany) attached to a water bath.

2.3.6 Determination of Fatty Acid Composition

The component fatty acids (FAs) of triacyglycerols (TGs) were determined by preparing their methyl esters and analysing them by gas liquid chromatography (GLC). Two methods were used, method A for samples containing only long chain FAs and method B for samples containing only long and short chain FAs.

(a) Determination of fat samples containing only long chain FAs

(i) Preparation of methyl esters

Adapted from the AOCS E2-66 (1973g).

0.2 ml of TGs were added to a 50 ml round-bottomed flask. To that was added 4 ml of 0.5M methanolic sodium hydroxide and a boiling chip. A condenser was attached and the mixture was heated in a steam bath until no oil droplets were visible in solution. This lasted approximately 10 min. 5 ml of boron trifluoride in methanol was added through the condenser and refluxed for 2 min. 5 ml of petroleum ether (40-50°C) was then added through the condenser and refluxed for a further minute. The apparatus was detached, sufficient water was added to float the solution of petroleum ether and FA methyl esters into the neck of the flask. 2 ml of this solution was transferred to a stoppered test-tube and 2.5 μl was analysed by GLC.

(ii) Gas liquid chromatography

The methyl esters of the FAs were analysed by GLC using a Varian aerograph 1400 gas chromatograph (Walnut Creek, California, USA). The equipment consisted of a hydrogen flame ionization detector and a stainless steel column (2m long and 3.1 mm in diameter) packed with 10% dietheylene glycol succinate (stabilised with phosphoric acid) on 80/100 mesh Supelcoport (Belefonte, Pennsylvania 16823). The flowrates of nitrogen (the carrier gas) and hydrogen were both 25 ml/min, while the flow of air to the detector was maintained at 300 ml/min. After injection of the sample at an initial column temperature of 160°C, the chromatograph was temperature programmed at 1°C/min until a temperature of 180°C was reached. It was then held at this temperature until the end of the run. The injector and detector temperature were maintained at 200°C. Peak areas were calculated by a Varian aerograph model 485 integrator (Walnut Creek, California, USA).

(b) Determination of fat samples containing long and ~~only~~ short chain fatty acids

(i) Preparation of methyl esters

Adapted from the method by Christopherson (1969).

The TGs were dissolved in petroleum ether to make a 10% solution (w/v). To 19 ml of this mixture was added 1 ml of 0.2M methanolic potassium hydroxide (prepared by dissolving the appropriate amount of potassium hydroxide in anhydrous methanol). The reactants were mixed by inversion until the solution became clear. This required approximately 20 sec. Almost immediately after clearing, the solution turned turbid again due to separation of glycerol. The solution was diluted with 76 ml of petroleum ether, shaken and allowed to stand for 2 min for the glycerol to precipitate out. 1.5 µl of the solution was analysed by GLC.

(ii) Gas liquid chromatography

The methyl esters of the FAs were analysed by GLC using a Hewlett Packard 5840A gas chromatograph (Hewlett Packard, Avondale, PA, USA) which was equipped with a hydrogen flame ionization detector and a stainless steel column (2m long and 3.1 mm in diameter) packed with 12% diethylene glycol succinate (stabilized with phosphoric acid) on 80/100 mesh chromasorb WHP. The flow rate of the carrier gas nitrogen was 20 ml/min, while the flow of air and hydrogen to the detector was 200 ml/min and 30 ml/min, respectively. The injector temperature and detector base were maintained at 230°C and 250°C, respectively. After injection of the sample at an initial column temperature of 50°C, the chromatograph was temperature programmed at 6°C/min for 20 min and then at 3°C/min until a temperature of 205°C was reached. It was then held at this temperature for 8 min. Peak areas were calculated by the 5840A gas chromatograph terminal. A typical chromatogram is shown in Figure 5.

Response factors for the FAs were obtained by preparing methyl

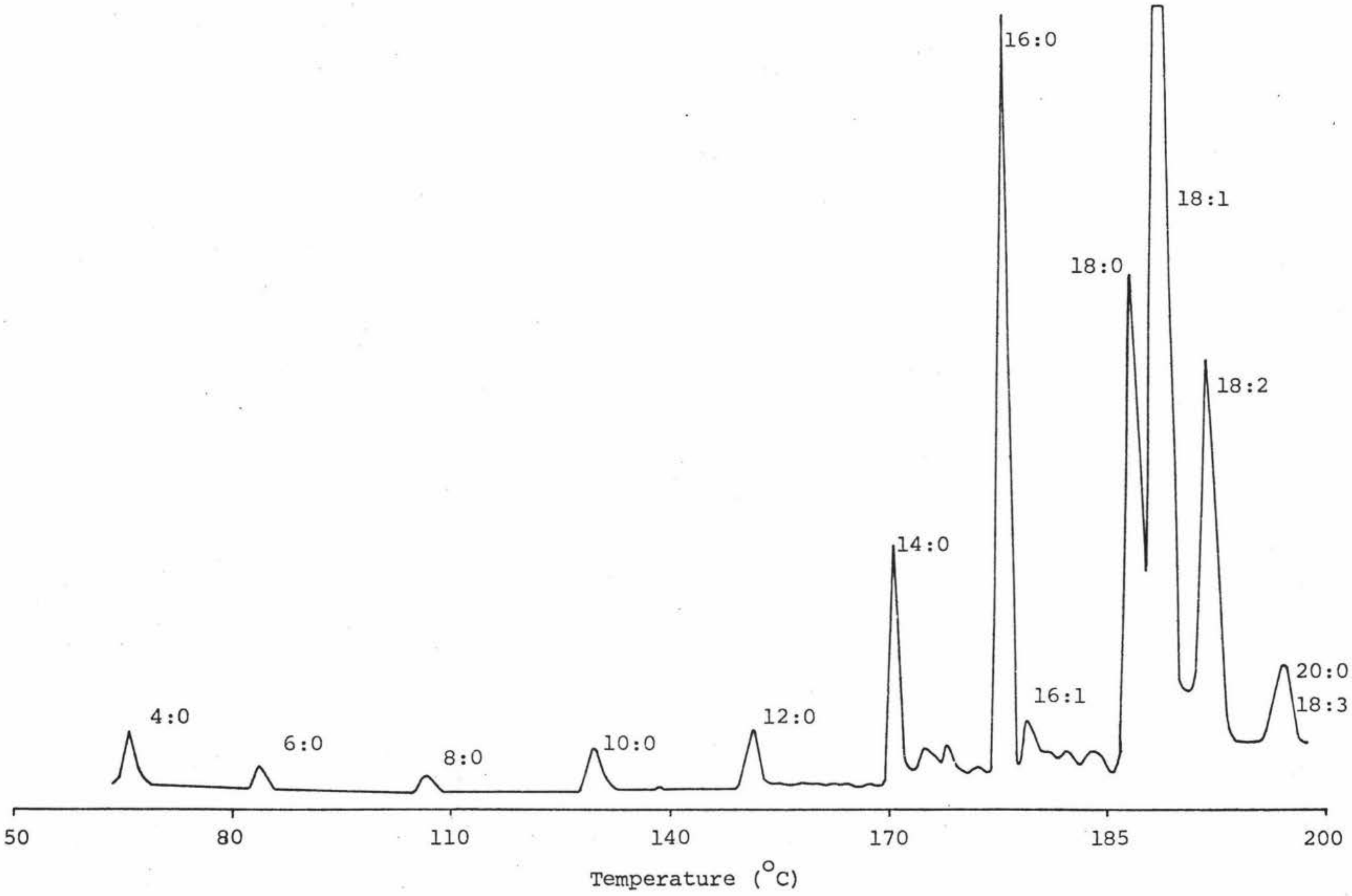

FIGURE 5: The chromatogram of Japanese pastry margarine which contains short chain fatty acids

esters from a mixture of pure TGs using method B. These factors were calculated using the equation:

$$\mathrm{Fw} = \frac{\text{Weight of TGs in standards}}{\text{Area of corresponding methyl ester peak}}$$

where Fw = response of factor.

Results of duplicate determinations are given in Table 1.

TABLE 1: Results of response factors

	Fw	Fw	Average Fw
methyl butyrate (C4)	1.26	1.36	1.31
methyl caproate (C6)	1.12	1.15	1.14
methyl caprylate (C8)	1.04	1.06	1.05
*methyl caprate (C10)	1.00	1.00	1.00

* Response factor for methyl caprate was set at 1.00

(c) Determination of unknown peaks

In vegetable oils, virtually all oleic acid (18:1) is in the cis - 9 form and linoleic acid (18:2) in the cis, cis-9,12 form. On hydrogenation, there is a decrease in the degree of unsaturation as hydrogen is added across some of the double bonds (Figure 6). Furthermore, a series of positional and geometrical isomers of 18:1 and 18:2 are formed which cause the tailing of the FA ester peaks. In the present work, it is difficult to identify the peaks which elute after the 18:1 peak as there are a number of possibilities. In addition, it is not possible to obtain retention times of the FA esters as the chromatographic runs were all temperature programmed. The data in Table 2 suggest that the 18:1 peak consists of cis and trans - isomers of 18:1 with double bonds at different positions (Jamieson, 1969). The two small peaks which elute after that are possibly cis, cis and trans, trans - isomers of 18:2 with the double bonds in the 7, 10 and 9, 12 position.

IV calculated from the assigned FA composition agreed closely with the experimentally determined IV.

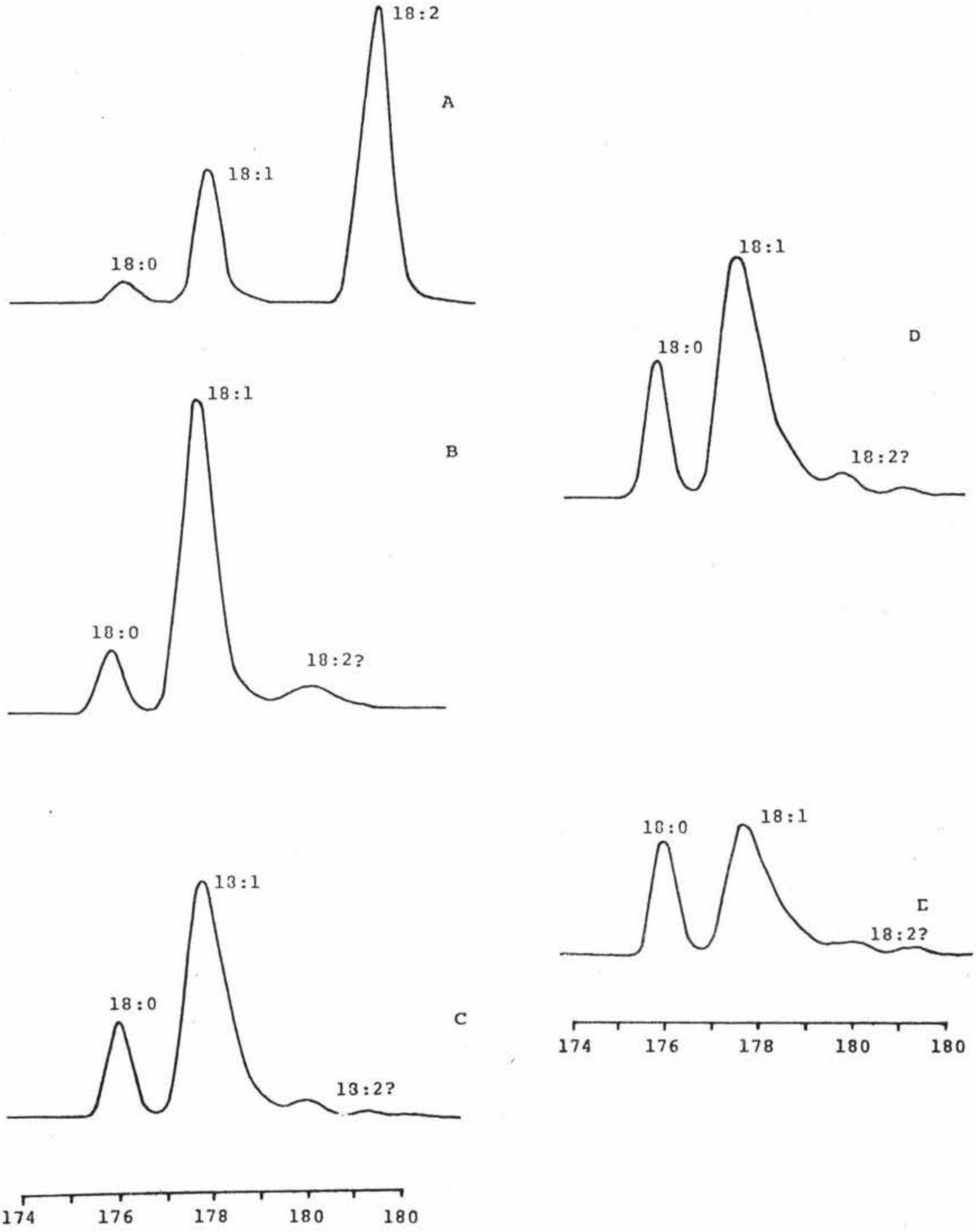

FIGURE 6: The chromatograms of cottonseed oil hydrogenated to different times by the very selective catalyst

A unhydrogenated cottonseed oil
B hydrogenated to 20 min
C hydrogenated to 45 min
D hydrogenated to 70 min
E hydrogenated to 120 min

TABLE 2: Retention times of positional and geometrical isomers of fatty acids*

Fatty acid		Retention time
18:1	9c; 9t; 10t	18.5
18:1	6c; 11t	18.6
18:1	12t	18.7
18:1	12c; 13c	18.8
18:1	14c; 15c	19.0
18:2	5,12cc; 6,10cc; 6,11cc	19.1
18:2	7,10cc; 6,9cc; 6,12cc; 9,12tt	19.2
18:2	8,11cc; 9,12cc	19.3
18:1	16c	19.4
18:2	9,12ct	19.5
18:2	9,12tc	19.6

* Jamieson (1969)

c is the cis - isomer
t is the trans - isomer

2.3.7 Determination of Triacylglycerol

TG analysis of fat samples were carried out by Mr D Moore, Te Puke Dairy Co., Bay of Plenty. They were analysed by gas liquid chromatography (GLC) using a Varian aerograph gas chromatograph (Walnut Creek, California, USA) equipped with a hydrogen flame ionization detector and linear temperature program. The chromatographic separations were made with a glass column (500 mm long and 4 mm in diameter) packed with 3% OV-1 on 100/120 gas chromosorb. After injection of the sample at 250°C, the chromatograph oven temperature was increased to 330°C at 4°C/min and then held at this temperature for 6 min. Peak areas were calculated by a CDS 401 data processor.

2.3.8 Determination of Trans-isomer

The trans-isomer content of the hydrogenated oils was determined by infrared spectroscopy (IR) using a Pye Unicam SP3-200 infrared spectrophotometer (Pye Unicam Ltd, York Street, Cambridge, England CB1 2PX). For this instrument, the scan time was set at 7 min to give a scan speed of 8 cm $^{-1}$/min. A double beam operation (in the auto smooth mode) was carried out with carbon disulphide in the reference cell. The procedure was based on that described by Madison <u>et al</u>. (1982). Two cells, one a 0.1 mm potassium bromide reference cell and the other a sodium chloride variable path length sample cell (adjusted to 0.23 mm) were filled with carbon disulphide solvent and the transmittance was measured from 900 cm^{-1} to 1505 cm^{-1} to obtain a straight baseline. The sample cell was then filled with either a calibration solution or a sample which had been methylated according to the procedure of Madison <u>et al</u>. (1982). It was then scanned from 900 cm^{-1} to 1505 cm^{-1}. The cells were rinsed with six washings of carbon disulphide between the measurements. A baseline tangent to the peak minima adjacent to the analytical peak at the wave number of 967 cm^{-1} was drawn. The baseline corrected transmittance at 967 cm^{-1} was obtained by subtracting the transmittance of the baseline tangent from that of the analytical peak. The percentage transmittance was obtained and then converted to absorbance. The results were expressed as a weight percentage of elaidic acid per gram of methyl ester sample.

A calibration curve was made by preparing a standard solution of methyl linoleate and methyl elaidate in carbon disulphide. The corrected absorbances at 967 cm^{-1} for each calibration standard was measured and plotted against the gram of elaidic acid equivalent (Table 3).

Methyl linoleate was synthesized from linoleic acid by refluxing 10g of the acid with 40 ml of methanol containing 0.8 ml of concentrated sulphuric acid for 2 hr. At the end of refluxing, 40 ml of water containing 5% sodium chloride was then added and the esters were extracted twice with petroleum ether : diethyl ether, 40:100 (v/v) using a separating funnel. The organic layer was then washed three times with 300 ml of water containing 0.6g of potassium bicarbonate and filtered over sodium sulphate. The solvent was then evaporated off in a rotary evaporator and the last traces of solvent was removed by applying a high vacuum for half an hour. Analysis by GLC showed that the methyl linoleate was 98.4% pure.

TABLE 3: Results of standards for the determination of *trans*-isomers

	Methyl linoleate (g)	Methyl elaidate (g)	Elaidic acid equivalent	Baseline corrected absorbance
1	0.5012	0	0	0
2	0.4883	0.0100	0.0095	0.005
3	0.4708	0.0306	0.0295	0.007
4	0.4659	0.0402	0.0383	0.012
5	0.5010	0.0500	0.0481	0.017
6	0.4118	0.1000	0.0953	0.037
7	0.2048	0.3134	0.2987	0.126
8	0.1019	0.4010	0.3822	0.162

2.4 PHYSICAL ANALYSIS

2.4.1 Determination of Softening Point

The softening points of fats were determined according to the method of Dolby (1961). It involves initially shock cooling fat samples to 0°C and holding them overnight. A ball bearing is then placed on the sample which is then heated at a rate of 0.5°C/min until the ball bearing sinks half way down the fat.

2.4.2 Determination of Thermal Properties

Thermal analysis was performed using a Perkin Elmer DSC-2 Differential Scanning Calorimeter (DSC) (Perkin Elmer Corporation, Main Ave MS-12, Norwalk, CT 06856, USA). Sealed aluminium sample pans and sample holder covers were used for all runs. The sample mass was generally 4-9 mg. The temperature scales were calibrated according to the DSC-2 manual.

Fats were then melted at 60-80°C and a 4-9 mg sample was quickly transferred to a sample pan using a glass capillary. The sample pan was then sealed and loaded into the instrument. The sample was maintained isothermally at 62°C for 20 min and then tempered in one of two ways.

In the first tempering method, (D1) the melted samples were shock-cooled to -48°C at a rate of 10°C/min, held at that temperature for 12 min and heated at a rate of 10°C/min to 62°C.

In the second tempering procedure (D2) the melted samples were shock-cooled to -48°C, held at that temperature for 12 min and then heated to 20°C at 10°C/min. They were then held at this temperature for 5 min and shock-cooled to -48°C again. After 12 min, the samples were heated to 62°C at 10°C/min.

A straight line was fitted to the initial linear portion of the melting curve and the first point which deviated significantly from this line was taken as the start of melting. The end of melting was determined in a similar way (Taylor & Norris, 1977).

2.4.3 Determination of Solid Fat Content

Solid fat contents (SFC) were determined by pulsed nuclear magnetic resonance spectroscopy (NMR) using a Minispec p-20 fitted with an analogue computation unit (Bruker-Physik AG, Karlsruhe, Germany). For this instrument, the 90° pulse was 3.5 μs long and the dead time of the receiver was 7 μs long. Measurements were made by subjecting each fat sample to two 90° pulses spaced 6 sec apart and observing the digital reading (Taylor & Norris, 1977). Measurements were done on duplicate fat samples.

Fats were melted at 80°C and NMR tubes (10 mm diameter) were filled to a height of 18 mm. The samples were then tempered in one of three ways prior to the measurement of their SFC at different temperatures. The first tempering procedure (S1) involved holding the samples at 60°C for half an hour, followed by shock-cooling to 0°C and holding at that temperature overnight. The samples were then held ~~at~~ for 45 min at each measuring temperature in turn (0°C to 50°C in 5°C steps) before the solid fat content of each sample was determined.

In the second tempering procedure (S2), the fat samples were held at 60°C for 30 min, at 0°C for 60 min, at 20°C for 60 min and then at 0°C overnight. Finally the samples were held for 45 min at each measuring temperature in turn (0°C to 50°C in 5°C steps) prior to the determination of solid fat.

Mixtures of tristearoyl glycerol and trioleoyl glycerol were prepared containing 10 to 60 percent by weight of tristearoyl glycerol. These standards were melted at 80°C, allowed to cool slowly to room temperature, and held at this temperature for 3 weeks. The TG mixtures were measured in the Minispec p-20 at 20°C and the gain of the computation unit was adjusted (230) so that the digital readings corresponded approximately to the proportions of tristeroyl glycerol in the mixtures. A standard curve was plotted and readings were obtained from the plot (Norris & Taylor, 1977).

2.4.4 Determination of Hardness

Hardness measurements were made with a FIRA/NIRD extrusion apparatus modified to measure sectility (Taylor *et al.*, 1971).

Samples of butter and margarine were forced into stainless steel rings, 2 cm thick and 5 cm in diameter. The excess fat was carefully removed by cutting around the rings with a wire. Longitudinal slots on opposite sides of the ring allowed the cylinder of butter to be cut along a diameter by a stainless steel wire 0.056 cm in diameter and 5.4 cm in length. The ring containing the sample was mounted so that the screw drive of the instrument moved it towards the cutting wire. A cutting speed of 36 cm/min (gear 4) was used.

The samples, which were done in duplicate, were tempered in one of two ways prior to measurement. In the first tempering procedure (H1) the freshly manufactured fat samples were held at 2^{O}C for 7 days and then at 15^{O}C for at least 4 hr. In the second tempering method (H2) the samples were held at 2^{O}C for 7 days, at 23^{O}C for 2 days, at room temperature (17-21^{O}C) for 1 day, at 2^{O}C for 7 days and then held at 15^{O}C for at least 4 hr.

2.5 HYDROGENATION OF VEGETABLE OILS

Hydrogenation of oils was carried out in a pilot scale hydrogenation vessel made at the New Zealand Dairy Research Institute. A diagram of the hydrogenator, the design of which is based on Harshaw's hydrogenation autoclave (Harshaw Chemical Company, Cleveland, Ohio, USA) is shown in Figure 7, while the engineering diagram of it is shown in Appendix I. The hydrogenator consists of an insulated pressure vessel fitted with a cooling coil and agitator. Initially, problems were encountered due to the leakage of hydrogen past the agitator seal. This was overcome by the insertion of two seals, a Bellows seal (9000 series) and a standard rear seal (1 in, 740 series). Both were supplied by Mark Pretch Ltd, Auckland, NZ. A heating element was fitted underneath the pressure vessel and the temperature could be controlled over the range 0^{O}C to 200^{O}C ± 3^{O}C. During the heating of the oil to the required temperature, a vacuum of 5 kPa (absolute pressure) was applied. On hydrogenation, hydrogen was released into the vessel until a hydrogen pressure of 300-400 kPa (absolute pressure) was obtained.

Hydrogenation experiments were carried out with two types of nickel catalyst, both from Unichema International.

One of these was a highly active general purpose nickel catalyst (Pricat 9900) which could be used to produce fully hydrogenated fats or soft fats. The other was a highly selective nickel catalyst ((Pricat 9908) which gave high trans-isomerization activity combined with extremely high selectivity and produced a fat with a steep SFC curve. Both nickel catalysts contained approximately 22% nickel.

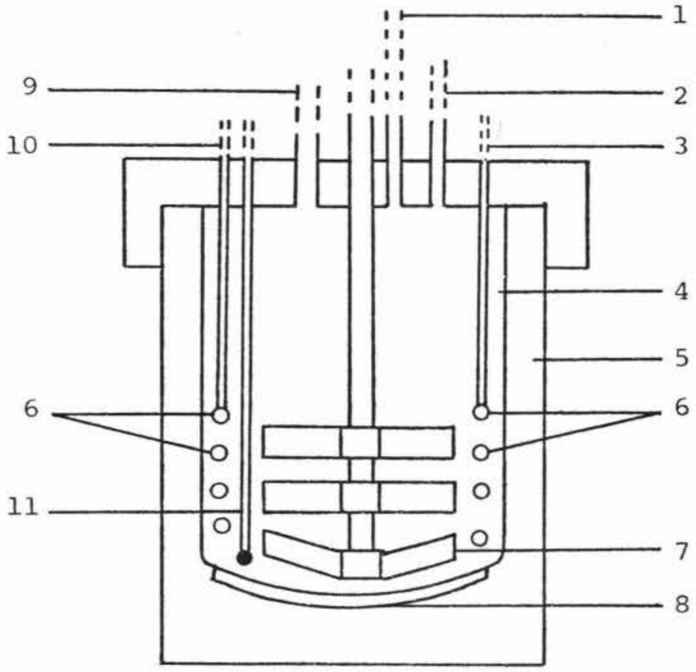

FIGURE 7: Diagram of hydrogenation vesssl

1. vacuum valve
2. oil inlet
3. water inlet
4. hydrogenating vessel
5. insulator
6. cooling coils
7. agitator
8. heating element
9. hydrogen inlet
10. water outlet
11. thermometer

Prior to hydrogenation, alkalinity and peroxide value tests on the cottonseed and palm oils showed the absence of soap and significant oxidation.

Three different hydrogenation techniques were carried out. In the first method (method A), the agitator was switched on to 450 rpm and 5 kg of melted cottonseed oil was poured into the vessel together with 0.2% of Pricat 9900 nickel catalyst. The vessel was closed,a vacuum was applied until an absolute pressure of 5 kPa was obtained. The fat was heated to 180°C and held at this temperature for 10 min. The vacuum valve was closed and hydrogenation was started by opening the hydrogen valve up to a pressure of 300 kPa (absolute pressure). The temperature of the oil in the vessel was kept at 180°C ± 3°C by adjusting the flow of water through the cooling coils. 50 ml samples were taken every 5 min (from 5-40 min) from the sample valve. The hydrogenator was stopped after the required time by closing the hydrogen valve, turning off the heater and increasing the flow of water through the cooling coils which lowered the temperature to 80°C.

The second method (method B) was similar to method A, except that 2% Pricat 9908 nickel catalyst was used and samples were taken at certain specified times.

The third method (method C) was similar to method B except that 0.5% Pricat 9908 catalyst was used and palm oil was hydrogenated (Beckman, 1983).

The hydrogenator was cleaned according to the procedure by Derrick _et_ _al_. (1980). It was first rinsed with hot water, washed with hot soapy water, filled with 2% sodium hydroxide solution at 70°C and agitated for 1 hr. The hydrogenator was then rinsed with hot water, filled with 1% nitric acid solution at 70°C and agitated for 1 hr. Finally, it was rinsed three times with hot distilled water and left to dry overnight.

2.6 FILTRATION OF HYDROGENATED OILS

Filtration of the hydrogenated fat samples was carried out in a pilot scale filter made by the New Zealand Dairy Research Institute, Palmerston North. A photograph of the filter is given in Figure 8, while an engineering diagram is shown in Appendix 2. The filter consisted of a cylinder made of polyvinylidenedifluoride, 11.7 cm in length, 5.1 cm in diameter, 0.6 cm in thickness and pores which were 25-35 μ in diameter (Type No. Kynar 5520, Industrial Plastics Division, Addington Engineering Co. Ltd, Christchurch, NZ). This cylinder was mounted and encased in a stainless steel jacket and the filter was attached to the hydrogenation vessel.

Prior to filtration, the hydrogenated oil was cooled to 80°C and the pressure in the vessel was lowered to 100 kPa. The outlet valve was then opened, allowing oil into the filter. The rate of filtration was determined by measuring the amount of oil filtered with respect to time. When operating normally, oil could be filtered at an initial rate of approximately 90 ml/min.

The filter was cleaned by scrubbing in hot water, soaking in hexane for 1 day after which it was rinsed with hot water and allowed to stand in 50% nitric acid for 1 day. It was then washed in water, soaked in 2% sodium hydroxide solution for a further day, rinsed in distilled water and then dried in the oven at 60°C.

2.7 DEODORIZATION OF HYDROGENATED OILS

Deodorization of the hydrogenated oils was carried out in a glass deodorization apparatus which was similar to that used by Heide-Jensen's (1963). A diagram of the apparatus is shown in Figure 9.

2.5 kg of fat was deodorized for a period of 2 hr with a steam rate of 30 ml/hr or 0.5 ml/min, a temperature of 210°C and an absolute pressure of 0.53 kPa. Samples were allowed to cool to 60°C before the vacuum was removed. 0.02% of an antioxidant

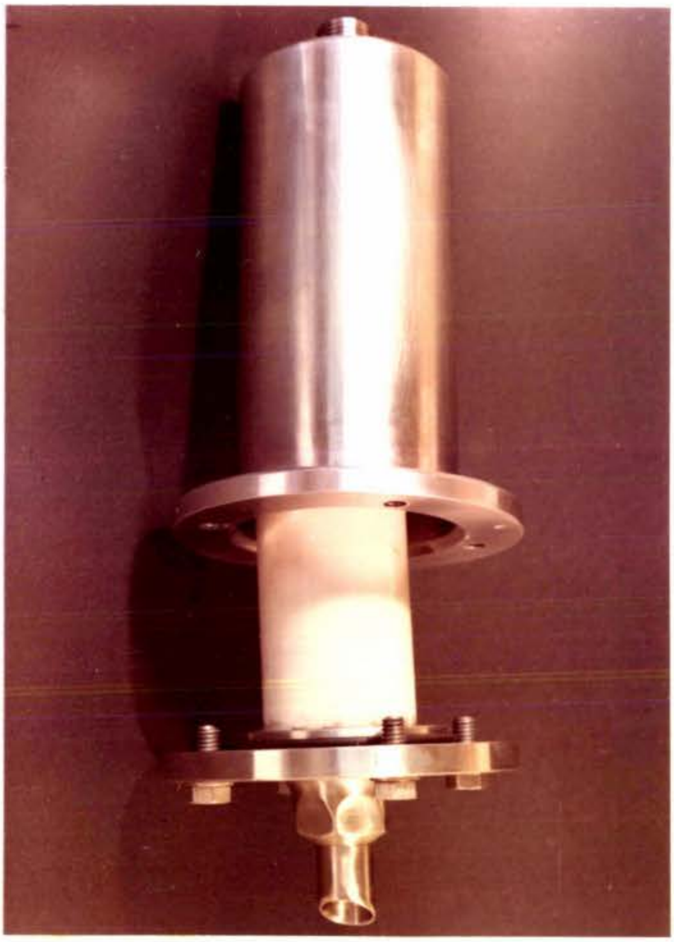

FIGURE 8: Photograph of filter

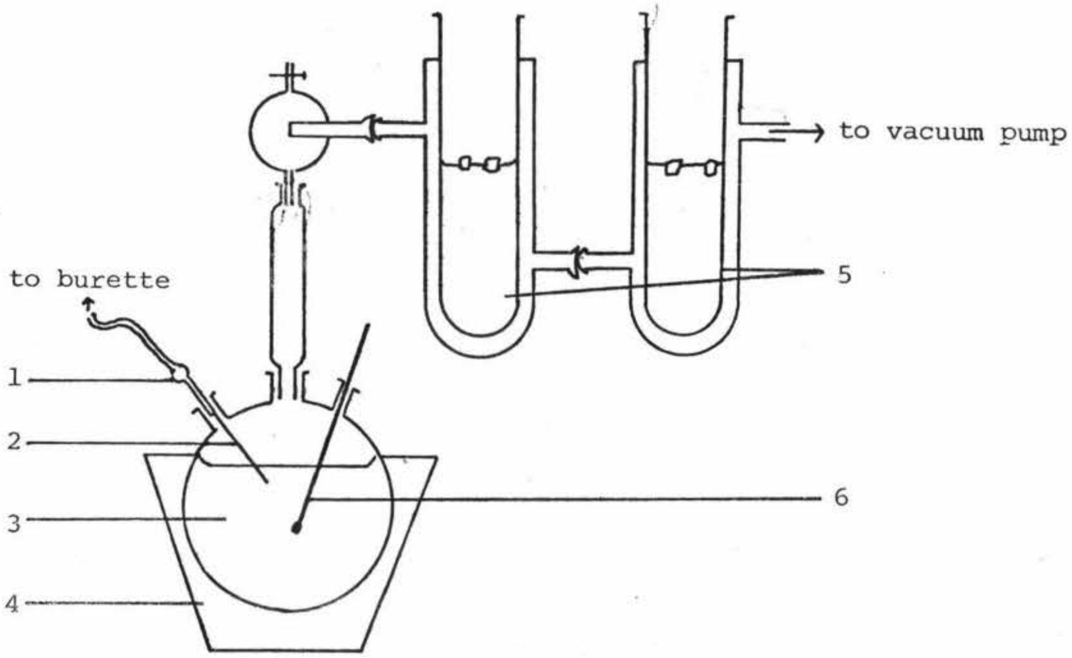

FIGURE 9: Diagram of deodorization apparatus*

1. valve to regulate amount of water
2. capillary tubing (stainless steel)
3. oil
4. heating element
5. ice traps (dry ice in methylated spirit)
6. thermometer

* Jensen (1963)

butylated hydroxytoluene was added to the deodorized oil.

2.8 FORMULATION OF FAT BLENDS

Various oil blends were made from three different types of oils, namely sunflower seed oil, milkfat and hydrogenated vegetable oils (cottonseed or palm oil). The amount of sunflower seed oil ranged between 7% and 15%, the milkfat varied from 55% to 70% while the hydrogenated oils ranged from 20% to 30%. Blends were prepared by melting these fats in an oven at 60°C and weighing the required amounts into 10 ml screw capped glass vials. The FA composition, softening points and SFC analysis of these blends were determined. Selected blends were also analysed by DSC.

2.9 PRODUCTION OF MARGARINE AND BUTTER

Four different manufacturing methods were used to manufacture a pastry margarine from milkfat and a fat blend. This blend comprised of 19.6% hydrogenated palm oil, 68.5% milkfat and 11.9% sunflower seed oil. Methods I and II involved the use of a z-blade reworker (Toledo Engineering Pty Ltd, Lidcombe, NSW, Australia) (Figure 10) while methods III and IV involved the use of a scraped surface heat exchanger (Votator, Continuous processing apparatus PR 7804, A Johnson and Co. London Ltd, Berkshire, England).

In method I, margarine or butter was manufactured as outlined in the flow process chart shown in Figure 11. A recombined cream comprising of 2.40 kg fat, 0.36 kg skim milk powder and 3.24 kg of water was prepared by heating to 60°C and pumping through a low pressure homogenizer (550 kPa) developed at the NZ Dairy Research Institute (Russell, 1969). The recombined cream was then cooled to 10°C by passing over a milk cooler and then held overnight in a cold room at 5°C. The next day the cream was churned in the z-blade reworker equipped with a chilled water jacket and a vacuum system.

In order to produce a satisfactory product, the speed of the reworker blades and the degree of chilling was varied through-

FIGURE 10: Photograph of a z-blade reworker

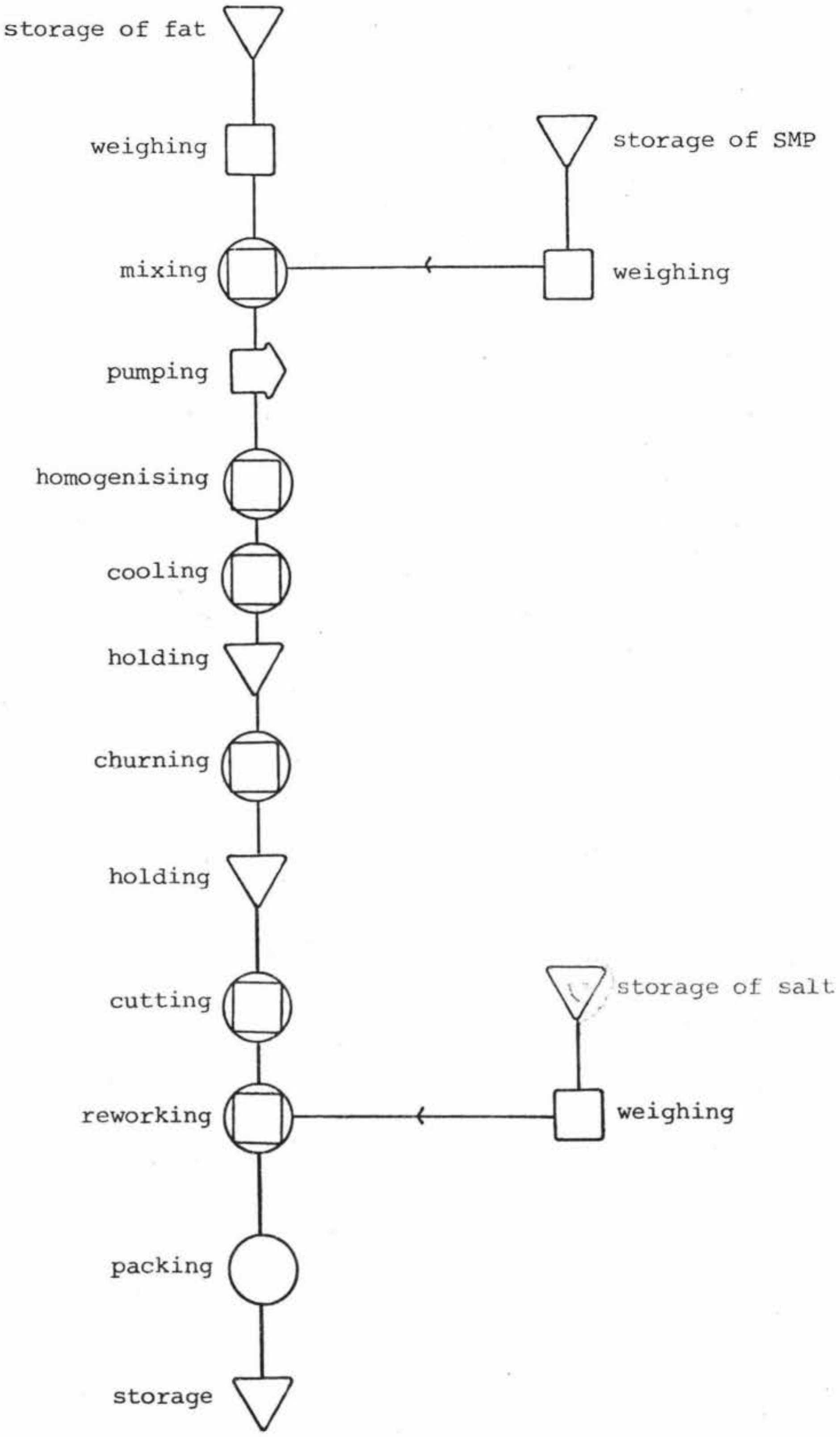

FIGURE 11: Flow process chart of manufacturing method I

out manufacture. In the case of milkfat, experience showed that the most suitable temperatures at breakpoint, end of churning and end of working were 8°C, 11°C and 15°C, respectively. In the case of the fat blend, however, the most suitable temperatures at breakpoint, end of churning and end of working were 14°C, 11°C and 14°C, respectively. For both cases, the speed of the blades was at 618 rpm during the initial stages of churning. The speed was lowered to 350 rpm once a thick whipped cream had been obtained and was reduced further to 150 rpm once breakpoint was reached. At this point, buttermilk started to separate out, the screen was fitted to the top and the buttermilk allowed to drain into a weighed pail. Further working of the product produced more buttermilk and the draining process was repeated. An estimation of the water content of the final product could be calculated at this point using the following formula:

$$\text{Moisture content} = \frac{Ww - 0.9x}{Wc - 0.9x}$$

where Ww = Weight of serum in cream.

Wc = weight of cream

x = weight of buttermilk to be removed

After removal of buttermilk, the product was worked at low speed (150 rpm) until there was no sign of free moisture and the product adhered to the walls of the reworker. At this stage, a moisture determination was carried out. The product was held at 5°C overnight, then cut into 1 cm pieces and reworked at an absolute pressure of 91.1 kPa (absolute pressure) for 6-8 min. The final temperature was 14-16°C. During reworking, the moisture content was adjusted to 17% and microfine salt was added to give a salt content of 1%.

In method II, margarine or butter was manufactured as outlined in the flow process chart shown in Figure 12. The processing steps were similar to those in method I, except for the cream cooling procedure which was a modification of the Alnarp process. The recombined cream was cooled at 5°C, held for 1 min, heated to 19°C, held for 2 hrs and then cooled to 10°C. After holding overnight at 5°C, the cream was churned.

In method III, margarine or butter was manufactured as out-

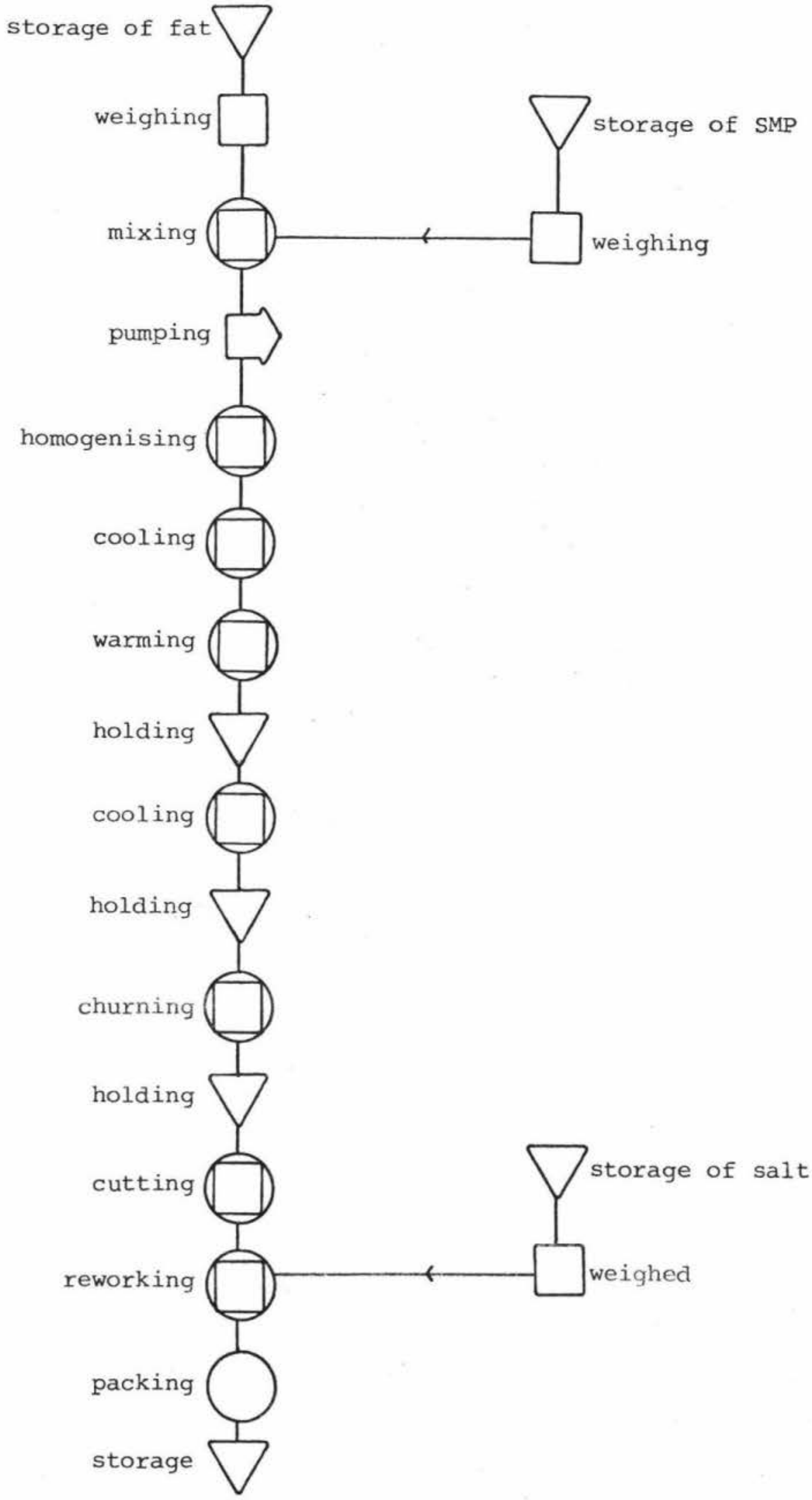

FIGURE 12: Flow process chart of manufacturing method II

lined in the flow process chart shown in Figure 13. The equipment used for this method was set up as shown in Figure 14. A mix comprising of 9.841 kg fat, 2.04 kg water and 0.12 kg skim milk powder was prepared, heated to 40°C and pumped (Howard proportiometer pump CHL 08-97SE 0-180 l/hr) into a *scraped surface heat exchanger to produce a final product with a temperature between 5-6°C. The flowrate of the product containing milkfat was 1.22 kg/min, while that of the fat blend mix was 0.83 kg/min. For both cases, the glycol cooling system was fully opened and the speed of the agitator shaft was at 500 rpm. Agitation was started as the product emerged from the scraped surface heat exchanger. This was carried out to prevent incorporation of air into the mix and also to ensure that the last traces of water were removed from the system.

The final product was held overnight at 5°C, cut into 1 cm pieces and reworked in the z-blade reworker as in method I.

In method IV, the product was manufactured as outlined in the flow process chart shown in Figure 15. The equipment used was set up as shown in Figure 16 and the processing steps were similar to those of method III, except that a pinworker was attached to the end of the scraped surface heat exchanger. The capacity of the pinworker was 3.2 l and the speed of the rotor shaft was at 300 rpm. As in method III, agitation was not started until product emerged from the pinworker. The product was held overnight at 5°C and reworked as in method I.

Hardness measurements, moisture, curd and salt determinations were carried out on all samples.

2.10 BAKING OF DANISH PASTRIES

Danish pastries were made with duplicate batches of Japanese pastry margarine (R1 and R2), butter (N1 and N2), margarine manufactured by method II (A1 and A2) and margarine manufactured by method IV (B1 and B2).

Four different batches of these products were made into

* SSHE 75mm diameter. 55mm shaft 300mm length
612.88 cc of nominal annular space.

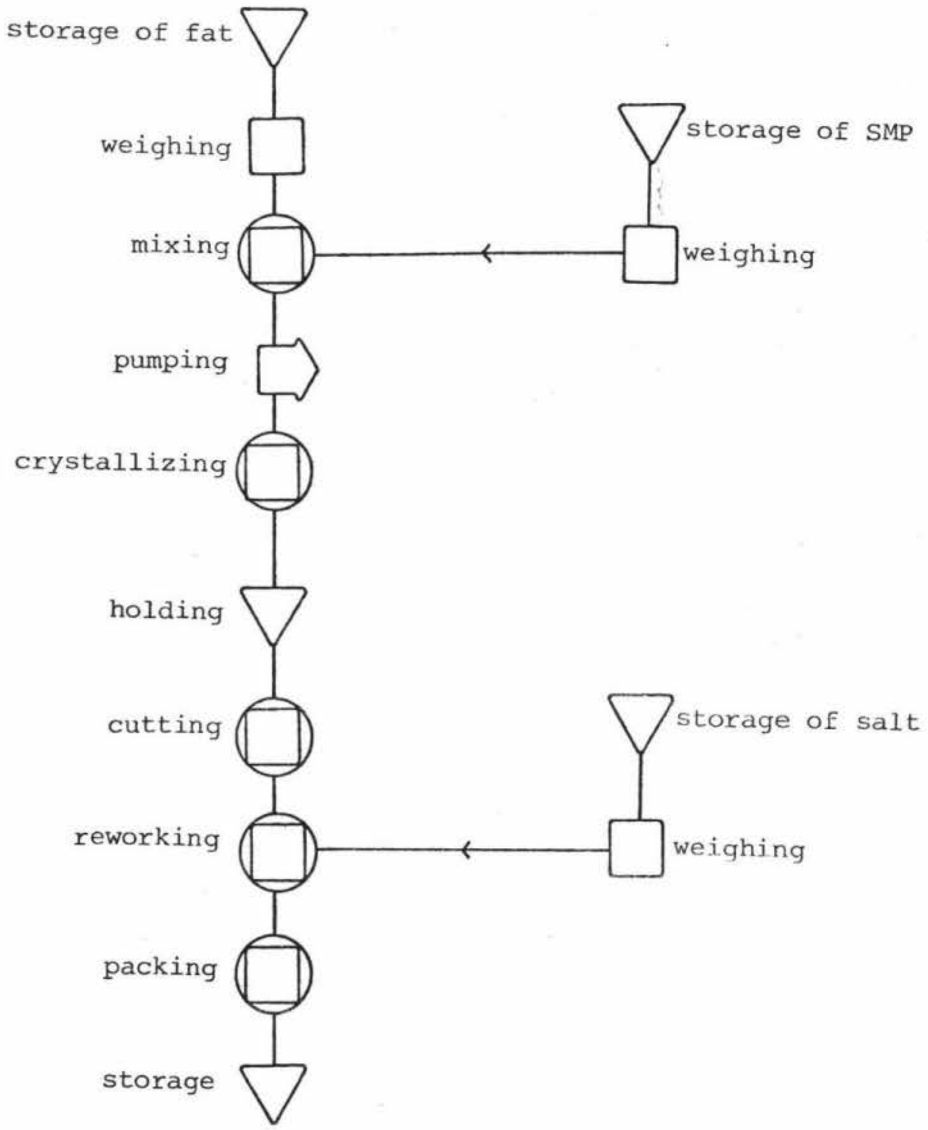

FIGURE 13: Flow process chart of manufacturing method III

<u>FIGURE 14</u>: Photograph of equipment used in manufacturing method III

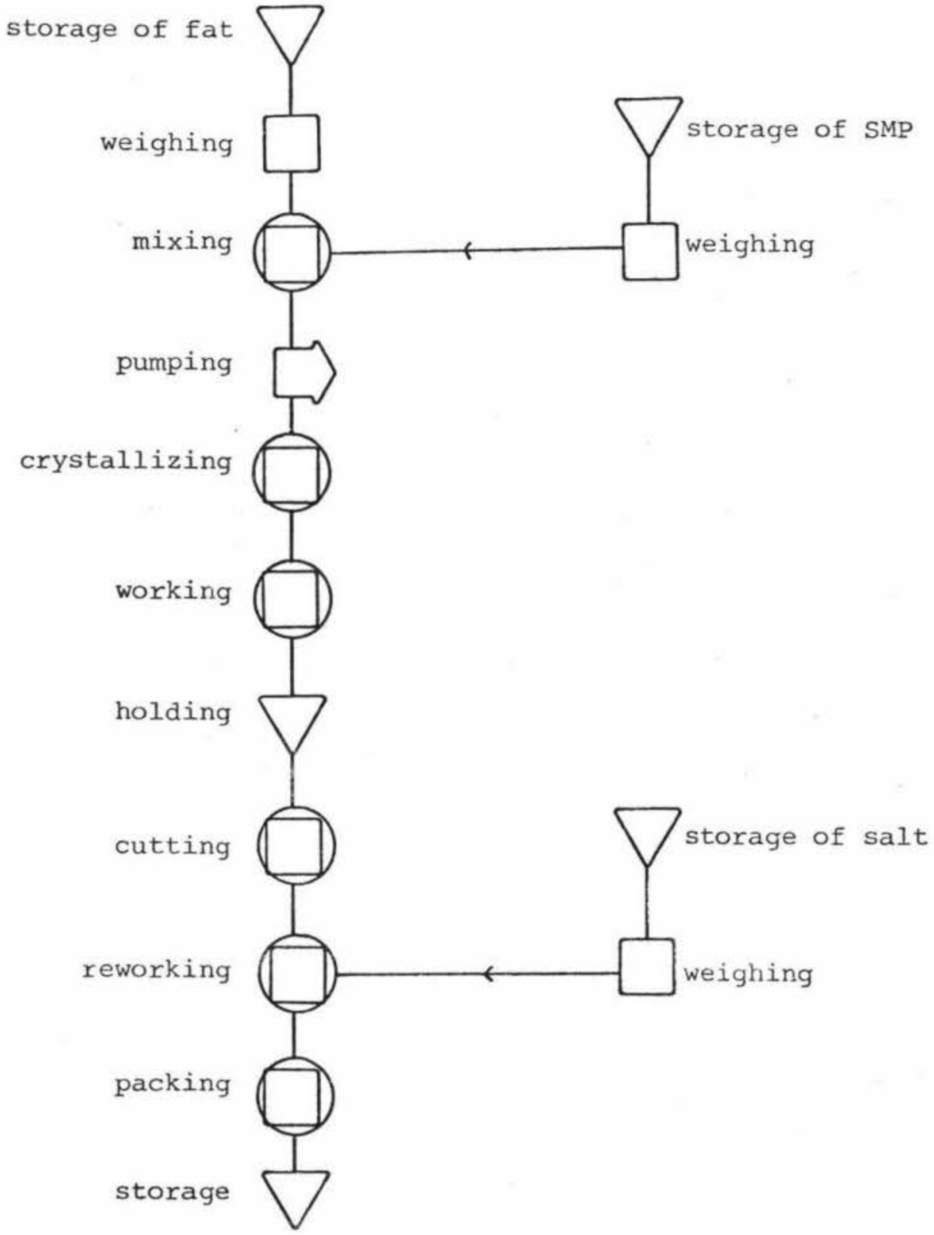

FIGURE 15: Flow process chart of manufacturing method IV

FIGURE 16: Photograph of equipment used in manufacturing method IV

pastries on each of three baking days. It was not possible to have more baking trials as there was a limited amount of margarine manufactured by methods II and IV. Each batch was made at different times of the day as follows:

Day 1 - R1; A2; B1; N1
Day 2 - A1; B2; R1; N2
Day 3 - B1; N1; A2; R2

The pastries were made according to a standardized procedure (Appendix 3) and a time schedule (Appendix 4).

2.10.1 Physical Measurements

The amount of spread in the pastry units was measured by tracing the outline of four randomly chosen 'butterfly' units before and after baking. The advantage of using this butterfly pattern was the ease in making standardized units and measuring the spread of the pastry on paper. The outline of each unit was cut out and weighed for comparison of sizes. A two-way analysis of variance was performed on the physical data using DSIR AMD program stats twoway on a VAX 11/780 computer.

Photographs of the cross-section and plane surface of the butterfly and windmill units were taken for visual comparison. The advantage of using the 'windmill' pattern was that the rise in volume was more easily detected than the 'butterfly' pattern.

2.10.2 Sensory Evaluation

Ten people from the staff at the NZDRI were chosen as panelists for the sensory evaluation of the danish pastries. They all have had some experience with sensory evaluation. Initially, a discussion was held to determine suitable characteristics for the evaluation of the pastries and as a result of this discussion, colour, external layering, flakiness, doughiness and fattiness were chosen.

Training was carried out by giving the panelists samples of flaky and doughy pastries plus a reference. They were then told the scores of the samples for each of the above characteristics in relation to the reference. Any disagreement on the scores was discussed until the panelists were satisfied. This procedure was repeated the following day.

Evaluation was carried out at the end of each baking day in sensory evaluation booths with controlled lighting. The pastries were evaluated at room temperature and each panelist was asked to taste the reference first, and then compare it with the other samples which were arranged in a random order An example of the questionnaire used is found in Appendix 3.

Wilcoxon's signed rank test (Bhattacharyya, 1977) was performed on the sensory evaluation data using the minitab computer program (Pennsylvania State University, 1981).

CHAPTER 3

RESULTS AND ANALYSIS

3.1 ANALYSIS OF A DANISH PASTRY MARGARINE

A sample of margarine used for manufacture of danish pastries in Japan was analysed to obtain its chemical and physical profile which was later used as a basis for the formulation of alternative blends. The product has a gross composition of 81.1% fat, 17.0% moisture, 1.0% curd and 0.9% salt.

Fatty acid (FA) composition results given in Table 4 show that the margarine contains both long and short chain FAs. The major FAs are palmitic (16:0), stearic (18:0) and oleic acid (18:1) and linoleic (18:2). The large proportion of 18:1 and 18:2 plus the significant quantity of butyric acid (4:0) and caproic acid (6:0) present suggest that the margarine consists largely of vegetable fat(s) in combination with a proportion of milkfat (20-30%).

As expected from the FA composition, the analysis of the intact triacyglycerols (TGs) show the presence of a large percentage of C_{52} TGs (22.6%) and C_{54} TGs (44.6%) in the margarine (Table 4).

The solid fat content (SFC) results given in Table 4 show the expected steady decline in the amount of solid fat as temperature is increased, e.g. from 72.0% at 5°C to 4.7% at 35°C. Tempering at 20°C (method S2) gives the expected decrease in the amount of solid fat at temperatures below 20°C, e.g. at 15°C, the SFC decreases from 53.8% to 40.6%. The softening point of the margarine is found to be 36°C, which corresponds to a solid fat content of 4-6% (Norris et al., 1973).

The hardness values of the margarine at 15°C are 219g and 238g when tempered by methods H1 and H2, respectively, indicating that the margarine is soft and maleable at that temperature. The relatively low hardness value obtained at 15°C

TABLE 4: Analysis of Japanese pastry margarine

	Fatty acid composition (weight %)																	
Fatty acid	4:0	6:0	8:0	10:0	11:0	12:0	14:0	15:0	15:1	16:0	16:1	16:2	17:0	18:0	18:1	18:2	18:3	20:0
	1.2	0.7	0.5	0.9	0.1	1.2	3.5	0.5	0.4	17.3	1.5	0.3	0.2	11.1	48.5	11.0	0.4	2.0

	Triacylglycerol composition (weight %)														
Triacylglycerol	30	32	34	36	38	40	42	44	46	48	50	52	54	56	58
	0.3	0.7	1.5	3.5	5.6	2.9	2.0	1.8	2.2	3.3	6.6	22.6	44.6	2.0	0.5

	Solid fat content (%)								
Temperature (°C)	0	5	10	15	20	25	30	35	40
*S1	74.7	72.0	63.4	53.8	37.7	26.3	15.8	4.7	0
**S2	61.3	55.7	48.8	40.6	37.6	27.4	14.9	6.7	0

* tempered by method S1
** tempered by method S2

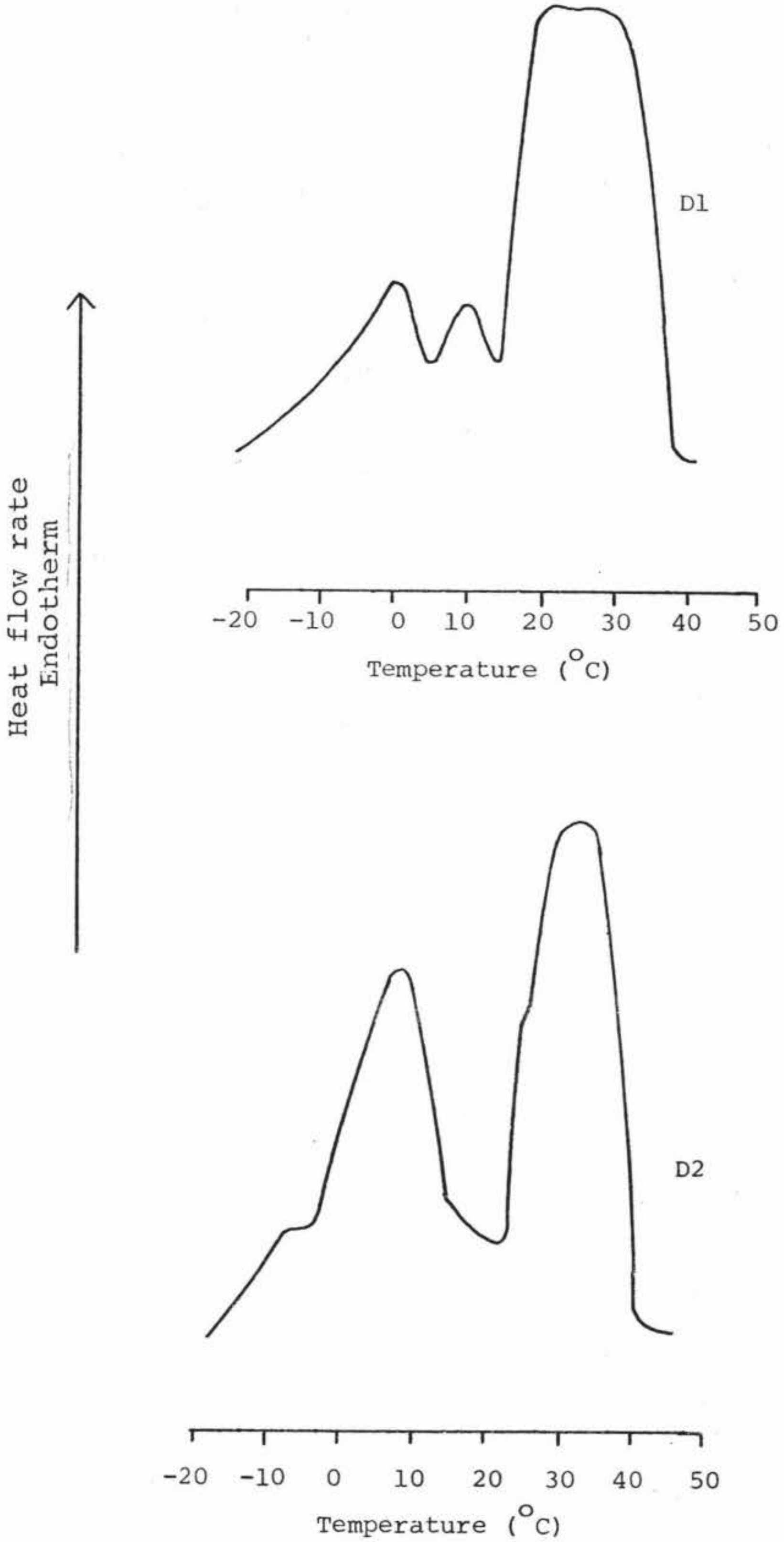

FIGURE 17: The melting thermograms of Japanese pastry margarine obtained after tempering by methods D1 and D2 (weight of sample 4.950 mg, scan speed 10°C/min, range 2).

implies that the product may have been tempered during manufacture.

Thermal analysis by differential scanning calorimetry (DSC) was performed on the pastry margarine. The sample tempered by method D1 gives a thermogram which has a large melting peak with a maximum at 30°C (Figure 17). Tempering at 20°C (method D2) causes a large dip at this temperature (20°C) and produces two large melting peaks with maxima at 8°C and 32°C, respectively. Comparison of these two melting thermograms (by methods D1 and D2) shows a marked increase in proportion of fat which melt below the tempering temperature, 20°C (method D1). This confirms the results obtained by the SFC analysis.

3.2 ANALYSIS OF MILKFAT

Milkfat obtained from cream produced during summer (February) was analysed.

FA composition given in Table 5 shows that milkfat contains both long and short chain FAs. The major FAs are 4:0, 16:0, 18:0 and 18:1.

As expected from the FA composition the milkfat has a varied TG composition with no preponderence of any one TG type. The major TGs present are C_{36}, C_{38}, C_{40}, C_{48}, C_{50} and C_{52}.

The SFC results (Table 5) show a decline in the amount of solid fat with increase in temperature from 70.7% at 0°C to 0% at 35°C. Tempering at 20°C (method S2) gives the expected decrease in solid fat at temperatures below 20°C, <u>e.g</u>. at 10°C, the SFC decreases from 61.8% to 52.9%. The softening point of the summer milkfat is found to be 34°C.

Thermal analysis by DSC was performed on milkfat. The rapidly cooled sample (method D1) gives a thermogram which has three small melting peaks with maxima about 11°C, 25°C and 33°C and a larger melting peak with a maximum about 18°C. Tempering at 20°C (method D2) causes a large dip at this temperature

TABLE 5: Analysis of milkfat

Fatty acid composition (weight %)

Fatty acid	4:0	6:0	8:0	10:0	11:0	12:0	14:0	15:0	15:1	16:0	16:1	16:2	17:0	18:0	18:1	18:2	18:3	20:0
	3.4	2.2	1.2	2.6	0.4	3.1	10.9	2.1	1.4	31.5	3.1	0.8	0.7	10.6	22.2	2.14	1.87	

Triacyglycerol composition (weight %)

Triacylglycerol	30	32	34	35	36	37	38	40	42	44	46	48	50	52	54	56	58
	0.8	1.9	5.1	0.8	10.6	1.1	13.3	9.7	6.9	6.1	7.6	9.8	12.2	10.1	4.0	0.1	-

Solid fat content (%)

Temperature (°C)	0	5	10	15	20	25	30	35
*S1	70.7	67.5	61.8	46.7	28.2	16.6	9.4	0
**S2	64.4	60.4	52.9	42.2	29.2	17.0	9.5	0

* tempered by method S1

** tempered by method S2

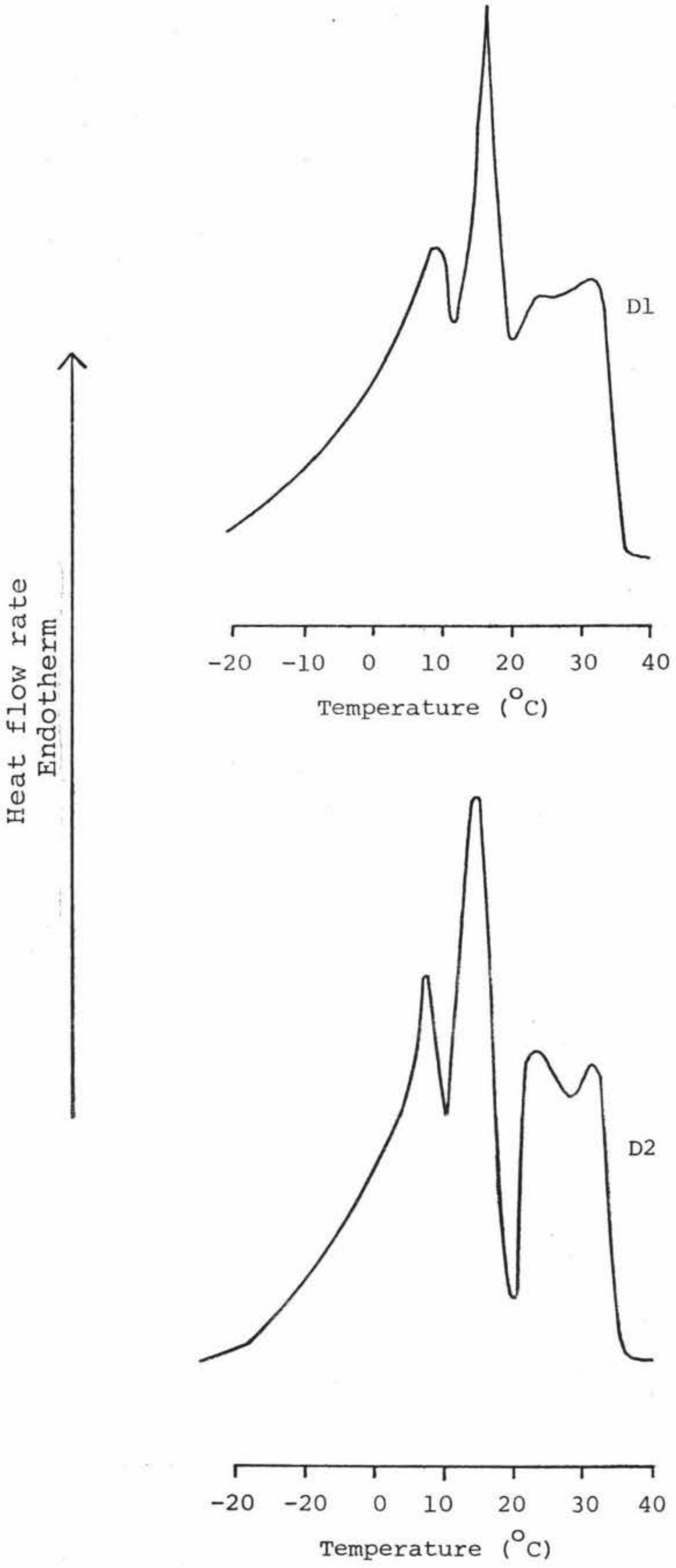

FIGURE 18: The melting thermograms of milkfat obtained after tempering by methods D1 and D2 (weight of sample 4.525 mg, scan speed 10°C/min, range 2).

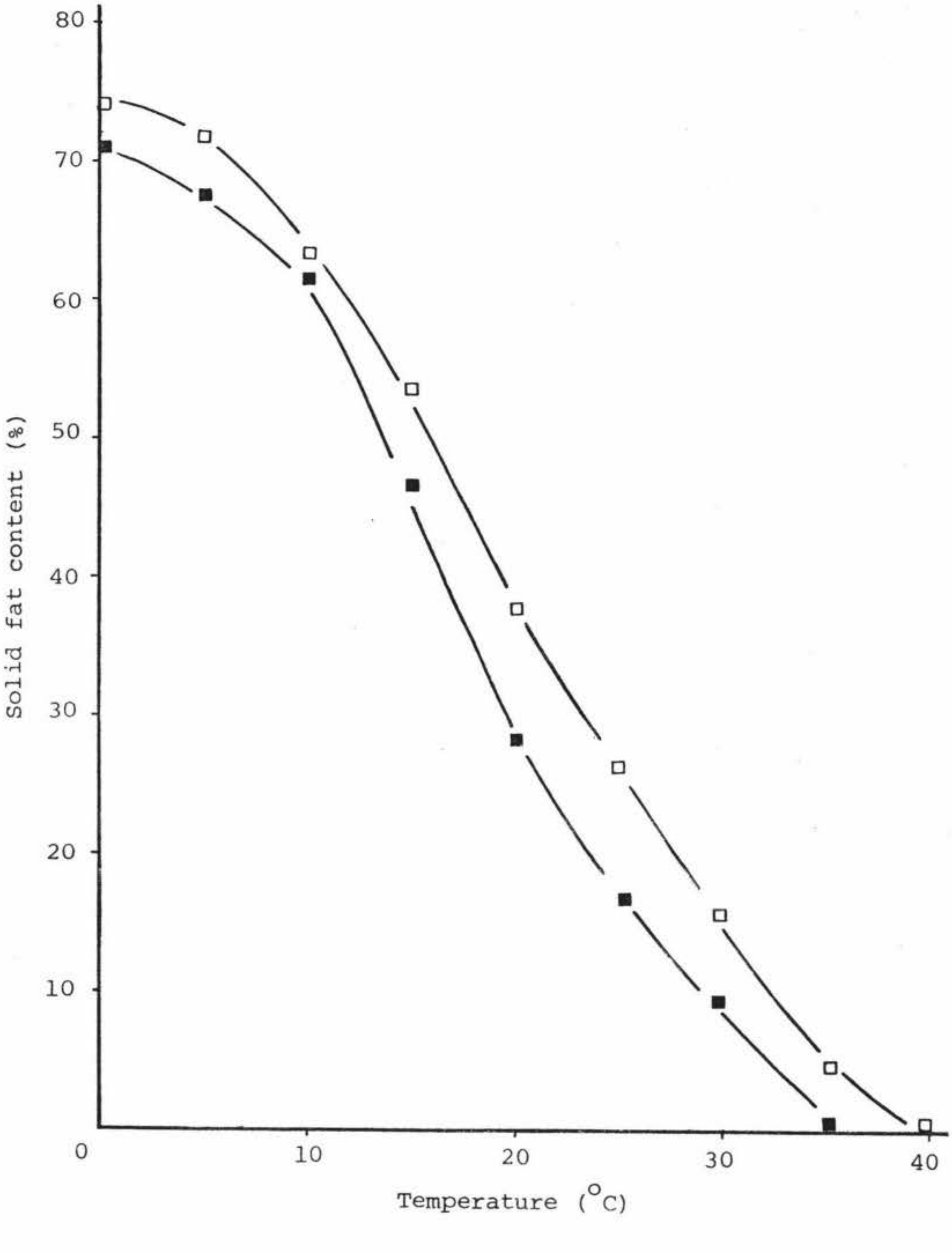

FIGURE 19: Curves of solid fat content of Japanese pastry margarine and milkfat obtained after tempering by method S1.

□ Japanese pastry margarine

■ Milkfat

(Figure 18).

Milkfat appears to be unsuitable for use in danish pastry because it lacks sufficient high melting TGs and a considerable proportion of TGs melt in the region of 15-20°C, the temperature at which rolling out takes place (Figure 19).

To formulate a blend containing a large proportion of milkfat which will be suitable for making danish pastry margarine, an oil melting below 5°C and a fat containing a large quantity of high melting TGs will have to be added. The high melting fat will increase the amount of solid fat throughout the whole range of temperatures while the oil will have the effect of reducing the SFC at low temperatures, thus producing a less steep melting curve.

3.3 HYDROGENATION OF VEGETABLE OILS

Hydrogenation studies were carried out to produce a series of samples with different melting properties. Cottonseed oil was hydrogenated using an active catalyst (method A) and a very selective catalyst (method B) while palm oil was hydrogenated using a very selective catalyst (method C). In each case, samples were taken for analysis at a series of different times during the hydrogenation reaction.

3.3.1 Variation in Iodine Value, Refractive Index and Softening Point

Figures 20, 23 and 26 show the corresponding curves of iodine value, refractive index and softening points. For each of the three hydrogenations, iodine value (IV) and refractive index (RI) decrease exponentially with increase in hydrogenation time. In each method, the IV and RI curves are similar to each other. This shows that RI measurements can be used to control the hydrogenation reaction to within ± 4 IV units.

In contrast to IV and RI, the softening point shows the expected increase as hydrogenation progresses.

3.3.2 Variation in Fatty Acid Composition and Solid Fat Content

For the hydrogenation of cottonseed oil using an active catalyst (method A), marked changes occur in the proportion of 18:0, 18:1 and 18:2 during the reaction (Table 6 and Figure 21). During the initial 10 min of the reaction, 18:2 decreases from 54.4% to 3.9%, 18:1 increases from 21.3% to 69.4% while 18:0 shows little variation. Subsequently, 18:1 declines from 69.4% to 0% while 18:0 increases from 5.4% to 78.7% at 40 min. These variations show that there is virtually no hydrogenation of 18:1 until the hydrogenation of 18:2 is almost completed. This is due to the difference in hydrogenation rates between 18:1 and 18:2. The amount of 18:0 at the end of the reaction closely corresponds to the total amount of 18 carbon FAs (C_{18}) present in the original cottonseed oil (78.5%).

As expected, there is little change in 16:0. The proportion of <u>trans</u>-isomers varies in a manner similar to that of the 18:1, increasing up to 35.0% during the first 10 min and thereafter decreasing to 0% at 40 min.

As hydrogenation progresses, the proportion of solid fat at each temperature increases, <u>e.g</u>. the proportions of solid fat at 15°C are 19.8%, 62.9% and 95.1% after 5, 10 and 15 min, respectively (Table 6). Furthermore, the SFC curve becomes steeper with increase in hydrogenation time (Figure 22). This is the expected trend since hydrogenation decreases the degree of unsaturation in a given fat.

For the hydrogenation of cottonseed oil using a very selective catalyst (method B), changes in the proportions of 18:0, 18:1 and 18:2 occur during the reaction ~~occur~~ (Table 7 and Figure 24). During the initial 20 min of the reaction, 18:2 decreases from 54.4% to 7.6%, 18:1 increases from 21.3% to 63.4% while 18:0 increases from 2.8% to 8.7%. Subsequently, 18:1 declines gradually from 63.4% to 52.5% while 18:0 continues to increase from 8.7% to 23.5% at 120 min. These variations are a consequence of the difference in hydrogenation rates between 18:2 and 18:1.

TABLE 6: Hydrogenation of cottonseed oil with an active catalyst (method A)

Reaction time (min)	0	5	10	15	20	30	40
Iodine value	113.0	87.3	66.4	48.7	31.6	5.7	1.8
Refractive index	1.4510	1.4485	1.4461	1.4442	1.4428	1.4400	1.4398
Softening point	-	27.8	36.1	48.4	56.5	64.0	64.7
Trans-isomers (%)	*t	18.3	35.0	34.6	23.6	-	0

Fatty acid	Fatty acid composition (weight %)						
12:0	0.1	0.1	0.1	0.1	0.1		t
14:0	0.7	0.8	0.7	0.7	1.0		0.7
16:0	20.4	20.8	20.1	20.2	22.9		20.6
16:1	0.4	0.3	0.4	t	-		-
18:0	2.8	3.7	5.4	23.0	41.6		78.7
18:1	21.3	47.1	69.4	55.9	34.5		-
18:2?	-	-	3.9	-	-		-
18:2	54.4	27.3		-	-		-

Temperature (°C)	Solid fat content (%)						
0		40.5	82.0	97.2	98.9		99.8
5		37.5	80.2	97.1	98.5		99.8
10		28.2	74.2	96.5	98.5		99.6
15		19.8	62.9	95.1	98.5		99.4
20		13.7	49.3	90.6	98.4		99.0
25		9.8	34.1	84.3	97.6		98.8
30		5.8	19.5	73.5	93.9		98.8
35		0	8.6	58.4	89.0		98.8
40			0	39.6	80.2		98.8
45				21.1	65.3		98.8
50				0	47.1		98.7
60					0		96.9

* trace

Hydrogenation of cottonseed oil with an active catalyst (method A)

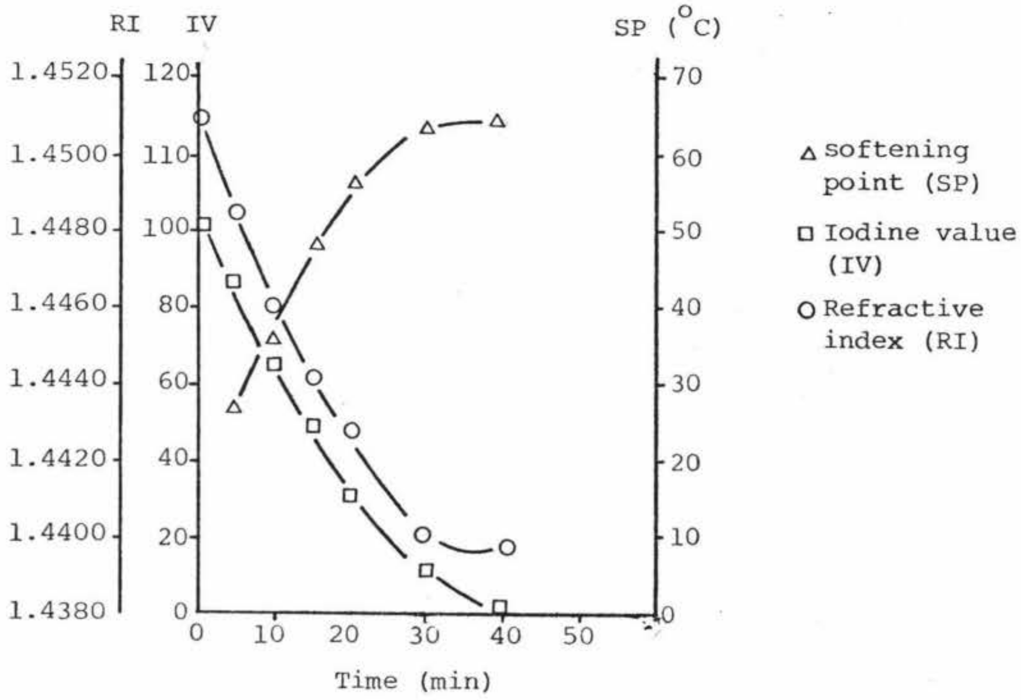

FIGURE 20: Curves of softening point, iodine value and refractive index.

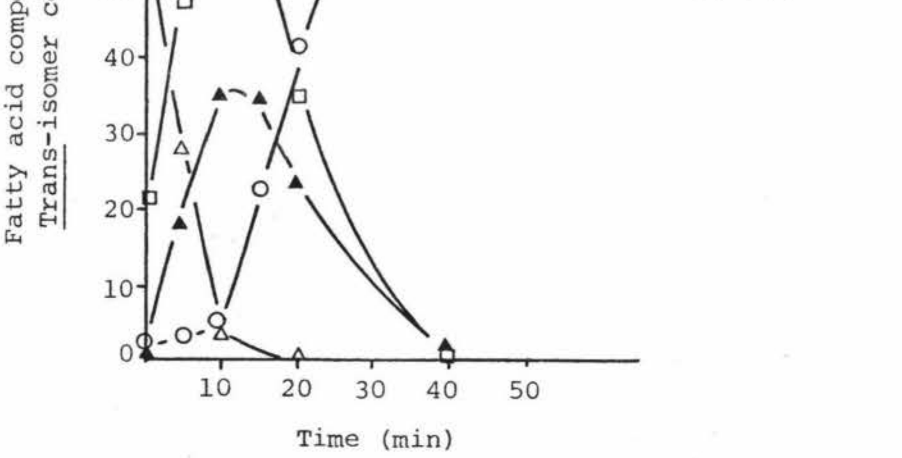

FIGURE 21: Curves of fatty acid composition

Hydrogenation of cottonseed oil with an active catalyst (method A)

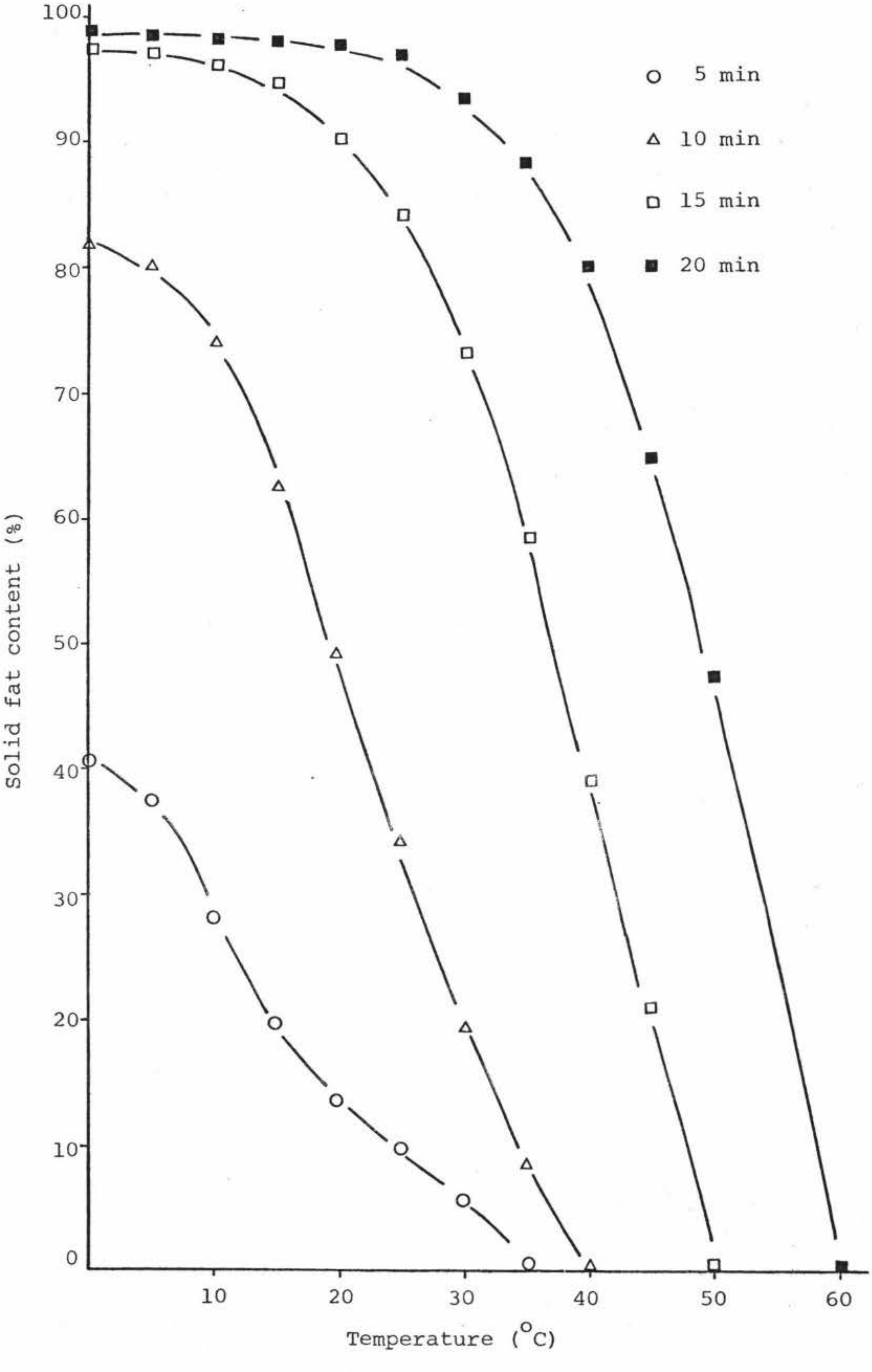

FIGURE 22: Curves of solid fat content hydrogenated to different times.

TABLE 7: Hydrogenation of cottonseed oil with a very selective catalyst (method B)

Reaction time (min)	0	20	40	45	70	90	120
Iodine value	113.0	66.7	59.0	58.2	55.1	52.4	49.1
Refractive index	1.4510	1.4453	1.4444	1.4442	1.4440	1.4439	1.4435
Softening point	-	44.4	46.7	47.1	48.3	49.2	50.3
trans-isomers (%)	*t	53.3	-	45.7	39.4	-	41.3

Fatty acid	Fatty acid composition (weight %)						
12:0	0.1	0.1		0.1	0.1		0.1
14:0	0.7	0.7		0.7	0.7		0.7
16:0	20.4	19.1		19.7	19.3		19.7
16:1	0.4	0.5		t	t		-
18:0	2.8	8.7		14.2	17.4		23.5
18:1	21.3	63.4		62.5	58.2		52.5
18:2?		7.6		3.6	4.4		3.6
18:2	54.4						

Temperature (°C)	Solid fat content (%)			
0	91.0	96.1	97.7	98.3
5	90.4	95.7	97.2	97.8
10	88.5	95.0	96.7	97.3
15	83.9	92.3	94.5	96.0
20	75.0	87.4	90.8	93.6
25	61.1	78.4	84.2	88.5
30	41.6	64.7	74.0	80.8
35	22.8	45.7	59.0	69.1
40	12.9	25.8	38.4	49.8
45	6.4	11.3	17.7	26.4
50	0	0	0	7.6
60	-	-	-	0

* trace

Hydrogenation of cottonseed oil with a very selective catalyst (method B)

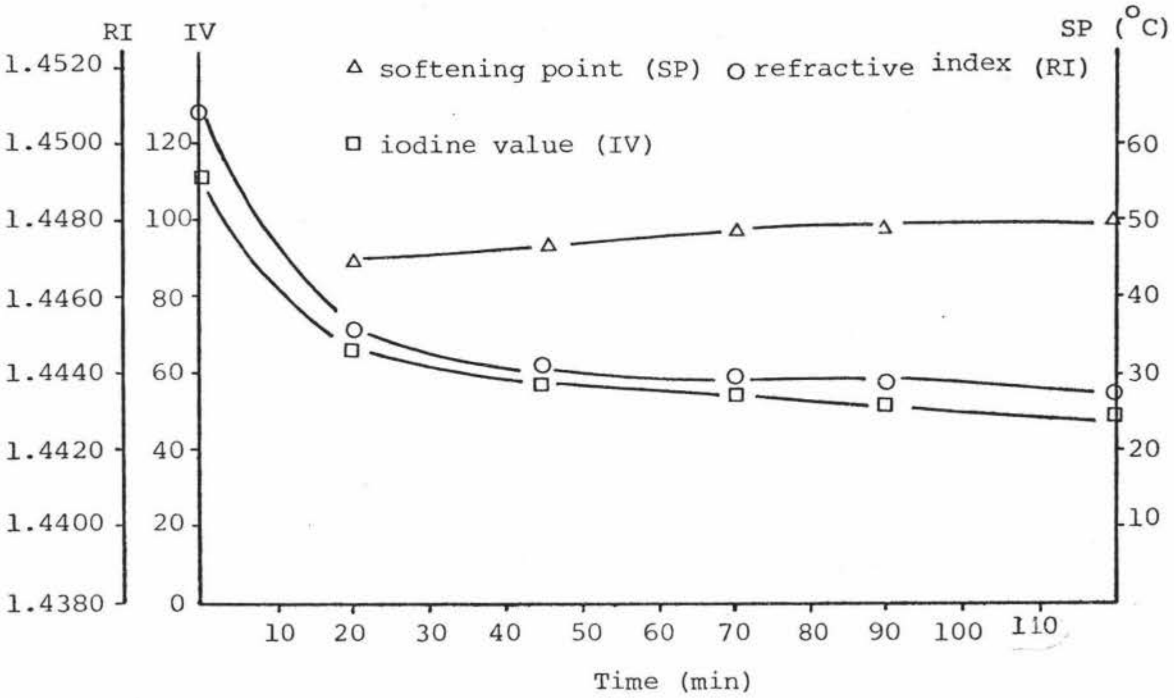

FIGURE 23: Curves of softening point, iodine value and refractive index

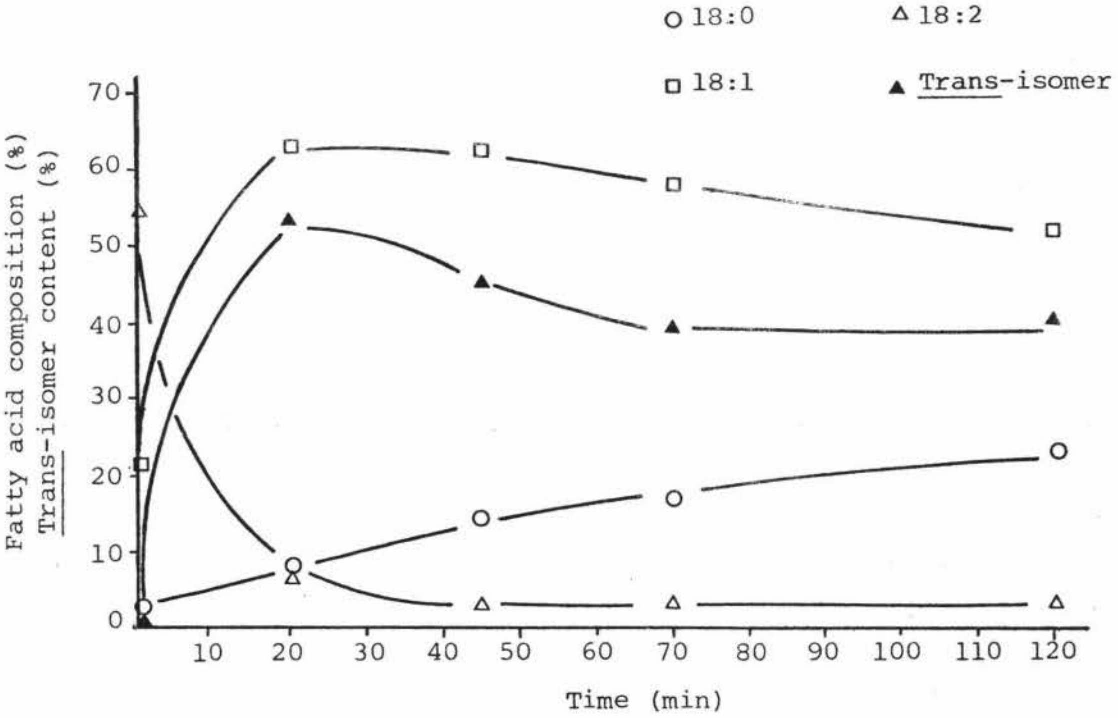

FIGURE 24: Curves of fatty acid composition

There is little change in 16:0. The proportion of *trans*-isomers varies in a manner similar to that of the 18:1, increasing up to 53.3% during the first 20 min and thereafter decreasing to 41.3% at 120 min.

As hydrogenation progresses, the proportion of solid fat at each temperature increases, *e.g.* the proportions of solid fat at 15°C are 83.9%, 92.3% and 94.5% after 20, 45 and 70 min, respectively (Table 7). Furthermore, the SFC curve becomes steeper with increase in hydrogenation time (Figure 25).

For the hydrogenation of palm oil using a very selective catalyst (method C), there are changes in the proportion of 18:0, 18:1 and 18:2 during the reaction (Table 8 and Figure 27). 18:2 decreases gradually from 12% to 0% at $\overset{45}{70}$ min, 18:1 increases from 40.2% to 47.0% during the first 15 min and decreases thereafter to 44.1% at 70 min. 18:0 increases gradually from 5.6% to 12.0% at 70 min.

As in the hydrogenation of cottonseed oil, there is little change in 16:0. The proportion of *trans*-isomers varies in a manner similar to 18:1, increasing from 0% to 34.7% during the first 15 min and then decreasing to 31.3% at 70 min.

As for methods A and B, the proportion of solid fat at each temperature increases with hydrogenation time, *e.g.* the proportions of solid fat at 15°C are 44.1%, 85.0% and 97.1% after 0, 5 and 15 min, respectively (Table 8). Furthermore, the SFC curve becomes steeper with increase in hydrogenation time (Figure 28).

3.3.3 The Effect of Different Catalysts

Cottonseed oil hydrogenated by the active catalyst shows a rapid increase in the proportion of 18:0 after the initial 10 min to a fully saturated fat at 40 min (Figure 21). In the case of the very selective catalyst, 18:0 increases gradually during the hydrogenation and a substantial amount of 18:1 is present when the reaction is terminated after 120 min, forming a partially hydrogenated fat (Figure 24). This

Hydrogenation of cottonseed oil with a very selective catalyst (Method B)

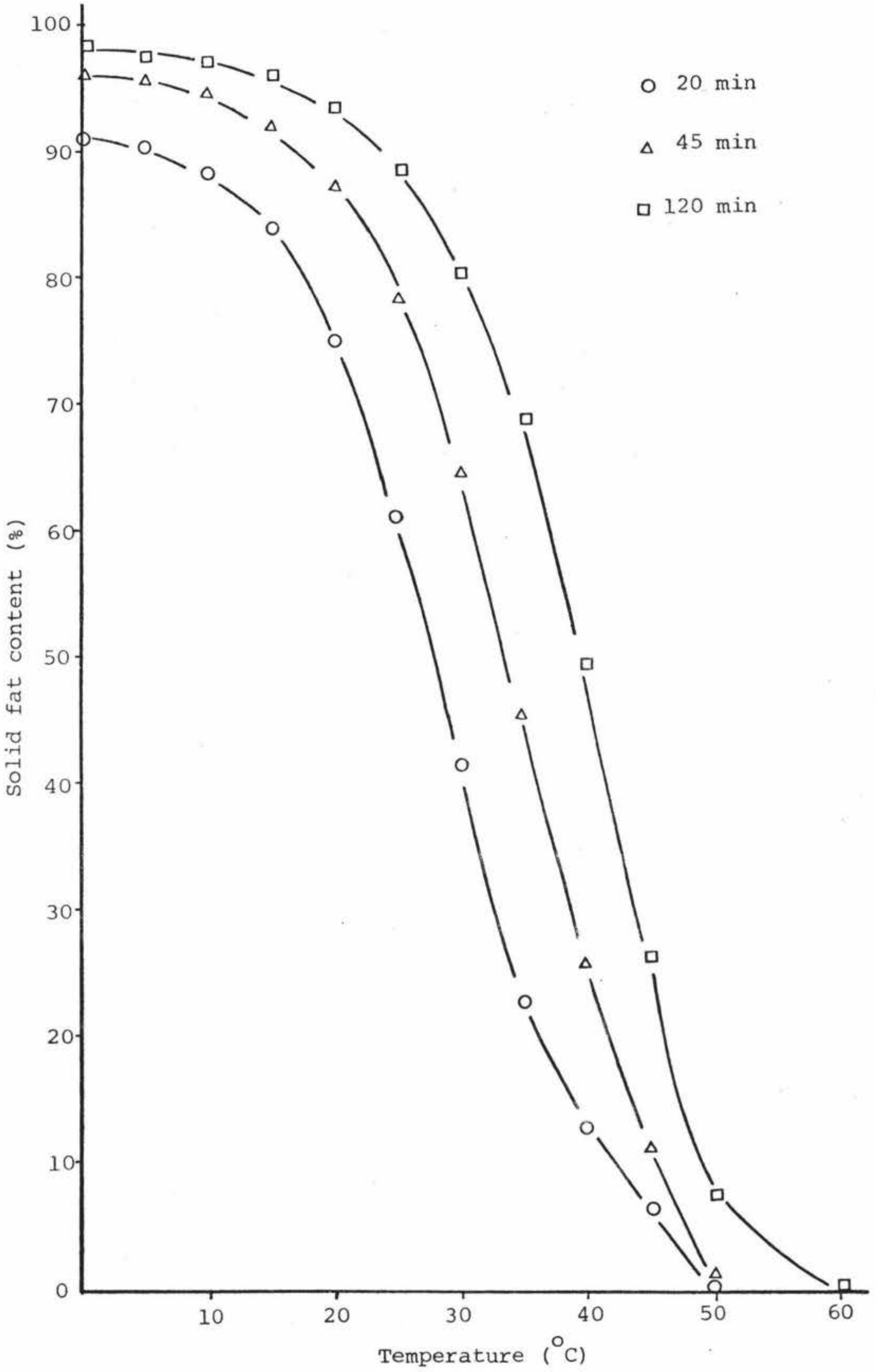

FIGURE 25: Curves of solid fat content hydrogenated to different times

TABLE 8: Hydrogenation of palm oil with a very selective catalyst (method C)

Reaction time (min)	0	5	10	15	30	45	70
Iodine value	56.2	48.3	45.7	43.8	42.3	41.8	40.0
Refractive index	1.4441	1.4430	1.4427	1.4422	1.4421	1.4421	1.4420
Softening point	36.5	44.6	46.3	47.0	47.7	48.0	48.5
Trans-isomers (%)	*t	23.8	-	34.7	-	33.1	31.3

Fatty acid	Fatty acid composition (weight %)				
12:0	0.1	0.2	0.1	0.2	0.2
14:0	1.0	0.9	0.9	1.1	1.0
16:0	40.2	39.1	40.0	43.3	42.7
16:1	0.3	t	t	-	-
18:0	5.6	8.2	9.6	10.3	12.0
18:1	40.2	43.7	47.0	45.1	44.1
18:?	-	-	-	t	t
18:2	12.0	8.0	2.5	t	-
18:3	0.4	t	-	-	-
20:0	t	t	t	t	t

Temperature (°C)	Solid fat content (%)				
0	75.8	94.4	98.6	99.0	98.8
5	70.4	93.4	98.3	98.8	98.6
10	59.8	91.5	97.9	98.5	97.8
15	44.1	85.0	97.1	98.0	97.8
20	30.3	75.9	93.9	97.2	97.4
25	19.4	62.7	87.8	91.8	93.2
30	11.5	46.5	76.4	83.6	85.7
35	7.4	33.2	60.4	69.3	72.9
40	0	18.9	39.7	48.2	51.8
45		4.8	15.8	23.0	26.2
50		0	0	0	0

* trace

Hydrogenation of palm oil with a very selective catalyst (method C)

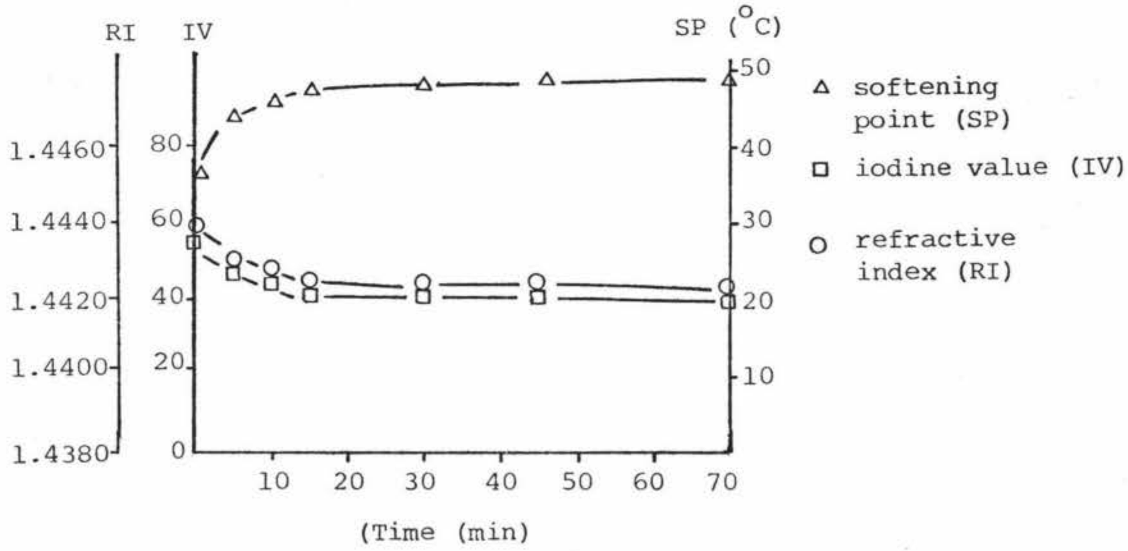

FIGURE 26: Curves of softening point, iodine value and refractive index

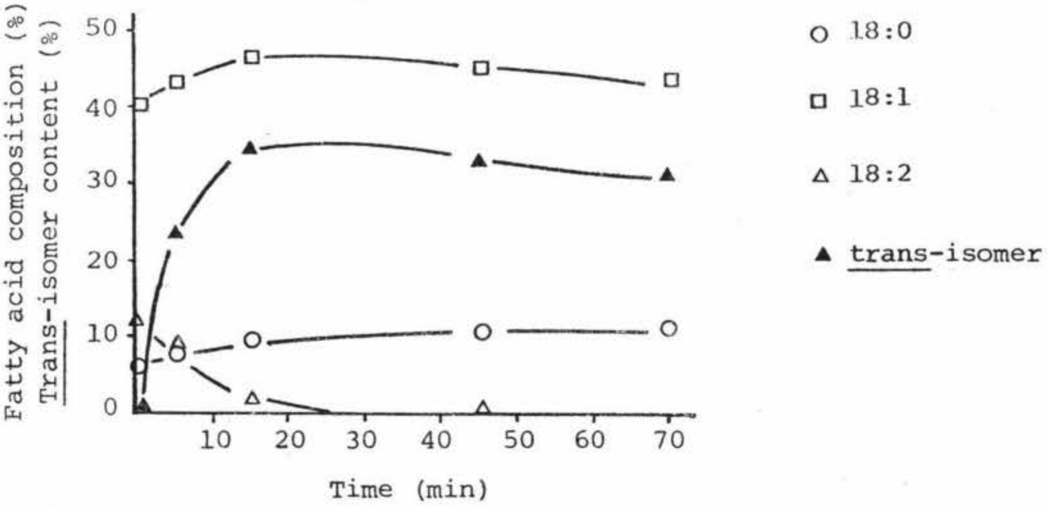

FIGURE 27: Curves of fatty acid composition

Hydrogenation of palm oil with a very selective catalyst (method C)

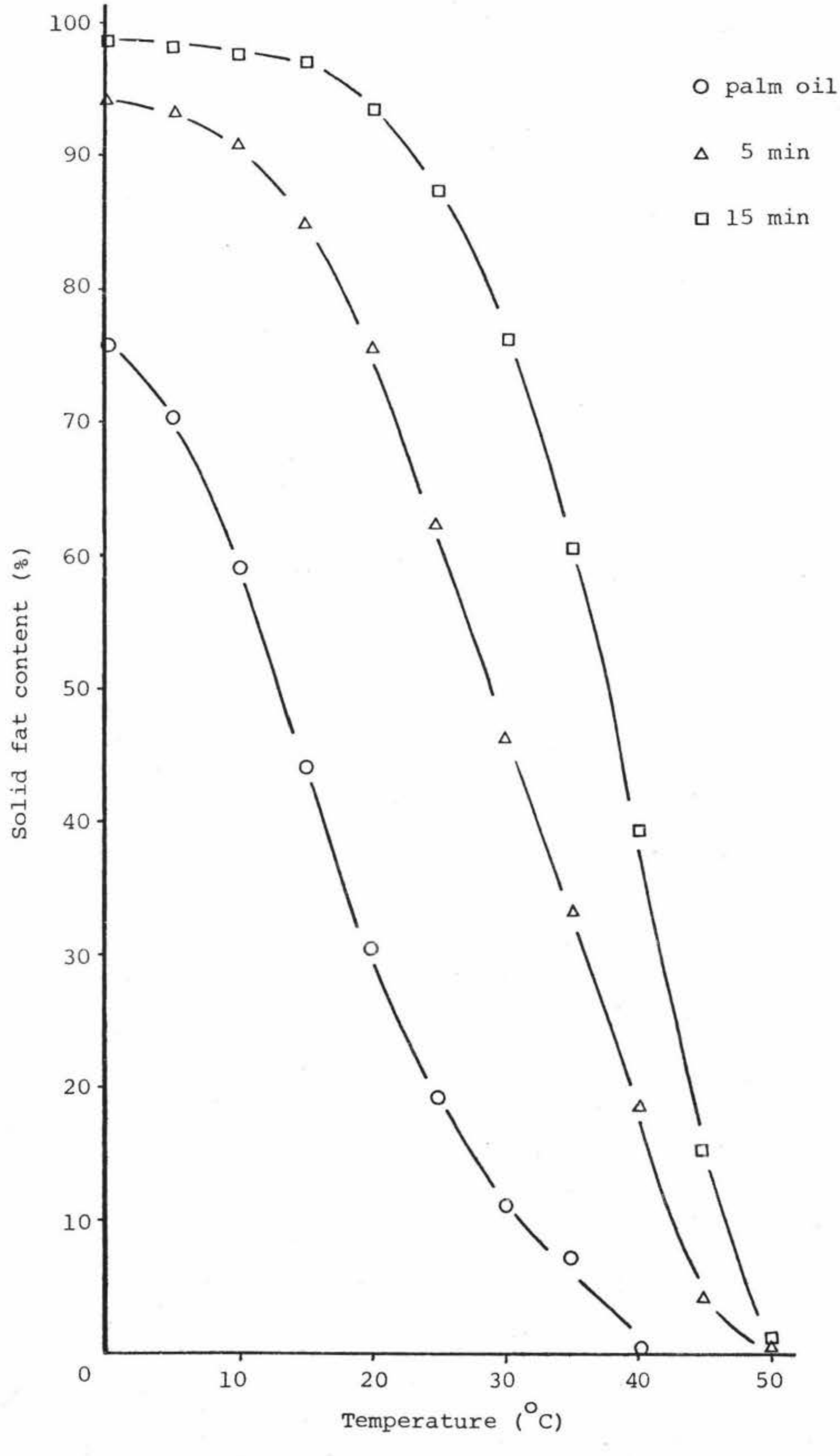

FIGURE 28: Curves of solid fat content hydrogenated to different times

catalyst also forms greater proportions of trans-isomer content. Examination of the two hydrogenation reactions shows that the active catalyst produces a maximum trans-isomer content of 35.0% at 10 min while the very selective catalyst produces a maximum of 53.3% at 20 min. The degree of unsaturation at these two reaction times is essentially the same (IV $\approx$ 66.5) and the greater trans-isomer content in the case of the more selective catalyst is probably the reason for the greater proportion of solid fat in these samples.

3.4 FORMULATION OF FAT BLENDS

3.4.1 Component Fats and Oils of the Blends

A series of blends containing different proportions of milkfat, an oil with a final melting point below 5°C, and a fat with a large proportion of high melting TGs were prepared with the intention of producing a product which will have similar melting properties to the Japanese pastry margarine. The milkfat used was the same as that analysed earlier (Section 3.2). The proportion of milkfat in the blend was set at 60-70%, as the aim of this research is to produce a product containing a large proportion of milkfat (Section 1.4). The oil used was sunflower seed oil which contains 6.4% 16:0, 68.7% 18:2, 19.9% 18:1, 4.5% 18:0 and only a trace of 18:3. A number of high melting fats were used in the blending experiments. These were chosen from the hydrogenation studies (Section 3.3). From the hydrogenation of cottonseed oil using the very selective catalyst, samples hydrogenated to 20 min (IV 66.7), 45 min (IV 58.2), 70 min (IV 55.1) and 120 min (IV 49.1) were used. Similarly, for the hydrogenated palm oil using the very selective catalyst, samples hydrogenated to 5 min (IV 48.3), 15 min (IV 43.8) and 70 min (IV 40.0) were selected.

The initial blending experiments involved the preparation of numerous blends containing various combinations of sunflower seed oil, milkfat and these high melting fats. Their SFC and softening points were determined.

3.4.2 Blends Containing Hydrogenated Cottonseed Oil

The results for the blend containing hydrogenated cottonseed oil are compared with those of Japanese pastry margarine. An example of this comparison is shown for a selected number of blends in Table 9. Blends 1 and 2 are considered unsuitable because they contain higher proportions of solid fat than the Japanese pastry margarine in the region of 15-40°C, *e.g.* at 35°C, blends 1 and 2 contain 17% and 14.6% solid fat, respectively, while Japanese pastry margarine only contains 4.7%. The softening points of blends 1 and 2 are noticeably higher than that of the Japanese pastry margarine. On the other hand, blend 4 contains a lesser proportion of solid fat between 15-30°C, which is also considered to be unsuitable. Blend 3 closely resembles the Japanese pastry margarine.

From the overall comparison of the results, cottonseed oil which was hydrogenated to 45 min was examined in greater detail. The SFC and softening point of four of these second series of blends together with that of the Japanese pastry margarine are shown in Table 10. These blends closely resemble that of the Japanese pastry margarine, especially between 15-20°C, the temperature at which danish pastries are normally rolled out.

3.4.3 Blends Containing Hydrogenated Palm Oil

Similarly, the results for the blends containing hydrogenated palm oil were compared with those of Japanese pastry margarine. A selection of these blends is shown in Table 11. Blend 9 is considered unsuitable because it contains a greater proportion of solid fat from 15-35°C and a higher softening point than that of the Japanese pastry margarine. On the other hand, blend 11 contains a lower proportion of solid fat in the region of 15-30°C and is also considered unsuitable. Blend 10 closely resembles the Japanese pastry margarine.

From the overall comparison of the results, palm oil which

TABLE 9: Solid fat contents and softening points of blends containing hydrogenated cottonseed oil and Japanese pastry margarine

Blend	**Composition H/M/S	*Hydrogenation time (min)	[a]Solid fat content (%)										Softening point (°C)
			0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	
1	29.9/58.8/11.3	120	74.5	72.3	67.4	55.9	42.0	33.7	24.4	17.0	7.2	0	40.7
2	30.4/59.7/ 9.9	70	75.3	72.8	67.7	56.7	41.8	32.0	24.4	14.6	9.5	0	39.0
3	30.0/60.1/ 9.9	45	74.3	71.9	65.6	53.4	36.8	26.8	19.3	9.3	0	0	37.9
4	30.1/60.1/ 9.8	20	72.2	69.4	63.1	48.0	30.2	19.5	12.6	5.8	0	0	35.5
[b]JPM			74.7	72.0	63.4	53.8	37.7	26.3	15.8	4.7	0	0	36.0

** hydrogenated cottonseed oil / milkfat / sunflower seed oil

* cottonseed oil hydrogenated to different times

[a] tempered by method S1

[b] Japanese pastry margarine

TABLE 10: Solid fat contents and softening points of blends containing hydrogenated cottonseed oil (45 min) and Japanese pastry margarine

Blend	**Composition H/M/S	[a]Solid fat content (%)										Softening point (°C)
		0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	
5	27.6/60.2/12.2	71.5	69.2	63.3	50.5	35.9	26.1	17.2	9.0	0	0	36.9
6	29.7/54.8/15.5	70.4	67.7	62.9	50.0	36.8	27.7	18.7	9.9	0	0	37.1
7	29.9/57.4/12.8	72.3	69.9	64.3	52.4	37.9	28.7	19.4	10.9	0	0	37.1
8	32.6/52.3/15.1	71.6	68.8	63.6	51.0	38.2	29.2	19.0	10.1	0	0	37.6
[b]JPM		74.7	72.0	63.4	53.8	37.7	26.3	15.8	4.7	0	0	36.0

** hydrogenated cottonseed oil / milkfat / sunflower seed oil

[a] tempered by method S1

[b] Japanese pastry margarine

TABLE 11: Solid fat contents and softening points of blends containing hydrogenated palm oil and Japanese pastry margarine

Blend	**Composition H/M/S	*Hydrogenation time (min)	[a]Solid fat content (%)										Softening point (°C)
			0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	
9	24.6/70.5/ 4.9	70	77.8	75.6	70.9	59.7	43.1	32.9	24.1	16.2	0	0	39.4
10	20.0/70.0/10.0	15	71.6	69.4	62.6	50.7	34.1	25.3	17.0	8.6	0	0	36.8
11	22.5/70.0/ 7.5	5	72.0	69.2	63.6	49.5	30.4	21.3	13.9	7.6	0	0	36.5
[b]JPM			74.7	72.0	63.4	53.8	37.7	26.3	15.8	4.7	0	0	36.0

** hydrogenated palm oil / milkfat / sunflower seed oil

* palm oil hydrogenated to different times

[a] tempered by method S1

[b] Japanese pastry margarine

was hydrogenated to 15 min was examined in greater detail. The SFC and softening point of four of these second series of blends which closely resemble the Japanese pastry margarine especially between 15-20°C are shown in Table 12.

From the second series of blending experiments, a blend containing cottonseed oil (blend 5) and a blend containing palm oil (blend 12) were selected for more detailed analysis because of the similarity of their melting curves and softening points to those of the Japanese pastry margarine.

The FA analysis shows that there is a marked overall difference between the FA composition of the blends and the Japanese pastry margarine (Table 13). Both blends contain greater proportions of low molecular weight FAs and 16:0 but a smaller proportion of 18:1 and total 18 carbon FAs (C_{18}) than the Japanese pastry margarine. This trend is a consequence of the larger proportion of milkfat present in the blends. The quantity of 18:1 in blends 5, 12 and Japanese pastry margarine are 32.4%, 27.1% and 48.5%, respectively.

As expected from the FA analysis, both blends contain a greater proportion of C_{36}, C_{38} and C_{40} TGs but a smaller proportion of C_{54} than the Japanese pastry margarine., e.g. the proportion of C_{54} TGs are 24.5% and 13.8% for blends 5 and 12, respectively, but 44.6% for that of the Japanese pastry margarine (Table 14). Additional SFC analysis shows that tempering of the fat at 20°C (S2) causes a decrease in the proportion of solid fat at all temperatures below 20°C, e.g. at 15°C, the amount of solid fat in blend 5 decreases by 8.8% on tempering (Table 15). This is a consequence of solid miscibility with diffusional delays.

Thermal analysis by DSC was performed on the blends 5 and 12 using the two tempering methods D1 and D2.

Figures 29 and 30 show a similarity in the shapes of the melting thermograms of the two blends for corresponding tempering methods. In the case of method D1, both blends have two main sets of melting peaks which are separated by a dip about 20°C,

TABLE 12: Solid fat contents and softening points of blends containing hydrogenated palm oil (15 min) and Japanese pastry margarine

Blend	**Composition H/M/S	[a]Solid fat content (%)										Softening point (°C)
		0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	
12	20/70/10	73.8	71.3	65.3	54.1	36.9	28.4	19.1	12.2	0	0	36.8
13	25/60/15	71.7	68.9	63.1	50.7	37.5	27.7	19.0	11.5	0	0	37.7
14	22.5/70/ 7.5	75.3	72.9	67.1	55.0	37.4	28.5	19.7	11.0	0	0	37.2
15	22.5/65/12.5	71.5	69.2	63.5	51.3	35.7	27.5	18.0	10.5	0	0	37.3
[b]JPM		74.7	72.0	63.4	53.8	37.7	26.3	15.8	4.7	0	0	36.0

** hydrogenated palm oil / milkfat / sunflower seed oil

[a] tempered by method S1

[b] Japanese pastry margarine

TABLE 13: Fatty acid compositions of blends 5 and 12, and Japanese pastry margarine

Fatty acid	Composition (weight %)		
	Blend 5	Blend 12	Japanese pastry margarine
4:0	2.0	2.2	1.2
6:0	1.3	1.5	0.7
8:0	0.7	0.8	0.5
10:0	1.5	1.8	0.9
11:0	0.2	0.2	0.1
12:0	1.8	2.3	1.2
14:0	6.7	7.7	3.5
15:0	1.3	1.5	0.5
15:1	0.9	1.0	0.4
16:0	24.7	30.8	17.3
16:1	2.0	2.2	1.5
16:2	0.5	0.5	0.3
17:0	0.4	0.5	0.2
18:0	10.3	9.4	11.1
18:1	32.4	27.1	48.5
18:2	11.8	9.1	11.0
18:3	1.6	1.40	0.42
20:0			2.0

TABLE 14: Triacylglycerol compositions of blends 5 and 12, and Japanese pastry margarine

Triacylglycerol	Composition (weight %)		
	Blend 5	Blend 12	Japanese pastry margarine
30	0.5	0.6	0.3
32	1.2	1.4	0.7
34	3.1	3.6	1.5
35	0.5	0.6	-
36	6.6	7.8	3.5
37	0.9	0.9	-
38	8.4	9.5	5.6
40	5.7	6.7	2.9
42	4.0	4.6	2.0
44	3.6	4.2	1.8
46	4.0	4.9	2.2
48	6.3	8.4	3.3
50	10.5	15.9	6.6
52	19.8	17.0	22.6
54	24.5	13.8	44.6
56	0.3	0.2	2.0
58	0.2	0.1	0.5

TABLE 15: Solid fat contents of blends 5 and 12, and Japanese pastry margarine

Temperature (^oC)	Solid fat content (%)					
	Blend 5		Blend 12		Japanese pastry margarine	
	*S1	**S2	*S1	**S2	*S1	**S2
0	71.5	63.2	73.8	64.3	74.7	61.3
5	69.2	58.1	71.3	60.4	72.0	55.7
10	63.3	51.8	65.3	53.9	63.4	48.8
15	50.5	41.7	54.1	42.5	53.8	40.6
20	35.9	35.6	36.9	35.0	37.7	37.6
25	26.1	26.2	28.4	26.1	26.3	27.4
30	17.2	16.0	19.1	16.2	15.8	14.9
35	9.0	7.8	12.2	8.9	4.7	6.7
40	0	0	0	0	0	0

* tempered by method S1

** tempered by method S2

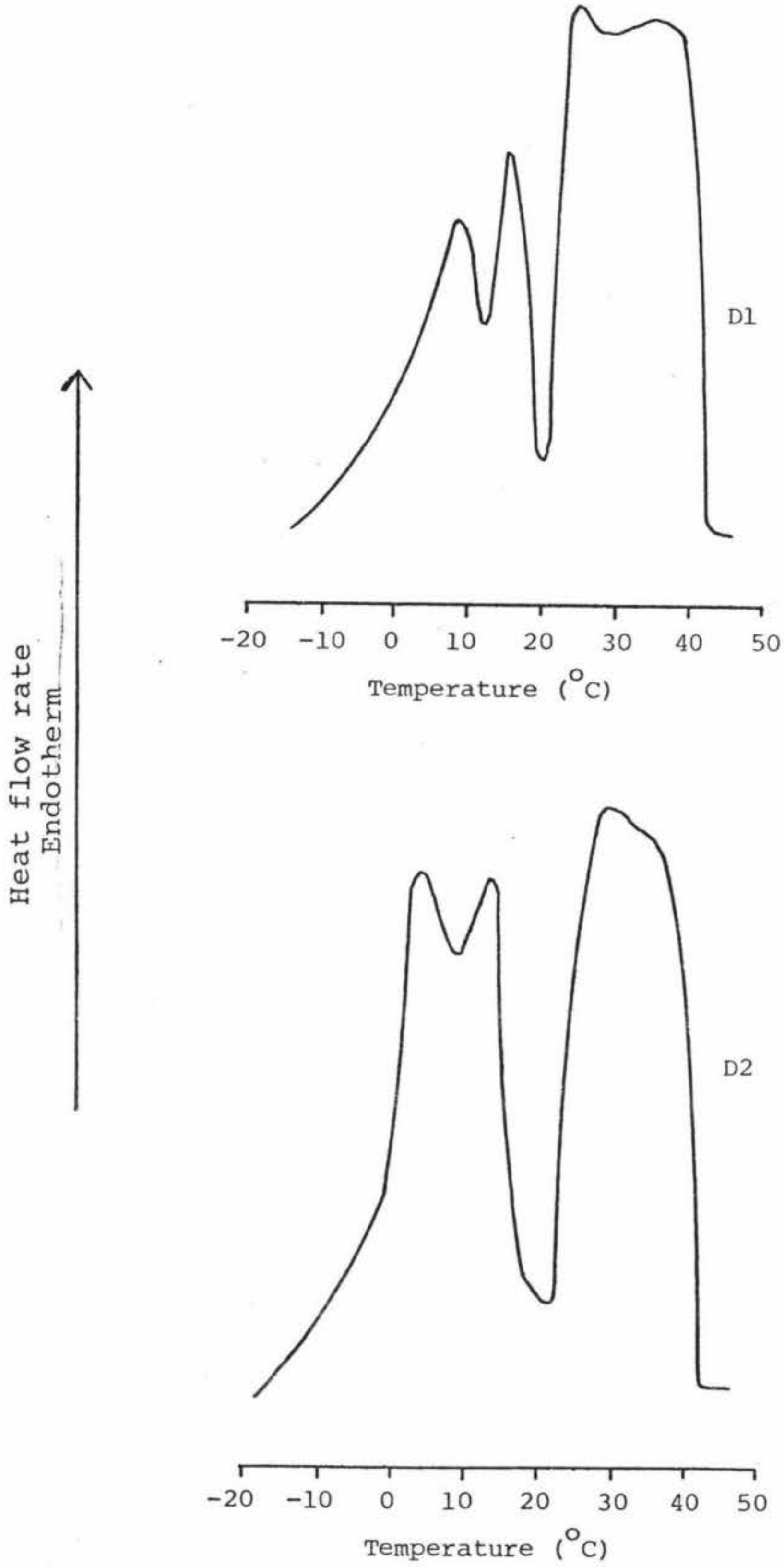

FIGURE 29: The melting thermograms for blend 5 obtained after tempering by methods D1 and D2 (weight of sample 6.920 mg, scan speed 10°C/min, range 2).

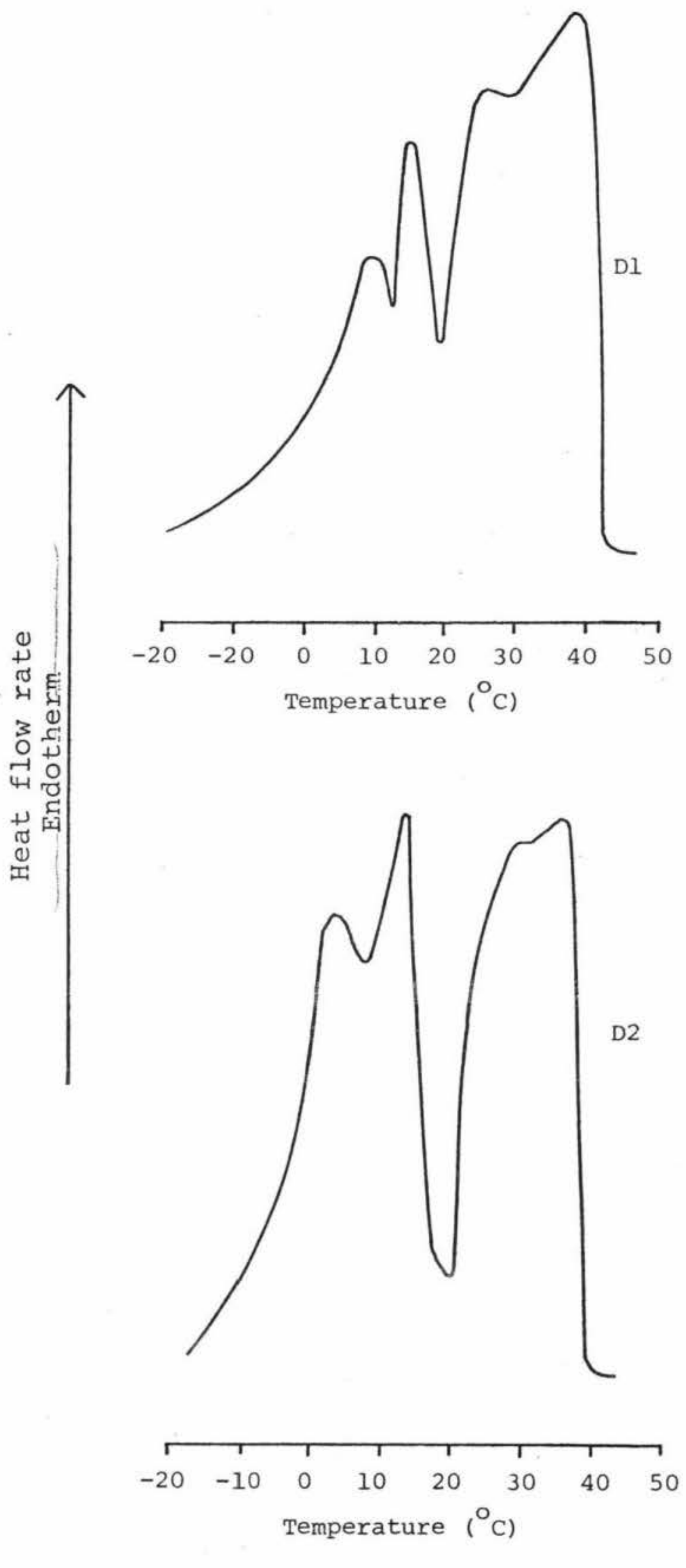

FIGURE 30: The melting thermograms of blend 12 obtained after tempering by methods D1 and D2 (weight of sample 6.570 mg, scan speed 10°C/min, range 2).

one with maxima about 5°C and 13°C and the other about 20°C and 36°C. However, on tempering the fat at 20°C (method D2) the pattern changes and the area under the lower melting peak is increased.

Comparison of the melting thermograms of these blends with that of Japanese pastry margarine (Figure 17) show a marked difference in their shapes when tempered by method D1. However, the shapes of the melting thermograms are more similar when tempered by method D2.

3.5 PRODUCTION OF MARGARINE AND BUTTER

The data presented in the previous section show that both blends 5 and 12 closely resemble the melting characteristics of Japanese pastry margarine. Of these two, blend 12 is preferred for making the pastry margarine because it contains a greater proportion of milkfat (70%) whereas blend 5 contains 10% less.

3.5.1 Preparation of the Blend

Three batches, each of approximately 5 kg of palm oil were hydrogenated to 15 min using the very selective catalyst (method C) to obtain a high melting fat similar to the hydrogenated palm oil used in blend 12. This high melting fat has an IV of 43.8 and a softening point of 47.0°C. The samples were bulked to obtain approximately 11 kg of hydrogenated oil. A blend 16 was prepared, consisting of 19.6% of this high melting fat, 68.5% of milkfat and 11.9% of sunflower seed oil. The milkfat used has similar chemical composition and melting characteristics to that used in the blending experiments.

The FA and TG compositions and SFC for this blend are given in Table 16 ~~which~~ while the melting thermograms obtained by DSC are presented in Figure 31.

Comparison of this data with the results obtained for blend 12 (Tables 13, 14 and 15) shows that there is marked similar-

TABLE 16: Analysis of blend 16

	Fatty acid composition (weight %)																	
Fatty acid	4:0	6:0	8:0	10:0	11:0	12:0	14:0	15:0	15:1	16:0	16:1	16:2	17:0	18:0	18:1	18:2	18:3	20:0
	2.5	1.7	1.0	2.1	0.2	2.7	8.1	1.6	1.1	30.6	2.1	0.4	0.4	9.7	25.1	9.3		1.9

	Triacylglycerol composition (weight %)															
Triacylglycerol	30	32	34	35	36	37	38	40	42	44	46	48	50	52	54	56
	0.7	1.5	3.8	0.5	7.7	0.9	9.4	6.9	5.1	4.9	5.6	7.9	14.7	15.9	14.2	0.1

	Solid fat content (%)								
Temperature (°C)	0	5	10	15	20	25	30	35	40
*S1	73.0	69.9	64.2	51.4	33.3	26.4	16.6	10.1	0
**S2	63.2	58.7	51.0	40.9	34.3	26.0	18.0	10.2	0

* tempered by method S1
** tempered by method S2

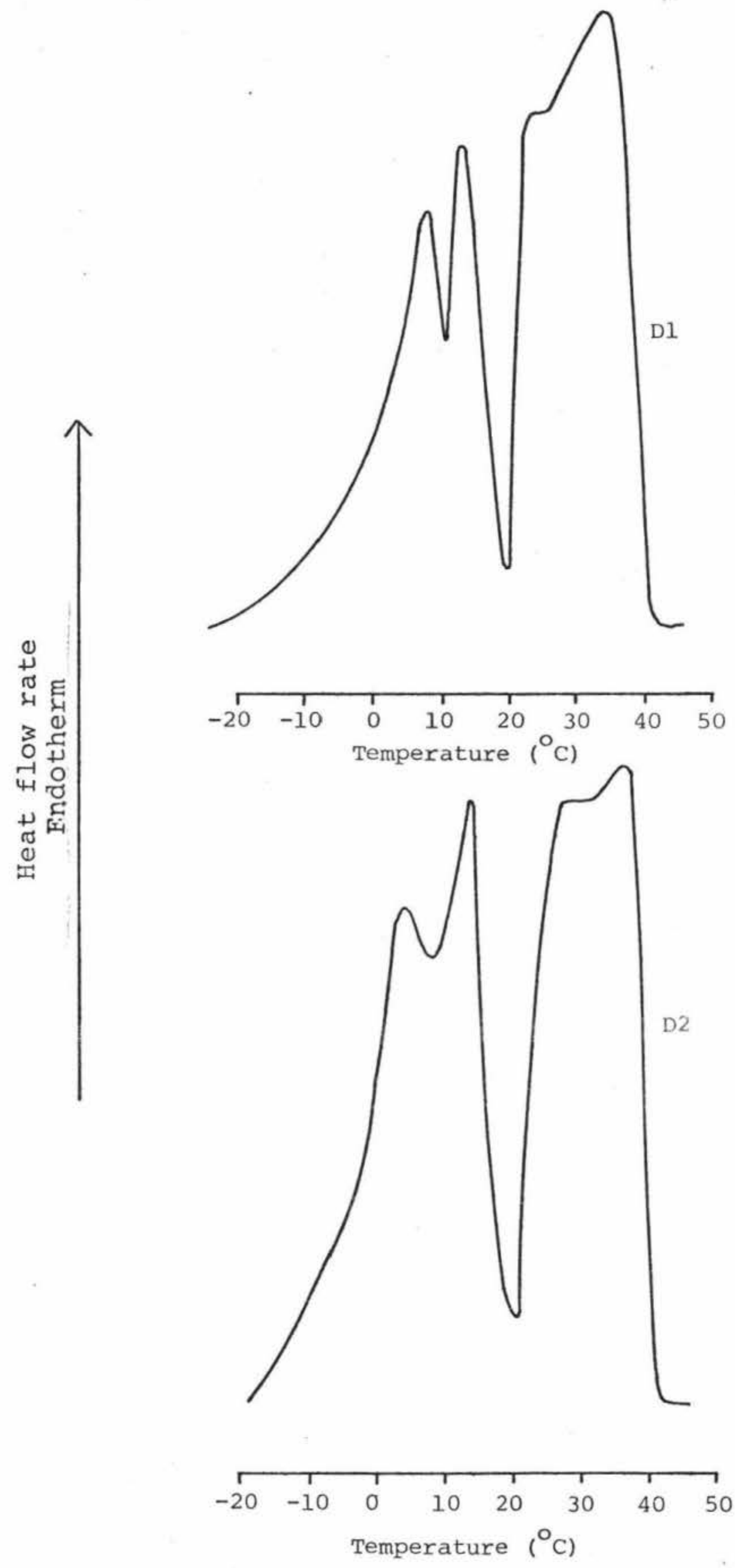

FIGURE 31: The melting thermograms of blend 16 obtained after tempering by methods D1 and D2 (weight of sample 8.405 mg, scan speed 10°C/min, range 2.)

ity in the chemical composition and melting properties of these two blends. This suggests that the blending technique used is able to reproduce blends accurately.

3.5.2 Manufacture of Margarine

The fat blend 16 prepared above was made into pastry margarine using four different techniques. Methods I and II involve churning in a z-blade reworker with the cream being shock-cooled for method I and cooled by a modified Alnarp process for method II. Method III involves the use of a scraped surface heat exchanger (SSHE) while method IV uses a SSHE in combination with a pinworker. For each method, duplicate products were made. Methods I, II and IV produce a smooth textured product while the margarine made by method III contains small lumps.

The pastry margarines were analysed for moisture, salt and curd and the results are given in Table 17. It can be seen that there is some variation in the moisture and curd contents of the products.

Hardness measurements were carried out on the products at $15^{o}C$ after tempering at $2^{o}C$ for 7 days (method H1). The margarines made by methods II and IV give markedly lower hardness values than the others (Table 17). Additional hardness measurements were carried out on the products after a period of tempering at $23^{o}C$ (method H2). This tempering technique dramatically reduces the difference in hardness between the various methods (Table 17). These trends hold despite a certain variability in the hardness values.

3.5.3 Manufacture of Butter

Milkfat obtained from cream produced during summer which was analysed (Section 3.2) was made into butter by the above methods. Methods I and II produce a smooth textured product while the butter made by methods III and IV contain lumps.

The products were analysed for moisture, salt and curd con-

TABLE 17: Composition and hardness values of pastry margarine made from blend 16

Method	Description	Hardness values (g)		Moisture (%)	Curd (%)	Salt (%)
		*H1	**H2			
I	Rapidly cooled cream	650	525	16.4	2.6	0.8
		738	713	15.9	2.5	0.9
II	Alnarp cooled cream	525	575	16.8	2.2	0.8
		525	875	16.0	2.3	0.9
III	SSHE	875	763	17.9	1.2	0.9
		988	738	17.3	1.2	0.9
IV	SSHE and pinworker	425	750	17.2	1.0	1.0
		438	775	18.1	1.2	0.9

* tempered by method H1

** tempered by method H2

tents (Table 18). Hardness measurements were carried out on the products using the tempering method H1 (method 18). The hardness values show the same trend as described for the margarines, namely that methods II and IV give lower hardness values.

3.5.4 Comparison of Margarine and Butter

Comparison of hardness values shows that for corresponding methods, margarine is softer than butter. In the case of method IV, (SSHE/pinworker) the hardness values (tempered by method H1) for pastry margarine and butter were 435g and 738g, respectively. This result is surprising as butter is expected to be softer because of its lower SFC at 15°C. This suggests that the different crystallization behaviour of the fats during manufacturing play an important part in the textural qualities of the pastry margarine and butter.

Of all the margarine samples, those made by the modified Alnarp method (method II) and the SSHE with pinworker (method IV) give hardness values which are closer to that of the Japanese pastry margarine. Hence, these were the margarines selected for the danish pastry test baking trials.

3.6 BAKING OF DANISH PASTRIES

Danish pastries were made with duplicate batches of Japanese pastry margarine (R), butter (N), margarine manufactured by method II (A) and margarine manufactured by method IV (B).

The two batches of Japanese pastry margarine were both purchased from Kanegafuchi Chemical Industry Co. Ltd. The first batch is the same as that analysed in section 3.1. Both margarines have similar SFC and hardness values (219g and 325g). The two batches of butter were made commercially in a continuous buttermaker from summer cream. These butters have hardness values of 675g and 900g which are similar to the value obtained for butter produced by method I. The milkfat samples from each of these butters have SFC which are similar to that of the milkfat analysed earlier (section 3.2). As

TABLE 18: Composition and hardness values of butter made from milkfat

Method	Description	Hardness values *H1	Moisture (%)	Curd (%)	Salt (%)
I	Rapidly cooled cream	863	16.4	2.0	0.8
		850	16.3	2.0	0.8
II	Alnarp cooled cream	700	16.1	2.1	0.8
		738	16.2	2.3	0.8
III	SSHE	925	16.0	1.4	0.9
		1063	14.6	1.3	0.7
IV	SSHE and pinworker	738	18.2	1.4	0.8
		675	18.9	1.3	0.9

* tempered by method H1

noted previously (section 3.5.4) the margarine manufactured by methods II and IV have hardness values which are closer to the Japanese pastry margarine than the other two experimental margarines. Consequently, they were selected for the baking trials.

Various combinations of these four different fat products were made into danish pastries on three separate days and physical and sensory evaluations were carried out on them. Table 19 summarizes the results of the physical evaluation of danish pastries for different pastry fats. Figures 32-39 show the photographs of four different fat products which were baked on the first of the three baking days. The pastries shown are typical of the results.

3.6.1 Physical Evaluation

Evaluation of the suitability of the fat product for rolling into the pastry dough during the preparation was carried out. Subsequently, the baked pastries were analysed for general appearance, size, distinct external layering and porosity. With the exception of pastry size, all physical evaluations were qualitative.

(a) Suitability of rolling

The Japanese pastry margarine rolls very easily when compared with the batter and margarines (A and B). Butter is difficult to roll initially as it is hard and causes the dough to tear. However, on further rolling, it rolls more easily and even becomes slightly greasy. The two margarines (A and B) roll well initially but become greasy with increased rolling.

(b) General appearance

All fat products produce pastries of satisfactory appearance on all three days. However, the pastries made from Japanese pastry margarine and the butter are slightly better in general appearance than those made from the margarines A and B. They generally give a larger rise in volume and better shape.

TABLE 19: Physical evaluation of danish pastries

Type of pastry fat	Suitability for rolling	General appearance	*Size of pastry	Porosity
R	good	good	2.36	good
N	lumpy initially greasy later	good	2.22	good
A	good initially greasy later	fair	1.89	fair
B	good initially greasy later	fair	1.88	good

R is Japanese pastry margarine

N is butter

A is margarine made from blend 16 manufactured by method II

B is margarine made from blend 16 manufactured by method IV

* mean of $\frac{\text{area of pastry after baking}}{\text{area of pastry before baking}}$

FIGURE 32: Photograph of danish pastries made from Japanese pastry margarine

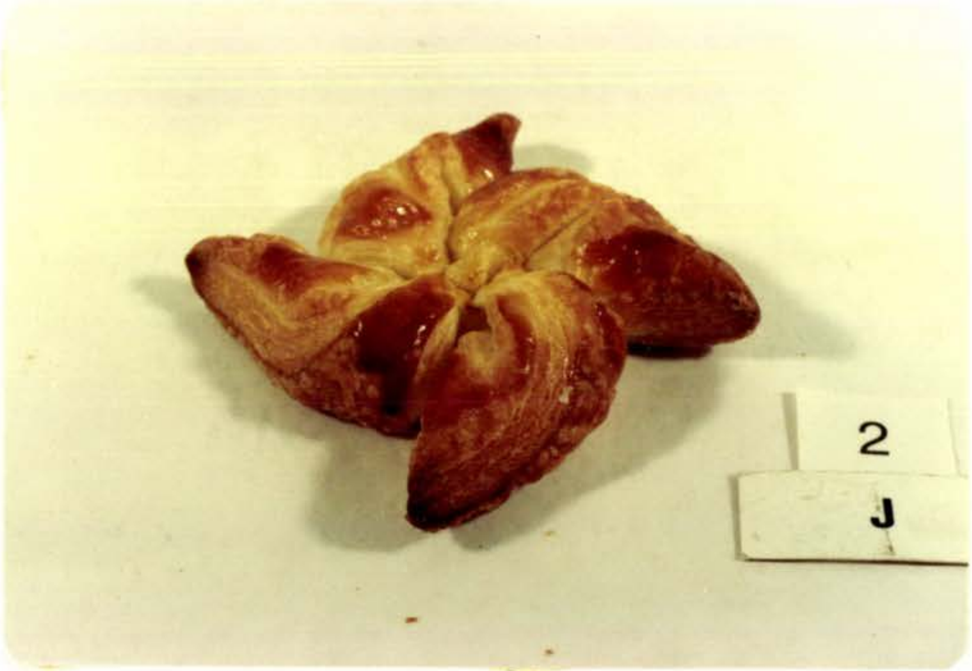

FIGURE 33: Photograph of 'windmill' danish pastry made from Japanese pastry margarine

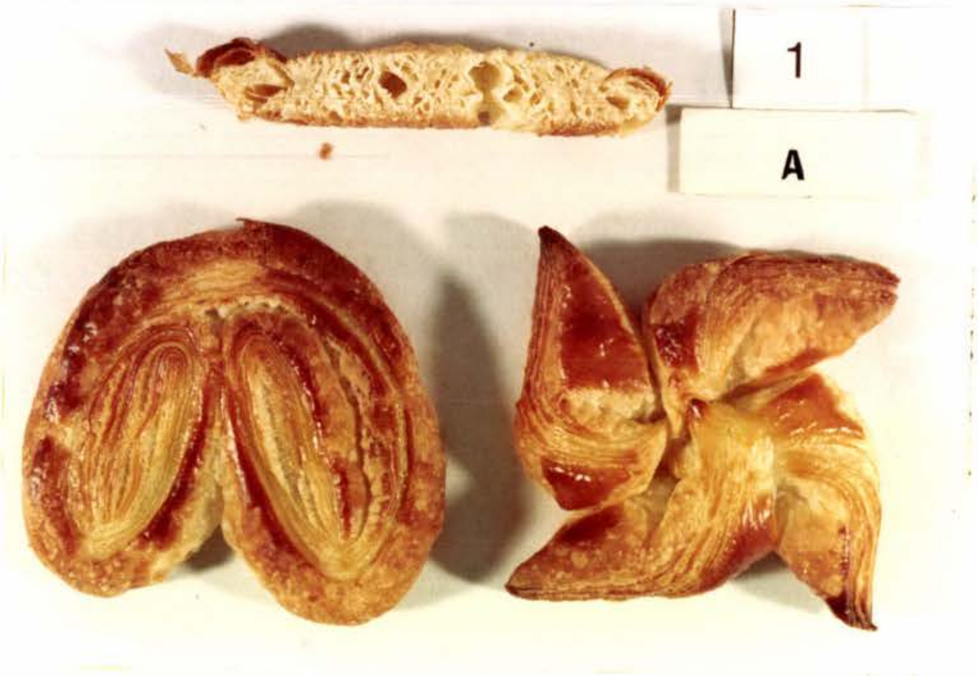

FIGURE 34: Photograph of danish pastries made from butter

FIGURE 35: Photograph of a 'windmill' danish pastry made from butter

FIGURE 36: Photograph of danish pastries made from pastry margarine A

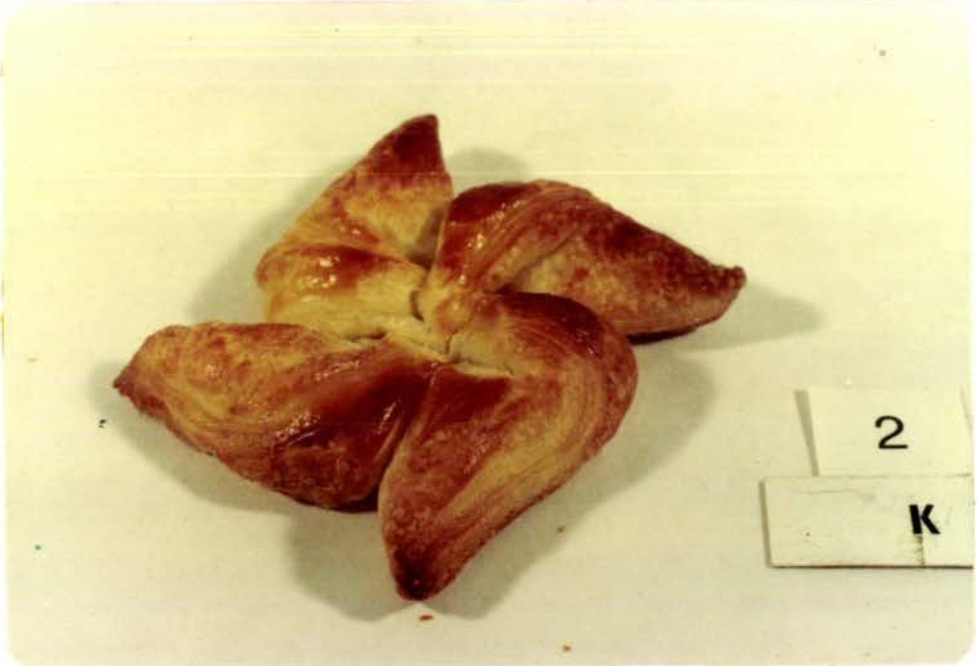

FIGURE 37: Photograph of a 'windmill' danish pastry made from pastry margarine A

FIGURE 38: Photograph of danish pastries made from pastry margarine B

FIGURE 39: Photograph of a 'windmill' danish pastry made from pastry margarine B

This is more clearly illustrated with the 'windmill' patterns (Figures 33, 35, 37 and 39).

(c) Size

The results on the expansion of the pastry after baking show that the pastries which are made from the Japanese pastry margarine and butter give a larger increase in spread than the other two margarines. On analysing the data using a two-way analysis of variance, the size differences are found to be significant at the 10% level (F (3,3) = 9.27).

(d) Porosity

On observing the cross-section of all the pastries (Figures 32, 34, 36 and 39) it is noted that all of the pastries have interiors of similar porosity except for the pastries made from margarine A.

3.6.2 Sensory Evaluation

Semi-trained panelists were asked to score the samples of danish pastries made from butter and the two margarines A and B against pastries made from Japanese pastry margarine. The samples were evaluated for colour, external layering, flakiness, doughiness and fattiness. A sample of the questionnaire used and the raw data of this sensory evaluation are given in Appendices 5 and 6-8.

A non-parametric test, Wilcoxon's signed rank test, was performed using the statistical computer package Minitab. It is noted that analysis of variance is not done on the sensory evaluation data as the usual assumptions required for such a parametric statistical test (e.g. continuity, normality and interval scale) are not followed (Amerine et al., 1965).

The results of the sensory evaluation which are summarized in Table 20 show that there are significant differences in certain characteristics between the pastries made from Japanese pastry margarine and the pastries made from the other fat products.

(a) Colour - Pastries made with butter are significantly darker in colour than the reference which is made from Japanese pastry margarine (R), while pastries made from margarine B are lighter in colour.

(b) Layering - Pastry samples made from butter give more distinct layering than the reference (Japanese pastry margarine), while pastries made from the margarines A and B give less distinct layers. The examination of the photographs in Figures 32-39 support this result.

(c) Flakiness - With the exception of pastries made from margarine A, there is no significant difference between the flakiness of the pastries.

(d) Fattiness - The pastries made from butter give a more fatty taste than the reference whereas the others are not significantly different from the reference.

(e) Doughiness - The results show that only the pastries made from margarine A are significantly more doughy than the reference.

Although the statistical results show that there are significant differences between the pastry samples and the reference for some characteristics, the mean difference in sensory scores are quite small (Table 20). They are less than ±1, with the exception of one result. A possible reason for this anomaly is that the Wilcoxon's signed rank test is designed to look for differences between scores and it ignores all the zero scores (i.e. when sample pastry was identified as identical to the reference). As there are many of these zero scores for each sample, the test may have been biased. Moreover, an examination of the raw data shows that there is considerable variation in the way in which panelists scored samples, e.g. scores on doughiness for a sample baked on one day range from -2 to +2. This indicates that there is some doubt regarding the preciseness of the base data.

TABLE 20: Sensory evaluation of danish pastries

Variable	Number of non-zero differences	z standard normal deviate	significant level $p < 0.05$	Mean sensory score
COLOUR:				
N vs R	20	2.31	*✓	0.6
A vs R	20	0.06		0.0
B vs R	13	-2.14	✓	-0.3
LAYERING:				
N vs R	22	2.18	✓	0.5
A vs R	20	-3.84	✓	-0.8
B vs R	22	-2.70	✓	-0.5
FLAKINESS:				
N vs R	23	1.68		0.5
A vs R	24	-4.24	✓	-1.2
B vs R	21	0.04		0.0
FATTINESS:				
N vs R	22	2.81	✓	0.7
A vs R	21	-1.75		-0.3
B vs R	14	-1.03		-0.2
DOUGHINESS:				
N vs R	22	-0.51		-0.1
A vs R	23	2.82	✓	0.6
B vs R	30	1.81		0.3

* significantly different

R is Japanese pastry margarine

N is butter

A is margarine made from blend 16 manufactured by method II

B is margarine made from blend 16 manufactured by method IV

CHAPTER 4

DISCUSSION

4.1 FACTORS AFFECTING MELTING BEHAVIOUR AND RHEOLOGICAL PROPERTIES OF MARGARINE AND BUTTER

There are a number of interrelated factors which influence the melting and rheological properties of margarine and butter. They are triacylglycerol (TG) composition, solid miscibility, polymorphism, manufacturing conditions and the presence of emulsifiers.

4.1.1 Triacylglycerol Composition

The type and proportion of TGs present in fat are directly related to its rheological and melting properties (Haighton, 1976). As the molecular weight and degree of saturation of fatty acids (FAs) increase, the melting points of the TGs increase. This causes the solid fat content (SFC) to increase and results in a fat which is harder (Swern, 1964c). The measurement of SFC can be used for controlling the type of product required because of the relationship between SFC and rheological properties of the fat (Norris *et al*., 1977; Bailey, 1950a).

It has been stated by Wiedermann (1978) that trisaturated TGs can only provide structure, monounsaturated TGs can provide structure and lubricity while poly-unsaturated TGs can only provide lubricity. Hence, a larger proportion of monounsaturated TGs has to be present in products where a firm and plastic consistency is required.

4.1.2 Polymorphism

Polymorphism is the ability of a substance to crystallize in more than one form, of which only one is completely stable at a given set of conditions (Mulder & Walstra, 1974a; Bailey, 1950a). In long chain hydrocarbon compounds like TGs, the FA chains can pack in a number of different lateral arrangements which are energetically almost equivalent (*i.e*. have similar Van der Waal interaction energies) (Norris, 1977). Due to the different crystal lattice, such polymorphic forms have different melting points which increase with stability. In the case of TGs, three main polymorphic forms exist, the α, β and β'. Rapid cooling of the melt gives the α form in which the hydrocarbon chains undergo torsional oscillation. The α form has the simplest lattice structure and the lowest melting point of the three TG polymorphs and it transforms irreversibly on heating to either β' or β (Norris, 1977; Mulder & Walstra, 1974a).

Although fats are complex mixtures of TGs they often show the same lattice arrangements as the polymorphic forms of simple TGs. It has been found that for fats in which the FA chain lengths vary considerably, the α → β' transition is more facile than the transitions α → β and β' → β so that the β' form is more stable in such mixtures. Hence fats with varying lengths of carbon chains. e.g. hydrogenated cottonseed oil are β' stable while fats in which the chain lengths show little variation, e.g. hydrogenated soyabean oil are β stable (Merker et al., 1958). Fats which stabilize in the β' form tend to produce products of 'sandy' nature. Hence it is important to select fats which are stable in the β' form whenever a margarine with a smooth and plastic consistency is required.

4.1.3 Solid Miscibility

The melting behaviour of fats is dependent not only on their polymorphic behaviour but also their tendency to solid miscibility (Bailey 1950b; Norris, 1977). This is the formation of mixed crystals due to the mixture of TGs present in fats. However, mixed crystals do not occur if the TGs are grossly different in molecular structure.

The degree of solid miscibility is dependent not only on the type of TGs present but also on the rate of cooling. Rapid cooling of fats gives a greater degree of mixed crystal formation which reduces the melting range of the fat and increases its SFC at a given temperature (Boekenoogen, 1964; Norris, 1977; Mulder & Walstra, 1974b). Consequently, solid miscibility is related to the crystal structure and SFC which in turn plays a part in influencing the consistency of the product.

4.1.4 Manufacturing Conditions

The melting and rheological properties of margarine and butter are controlled by not only TG composition but also processing conditions during production, i.e. chilling, tempering and reworking (Haighton, 1976). These conditions affect the degree, type and rate of crystallization, postcrystallization, setting and work softening which are related to the rheological properties of the product.

(a) Crystallization

When a fat is crystallized, the crystal habit (external shape of crystals) can vary in the form of needles or platelets. The type of crystal habit is related to polymorphic behaviour, solid miscibility and SFC of the fat. The fat crystals can grow together to form a strong network which can contain liquid oil better and produce a harder margarine. Alternatively, they may agglomerate, forming tiny crystal clusters with considerably fewer contact points which allow oil to exude out, producing a soft, sloppy and oily margarine. Haighton (1976) believed that a good margarine should take a position between these two types.

Certain fats crystallize slowly and may take a few hours to go to completion. However, the rate of crystallization can be increased with agitation during chilling (Haighton, 1976).

(b) Postcrystallization

Postcrystallization (i.e. the continuation of crystallization after chilling) always occurs in the case of products made in the scraped surface heat exchanger (SSHE) but may not occur in products manufactured using the chilled drum process (Grinsted, 1981). In addition to this type of postcrystallization, there is the transition of polymorphic forms to the more stable arrangement. The heat which is liberated during postcrystallization causes remelting and recrystallization of fats which result in a change in the rheological properties of the product (Alexander, 1978; Haighton, 1976).

A series of tempering and kneading procedures can be carried out after the chilling process to reduce the effect of post-crystallization on the rheological properties of the product.

(c) Setting

The formation of a crystal network which occurs during crystallization continues during storage. This process is known as setting and is considered to be due to the flocculation of crystals into a network which results in an increase in firmness (De Man & Wood, 1958b, 1959). There are two types of bonds which are formed in such a network, weak secondary bonds which are reversible and strong primary bonds which are irreversible. The hardness caused by the crystal network can be reduced by subjecting the fat to large shearing forces which break down both secondary and primary bonds. Since only the secondary bonds can be reformed a softer product can be obtained (Haighton, 1965; Shama & Sherman, 1970). This process is known as kneading or working. The extent of the reduction of hardness caused by the process is sometimes referred to as worksoftening.

4.1.5 Emulsifiers

Emulsifiers reduce the interfacial tension between water and fat phases. As a consequence of this, they stabilize the liquid emulsion and produce a fine and stable dispersion (Andersen & Williams, 1965d). In addition, it is considered that they influence the crystallization of the fat and hence affect the rheological properties of the product (Van Boekel, 1980).

The above discussion suggests that if the manufacturing conditions are constant, there is a close correlation between

SFC and the rheological properties of the margarine produced. Conversely, it is evident that changes in the manufacturing techniques can markedly alter the rheological properties of margarines containing the same fat blend.

4.2 FORMULATION OF FAT BLENDS

As noted above, when manufacturing conditions are constant, SFC and rheological properties of a fat are strongly correlated. As a consequence of this relationship, SFC measured under standard cooling conditions was used as a control technique for the formulation of blends which were designed to imitate the Japanese pastry margarine.

The SFC curve of Japanese pastry margarine shows that it has the requirements for a danish pastry margarine as described in section 1.3, namely reasonably high SFC at rolling temperatures, a small proportion of solid fat at proofing temperatures (25-30°C) and a melting point at body temperature (36°C). In order to obtain such a blend with a large proportion of milkfat, a balance of low and high melting fats is required. The high melting fat increases the amount of solid fat throughout the range of temperatures while the low melting fat decreases the proportion of solid fat at low temperatures, hence producing a less steep melting curve. The addition of this oil also helps to improve product control and flexibility (Wiedermann, 1978).

In addition to the proper level of solids, care has to be taken to ensure that the product is composed of fats which give the proper crystal habit and polymorphic forms (Merker *et al*., 1958; Knightly, 1981). Fats which stabilize in β form tend to produce a product of 'sandy' nature, hence it is usual to select fats which stabilize in the β' form when a product of a firm and plastic consistency is required. In this study, hydrogenated cottonseed and palm oil were used because they are β' fats (Merker *et al*., 1958; Berger, 1975).

The blending experiments were done on a trial and error basis although computer programs have been used in the formulation of simple blends especially when relationships between the characteristics of the components and mixtures are known. However, in this study, such computer programs cannot be used because the crystal system of these blends are relatively complex (Lefebvre, 1983).

4.3 RHEOLOGICAL PROPERTIES OF MARGARINE AND BUTTER

4.3.1 Experimental Margarine made by Different Methods

The different manufacturing techniques used in this study produce margarines from the same fat blend with markedly different hardness values (Table 21).

The modified Alnarp method (i.e. cooling cream to 5°C, holding at 19°C for 2 hr, cooling to 10°C and holding overnight at 5°C) gives a softer product than that obtained by the other churning method (i.e. rapidly cooling cream). These results are consistent with that obtained by Dolby (1965) and Dixon (1970). The principal reason for this difference is that the rapidly cooled cream gives a greater degree of mixed crystal formation and hence a greater proportion of solid fat at a given temperature (section 4.1.3).

The margarine obtained from the manufacturing process using just the SSHE is harder than the product made by the SSHE/pinworker system. These results are consistent with those obtained by Madsen (Grinsted, 1981). The principal cause of the marked difference in hardness value is the breaking down of crystal networks by agitation in the pinworker (section 4.1.7).

On comparing the hardness values of margarines manufactured by the churning process with those made from the SSHE (without the pinworker) the latter products are much harder. This is presumably due to the extremely rapid cooling rate in the SSHE and a lack of agitation during postcrystallization (section 4.1.4).

4.3.2 Butter made by Different Methods

The different manufacturing techniques also produce butters with different hardness values. Furthermore, the trend in these values is the same as that obtained from the experimental margarines. For example, the modified Alnarp butter is softer than that made from rapidly cooled cream, while the butter made from the SSHE / pinworker system produces a softer product than that made from just the SSHE.

4.3.3 Comparison of Margarine with Butter made by Similar Methods

Table 21 shows that for corresponding manufacturing processes butter has higher hardness values than the experimental margarines. The difference in hardness values varies, for example, considering the products manufactured by just the SSHE, the difference is 65 units while for the products made from the SSHE / pinworker system, the difference is 280 units.

This trend in hardness values is somewhat surprising when results are examined (Table 22). The SFC of butter at 15°C is lower than that of the blend when tempered by method S1. In contrast, similar SFC ~~is~~ was obtained at 15°C when tempered by method S2. These results appear to contradict the hypothesis that SFC and rheological properties are strongly correlated when manufacturing conditions are constant (section 4.2). A possible reason for this anomaly may be that the tempering conditions used in S1 and S2 are different from those present in the manufacturing conditions. Furthermore, the marked difference in the TG composition between the two products may cause differences in solid miscibility, polymorphic behaviour and crystallization conditions even though similar manufacturing conditions were used (section 4.1).

4.3.4 Comparison of Experimental Margarine with the Japanese Pastry Margarine

For the experimental and Japanese pastry margarines, the SFC results at 15°C are similar when tempered by method S1 (51.4%

TABLE 21: Average hardness values of butter, experimental pastry margarine and Japanese pastry margarine

Manufacturing method	Hardness values (g) at 15°C			Margarine used for baking
	Butter	Experi-mental pastry margarine	Japanese pastry margarine	
I churning shock cooled	855	695		
II churning Alnarp	720	525		✓
III SSHE	995	930		
IV SSHE / pinworker	705	425		✓
unknown			219	✓

TABLE 22: Solid fat contents of butter, blend 16 and Japanese pastry margarine

Type of tempering	Temperature (°C)	Solid fat content %		
		Butter	Blend 16	JPM
S1*	15	46.7	51.4	53.8
S2**	15	42.2	40.9	40.6
S1*	20	28.2	33.3	37.7
S2**	20	29.2	34.3	37.6

* tempered by method S1

** tempered by method S2

and 53.8%, respectively) and when tempered by method S2 (40.9% and 40.6%, respectively). Despite this similarity, the commercial margarine is softer than any of the experimental margarines. This difference in rheological properties may have been caused by manufacturing techniques since the manufacturing process for the Japanese pastry margarine is unknown. In addition, there is a difference in TG composition between the two margarines and this may influence the degree, type and rate of crystallization (section 4.1).

Although the experimental margarine has a higher hardness value than the Japanese pastry margarine, the former lost its firmness on rolling. This resulted in a lesser increase in volume and a loss in the external layering of the pastries. A possible reason for this behaviour is the greater degree of melting between 15°C and 20°C for the experimental margarine. Additionally, work softening may also have caused the blend to lose its firmness on rolling (section 4.1.4 (c)).

During the production of the experimental margarine, emulsifiers were not added. This may also be another reason for the difference between the rheological properties of the two margarine types since it is considered that emulsifiers can influence fat crystallization (4.1.5).

4.4 BAKING OF DANISH PASTRIES

The rolling procedure is important in the making of danish pastries. Improper rolling and loss in the firmness of the roll-in fat may produce a product with less distinct layering and volume increase (Sultan, 1969b).

The Japanese pastry margarine is sufficiently plastic to be rolled easily and firm enough to keep the dough layers separate. As a result, there is a large volume increase and distinct external layering in the pastries. In contrast, margarine made from the blend is easy to roll initially but loses its firmness during the last few rolls. This causes a lesser increase in volume and a loss in external layering of the pastries. Butter gives pastries which have distinct layers and large volume increases. However, it is difficult to roll-in because of its hardness during the first roll which causes the dough to tear. This problem can be overcome by taking considerable time and care during the rolling process but this will not be practical in a commercial situation. Moreover, the difficulty in obtaining butter of a consistent hardness due to seasonal differences adds to its disadvantage (De Man & Wood, 1958a; Dolby 1954).

The pastries made from butter and the margarine blend containing 70% milkfat have a distinctive buttery taste which is considered to be a positive feature. It therefore follows that the ideal pastry margarine will have the physical properties of the Japanese pastry margarine and a distinctive buttery taste.

4.5 FUTURE INVESTIGATIONS

The baking trial shows that the consistency of the roll-in fat is very important and it suggests that additional research will have to be done to determine why the margarines manufactured in the present study softened on working. Although these products have been reworked after 24 hr to reduce the formation of crystal networks and lower the effect of worksoftening, the experimental margarines used in the baking trials still lose firmness on rolling.

In addition, the effect of emulsifiers on the rheological properties of margarines can possibly be investigated.

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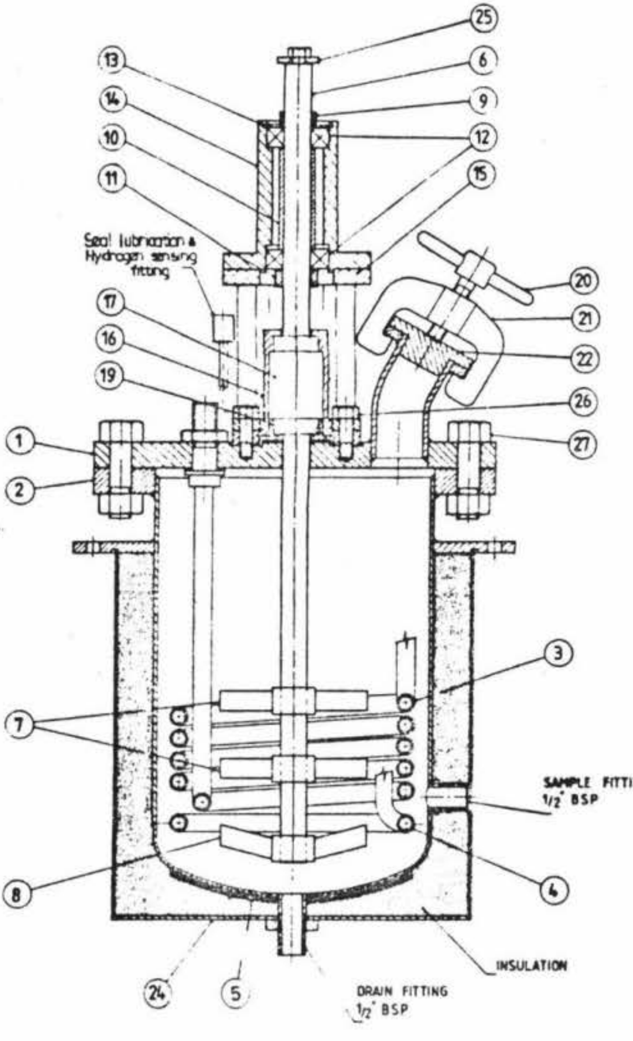
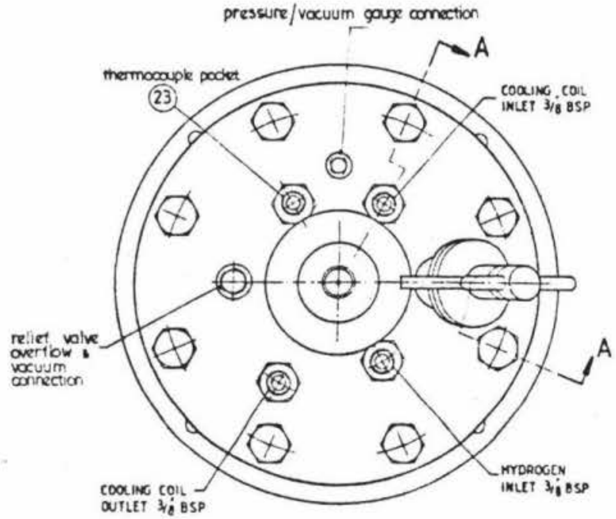
NOTES



SECTION AA



MAXIMUM WORKING PRESSURE 75 psig

APPENDIX 1: Hydrogenation vessel

STAINLESS STEEL SPECIFICATION			
ITEM	GRADE	ASME SPECIFICATION	PRODUCT FORM
1	316 TP 316 316	SA-240 SA-312 SA-479	PLATE SEAMLESS PIPE BAR
2	316 316	SA-240 SA-479	PLATE BAR
3	TP 316 316	SA-312 SA-479	SEAMLESS PIPE BAR
4	TP 316 316	SA-312 SA-479	SEAMLESS PIPE BAR
6	316	SA-479	BAR
7	316 316	SA-240 SA-479	PLATE BAR
8	316 316	SA-240 SA-479	PLATE BAR
20	304	SA-479	BAR
21	304 304	SA-240 SA-479	PLATE BAR
22	316	SA-479	BAR
23	TP 316 316	SA-213 SA-479	SEAMLESS TUBE BAR
26	B8MCl.1	SA-193	BOLT
27	B8MCl.1	SA-193	BOLT

◆ SEE ADJACENT TABLE FOR ST STL SPECIFICATION

ITEM	DESCRIPTION	REQD	REMARKS
27	BOLT 5/8 BSW × 2 1/2 Lg	8	ST STL ◆
26	BOLT M 10 × 30 Lg	4	ST STL ◆
25	WASHER	1	ST STL 304
24	OUTER CASE	1	ST STL 304
23	THERMOCOUPLE POCKET	1	ST STL ◆
22	SEALING BLANK	1	ST STL ◆
21	CLAMP	1	ST STL ◆
20	CLAMP SCREW	1	ST STL ◆
19	BOTTOM BUSH	1	BRONZE
18			
17	SEAL		
16	SEAL HOUSING	1	ST STL 304
15	SPACING BRACKET	1	ST STL 304
14	BEARING HOUSING	1	MILD STEEL
13	CIRCLIP	1	SEEGER TYPE J ⌀ 47 BORE
12	BEARING	2	SKF 6204 2RS
11	LOCATING COLLAR	1	ST STL
10	BEARING SPACING	1	MILD STEEL
9	SPACER	1	ST STL 304
8	BOTTOM AGITATOR	1	ST STL ◆
7	TOP AGITATOR	2	ST STL ◆
6	AGITATOR SHAFT	1	ST STL ◆
5	HEATING ELEMENT 2 kW	1	
4	HYDROGEN SPARGE PIPE	1	ST STL ◆ SCHED 40
3	COOLING COIL	1	ST STL ◆ SCHED 40
2	MAIN BODY	1	ST STL ◆
1	TOP PLATE	1	ST STL ◆

No.	REVISION DETAILS	BY	DATE
2	ASME SPEC ADDED	IWH	21 7
1	ITEM NOS ADDED	IWH	30 4

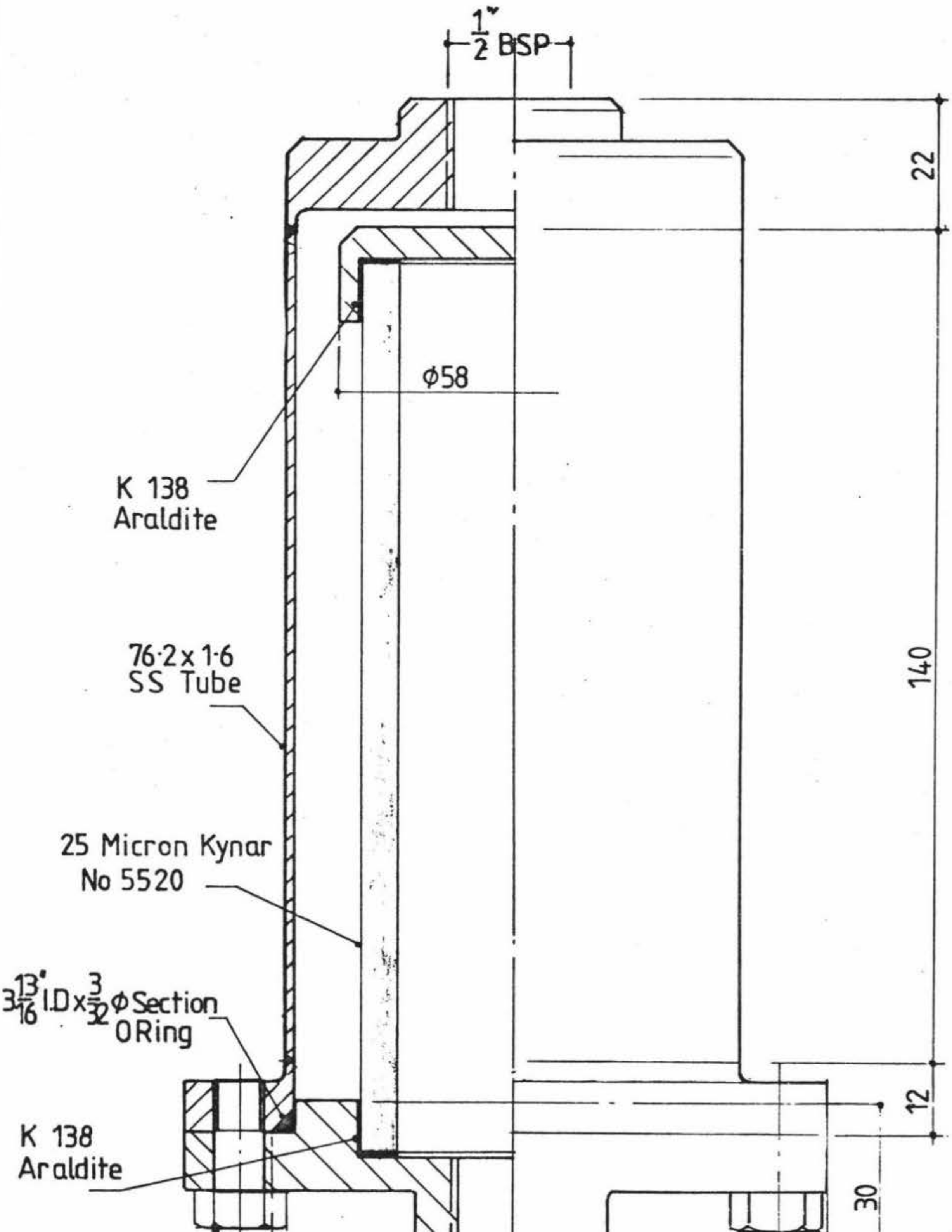
DESIGN
DRAWN IWH
CHECKED
APPROVED
DATE 15-4-80

JOB TITLE

DRAWING TITLE
HYDROGENATION VESSEL

DRAWN SCALE 1:2
REVISION 2
JOB No
CODE L
DRAWING No 2-212

Original Size 0 10 50 mm



Material 316 SS

Title APPENDIX 2: Hydrogenation Filter

Drawn IWH | Date 28-6-82 | Scale 1:1 | Ref. No. S 2-212

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APPENDIX 3: Method of baking danish pastries

Ingredients

185	ml	water	For making the dough
21	g	skim milk powder (SMP)	
63.5	g	sugar	
478	g	pastry flour	
28	g	compressed baker's yeast	
3.5	g	salt	
56.5	g	butter	
50	g	egg (two days old)	
7.5	ml	vanilla essence	
250	g	roll-in fat (1 cm thick slab)	

The rolling and make up of units were done in a temperature controlled laboratory at 21°C.

The dry ingredients (skim milk powder, sugar, pastry flour, (sifted), yeast, salt and butter) were mixed for 1 min in a Kenwood mixer at a low speed (position 1 on scale). The wet ingredients (water, eggs and vanilla essence) were then added and the mixing continued until a clear dough was obtained, which did not stick to the sides of the mixing bowl. The dough was then kneaded by hand for 1 min. This involved a pressing motion by the palm and a lifting motion by the fingertips so that the ball of the dough was turned in a circular manner. The dough was then allowed to rest for 5 min after which it had reached a temperature of 22°C.

750 g of the dough was rolled to a thickness of 1 cm with a pastry brake (Henry Berry Bench Handbrake, Figure 1) by lowering the rollers 0.15 cm at a time. It was placed on a flat surface and excess flour was dusted off with a 2 in brush. 250 g of roll-in fat in the form of a 1 cm thick slab at a temperature of 10-12°C was placed over 2/3 of the rolled out dough as shown in Figure 2. The uncovered part of the dough was folded onto the fat slab (Figure 3) and the half turn was completed by folding over the other half portion of fat covered dough (Figure 4). The pastry was passed through the rollers of the pastry break again until a thickness of

0.5 cm was obtained. At this stage, the temperature of the dough was 16°C. The pastry was dusted and a half turn was performed again after which it was allowed to rest for 5 min at 2°C. The pastry was rolled out and given another half turn before being allowed to rest for 3 min at 2°C. The procedure of rolling and making half turns was repeated two more times, after which the pastry was rolled to 0.5 cm and then to a final thickness of 0.4 cm by hand (Figure 5). The temperature of the pastry was approximately 18°C. A sheet (27 x 27 x 0.4 cm) was cut from the pastry and several small pastries of the 'butterfly' pattern were made. This involved folding the two sides of the sheet inwards three times and then cutting the roll into 1 cm pieces (Figures 6 and 7). A further sheet (6 x 6 x 0.4 cm) was cut and one pastry of the 'windmill' pattern was made as shown in Figure 8.

The units of pastries were proofed for 40 min in a cabinet (MLS contherm) set at 30°C with a damp cloth at the bottom shelf. They were then baked in a thermowave oven (Atlas Hilton 610) for 6 min at 200°C.

FIGURE 1: Rolling of dough

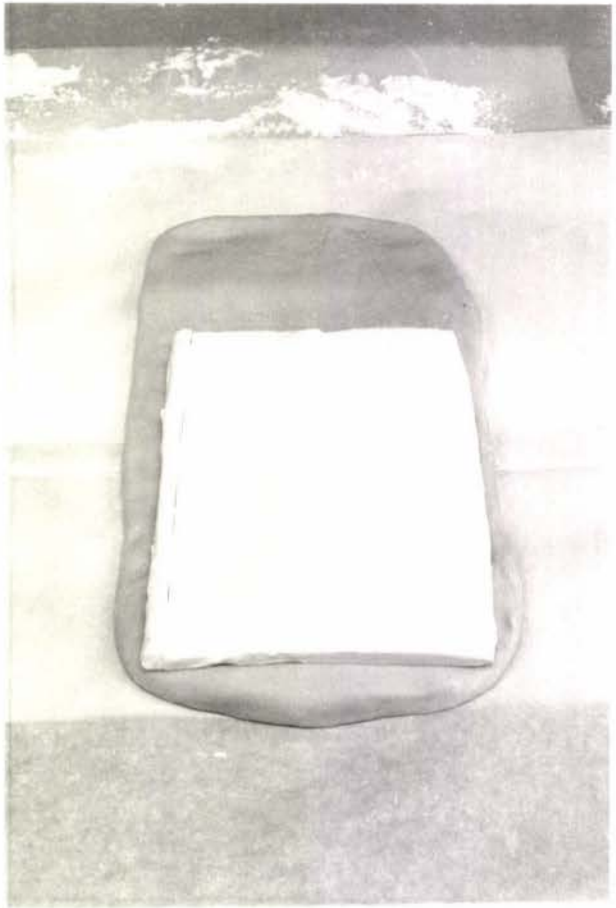


FIGURE 2: The roll-in fat is placed over dough

FIGURE 3: The uncovered part of the dough is folded onto half of the fat covered dough

FIGURE 4: The half turn is completed

FIGURE 5: The pastry is rolled to 0.4 cm by hand

FIGURE 6: Folding of the pastry before cutting into the butterfly shapes

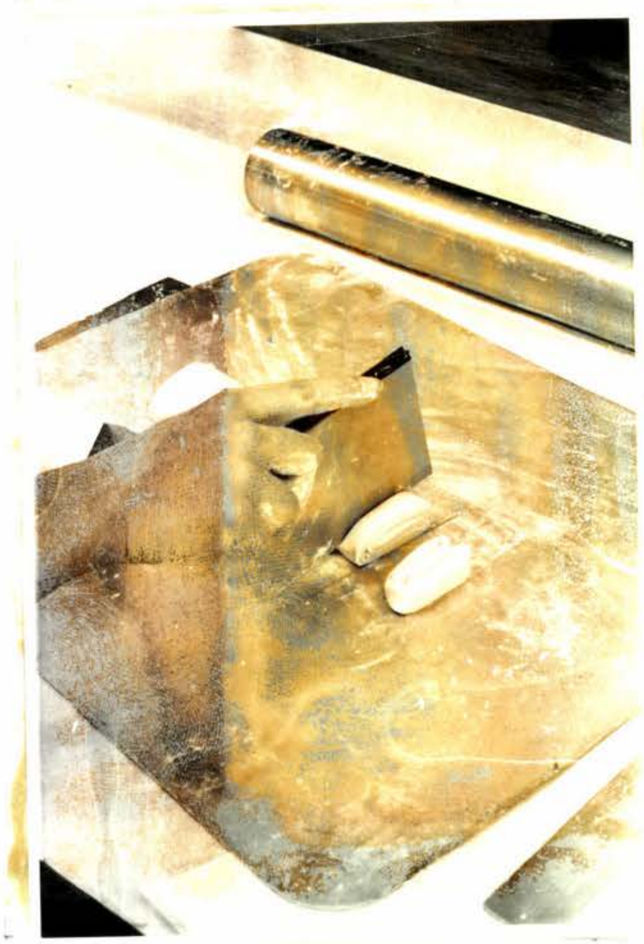


FIGURE 7: Completed 'butterfly' unit

FIGURE 8: Steps in making a 'windmill' unit

APPENDIX 4: Schedule for making danish pastries

Time	Method
8.30 am	The roll-in fat (A) is taken out of the cold room (2°C). The ingredients are mixed for 11 min.
8.42	The dough is kneaded by hand.
8.44	It is allowed to rest for 5 min at 21°C.
8.49	750g of dough is weighed out and rolled to 1 cm. 250g of fat is rolled in.
8.57	The pastry is allowed to rest for 5 min.
9.02	It is rolled to 0.5 cm and given a half turn.
9.04	The pastry is allowed to rest for 3 min.
9.07	It is rolled to 0.5 cm and given a half turn twice. It is made into butterfly and windmill units and washed with egg.
9.25	The units are proofed for 40 min.
10.05	They are baked for 6 min.
10.10	They are removed from the oven.
10.13	The roll-in fat (B) is taken out of the cold room. The ingredients are mixed for 11 min.
10.25	The dough is kneaded by hand.
10.27	It is allowed to rest for 5 min at 21°C.
10.32	750g of dough is weighed out and rolled to 1 cm. 250g of fat (B) is rolled in.

10.40 The pastry is allowed to rest for 5 min.

10.45 The pastry is rolled to 0.5 cm and given a half turn.

10.47 It is allowed to rest for 3 min.

10.50 The pastry is rolled to 0.5 cm and given a half turn twice. It is made into the units and washed with egg.

11.08 The units are proofed.

11.30 The roll-in fat (C) is taken out of the cold room. The ingredients are mixed for 11 min.

11.42 The dough is keaded by hand.

11.44 It is allowed to rest for 5 min at 21°C.

11.48 The pastry units (B) are baked for 6 min.

11.49 750g of the dough (C) is weighed out and rolled to 1 cm. 250 of fat (C) is rolled in.

11.54 The pastries (B) are removed from the oven.

11.57 The pastry (C) is allowed to rest for 5 min at 2°C.

12.02 pm The pastry (C) is rolled to 0.5 cm and given a half turn.

12.04 It is allowed to rest for 3 min.

12.07 The pastry (C) is rolled to 0.5 cm and given a half turn twice. It is made into the units and washed with egg.

12.25 They are proofed for 40 min.

12.30 The roll-in fat (D) is taken out of the cold room. The ingredients are mixed for 11 min.

12.42 The dough is kneaded by hand.

12.44 It is allowed to rest for 5 min at 21°C.

12.49 750 of dough (D) is weighed out and rolled to 1 cm. 250g of fat (D) is rolled in.

12.57 It is allowed to rest for 5 min at 2°C.

1.02 It is rolled to 0.5 cm and given a half turn.

1.04 It is allowed to rest for 3 min.

1.05 The pastry units (C) are baked for 6 min.

1.07 The pastry (D) is rolled to 0.5 cm and given a half turn twice. It is made into the units and washed with egg.

1.11 The pastries (C) are removed from the oven.

1.25 The pastry units (D) are proofed for 40 min.

2.05 The pastry units (D) are baked for 6 min.

2.11 The pastries (D) are removed from the oven.

APPENDIX 5: Sensory evaluation of danish pastry

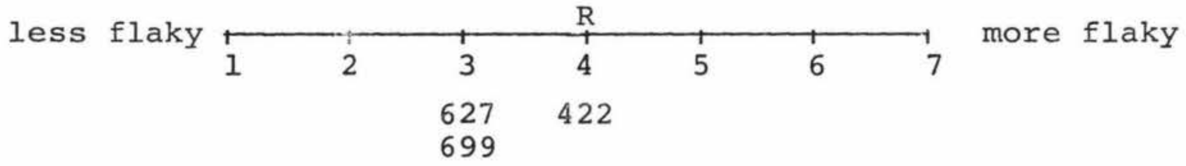
Name: ______________________________ Date: ____________

You will be given a reference R and 3 samples coded 699, 422, 627. Taste R first and leave enough of it to evaluate the next 3 samples. R is given a score of 4 in all characteristics.

The scoring is as follows:-

7 = much more than
6 = more than
5 = slightly more than
4 = same as reference
3 = slightly less than
2 = less than
1 = much less than

Evaluate each sample by writing the number code below the appropriate score. Please rinse your mouth thoroughly before tasting each sample. An example is shown below:



Please rate the appearance and texture of each sample in relation to R by writing the number code below the appropriate score.

External Appearance

less dark				R				more dark
in colour	1	2	3	4	5	6	7	in colour
less distinct				R				more distinct
layering	1	2	3	4	5	6	7	layering

Mouthfeel

less flaky				R				more flaky
	1	2	3	4	5	6	7	
less fatty				R				more fatty
or greasy	1	2	3	4	5	6	7	or greasy
less doughy				R				more doughy
	1	2	3	4	5	6	7	

APPENDIX 6: Sensory evaluation of danish pastries on the first baking day

Panelist	Colour			Layering			Flakiness			Fattiness			Doughiness		
	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1
1	0	0	0	0	1	1	-1	1	0	-1	0	0	2	0	-1
2	0	0	1	1	-1	-1	-2	0	-1	-1	0	2	-2	1	-2
3	-1	-1	-1	-1	-2	-3	-1	0	-2	-1	0	1	1	2	2
4	-1	-1	0	-1	0	-1	-1	2	-2	1	2	1	2	1	2
5	0	0	0	-1	0	1	-2	0	-1	-2	0	0	0	-1	1
6	-1	0	1	0	0	-1	-1	-1	-1	0	0	0	1	1	2
7	0	0	1	-2	0	-1	-2	1	0	-2	-1	1	1	-1	0
8	0	0	1	-1	1	1	-2	1	0	-2	1	0	0	0	-1
9	0	0	0	0	-1	-1	0	2	1	-1	0	-1	1	0	-1
10	-1	0	0	0	1	0	-1	1	1	0	1	0	1	0	0
Mean score	-0.4	-0.2	0.3	-0.6	-0.1	-0.5	-1.3	0.7	-0.5	-0.9	0.3	0.4	0.7	0.3	0.2

A is margarine made from blend 16 manufactured by method II
B is margarine made from blend 16 manufactured by method IV
N is butter

APPENDIX 7: Sensory evaluation of danish pastries on the second baking day

Panelist	Colour			Layering			Flakiness			Fattiness			Doughiness		
	A_1	B_2	N_2	A_1	B_2	N_2	A_1	B_2	N_2	A_1	B_2	N_2	A_1	B_2	N_2
1	1	-1	1	-1	-1	1	0	-1	2	0	-1	2	1	2	2
2	1	0	2	0	-1	2	0	0	3	-1	0	0	-1	-1	-1
3	2	0	1	0	1	2	-2	-1	2	0	-2	2	0	0	-1
4	1	0	3	-1	-2	0	0	-2	3	1	-2	2	0	1	-1
5	1	0	3	-3	-1	2	-2	-1	2	-2	0	2	0	1	-2
6	1	0	2	-1	0	0	-1	-1	1	0	0	0	0	0	1
7	2	0	2	0	0	2	1	2	3	0	0	1	-2	-1	-1
8	2	1	3	-1	-1	0	-1	1	2	0	1	1	1	0	-1
9	0	0	2	-1	-1	2	-2	-1	2	-1	-1	1	1	0	-2
10	1	0	2	-3	-1	1	-2	-2	2	-1	-1	1	2	2	0
Mean score	1.2	0	2.1	-1.1	-0.9	1.2	-0.9	0.6	2.2	-0.4	-0.6	1.2	0.2	0.4	-0.6

A is margarine made from blend 16 manufactured by method II
B is margarine made from blend 16 manufactured by method IV
N is butter

APPENDIX 8: Sensory evaluation of danish pastries on the third baking day

Panelist	Colour			Layering			Flakiness			Fattiness			Doughiness		
	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1	A_2	B_1	N_1
1	0	1	0	-1	0	2	-2	1	-1	1	0	1	0	0	1
2	0	1	0	-1	0	1	-1	1	0	1	-1	-2	1	1	0
3	-1	-1	0	-1	-1	0	-2	-1	1	-1	0	1	1	-1	-1
4	-1	-1	-2	-1	-1	0	-2	0	-1	1	-1	3	1	-1	-2
5	0	0	0	0	1	1	-2	0	1	0	0	0	1	0	0
6	-1	-2	-1	-2	-1	1	-1	0	0	1	0	2	1	1	0
7	-1	-2	-1	-1	-1	1	-2	0	-2	-2	1	-1	2	-1	0
8	-2	-2	-1	0	-2	0	-1	-1	-1	1	0	1	1	1	1
9	-1	-1	0	0	-1	1	0	-1	0	0	-1	-1	1	2	1
10	-1	-1	-1	-1	-1	0	0	0	0	1	0	1	1	1	0
Mean score	-0.8	-0.8	-0.6	-0.8	-0.7	0.7	-1.3	-0.1	-0.3	0.3	-0.2	0.5	1.0	0.3	0

A is margarine made from blend 16 manufactured by method II
B is margarine made from blend 16 manufactured by method IV
N is butter

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