The Production of a High Free-Fat Whole Milk Powder for the Chocolate Industry; The Spray Chilling Technology

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A Thesis presented in partial fulfilment of the requirements for the degree of Master of Technology at Massey University.

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" I find the great thing in this world is not so much where we stand, as in what direction we are moving " O. W. Holmes

" There is always room at the top " Daniel Webster

ABSTRACT

Whole milk powder containing down to 80 percent free fat was manufactured by spray chilling suspensions of skim milk in milk fat, using a modified laboratory spray drier. Also, the pure unmodified milk fat, and the soft (SBF23), medium (SBF27) and hard (SBF42) fractions of the same were transformed into powder by spray chilling the molten samples. The effect of chilling with air and nitrogen was investigated. The powders were satisfactorily stable at 5°C, but were relatively unstable at ambient temperatures. The powders' particle size distributions ranged from 4.44 to 215.56 μm. The powder characteristics were influenced by the size of the nozzle, the atomising gas pressure, the chilling temperature, the feed flow rate, and to a lesser extent, the feed temperature.

The shelf life of the unmodified milk fat powders stored at 20°C, 5°C and -10°C was assessed. The powders chilled with air had excessively oxidised after one month of storage at all the temperatures, whereas powders processed with nitrogen were still usable after the same period of storage. Lower peroxide values were recorded for the powders stored at -10°C and 5°C, while significantly higher values were obtained for the samples stored at 20°C.

The powdered fats dry-blended successfully with skim milk and calcium caseinate powders at the ambient temperature. In comparison, the hard fraction mixed better than the other softer fractions. Up to 50 percent of the hard fraction, and just 30 percent of the softer fractions, could be blended with the skim milk powder. An upper level of 70 percent hard fraction, and of 50 percent for the softer fractions, were mixed with calcium caseinate. The repose angles of the skim milk and milk fat blends increased with the increasing fat content, and the blends containing up to 20 percent fat were free flowing. For the calcium caseinate and skim milk blends, the repose angle decreased with the increasing fat content, and all the blends were not free flowing. The bulk densities of the skim milk blends decreased with the increasing amount of fat, while those of the calcium caseinate blends increased with the increasing fat content.

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1 INTRODUCTION

Spray chilling is often regarded as the converse of spray drying (Lamb, 1987; Anon, 1970). Not surprisingly so because the two processes share the same basic operating principles. Perhaps the only notable difference is that spray chilling is achieved by circulating cold gas in the system, whereas spray drying is effected by circulating hot air.

Records describing spray chilling date as far back as the 1970s (Anon, 1970; Grolistch, 1975), but up to now widespread application of this technology has not followed, especially in the processing of food materials. By far, the slackness in the adoption of this process has been attributed to the processing difficulties (Grolistch, 1975; Lamb, 1987), in particular, the need for very low cooling temperatures, long product residence times in the crystallising chambers, and more importantly, poor physical properties of the spray chilled product during storage. However, research is now advancing the spray chilling technology, addressing these stumbling blocks by building into the system highly specific release properties (Lamb, 1987; BOC gases Ltd, 1995).

Despite the hampering factors, the envisaged application of the spray chilling process is very broad. Nevertheless, so far almost all the attention has been focused on lipid processing. By using this technology, the fat which is usually in block form or liquid can be handled as powder, ideal for incorporation into other ingredients by dry blending. Additional advantages associated with powdered fats include improved storage life at ambient temperatures (Claypool, 1984; Frede *et al* , 1991), enhanced handling properties which make storage and transportation more easier(Frede *et al*, 1991), and flexibility in product formulation, with subsequent potential for new product opportunities.

In the work discussed here, the potential for application of the spray chilling technique in manufacturing high-fat whole milk powders, specifically targeted for the chocolate

confectionery, was investigated. Moreover, it was sought to gain more insight into the operating parameters which have significant effect on the success of the spray chilling process *per se*, and therefrom, optimise the processing conditions for the purpose of manufacturing milk fat powders efficiently. The processing equipment used for this investigation comprised a converted laboratory spray drier, in which liquid nitrogen and blast-freezer-generated cold air were separately tested as the chilling media. Anhydrous milk fat and three different melting fractions of the same (soft, medium and hard fractions) were processed.

The actual production of the high-fat whole milk powder was approached in two strategies. The first tactic, which was derived from the work of Teo (1993), involved formulation of suspensions of skim milk powder in milk fat, which upon spray chilling gave powders whose particles were coated with milk fat. The second strategy entailed spray chilling pure anhydrous milk fat (AMF) to produce powders which were thereafter dry-blended with skim milk powder.

Following the production of the AMF powders, their physical and oxidative stability at three different storage temperatures were studied. The oxidation was assessed at intervals up to four months. In addition, the potential for the powdered fats to be dry-blended with other powders of differing physical properties was appraised.

2 LITERATURE REVIEW

The available literature concerning the spray chilling of fats to form powder was reviewed. This review focuses on three areas. First, the chemical and physical properties of milk fat, and their relation to the functional role of milk fat in chocolate confectionery; second, the processing conditions of the spray cooling technique, and their influence on the processed powder; and third, the potential for spoilage of milk fat powders by oxidation.

2.1 The Chemical and Physical Properties of Milk fat

The composition of milk fat influences the physical properties of the fat, and, hence, affects the properties of the food products in which it is used. This subject is extensively discussed in literature by Kessler (1989), Taylor *et al* (1975), Rajah (1991), and Moulder (1980). Banks (1991) and Webb *et al* (1965) have given a detailed account of the overall composition of the milk fat. However, for this study, only a brief outline of the milk fat components relevant to the role of milk fat as an ingredient of chocolate confectionery are considered.

The composition of milk fat is complex. Most importantly, milk fat consists mainly of glycerides, with the triglycerides making up 98% of the total glycerides content. The rest of the glycerides are small amounts of diglycerides, monoglycerides, and free fatty acids (Boudreau *et al*, 1991; Banks, 1991; Webb *et al*, 1965). Also present are small quantities of complex lipids, such as phospholipids; cerebrosides; and sterols, mainly cholesterol and cholesterol esters. In addition, milk fat contains fat-soluble vitamins, A, D and E; antioxidants, such as tocopherol; pigments, notably carotene; and flavour components, which include lactones, aldehydes and ketones.

The glycerides are esters of glycerol and fatty acids. Their fatty acid spectrum is dominated by acids containing from four to eighteen carbon atoms, notably, the oleic acid, C18:1; butyric acid, C4:0; myristic acid, C14:0; palmitic acid, C16:0; and stearic acid, C18:0 (Shukla, 1994). A large amount (about 70%) of the fatty acids are saturated, that is, they do not possess double bonds in their chemical structure. The rest of the acids are unsaturated (about 30%), and are usually associated with the oxidative spoilage of the fat.

Of the unsaturated acids, oleic acid is the only one which is present in appreciable amounts (Shukla, 1994; Banks, 1991; Wilster, 1943), and it exists in two structural forms, the *cis* and the *trans*. The *cis* is the dominant form, while the *trans* constitute about 2 to 11% of the total oleic acid content (Shukla, 1994). Unfortunately, in spoilage terms, the *cis* acids oxidize more readily than their *trans* couterparts (Nawar, 1985). It is known that oleic acid and butyric acid contribute to the softness of the fat, whereas high amounts of stearic acid and palmitic acid make the fat firm (Rajah, 1991; Kerry *et al*, 1972; Banks *et al*, 1990). Table 2.1 below illustrates the typical distribution of fatty acids in milk fat from New Zealand cows.

Table 2.1 Fatty Acid Profile of Milk fat from New Zealand Cows (Taylor and Hawke 1975)

Fatty Acid	Summer (%)	Winter (%)
C4:0	9.6	12.0
C6:0	4.5	4.5
C8:0	2.2	2.3
C10:0	4.2	4.2
C12:0	4.1	4.0
C14:0	11.5	10.8
C14:1/C15:0	2.9	2.2
C16:0	27.6	22.0
C18:0	10.1	13.1
C18:1	17.8	21.5
C18:2	1.4	0.7
C18:3	0.8	0.3

Most researchers have found that the fatty acid composition of milk fat varies with the breed of the cow and seasons of the year. They found that in Europe, the unsaturated acids are least in winter and greatest in summer (Wilster, 1943). Hence, the fat is softer in summer and harder in winter. But in New Zealand (McDowall, 1953; Taylor *et al*, 1975), the fat is softer in spring and late autumn, and is harder in the summer. These variations suggest that for manufacturing a consistant product throughout the year, it would be necessary to adjust the composition of the raw material as and when it changes.

2.2 The Functional Role of Milk fat in Chocolate

The chocolate industry is the largest user of milk fat in the confectionery industry (Shukla, 1994). This is because milk fat, which is less expensive than cocoa butter, is one of the few fats which is compatible with cocoa butter, the most important ingredient in chocolate. A typical milk chocolate is composed of cocoa mass (12%, of which 55% is fat), cocoa butter (19.5%), sugar (45%), milk solids (22.7%, of which 28% is fat), emulsifiers, and flavours (0.3%). Dark chocolate also contains milk fat and milk solids, but at lower levels than milk chocolate (Shukla, 1994; Barts, 1991). Milk fat is used primarily to reduce the costs of cocoa butter used in the production, and also to add to the chocolate some desirable qualities inherent in the milk fat.

Milk fat may constitute up to 30% of the total fat phase in chocolate, with the rest of the fat being made up by cocoa butter. The amount of the milk fat mixed with cocoa butter depends on the softening point of the milk fat, essentially, its fatty acid composition (Barts, 1991; Kessler, 1989; Shukla, 1994), but it is often fixed by law in most countries. For example, in New Zealand the amount of milk fat in milk chocolate must not to be less than 4.5%, and it should not exceed 3% in dark chocolate. In chocolates other than "milk" and "dark" the milk fat is not allowed to be more than 5% (New Zealand Food Regulations, 1984). It is worth noting that cocoa butter has a uniform composition of the fatty acids and the triglycerides, and a very narrow melting temperature range. It softens at 30 to 32°C and melts at 32 to 35°C. By comparison, milk fat melts over a wide temperature range, between -40 and 38°C. This is caused by the milk fat's diverse

fatty acid profile (Shukla, 1994).

To date, the wide melting-temperature range of milk fat has limited its usefulness as an ingredient of chocolate. This is because the addition of milk fat to cocoa butter results in a significant lowering of the melting point of the mixture, adversely affecting the crystallization and, subsequently, the hardening of the chocolate (Shukla, 1994; Barts, 1991). This effect has been attributed to the fluid nature of the low melting components of milk fat, and the formation of an eutectic by cocoa butter with milk fat (Shukla, 1994; Barts, 1991; Rajah, 1994). A solution to this problem was suggested by Rajah (1994) and Iversen (1991), who reported that when higher melting milk fat fractions are used, instead of unmodified milk fat, the chocolate softening effect is minimised.

In addition to being used to reduce chocolate production costs, milk fat is also added to chocolate for distinctive taste and flavour. Milk fat also plays a special role as a natural stabiliser of chocolate by inhibiting the formation of fat blooms, that is, the formation of grey and white surface colouring on chocolate. It inhibits fat blooms by preventing the transition of cocoa butter crystals from the stable form V polymorph to the form VI polymorph (Jebson *et al.* 1974; Barts, 1991; Shukla, 1994).

Milk fat is incorporated into the chocolate mixture as molten fat; milk crumbs, a dried mixture of chocolate ingredients; and, most commonly, as whole-milk powder (Barts, 1991). The suitability of the latter as the fat base depends on the method used to manufacture the powder.

Production of whole-milk powder for chocolate making can be done by two processes: spray drying or roller drying. Spray dried powder has small, spherical particles with milk fat encapsulated by a protein film. These milk particles do not readily combine with cocoa butter. On the other hand, roller dried powder has large, flat particles with a high level of surface free fat which readily mixes with cocoa butter (Barts, 1991). This superior mixing ability makes roller dried powder more favourable as a chocolate ingredient. Its disadvantage is that roller drying is an expensive process, and this has led to increased use

of the cheaper, but less suitable, spray dried powders (Barts, 1991). The use of spray dried powder requires the addition of AMF to achieve the necessary fat levels in the mixture. AMF is usually supplied separate in drums, and it has to be melted down. This of course means extra equipment and handling. Besides, the techniques commonly applied for this fat addition are often messy, and sometimes they even promote the oxidation of the mixture, or the final product (Anon, 1970).

The aim of this project, therefore, is to assess the potential of the spray chilling technique, for manufacturing a fat-based powder which is both inexpensive and more suitable for application in the chocolate confectionery, or any other desired applications.

2.3 Production of Powdered Fats by Spray Chilling

Literature is sparse concerning studies on production of powdered fats by the spray chilling, or other similar, techniques. By definition, spray chilling is considered the converse of spray drying in that cold gas, rather than heat, is used to solidify a spray of material (Lamb, 1987). In a strict sense, the term *spray chilling* is used to refer to a process in which materials (commonly lipids) with melting points lower than 42°C are processed. For lipids with higher melting points, *spray cooling* is preferred, to make a distinction (Lauren *et al*, 1991).

Most published information refers to butter powders or other high-fat powders with a 40 to 80 percent fat content, produced mainly by the spray drying processes. Spray dried powders have the fat encapsulated by carrier materials such as starch, milk powders, gum arabic, or sugars. These do not readily give sufficiently high free fat when mixed with cocoa butter, or any other mixtures. Some of the fat ends up being bound to the encapsulating material.

In spray chilled powdered fats, the powder is either composed entirely of fat, or the fat is used to coat other materials. That is, the fat forms the outer layer of the particles, as opposed to being the core (Frede *et al*, 1991; Teo, 1993; Podmore, 1994). Since their fat

is contained outside the particles, it is released rapidly to the mixture into which they are incorporated (Anon, 1970).

2.3.1 The Spray Chilling Process

The production of powdered fats involves atomising molten fat, or a mixture of fat and the powder to be coated (carrier powder), into a stream of cold air or nitrogen (Podmore, 1994; Frede *et al*,1991; Lamb, 1987; Grolitsch, 1975). The carrier powder can be fed separately, but simultaneously with the liquid fat, into the area of atomization. This is highly recommended if softer fats are being processed (Lamb, 1987). Through shock cooling, the atomised fine fat droplets are immediately crystallised, and are discharged from the bottom of the cooling chamber as powder (Frede *et al*, 1991; Teo, 1993; Lamb, 1987). The cooling gas is then recirculated to the chamber, via a filter which traps the fines. Frede *et al* (1987) stated that crystallisation of the fat can be effected with ambient atmosphere if fat containing sufficiently high amounts of high melting triglycerides is used. The discharged powdered fat is then mixed with carrier powders, such as skim milk powder, casein, and others, to prevent it from lumping during storage. The choice of the carrier powder is based on the ultimate use of the powdered fat (Frede *et al* 1991; Lamb 1987; Anon, 1970).

In a patent produced by Grolitsch (1975), it was asserted that stable powdered fat, which maintains good flowability properties even after long storage periods at room temperatures, can be achieved without using carrier powders. He stated that this is possible if the crystalline powder is subjected to suitable pre- and post- temperature treatments, so that maximum stable high-melting β-crystals are achieved in the powder particles.

The stability and functional properties of the powder can be improved further if antioxidants and liquid emulsifiers are added to the fat prior to crystallisation (Anon, 1970). Further, Grolitsch (1975) claimed that good quality powders can be obtained if naturally occurring milk fat constituents, such as phospholipids and sterols, have been removed. However, in this study, it was desired to use milk fat in its most natural form.

The only modifications of the fat which were investigated were the performance of its different melting fractions.

2.3.2 The Processing Conditions

The fundamental parameter governing the success of the spray chilling process is the size of the fat globule. The globule size should be such that the total particle is fully solidified before it leaves the tower. This whole process is dependent on the design of the spray chiller and the operating conditions of the chiller.

Lamb (1987) and Teo (1993) carried out trials to produce powdered fats using the laboratory spray drier as the crystallising chamber, and cold air as the cooling medium. Their investigations were aimed at evaluating the effect of various operating parameters on the fats produced. Their research revealed that the production of good powders is determined by four key factors. These are the operating parameters and the type of the atomizer, the temperature of the chilling gas, the feed flow rate, and the feed composition and feed temperature. Pre- and post- temperature treatment of the fat was also found to have a marked influence on the physical properties of the powders (Grolitsch, 1975).

Atomising System

Two types of atomizers, the centrifugal disc atomizer and the nozzle atomizer, high pressure or two-fluid nozzle, can be used successfully to generate fine milk fat globules in the spray chiller. These influence the size and the shape of the particles produced. Teo (1993) noted that when the feed flow rate was kept constant, increasing the speed of the disc atomizer resulted in a corresponding reduction in the size of the particles. Using a standard laboratory disc atomizer revolving at 20 000 r.p.m, and the feed flow rate fixed at 40 ml/min, Teo (1993) produced good spherical milk fat particles which ranged in size from 180 - 300 μm. In a similar work done by Zanker in 1994 (through verbal communication), the smallest possible particle diameter of 28 μm was achieved with the disc revolving at 55 000 r.p.m., with the feed flow rate fixed at 0.6 Kg/h. Masters (1991) correlated the size of the particles to the disc atomizer speed by the following

approximation:

$$d \approx N^{-0.6} \qquad (2.1)$$

Where

d = mean diameter of the particle

N = number of revolutions per minute

Atomization of fat with two-fluid nozzle atomizers is highly recommended for laboratory trials (Lamb, 1987). These atomizers are able to produce particles with suitable sizes, of about 10 - 50 μm, for spray chilling (Lamb 1987; Grolitsch 1975). In his comprehensive review of spraying systems, Masters (1991) stated that pneumatic nozzles have great flexibility in producing small droplet sizes over a wide range of feed rates. It has been established that the droplet size characteristics can be varied over a wide range by adjustment of the feed-air (atomising gas) flow ratio at the nozzle head. Moreover, several complex mathematical models have been proposed for predicting the particle sizes which result under given sets of operating conditions (Masters, 1991). One such model, known as the Kim-Marshall equation, which is applicable for the design of the nozzles which were to be used in this study is stated as;

$$D_{MMD} = \left[\frac{249\,\sigma^{0.41}\mu_l^{0.32}}{(V_{rel}^2\,\rho_a)^{0.57} A^{0.36} \rho_l^{0.16}} \right] + 1260 \left[\left(\frac{\mu_l}{\rho_l \sigma}\right)^{0.17} \left(\frac{1}{V_{rel}^{0.54}}\right) \left(\frac{M_a}{M_l}\right)^m \right] \qquad (2.2)$$

Where $m = -1$ at $\left(\frac{M_a}{M_l}\right) < 3$ also $m = -0.5$ at $\left(\frac{M_a}{M_l}\right) > 3$

M_l = feed flow rate (lb/min) $A = in^2$ μ_l = Viscosity of the feed (cP)

σ = surface tension of the feed (dynes/cm) ρ = density of the feed (lb/ft^3)

D_{MMD} = mass median diameter V_{rel} = relative velocity of the air

In some earlier studies done here at Massey University two nozzles with aperture diameters of 1 mm and 2 mm were used to evaluate the effect of the nozzle size and the atomising pressure on the size of the particles atomised. In these studies, the size of the particles was found to decrease with the increasing pressure at the nozzle, the reduction in nozzle aperture, and the decreasing feed flow rate. With the feed flow rate fixed at 0.6 Kg/hr, and atomising with a pressure of 3 bar, particle sizes in the range of 3.5 - 27.0 μm were produced. Grolitsch (1975) claimed that with proper temperature pre-treatment of the feed, it is possible to achieve particle sizes in the range of 0.5 - 5.0 μm.

Temperature of Cooling Gas (Crystallising Temperature)

The difference between the cooling gas temperature and the temperature of the liquid fat entering the cooling chamber is the crucial driving force that effects crystallisation of the fat droplets. This temperature difference determines the rate at which the fat globules solidify (Podmore,1994; Teo,1993). The higher the temperature difference, the faster the rate at which the particles solidify.

Teo (1993) determined the range of temperatures within which a standard laboratory spray drier can be operated to crystallise milk fat into powder (see figure 2.1). This temperature regime was determined using cold air generated by a blast freezer, and a standard laboratory centrifugal disc atomizer set at 20 000 r.p.m.

It is claimed that reasonably stable and free flowing powders were achieved when the inlet air temperature was maintained between 2 and 5°C, with the feed flow rate fixed at 40 ml/min (Teo,1993). In contrast, cooling at temperatures below 0°C gave particles with 'tails', while crystallisation at temperatures above 5°C resulted in sticky powders. The latter finding is supported by Snow *et al* (1967), whose dilatation studies of fat particles crystallised at 4.4°C revealed that approximately 44 percent of the fat in the particles was crystallised.

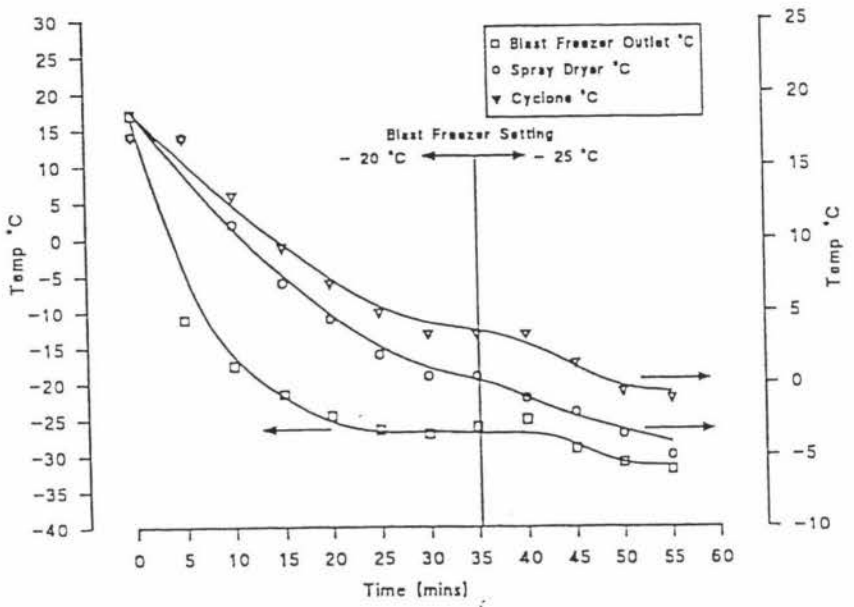


Fig 2.1 Temperature regimes within which spray chilling of milk fat can be effected in a laboratory spray drier , using a blast freezer (Teo, 1993)

The cooling temperatures ranging between -15°C and -30°C are cited (Grolitsch, 1975; Anon, 1970) for spray chillers which utilise high pressure nozzle atomisers. This temperature regime is used to effect rapid crystallisation. However, it is known that rapid crystallisation of molten triglycerides promotes the immediate formation of the less stable α-crystals. After leaving the chiller, the α-crystals then change to the short-lived β'-form, and, eventually, to the more stable β-form (Guly *et al*, 1993; Lamb,1987; Grolitsch,1975). These polymorphic crystal transformations are accompanied by generation of heat and changes in density. The heat generated causes the melting and lumping of the powders (Lamb, 1987).

Two requirements are crucial for the successful use of very low crystallising temperatures. One requirement is that the atomised particles must be sufficiently small, preferably having diameters in the range 10 - 50μm (Grolitsch, 1975; Lamb, 1987). The second requirement is that the humidity in the cooling chamber must be kept as low as possible; high humidity affects the quality of the final product (Grolitsch, 1975).

Feed Temperature

It has been recommended that the temperature of the fat should be raised 15 to 20°C above its melting point before it is processed into powder (Lamb, 1987). Heating the fat to above this temperature range is not recommended because it is costly and may encourage oxidative spoilage of the fat (Grolitsch, 1975).

For milk fat, it is commonplace to heat the melt to about 50°C before crystallising it. This is done to destroy all the present crystal nuclei so that fresh nuclei can be formed, and to lower the viscosity of the fat and enhance the flow of the fat to the atomiser (Anon, 1970; Lamb, 1987).

Low melt temperatures increase the viscosity of the melt. Increased viscosity, coupled with high feed rates, inevitably causes wide droplet size when the melt is atomised.

Composition of the Feed

Composition of the feed also plays a vital role in determining the success of the spray chilling process. It has been demonstrated that the fat which contains high amounts of high melting triglycerides crystallises easily, and also forms relatively stable powders (Teo, 1993). The proportions of other components of the feed also influence the properties of the powder which is being manufactured. They affect the viscosity and the homogeneity of the feed, which in turn affects the size of the powder particles. If milk fat is being used to coat other powdery materials, like milk powder, the composition of the feed may affect the efficiency of coating (Teo, 1993). The ratio of the powder to the fat, for sufficient coating of the powder, can only be determined effectively by trials.

2.4 Potential for Spoilage of Milk fat

Spoilage of milk fat, or products containing high amounts of milk fat, can take place hydrolytically or oxidatively. These two processes, which are discussed below, result in the development of off-flavours in the product (Keogh *et al*, 1986; Jebson *et al*, 1973; Illingworth *et al*, 1994).

2.4.1 Hydrolytic Spoilage of Milk fat

Hydrolytic spoilage of milk fat results from the breakdown of triglycerides by lipolytic enzymes, to give diglycerides, monoglycerides, and free fatty acids (Keogh *et al*, 1986; Nawar, 1985). Contributing most to the off-flavour development are the free fatty acids (FFA), especially the short chain (C4 - C12) acids (Deeth *et al*, 1983; Keogh *et al*,1986). It therefore follows that flavour deterioration can be minimised by controlling levels of FFA in the product.

The production of FFA in lipids can be controlled directly by controlling the development, and action, of lipolytic enzymes in the product. It is known that the action of lipolytic enzymes is promoted primarily by high levels of moisture in the product, and relatively high storage temperatures (Illingworth *et al*, 1994). High moisture levels encourage the growth of microorganisms, which in turn produce lipolytic enzymes. Raised storage temperatures increase their reproductive rate. Therefore, limiting the amount of moisture in the product, and lowering the storage temperatures will reduce this type of spoilage. In the system being considered, hydrolytic spoilage is unlikely, provided the cooling air is not excessively humid.

The maximum FFA permitted in milk fat by the International Dairy Federation standards (1977) is 0.3%, expressed as oleic acid. This is determined by titrometric neutralisation of the FFA, using standardised potassium hydroxide solution (IDF 1989).

2.4.2. Oxidative Spoilage of Milk fat

Oxidative spoilage of fats has been well researched and reported in the literature (Gray, 1978; Keogh *et al*, 1986), and is rated as the major cause of flavour deterioration in milk

fat (Cant, 1991; Illingworth *et al*, 1994; Wilbey, 1991). The oxidation process involves the reaction between oxygen and the double bonds of the unsaturated glycerides. This reaction yields peroxides, which subsequently breakdown into a range of unstable off-flavour compounds, including saturated and unsaturated aldehydes, lactones, fatty acids, and alkanes (Tamsma *et al*, 1974; Richardson *et al*, 1983).

The oxidation reaction commonly proceeds by a free radical mechanism. This reaction is autocatalytic, that is, the products of the reaction act as a catalyst to promote further reactions (Illingworth *et al*, 1994; Cant, 1991). Comprehensive descriptions of the mechanisms involved in the oxidation of fats are given by Urbach and Gordon (1994), Nawar (1985), and Gray (1978).

There are several factors which influence the onset and progress of oxidation in fats. Swern (1979) has reviewed the various roles played by these elements in the off-flavour development of the fats. Keogh and Higgins (1986) have also studied the effect of these factors on the rate of milk fat oxidation. In all the oxidation studies carried out, it was found that the critical requirement for oxidation to take place is the availability of oxygen (Webb *et al*, 1965; Richardson *et al*, 1983). The other factors which have a profound influence on the oxidative spoilage are the temperature of storage (Keogh *et al*, 1986; Jebson *et al*, 1973), light (Mottar,1982), the degree of unsaturation in fat, the presence of pro-oxidants (Cant, 1991), the length of storage, and the presence of anti-oxidants (Timmen, 1978). Some other factors which have a minor impact on the oxidation of dairy products include the maillard compounds (Urbach *et al*, 1994), pH, and the presence of ascorbic acid.

Any milk fat (AMF) surface exposed to air will absorb oxygen rapidly (Cant, 1991). The amount of oxygen absorbed varies with the temperature of the milk fat and the proportion of solid fat to liquid fat. Keogh *et al* (1986), Jebson *et al* (1973), and Timms *et al* (1982) have determined the amount of oxygen that can dissolve in liquid milk fat over several temperature ranges between 0°C and 110°C. Moreover, Wilbey (1991) graphically demonstrated the variation in the amount of oxygen absorbed with changes in

temperature, using data from several sources (see figure 2.2).

Further, it has been demonstrated that if liquid milk fat is allowed to equilibrate with the air, amounts of oxygen as high as 33 ppm can be absorbed (McDowell, 1963; Jebson *et al*, 1973; Timms *et al*, 1982). Such high concentrations of oxygen accelerate the rate of oxidation of the fat (Wilbey, 1991). Oxygen absorption can be minimised by processing and packing milk fat under nitrogen. Less stirring of milk fat also limits the quantity of oxygen that can be absorbed (Cant, 1991). In addition, it has been suggested that when the fat is packaged, the head space of the pack should be reduced as much as possible. It has been recommended that the amount of oxygen dissolved in milk fat during packaging should be maintained below 3 ppm (CSIRO report, 1944 - 1945), but generally, levels lower than 2 ppm are preferred.

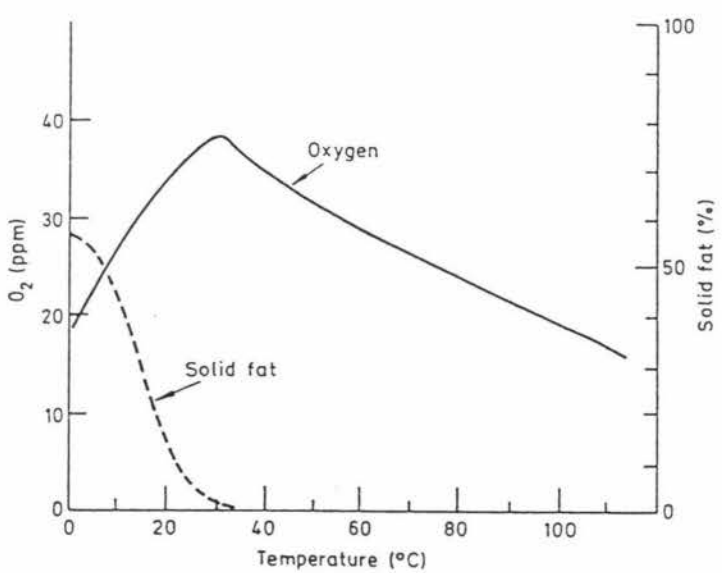


Fig. 2.2 The effect of temperature on the solid fat content and solubility of oxygen in milk fat (Wilbey 1991).

Several researchers have studied the influence of temperature on the rate of oxidation (Wilbey, 1994; Russell, 1973; Keogh *et al*, 1986). They found that the oxidation of fat accelerates as the temperature increases, and becomes significantly faster at storage temperatures in excess of 30°C. Because of this observation, it has been recommended that if pure milk fat is stored at 5°C it is best used within 3 months, and that the shelf life can be doubled by storing at -20°C (Wilbey, 1991). However, regardless of the storage temperature, the rate of oxidation reaction accelerates exponentially with the increase in time (Cant, 1994). In addition, Hamm *et al* (1968) found that the reaction rate is proportional to the reciprocal of the absolute temperature between -10°C and 50°C, with no deflection at the melting area of the fat as might be expected. If all other factors are controlled, pure milk fat should store for 3 months at ambient temperatures (<35°C), or more than 12 months at 5°C, without detectable deterioration (Wilbey, 1991).

Iron and copper are good catalysts for oxidation. For this reason, equipment made of stainless steel should be used at all times. Contamination of fat by these metal ions can easily come from the processing equipment unless proper care is observed. The maximum level of copper allowed in milk fat by IDF standards is 0.05 ppm. When working with copper levels of 0.01 ppm - 0.04 ppm, Keogh *et al* (1986) did not notice any relationship between milk fat storage stability and the copper levels, even after 8 months of storage. Perhaps at levels lower than 0.05 ppm, the effect of the catalyst is arrested.

Light damage as a flavour defect in dairy products has long been recognised (Farrer, 1984). A good review by Bradley (1980) discussed this subject. Furthermore, Keogh *et al* (1986) showed that the peroxide level of milk fat doubled after exposing the fat to fluorescent light for two hours, and tripled after four hours. To minimise the light damage, the IDF has recommended that the maximum permissible light transmission of packaging materials for dairy products should be 8% at 500 nm and 2% at 400 nm (Mottar, 1982).

Natural antioxidants can be used to retard the rate of oxidation in stored milk fat. It has been shown that the presence of α-tocopherol reduces the rate of oxidation in milk fat,

but the effect varies with changes in storage temperature and the amount of the antioxidant added (Keogh *et al*, 1986; Wilbey, 1991). Keogh *et al*, (1986) found that α-tocopherol behaved as an antioxidant when used at levels up to 100 ppm, but above 200 ppm it became pro-oxidant. Similar observations were made by Timmen (1978). At ambient temperatures (25°C), the anti-oxidant effect of tocopherol was not observed (Keogh *et al*, 1986). When α-tocopherol is used with lecithin and ascorbyl palminate, the anti-oxidant effect is more pronounced (Wilbey, 1991). Moreover, a combination of lecithin and ascorbyl palminate was shown to be an effective anti-oxidant at ambient temperatures (Keogh *et al*, 1986).

2.4.3 Assessing oxidation in milk fat

Gray (1978) has reviewed the techniques available for assessing fat oxidation. In addition, Jebson *et al* (1973) and Timms *et al* (1982) have compared some physical and chemical methods for quantifying oxidative deterioration in milk fat.

The amount of dissolved oxygen in liquid fat can be rapidly determined using an amperometric method (Jebson *et al*, 1973). This method involves the use of an oxygen meter and an oxygen probe. The probe is comprised of a gold cathode and a silver anode, which are coated with an electrolytic gel to measure the partial pressure of oxygen in the fat. In solid or partially crystalline samples, a chemical method can be used to estimate the amount of dissolved oxygen (McDowell, 1963). Both chemical and amperometric methods give similar results (Jebson, 1973; Timms, 1982).

Two basic tests are usually carried out to quantify the progress of oxidation in milk fat and other dairy products. These are the peroxide value (PV) test, which determines the amount of peroxides formed in the sample and the free fatty acid test, which quantifies the level of the free fatty acids.

Free fatty acids are normally assessed by titration of the sample against a standardised potassium hydroxide solution to phenolphthalein endpoint. For the PV test, two methods can be used. One involves complexometric titration of the sample (AOCS, 1986), and the

other, which is recommended by the IDF (1974) for its sensitivity at low PV values, is a colourimetric method. The latter involves measuring absorbance of colour formed by the iron (III) ions and the thiocyanate ions. The former ions are produced when iron (II) is oxidised by peroxides in the sample.

In practice, by the time milk fat has reached a peroxide value of 0.3 - 0.4 mEq/kg, the flavour is oxidised to an unacceptable level for some uses (Cant, 1991). For this reason, the IDF (1977) set specifications of PV for milk fat, at the time of manufacture, to be 0.2 mEq oxygen/kg of fat. Many researchers cited instances of poor correlation between flavour deterioration and the PV results.

Since the PV test is based on the oxidation of iron (II), erroneous results may be obtained if other oxidants beside the peroxides in the material tested are allowed to mix with the sample. Jebson *et al* (1979) cautioned that care must be taken in handling the samples before PV determinations, otherwise higher results may be obtained.

Podmore (1994) stated that in the case where milk fat is combined with a carrier, there are increased microbiological hazards. This was deduced from the observation that fat powders, which contain milk proteins, oxidatively deteriorated faster than powdered fats.

In view of the foregoing arguments, it would seem logical to conduct a complete study of the oxidation of the powdered fats at several storage temperatures, and with different levels of oxygen in the gas surrounding the powder.

2.5 Summary

All the literature surveyed solidly hold that it is possible to convert fats and oils into powder by spray chilling, and or spray cooling. There is however, no clear evidence to support that such powders are commercially viable. In fact, attempts to source for powders manufactured in the manner discussed drew blanks.

One of the crucial stages in the life-cycle of a product is the post-production stage. This stage encompases the handling processes, such as packaging, storage and distribution of the product. Non of the papers encountered discussed any of these processes. Also, no information is available concerning the shelf life of typical powdered fats.

This study, therefore, attempts to address some of the quiries mentioned above.

3 MATERIALS AND METHODS

The following is a general outline of the various materials and methods which were employed at one stage or another in this project. The finer details for each method are furnished at the relevant chapters where the particular method was used.

3.1 Materials

All the raw materials were obtained from Bay Milk Products Ltd. These included Anhydrous Milk Fat (AMF) and its fractions (SBF23 (soft), SBF27(intermediate) and SBF42(hard)), Fresh Frozen Milk Fat for Recombining (FFMR), medium heat skim milk powder and edible calcium caseinate (380) powder.

The liquid nitrogen used for cooling was of industrial grade, and was supplied by BOC New Zealand Ltd. This came in 176 litre Dewar vessels.

All the chemicals (and organic solvents) used for the various tests were of AR grade, purchased from various suppliers in New Zealand. 18 milliQ water, prepared in our lab, was used for the preparation of the solutions.

3.2 Viscosity Measurements

The viscosities of milk fat, and suspensions formulated from milk fat and skim milk powder were determined using Ferranti-Shirley viscometer. This viscometer is based on a cone and plate principle. Figure 3.1 below illustrates the essential elements of this instrument.

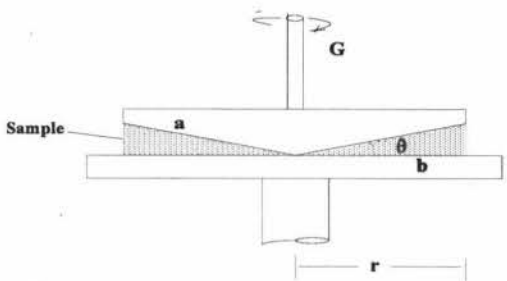


Fig.3.1 The essential elements of the Ferranti Shirley viscometer. a=cone; b=stationery plate; r=radius of the cone; θ=cone angle; G=angular velocity.

The sample is sheared in the gap between a rotating cone (a) and a stationery plate (b). The angle of the cone (θ) is about 0.5°, and at this small angle the shear rate across the conical gap, as well as the shear stress, are considered to be consistent with radius (r). In this geometry, the torque M is measured as the torque required to rotate the cone at a constant angular velocity (G), and the viscometer provides meter readings which are proportional to this torque. The readings obtained are then converted to shear stress units by multiplying with a shear stress multiplier constant $K\tau$, which is supplied by the manufacturer for the various possible settings of the machine. Thus

$$Shear\ \ Stress \ = \ K_{\tau} \ \times \ meter\ \ divisions \qquad (3.1)$$

Similarly, a shear rate multiplier constant K_D is used to convert cone rotational speed to shear rate units. Thus

$$Shear\ \ Rate \ = \ K_{D} \ \times \ rpm \qquad (3.2)$$

The viscosity of the test material was then worked out by dividing the shear stress by the

shear rate. i.e

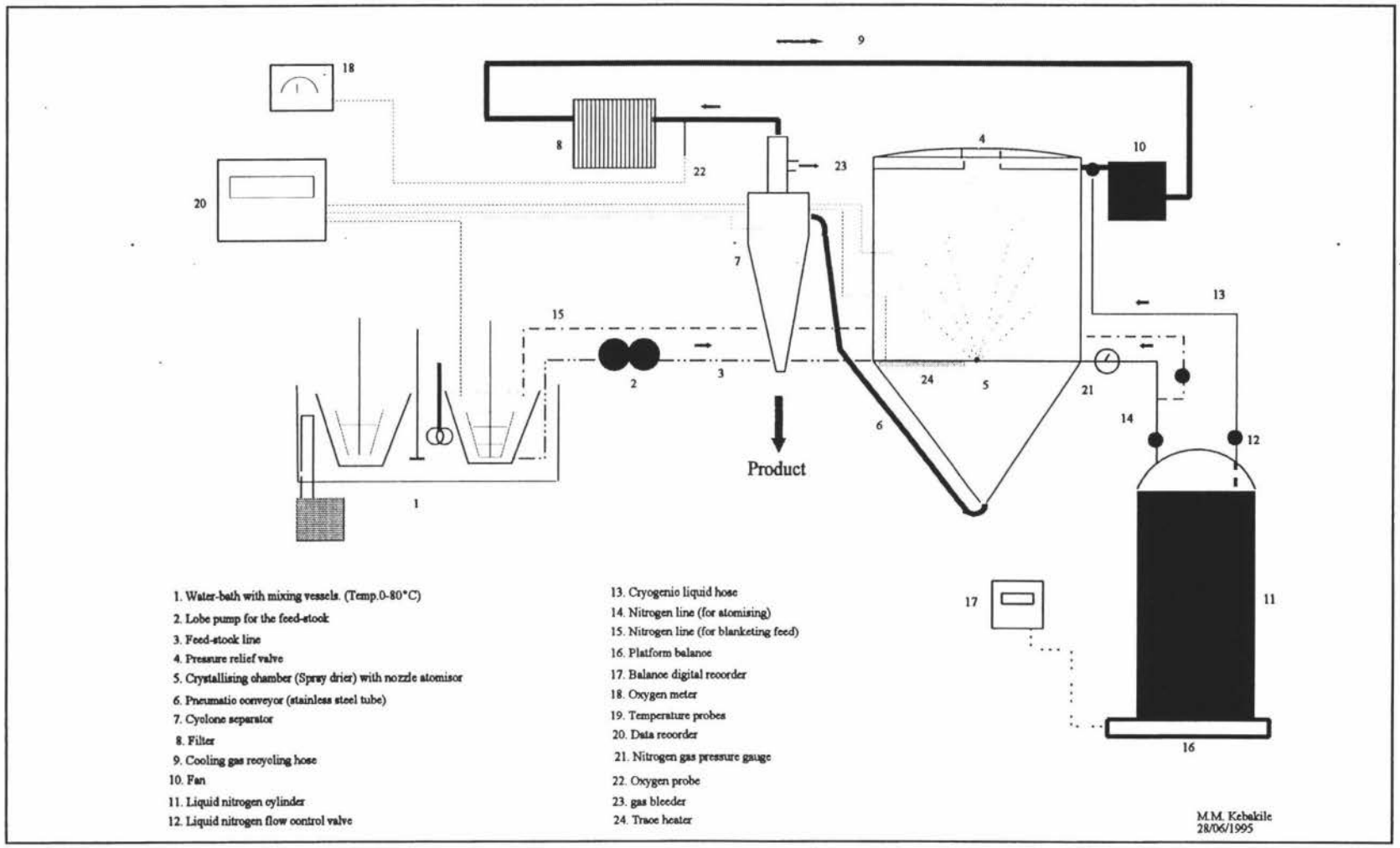
$$Viscosity = \frac{Shear\ Stress}{Shear\ Rate} \qquad (3.3)$$

3.3 Equipment Layout for Production of the Fat Powders

The plant layout for the powdered fats production consisted of feed preparation section, feed pumping to the nozzle atomizer, solidified powder conveying and recovery, and the chilling media sources. A counter-current crystallising chamber was adopted in two cycle layouts; i) a *semi-closed cycle layout*, in which nitrogen was used as a chilling medium, and ii) a *closed cycle layout*, where air was the chilling medium. The two set-up are shown in figures 3.2 and 3.3 respectively.

The feed preparation unit (1) (refer to fig.3.2) comprised of a temperature-programmable water-bath, having a heating and refrigeration unit, and two stainless steel mixing vessels of seven litres capacity, with gate stirrers and clear perspex lids. From the mixing vessels the feed was pumped to the nozzle, in the crystalliser, using either a peristaltic pump (model, Masterflex No. 7521-25), for less viscous material, or a high pressure lobe pump (APV, model CL/0/006/10) for highly viscous materials. These pumps were pre-calibrated by correlating their selected rev speeds to the corresponding volumes of feed material delivered. Three two-fluid nozzle atomizers described in table 3.1 were used. These nozzles were designed to mix the feed and the gas jet externally. All these nozzles were acquired from Spraying Systems Ltd, New Zealand. A trace heater (24), connected to a variable voltage controller, was used to keep the fat molten in the feed line inside the chamber, before it reached the atomizer. The voltage controller was initially calibrated for the temperatures maintained by the trace heater.

Fig.3.2 Equipment Layout for Chilling with Liquid Nitrogen



1. Water-bath with mixing vessels. (Temp.0-80°C)
2. Lobe pump for the feed-stock
3. Feed-stock line
4. Pressure relief valve
5. Crystallising chamber (Spray drier) with nozzle atomisor
6. Pneumatic conveyor (stainless steel tube)
7. Cyclone separator
8. Filter
9. Cooling gas recycling hose
10. Fan
11. Liquid nitrogen cylinder
12. Liquid nitrogen flow control valve
13. Cryogenic liquid hose
14. Nitrogen line (for atomising)
15. Nitrogen line (for blanketing feed)
16. Platform balance
17. Balance digital recorder
18. Oxygen meter
19. Temperature probes
20. Data recorder
21. Nitrogen gas pressure gauge
22. Oxygen probe
23. gas bleeder
24. Trace heater

Fig.3.3 Equipment Layout for Chilling with Air

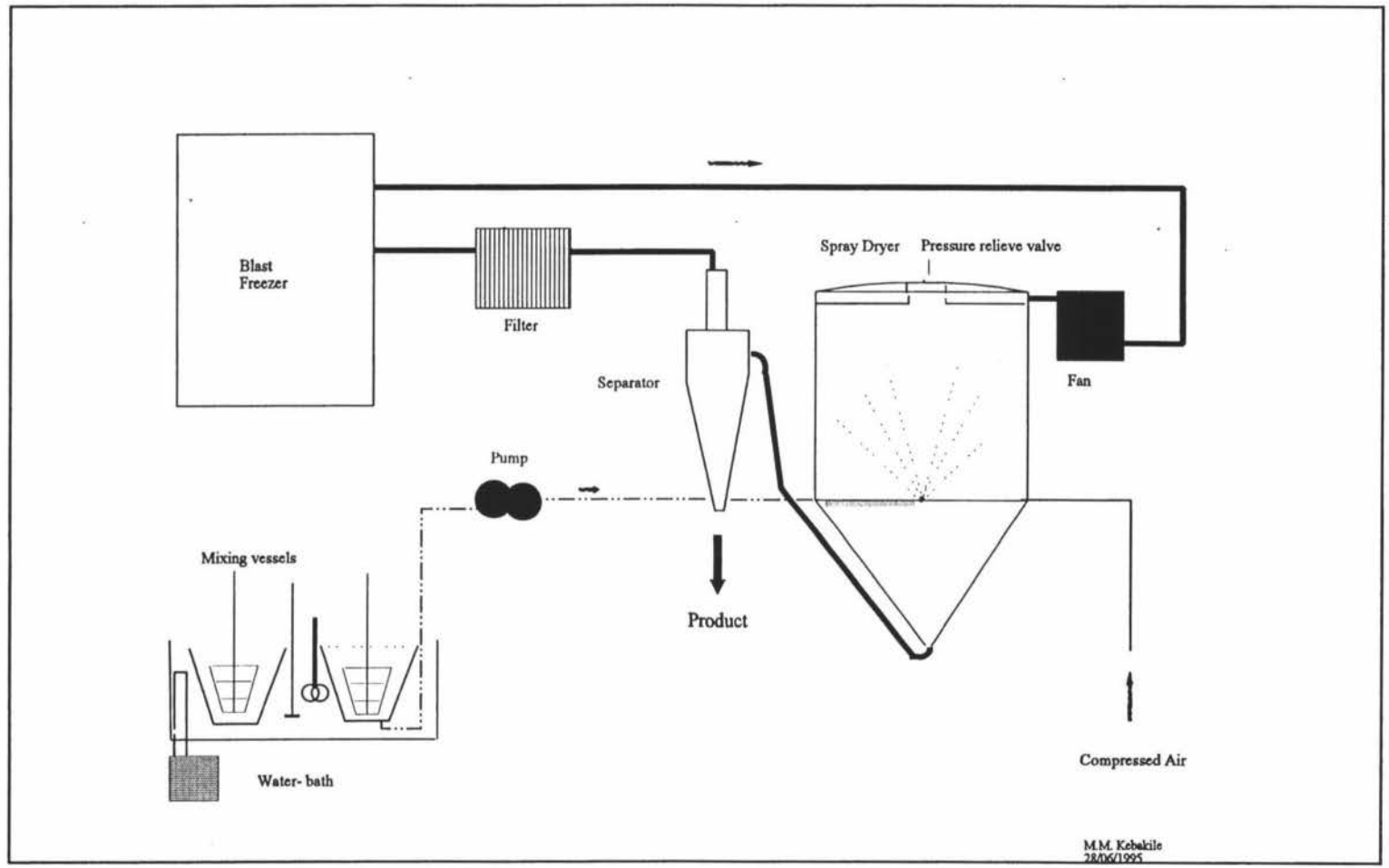


Table 3.1 The Two-Fluid Nozzle Atomizers used for the Trials

Nozzle No.	Fluid Cap	Air Cap	Angle of Spray	Orifice (mm)	Shape of spray	Nozzle Description
1	2050	67228	45°	0.5	solid cone	fine
2	60100	122281	60°	1.5	solid cone	large
3	40100	134255	45°	1.0	solid cone	medium

The crystallising vessel was a converted pilot scale spray dryer, ANHYDRO A/S; TYPE LAB.S1, with a height of 2.6 metres, width 1.2 metres, length 1.3 metres and a chamber diameter of 1.0 metre. In this vessel, the feed spray mixed counter-current with the chilling gas, and was immediately shock cooled and solidified into powder. The powder then left the base of the chamber pneumatically, via a stainless steel tube (6) to the cyclone (7), where it was separated from the cooling gas and was collected for storage. The spent cooling gas was recycled in the system, passing through a filter (8) which trapped the fine particles. Circulation of the cooling gas through the entire system was effected by a fixed-speed fan (10) attached at the top of the chamber. In the nitrogen's semi-closed cycle, some of the spent gas was released to the atmosphere through a gas bleeder (23), situated on the cyclone exhaust. This was done to maintain low crystallizing temperatures and low pressure in the chamber.

The nitrogen used for chilling was supplied in 176 litre cryogenic cylinders (Dura-Cyl) (11). Nitrogen was tapped from this cylinder as a liquid (12) and/or as a gas (14). The liquid nitrogen was conveyed through a cryogenic-liquids duct (12mm inside dia.) (13) into the spray chamber, where it vaporised and mixed with the fat spray. The flow of liquid nitrogen was regulated using the liquid valve (12), and its control was enhanced by a 1.2 mm gap Venturi fixed at the end of the conveying duct. Gaseous nitrogen (14) was used for atomising the feed, and also for blanketing the fat in the mixing vessels (15). The flow of the gas to the atomizer was monitored through a pressure gauge (21), and controlled using a gas valve (14). The amount of nitrogen spent, from the cylinder, was determined by weight difference, using a 500 kg (±0.1kg) digital platform balance (16) (Teraoka Weighing System, Model D1-10).

For chilling with the air, a blast freezer was used to generate the cold air. This freezer was able to produce up to 300kg per hour of cold air at -40°C. The spent cooling air was recirculated in the system.

The oxygen content of the gas circulating in the system was ascertained using an oxygen meter (18) connected to an oxygen electrode (22). The electrode was fitted with a standard oxygen membrane, and filled with saturated potassium chloride electrolyte. Before use, the meter was prepared as instructed in the manufacturer's manual. The same meter was used for determining the amount of oxygen dissolved in the fat before crystallizing.

A data recorder (Yokogawa 3088 Hybrid Recorder) (20) was employed to record temperature at various points of the plant. Thermocouples (19) of type T were used for this process.

3.4 Particle Size Measurement

The particles sizes of the powders were determined using a microscopic imaging technique. Out of the methods tried for this analysis, including the use of a marlven particle analyzer, this image analysis technique was found to be better suitable for handling these powders.

Slides of the powdered fats were prepared by gently sprinkling the powder thinly on microscope slides, which were previously stored at 5°C. The prepared slides were then kept cool (in a cool box with ice packs) until they were observed. Observations were carried under a pre-calibrated microscope, mounted with a video camera, which was connected to a Power-Mac computer. The computer was loaded with an NIH image analysis program (Ver.1.53). Images of the powders were captured and analysed. With this set-up, the particle diameters could be measured manually and/or automatically. However, because of the sticky nature of the particles under the test conditions, and the inability of the software to discriminate the agglomerated particles, it was preferred to

analyse the images manually. A detailed description of this technique is given by Russ *et al* (1988).

For each slide examined, three fields were randomly selected for particle counting. In the fields where less than 20 particles were present, all the particles were measured. Where numerous particles were present, only particles in half the area of the field were analysed.

3.5 Blending of the powders

The mixing of the powdered fats with other powders was effected using a kitchen scale Kenwood blender, for small quantities (up to 1 kg). For larger amounts of the powder (2-4 kg), a pilot scale Kenwood mixer was employed.

3.6 Bulk Density

The bulk density of the blended powders was expressed as their poured density. This was determined by measuring the volume occupied by a known amount of powder when it is freely poured into a measuring cylinder. Thus,

$$Poured\ \ Density = \frac{Weight\ \ of\ powder\ (g)}{Volume\ \ of\ powder\ (ml)} \qquad (3.4)$$

3.7 Flowability

The flowability of the powders was assessed by the angle of repose method. This is a commonly used technique for assessing this parameter in dry powders. 80 grams of the powder was allowed to flow through a vibrating plastic funnel having the diameters of 2.5cm and 12.0cm, to form a heap on a flat surface placed at 10 cm below the funnel. The height (h) of the powder pile and the radius (r) of the base of the pile were determined. The angle of repose (θ) was expressed as

$$\theta = cotan\ \frac{h}{r} \qquad (3.5)$$

3.8 Packing of the Powders for Oxidation studies

The powder samples, contained in small laminated bags were sealed using a standard heat sealer. Some of the bags were sealed using a Trigon vacuum packer (model; VC999/09 TF DD KNN). This vacuum packer was set to flash the bags with nitrogen gas, before pulling a weak vacuum (700 mbar) in the bag.

3.9 Peroxide Value

The peroxides in the fat were quantified by the Ferric Thiocyanate Method of the New Zealand Dairy Research Institute (also outlined by the Ministry of Agriculture and Fisheries - Dairy Division Standard Laboratory Methods). This method is a modified version of the international standard method 74A:1991 of the International Dairy Federation. The analysis is based on the principle that any peroxides present in the sample, resulting from oxidation of the fat, cause stoichiometric oxidation of the iron (II) to iron (III). The resulting iron (III) ions then react with thiocyanate to form a red complex, whose colour intensity is proportional to the concentration of the peroxides concentration. The colour intensity of the complexes formed by the samples were quantified using a UV/visible spectrophotometer (model; 80-2091-73, Pharmacia LKB).

3.10 Free Fatty Acids

The amount of free fatty acids in the FFMR and AMF used for the trials was ascertained by the alikametric titration (IDF, 1989) of a known amount of the fat sample.

3.11 Statistical Analysis of the Results

The results obtained were statistically tested using Minitab linear regression software (ver. 9.0).

4 PRODUCTION OF SPRAY CHILLED POWDERED FATS USING SKIM MILK AND MILK FAT SUSPENSIONS.

With reference to the work of Teo (1993), and through the adoption of his strategy of coating particulate material with fat, it was intended at the start of this project to produce whole milk powder containing high levels of free fat, whereby the skim milk powder particles were coated with milk fat. This was to be achieved by spray crystallizing suspensions containing molten AMF and skim milk powder. It became apparent that this exercise called for an understanding of the rheological characteristics of the suspensions which were to be formulated. A literature search for such information was commenced, but no records concerning the milk fat-skim milk blends, or any other similar formulations, were found. Hence, it was found necessary to characterise the viscosity behaviour of various blends of these materials, as a function of temperature. Viscosity is a measure of the internal friction of a liquid and therefore, it can be considered as a measure of the liquid resistance to flow. This rheological information was necessary for predicting the likely behaviour of the formulated feed-stock matrix during transportation in pipes, and during atomization.

4.1 Rheological Behaviour of Milk Fat and Skim milk Blends.

This investigation employed a full factorial experimental design, encompassing six ratios of skim milk to milk fat, and four holding temperatures. The response variable was the change in the viscosity.

4.1.1 Method

Milk fat - skim milk suspensions containing 10%, 20%, 30%, 40% and 50%, by weight, of skim milk powder were prepared by dispersing appropriate amounts of the powder in liquid

fat to make a total of 200g of the mixture. The mixtures were then held at the temperature required for viscosity measurements for at least 30 minutes, before sampling for analysis. A 200g sample of liquid AMF was subjected to the same treatment as the suspensions.

Liquid viscosities of the samples were determined using Ferranti Shirley cone plate viscometer. The optimum operating settings for the viscometer were determined using the suspension containing 20% solids, measured at 40°C. The analysis was carried with a cone of radius 0.035 m. Measurements for all the samples were then taken at 35°C, 40°C, 50°C and 60°C (± 0.1°C). The temperature of the sample stage was adjusted and stabilised for 15 minutes by circulating water through the same from a water-bath. The sample was then loaded and the test performed immediately. A sweeping shear rate range of 460 - 1870 s^{-1} was used to generate flow curves at all the temperatures, except at 60°C. For the latter, 920 - 1870 s^{-1} were used. The tests were repeated three times for each mixture, loading a fresh sample each time.

From the flow curves, meter readings corresponding to chosen rotational speeds were extrapolated, and these were multiplied by the shear stress multiplier constant $K\tau$ (1.95) to give shear stress values. Similarly, a shear rate constant multiplier (18.7) was used to convert the cone rotational speeds to shear rate units. Using the converted parameters, the viscosity was worked out, and rheographs were generated.

4.1.2 Results and Discussions

There were distinct differences between pure AMF and AMF-skim milk suspensions. AMF was found to exhibit Newtonian behaviour in the temperature range 35 - 50°C, and above 50°C it displayed non-Newtonian characteristics. Newtonian fluids have viscosity that is independent of shear rates (Campanella, through verbal communication), that is, there is a strict proportionality between shear stress (τ) and shear rate (γ). This behaviour is often described by the expression

$$\tau = \mu\gamma = \mu \frac{dv}{dy} \qquad (4.1)$$

commonly known as the Newtonian law of viscosity. The proportionality constant, μ, is the viscosity of the liquid. In their rheological studies of milk fat and milk fat substitutes, Drake *et al* (1994) also noted the Newtonian characteristics of milk fat at 50°C. Similar findings were reported by Dvoeglazova et al (1987), with the Newtonian behaviour observed over the temperature range of 40 - 90°C.

The viscosity of AMF was found to decrease with the increasing temperature. Increasing the temperature by five units from 35°C to 40°C reduced the viscosity by 22%. A further increase in temperature by 10°C, from 40°C, took the viscosity further down by 27%. The average results for AMF at different temperatures are collected in table 4.1 below.

Table 4.1 The Viscosity of AMF at Various Temperatures

Temperature	Viscosity (Pa.s)	Standard deviation
35°C	0.0082	±0.0001
40°C	0.0064	±0.0004
50°C	0.0047	±0.0006

$P < 0.05$

In contrast, all the AMF-skim milk mixtures displayed non-Newtonian behaviour at all the test temperatures. These mixtures were shear thinning (pseudo-plastic), that is, their viscosity decreased with the increasing shear rate (refer to figures 4.1a - 4.1d). A constitutive empirical equation

$$\tau = \mu \gamma^n \qquad (4.2)$$

or

$$\log \tau = (n-1) \log \gamma + \log K \qquad (4.3)$$

referred to as the Ostwald-de-Waele equation, or more commonly, the power law, fits the behaviour of these pseudo-plastic materials. In this equation K is called the consistency index, while n is the flow behaviour index.

Since the viscosity of the suspensions varied with the shear rate, this viscosity is said to be apparent (μ_{app}) (Carr, 1994), and it fitted the expression

$$\mu_{app} = \frac{\tau}{\gamma} = \frac{K\gamma^n}{\gamma} = K\gamma^{n-1} \qquad (4.4)$$

Plots of log μ_{app} versus log γ gave straight lines with slopes n-1, and the Y-intercept as log K. n and K values were calculated for the suspensions tested and are given in table 4.2. The value of n is a measure of the liquid's departure from Newtonian behaviour, and it is generally accepted that for n=1 the liquid displays Newtonian behaviour, whilst n<1 signifies pseudo-plasticity. If n>1 the liquid is said to be dilatant (i.e. viscosity increases with increasing shear rate). It can be seen from the table that n is about unity for AMF at all the temperatures, except at 60°C, verifying the Newtonian characteristic at these temperatures. For the skim milk suspensions n is significantly below one, confirming the non-Newtonian flow.

The larger the value of K at a given n and rotational velocity, the more viscous the liquid (Backhurst *et al*, 1974). There was a strong positive correlation (r = 0.94) between the amount of skim milk added to the mixture and the K value. That is, K increased with the increasing amount of powder in the mixture. For example, at 40°C every 10 percent increment of the skim milk in the mixture produced about 10 units of K. A similar trend was observed at 50°C, but with K increasing gently for the skim milk content of up to 20 percent. Beyond 20 percent solids, the K values increased rapidly. These results are graphically demonstrated in figure 4.2. As was expected, when the temperature was increased the viscosity of the suspensions decreased.

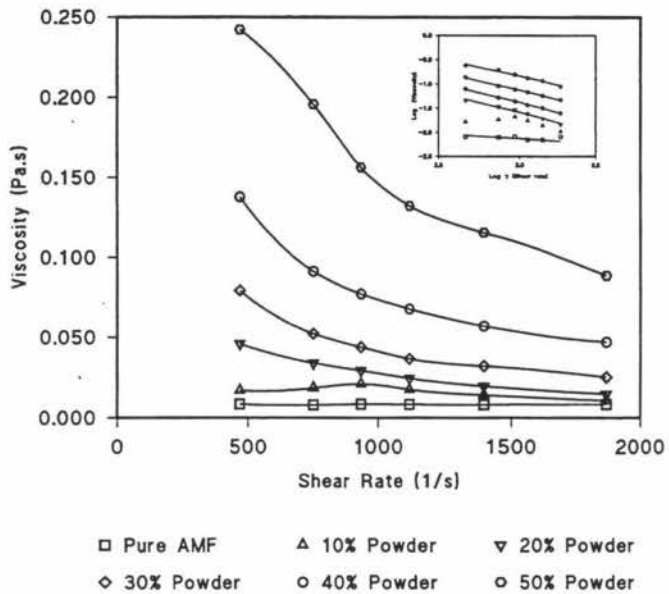


Fig. 4.1a Viscosity of skim milk-milk fat suspensions at 35°C

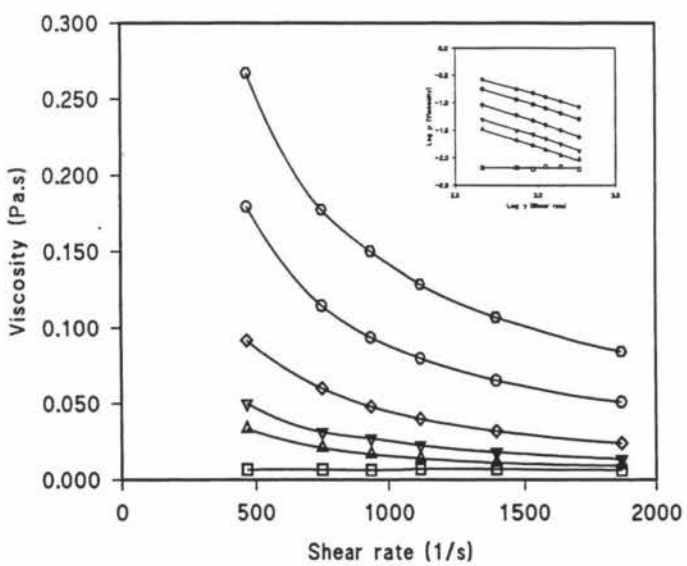


Fig. 4.1b Viscosity of the suspensions at 40°C

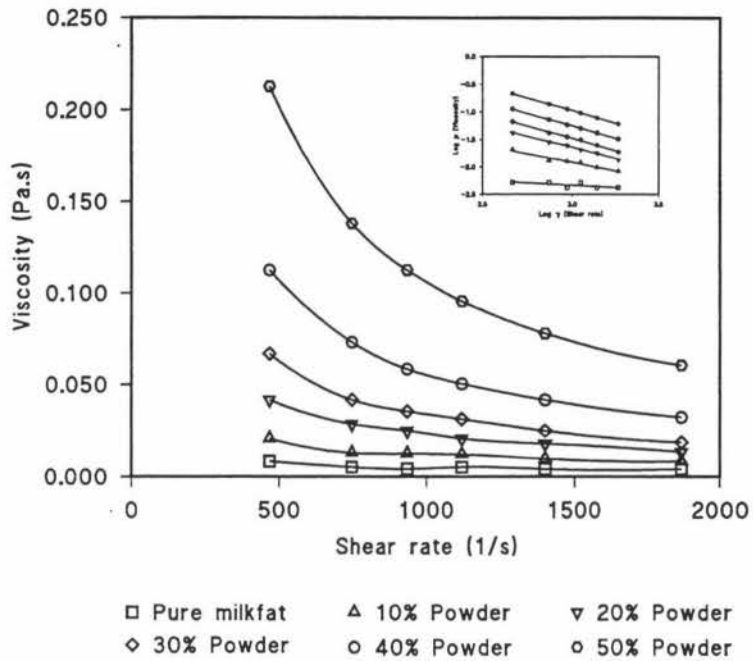


Fig. 4.1c **Viscosity of Skim milk-milk fat Suspensions at 50°C**

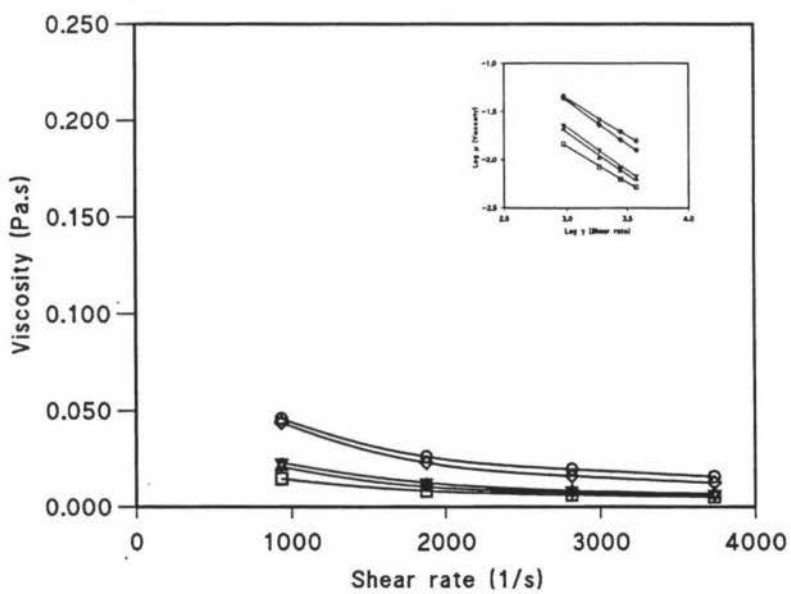


Fig. 4.1d **Viscosity of the suspensions at 60°C**

Table 4.2 Calculated K and n values of the milk fat-skim milk suspensions

Test Temperature	Sample Composition		K value	n value
	Milk fat (%)	Skim milk (%)		
35°C	100	0	0.01	0.95
	90	10	0.16	0.67
	80	20	7.94	0.17
	70	30	12.59	0.17
	60	40	15.85	0.23
	50	50	23.99	0.26
40°C	100	0	0.01	0.99
	90	10	10.23	0.06
	80	20	15.14	0.07
	70	30	36.31	0.03
	60	40	46.77	0.09
	50	50	42.58	0.17
50°C	100	0	0.07	0.83
	90	10	0.93	0.37
	80	20	5.62	0.20
	70	30	16.22	0.11
	60	40	28.18	0.10
	50	50	56.23	0.09
60°C	100	0	2.40	0.25
	90	10	7.94	0.13
	80	20	10.23	0.11
	70	30	21.38	0.09
	60	40	9.12	0.24

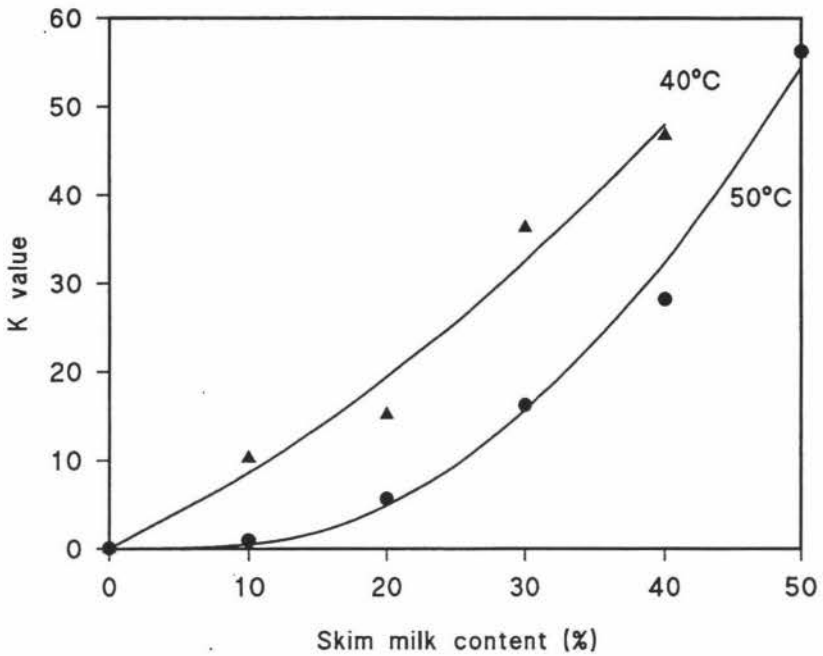


Fig. 4.2 The Variation of K value as a Function of Temperature and the Skim Milk Content.

Explanations for the observed changes in viscosity

The Newtonian flow behaviour displayed by AMF may be explained in the light of the molecular interactions proposed by Van den Tempel (1961). This proposition holds that two distinct types of molecular bonds are involved in the formation of the viscoelastic network of fats. One type of these bonds are the primary bonds, which are not broken at tests of low shear stress. The other type are the secondary bonds, which tend to break during a test period and may be re-established. These secondary bonds are believed to be caused by weak Van der Waal's forces between the neighbouring molecules (Nawar, 1985; Van den Tempel,1961). It is known that the triglyceride structure of milk fat allows stable and ordered interactions between molecules, consequent of their ability to pack close together (Nawar, 1985). Because of this close packing, secondary bonds broken during a test cycle in milk fat triglycerides are easily reformed, and as a result the original structure of the fat is maintained, and so is the viscosity of the material. Hence, the Newtonian behaviour is observed.

When the temperature of the liquid fat is increased the molecules gain increased freedom of movement and the Van de Waal's forces get weakened. This give rise to a decrease in the viscosity of the fat, and accounts for the loss of the Newtonian characteristic.

The non-Newtonian flow characteristic observed for the skim milk - milk fat suspensions can be attributed to a number of factors. These may be explained as follows;

i) The suspension matrix is composed of milk powder particles of irregular shapes, and entangled molecular chains of the fat. At rest all these materials maintain irregular internal order, and a corresponding high viscosity. When the shear rate is increased, the particles randomly oriented in the suspension become aligned in the direction of the flow, and molecular chains get stretched and oriented parallel to the flow (Nawar, 1985). This particle and molecular rearrangement allow particles and molecules to slip past each other more easily, and this shows as reduced viscosity.

ii) Aggregates of particles, or individual large particles, break up due to flow, thus allowing easy flow of the solids in the suspension.

iii) Interactions between fat and casein micelles are known to impart characteristic non-Newtonian behaviour (Campanella, verbal communication). Permanent deformation of the secondary bonds during the test period causes gradual decline in the viscosity of the material under test (Nawar, 1985).

Interpretation of the findings

The inferences drawn from the foregoing rheological results, which may hold true, from the practical point of view are;

i) the pseudoplastic nature of the skim milk suspensions suggest that the more vigorous the suspension is stirred (intensely mixed), and the faster it is

pumped through the pipelines, the less viscous it would become. This would positively influence the atomization process.

ii) technically, pseudoplasticity implies that for a given force or pressure the flow of the suspensions would not be consistent. Hence, a good feed flow controlling mechanism would be required to maintain a smoothly running process.

iii) pumping AMF through pipelines would be easily manageable at temperatures not exceeding 50°C. This is so because below 50°C the flow was Newtonian, and Newtonian liquids are easier to handle than their non-Newtonian counterparts (Campanella, personal communication)

4.2 Production of the Powders From the Suspensions.

4.2.1. Method

Whole-milk powders, containing 90 percent and 80 percent fat were prepared by spray chilling suspensions of milk fat and skim milk powder formulated as described in 4.1.1 above. The processing sequence was as follows: Milk fat was melted by immersing the container in hot water, then transferred into the mixing vessels where it was held at 50°C. Skim milk powder was dispersed, with constant stirring, into the molten fat to make slurries containing 10 percent and 20 percent total solids. Each suspension was pumped to the nozzle where it was atomised and crystallised at -5°C, using cold air as the chilling medium. The feed flow rate was fixed at 6 litres per hour, using the APV pump, while nozzle No 2 (table 3.1) was used for atomising. The pressure of the atomising air was maintained at 2 atmospheres. The powders formed were immediately stored at 5°C to await physical tests. The trials were done in batches of 3 kilograms, and only unmodified AMF was used. Following their production, the powders were examined under the microscope.

4.2.2 Results and Discussions

Although suspensions containing 30, 40 and 50 percent total solids were also prepared, they could not be processed into powder. Only slurries containing 10 and 20 percent solids could be run successfully through the spray chilling system. Beyond 20 percent solids, intermittent blockages of the nozzle and the pump were experienced. This outcome can be explained as follows; with solids content in excess of 20 percent, the milk fat started to become saturated with the powder such that the solids could not be suspended adequately any more. This resulted in rapid settling of a lot of the particles. That is, the rate at which the particles were separating from the fat in the conveying system was exceeding the rate at which the feed was atomised, and hence, the occurrence of non-uniform flow of the feed, which eventuated into blockage of the system. The difference in the densities of the suspension components contributed significantly to the separation of the mixture. Also, the

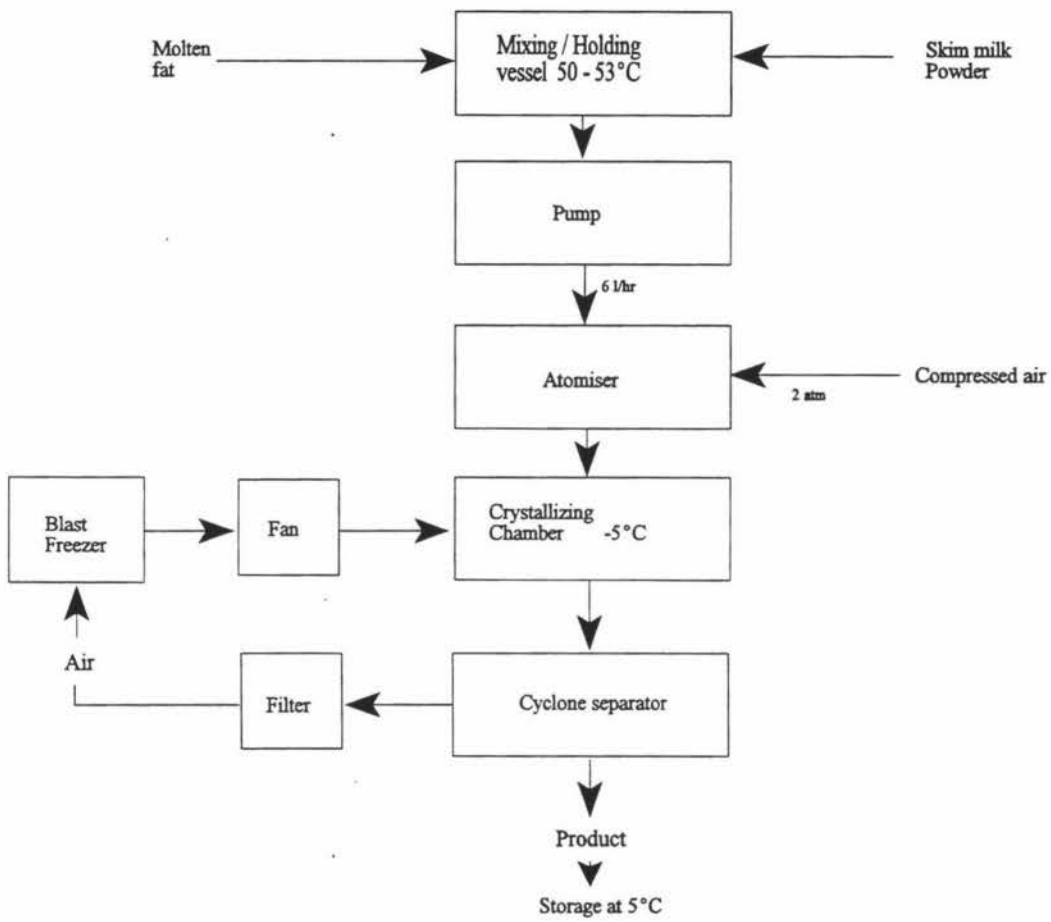


Fig. 4.3 Coated Milk Powder; Product and air passage through the spray crystallizer

rate at which the particles settled is known to be dependent on the size of the particles. Large particles settle faster than the smaller particles of the same material. Because of this separation, the suspensions had to be constantly agitated in the mixing vessels. Unfortunately, agitation can actively promote dissolution of undesirable quantities of oxygen in the liquid fat, and so this process appeared to be one of the potential setbacks for manufacturing fat powders from suspensions.

If mixtures containing more than 20 percent solids were to be spray chilled, a better suited feed line such as a screw type auger system, and a disc atomizer instead of a nozzle atomizer, could be adopted for the task.

The powders produced had well formed spherical particles which contained one or more skim milk particles coated entirely by a milk fat layer. The fat layer ranged in size from thick to thin, among the individual particles. No obvious distinctions could be made between the particles of the powders containing 10 percent skim milk and those containing 20 percent of the same. The general appearance of the particles produced from the suspension containing 10 percent solids was captured in fig. 4.4. Also, fig.4.5 displays the exposed skim milk particles, which formed the core of the coated particles, and the melted fat coat. Most of the particles are shown fused together. It is believed that this agglomeration process took place during storage of the powders, and at the time of microscopic examinations, and were caused by changes in temperature. It can be deduced from this micrograph that one likely advantage of these powders would be quick release of the free fat to the mixture in which the powder is applied. Generally, the powders produced were coarse, having a particle size range of 13.3μm - 220.0μm. For the powder containing 10 percent skim milk, a mean particle diameter of 68.9μm was recorded.

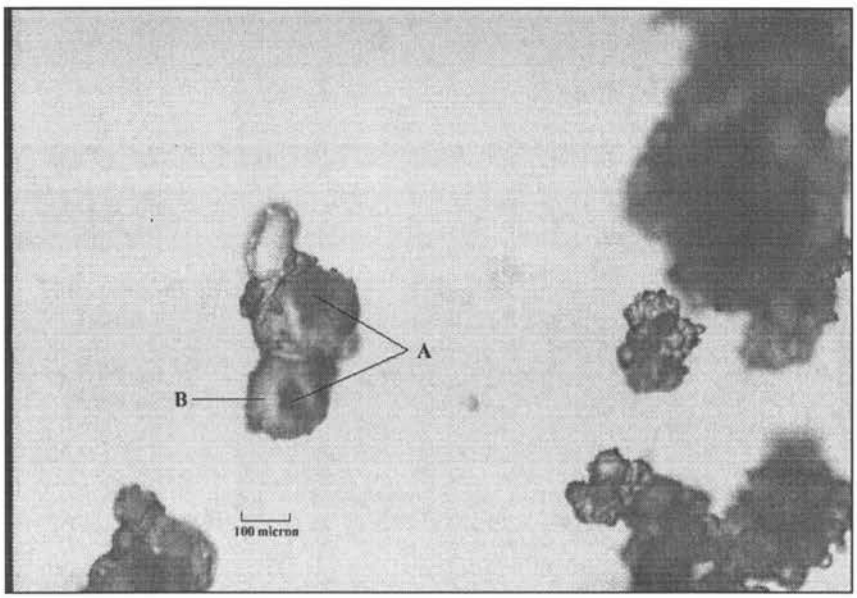


Fig. 4.4 Micrograph of whole milk powder produced from a suspension containing 10% powder. The darker centres (A) of the particles are the encapsulated skim milk particles. B = the fat coat. Magnification; x 40.

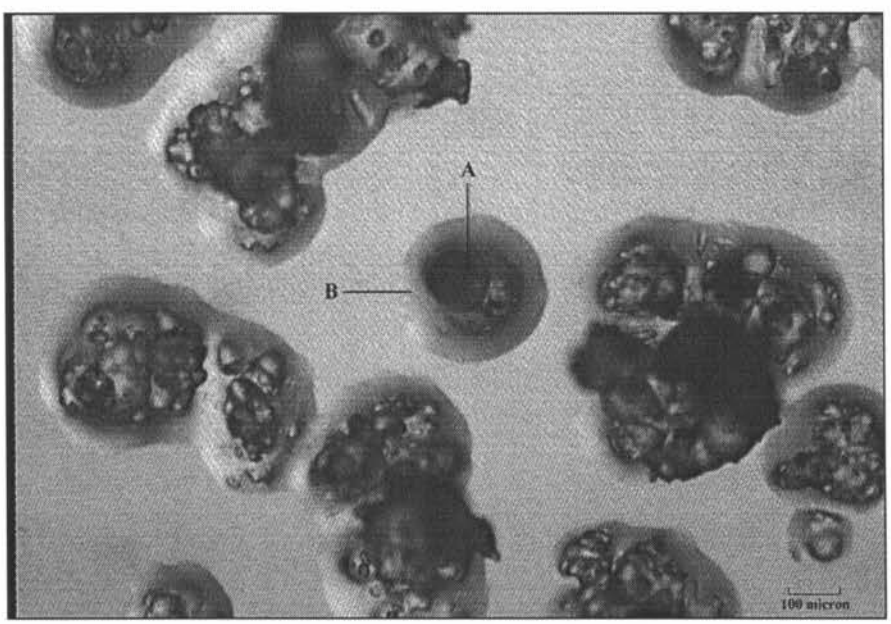


Fig. 4.5 Micrograph showing the melted powder particles. A = the exposed skim milk nuclei; B = melted fat coat. Magnification; x 40.

It was observed that these powders were susceptible to ambient temperatures, and because of this, their flowability could not be quantitatively determined. However, by visual inspection, the freshly prepared powder was very flowable, and remained flowable for up to five minutes at ambient temperatures (18°C - 23°C). After immediate storage at 5°C for at least one hour, the powders formed soft lumps but were still flowable. Factors which could be contributing to the formation of these lumps are discussed in chapter 5.

4.2.3 Conclusions

Whole milk powders containing up to 20 percent skim milk solids could be produced from liquid mixtures of milk fat and skim milk powder by spray chilling. Owing to their relatively thin particle fat-coat, the powders produced were sensitive to the room temperature.

At the solid content in excess of 20 percent the production process was too cumbersome, and in view of the problems encountered it was decided to abandon using milk fat and skim milk powder premixes, but instead, produce the fat powder from pure AMF, and mix it thereafter with the skim milk powder, to achieve the desired fat levels in the powder.

5 PRODUCTION OF POWDERED FATS USING PURE ANHYDROUS MILK FAT (AMF)

Liquid AMF was found to exhibit Newtonian characteristics at temperatures of up to 50°C. It was expected, therefore, that unlike the skim milk-AMF suspensions, the flow of AMF through the pumping system, and its subsequent atomisation, would be trouble free. Following this, powdered AMF was manufatured, using pure fat.

By using the same pure fat, the operating conditions for the crystallising process, viz, size of nozzle, feed flow rate, atomising gas pressure and crystallising temperature, were optimised for the modified standard laboratory spray drier. Also, the performance of three fat fractions, SBF23 (soft fraction), SBF27 (intermediate fration) and SBF42 (hard fraction), were investigated. According to the literature, one other factor which influences the physical properties of the powders produced by nebulising the feed is the feed holding temperature. However, in the light of the rheological properties reported earlier, it was deemed that varying the feed temperature, especially for most of the fat fractions, would not cause any significant variation in the physical characteristics of the powder. As a result, the feed temperature was varied for the SBF42 only. The latter seemed to change significantly over a narrow range of temperature change.

The dependent variables of interest for all the investigated parameters were the particles shapes and size distributions, flowability of the powder and its ability to dry blend with skim milk and calcium caseinate powders. Also, the physical stability of powdered fats at selected temperatures were examined.

Two chilling media, cold air and liquid nitrogen, and two atomising gases, compressed air and nitrogen, were tried.

5.1 Methods

5.1.1 Chilling with Cold Air

A weighed amount of fat, about 2.5 kg, was melted by immersing the fat container in hot water until the melt reached 50 - 55°C. The melt was then held at 50°C in a water-bath, at the same time being fed at a rate of 50ml per minute to the spray crystalliser. Compressed air was used to effect atomisation of the fat at a pressure of 2 atmospheres (Kg/cm^2). Cold air generated by the blast freezer at -30°C was circulated through the system at a fixed estimated mass flow rate of 95Kg per hour. This air contained 9.0 to 12.5 ppm of oxygen. The crystallising chamber temperature was regulated between -0.1°C and 2.8°C, with the cyclone temperature fluctuating between 1.4 and 4.5°C. The powder was recovered from the cyclone, and was stored at 5°C to await further processing. The spent air was recycled through the system.

5.1.2 Chilling with liquid nitrogen

Liquid nitrogen was used primarily to attain lower crystallising temperatures, and to protect the fat from the environmental oxygen. The two functions were possible because, firstly, nitrogen vapourises at about -196°C and was therefore expected to drop the chiller temperature well below zero, effecting rapid heat exchange between the liquid droplets and the gaseous medium. Secondly, the gas is inert and odourless, hence, it could not impart any foreign odours or cause any chemical reaction which could modify the fat. The equipment layout depicted in figure 3.2 was used.

The production process was carried as follows; The fat was melted by immersing the 25 liter drum, containing the same, in hot water for 2 to 2½ hours, shaking the drum at intervals to stirr. After melting, the fat was weighed by difference into the holding vessels, in the water bath. The water bath was previously stabilised, and constantly maintained,

at 50°C. Batches ranging in size from 2 kilograms to 6 kilograms were processed at a time. For every run intended for oxidation studies, a new unopened drum of AMF was used. To minimise contact with air, the holding vessels were covered with perspex lids, complemented with a film of aluminium foil to exclude light. In addition, nitrogen gas was blown over the surface of the molten fat under low pressure. The heat was uniformly distributed within the fat by stirring for half a minute at 10 minute intervals, revolving the agitator at five revs per minute. The oxygen content of the fat was determined immediately before spray crystallizing.

The crystallising chamber was prepared by first purging with gaseous nitrogen (through the atomiser), while the system was running, until the oxygen meter recorded 1.5 - 3.5 ppm. Liquid nitrogen was then started, and as soon as the desired crystallising temperature was reached the feed line was started. Atomisation was effected with gaseous nitrogen. The powder produced was immediately stored in the dark at 5°C. Different fat fractions were tried, and the exact processing conditions for each particular fraction are given in table 5.1.

The chilling temperature was regulated by manually controlling the flow rate of the liquid nitrogen to the chamber. This arrangement made it difficult to accurately maintain a steady fixed-point temperature. Owing to this, temperature ranges (refer to table 5.1) with five units intervals were chosen.

The optimum processing conditions for the crystallising chamber were determined by trying several different combinations of the operating variables, using the unmodified fat and the SBF42. The two fats were chosen for their ease of handling. The experimental combinations are furnished in tables 5.2 and 5.3 for the unmodified fat and SBF42 respectively. Each run yielded 500 g to 1 Kg of powder, which was used for microscopic observations and other physical tests. For the most successful runs, up to 4 kg of powder was processed, and was used for storage and dry blending trials. The other fat fractions were processed using the determined optimum conditions.

The amount of liquid nitrogen spent per kilogram of fat was estimated from the amount of nitrogen spent per run, which also included the initial amount of nitrogen required to cool the crystallising chamber to the necessary chilling temperature.

Table 5.1 **The Processing conditions used for crystallising the different fat fractions used for the trials.**

Processing Conditions	Milk Fat Fraction			
	Unmodified AMF	SBF42	SBF27	SBF23
Feed Temperature	50°C	50°C 35°C	50°C	50°C
Feed Flow Rate	6 litres/hr 12 litres/hr	6 litres/hr 12 litres/hr	6 litres/hr -	6 litres/hr -
Atomising pressure	1 atm (1.013 bar) 2 atm (2.026 bar)	1 atm 2 atm	2 atm	2 atm
Crystallising temperature	-5 to 0°C -15 to -10°C	-5 to 0°C -15 to -10°C	-15 to -10°C	-15 to -10°C
Atomiser (nozzle)*	#1 #2 #3	#2 #3	#3	#3

* Descriptions are in table 3.1

Table 5.2 Combinations of the Processing Conditions for the Unmodified Fat.

Experiment No	Feed flow rate	Atomising pressure	Crystallising temperature	Nozzle
1	+	-	c	1
2	+	-	c	1
3	+	- -	c	1
4	+	- -	c	1
5	+	-	c	2
6	+	-	c	2
7	+	- -	c	2
8	+	- -	c	2
9	+	-	c	3
10	+	-	c	3
11	+	- -	c	3
12	+	- -	c	3
13	++	-	cc	1
14	++	-	cc	1
15	++	- -	cc	1
16	++	- -	cc	1
17	++	-	cc	2
18	++	-	cc	2
19	++	- -	cc	2
20	++	- -	cc	2
21	++	-	cc	3
22	++	-	cc	3
23	++	- -	cc	3
24	++	- -	cc	3

+ = 6 l/hr - = 1 atm c = -5 to 0°C

++ = 12 l/hr - - = 2 atm cc = -15 to -10°C

1, 2, 3 = nozzles, as described in table 3.1

Table 5.3 Combinations of the Processing Conditions for the SBF42 (hard fraction).

Experiment No	Feed temperature	Feed flow rate	Atomising pressure	Crystallising temperature	Nozzle
1	*	+	-	c	2
2	*	+	-	cc	2
3	*	+	- -	c	2
4	*	+	- -	cc	2
5	*	+	-	c	3
6	*	+	-	cc	3
7	*	+	- -	c	3
8	*	+	- -	cc	3
9	*	++	-	c	2
10	*	++	-	cc	2
11	*	++	- -	c	2
12	*	++	- -	cc	2
13	*	++	-	c	3
14	*	++	-	cc	3
15	*	++	- -	c	3
16	*	++	- -	cc	3
17	**	++	-	c	2
18	**	++	-	cc	2
19	**	++	- -	c	2
20	**	++	- -	cc	2

+ = 6 l/hr - = 1 atm c = -5 to 0°C * = 50°C

++ = 12 l/hr - - = 2 atm cc = -15 to -10°C ** = 35°C

2, 3 nozzles, as described in table 3.1

5.2 Results and Discussions

5.2.1. The physical appearance of the powders

Generally, fresh powders produced at the temperature range of 0°C to -5°C were sticky and slightly resistant to flow. These appeared 'wet', and were intensely yellow in colour. Even varying all the other parameters within the defined limits did not produce any positive impact. This observation was more pronounced for the SBF23 (soft fraction), which did not produce a flowable powder at all. Based on these observations, it may be concluded that the particles were not fully solidified.

On the other hand, free flowing powders were archieved by chilling at temperatures below -10°C. However, these powders formed soft lumps upon storage at 5°C. A collection of explanations may be advanced for this outcome. These are;

i) It is known that rapid cooling of fat causes the formation of weak unstable α-polymorphic fat crystals (Nawar,1985). Therefore, since the fat was shock crystallised, it was expected that the α-polymorphs would be present in numerous quantities. Because the powder exiting the chilling system was immediately exposed to the ambient temperature, some of the small unstable particles may have melted immediately, with their liquid fat binding the other particles, hence forming the lumps.

ii) When the powders were stored at 5°C, their particles transformed through a series of polymorphic stages, to acquire the most stable β-form. These transitions are usually accompanied by energy changes which involve generation of some heat (Lamb, 1987). It is therefore suspected that the heat evolved was sufficient to soften the weaker fat particles, enabling them to agglomerate to their neighbours, before resolidifying.

Samples of the unmodified AMF and SBF42 powders are displayed in figure 5.1. These

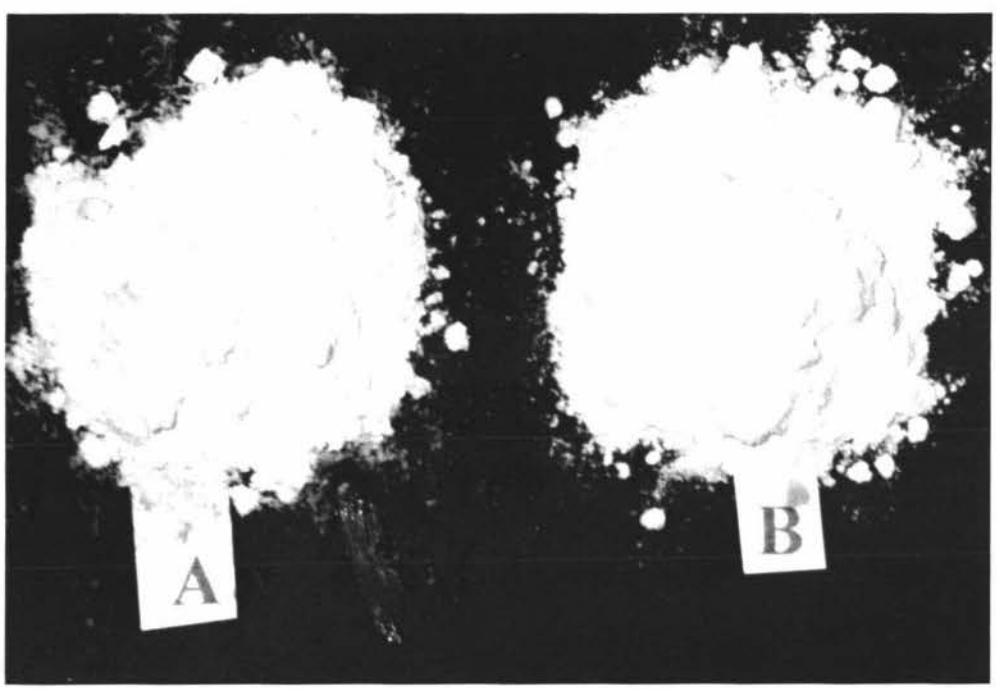


Fig. 5.1 The appearance of the powdered fats after standing for five minutes at ambient temperature; A = Unmodified AMF; B = SBF42 (Hard Fraction).

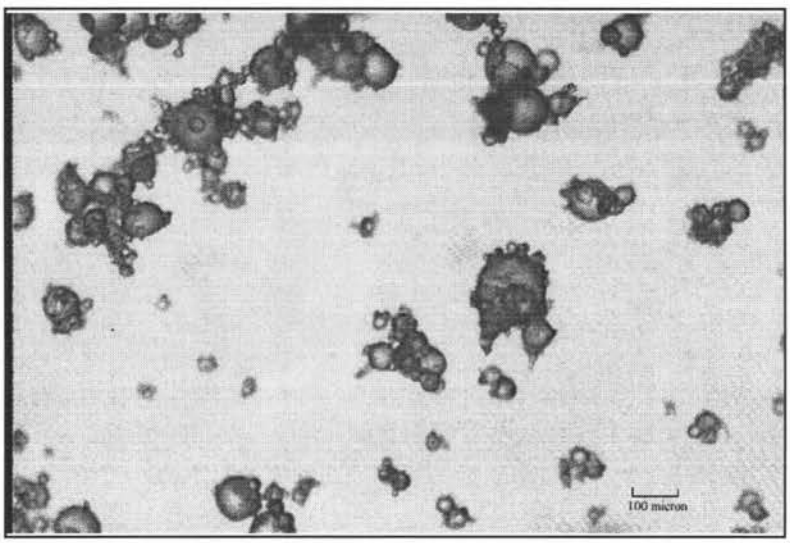


Fig. 5.2 The micrograph of the hard fraction (SBF42) powder produced using a large nozzle (nozzle #2), feed flow rate of 12 l/hr, atomising pressure of 1atm and a crystallising temperature of -15 to -10°C. Mag; x10.

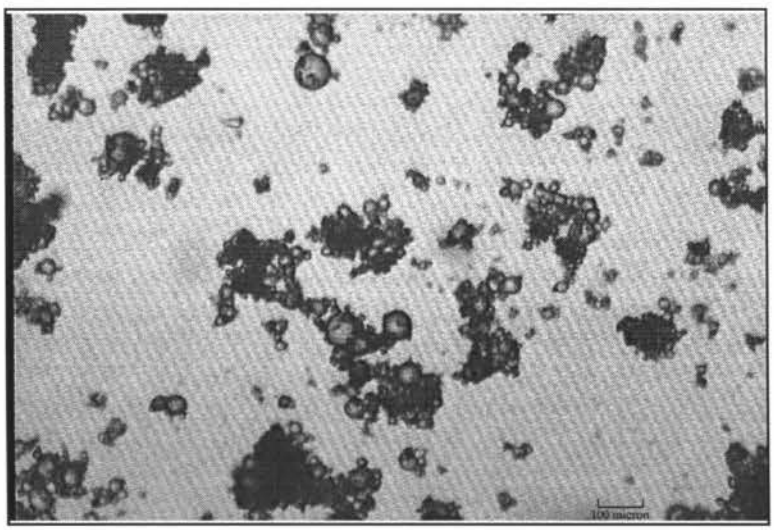


Fig. 5.3 Micrograph of the hard fraction powder produced using a medium size nozzle (nozzle #3), an atomising gas pressure of 1 atm, and a feed flow rate of 12 l/hr. Mag; x10

were produced using the following conditions; -15 to -10°C for chilling, an atomising pressure of 2 atmospheres, a feed flow rate of 12 litres per hour, and nozzle number 3.

Unlike the powders produced using the higher chilling temperature, the powders manufactured using -15 to -10°C were pale yellow, with the SBF23 and SBF27 being more yellowish than the AMF. In comparison, the SBF42 powders were almost white. This variation in colour was associated with the concentration of the carotene, because it is known that during fractionation of the fat more carotene is retained in the softer fractions than in the harder fractions (Boudreau *et al*, 1991). Microscopic examinations of the powders revealed well solidified spherical particles, the majority of which were agglomerated. These are depicted in figures 5.2 and 5.3.

5.2.2 The Influence of the Operating Variables on the Particle Size Distribution

To illucidate the shapes and the size distributions of the particles the hard fraction powders were used. Powders produced from the other fractions were not stable enough, under the test conditions, to allow adequate sampling of the particles. The following observations were made.

The frequency curves of the particles' diameters were skewed in shape, reflecting the presence of numerous small particles in the distribution (see figure 5.4). The resultant skewed shape may be considered indicative of a high degree of homogeniety of the particles. These distributions are numerically presented in table 5.4.

The effect of the atomising gas pressure

Varying the atomising pressure was in essence varying the gas to feed flow ratio at the nozzle head. In other words, this was changing the atomising energy. Increasing the gas pressure decreased the particle sizes. For example, with the other variables kept constant, changing the pressure from 1 atmospheres to 2 atmospheres changed the mean diameter (measured as the median diameter, Dm) from 24.44μm to 18.89μm, using a medium size

nozzle. Similarly, a decrease from 28.89μm to 26.67μm resulted when a larger nozzle was used. This transformation is graphically demostrated in figure 5.4.

Table 5.4: The Particle Size Distributions of the SBF42 Powders.

Processing conditions	Median(Dm)(μm)	Q1	Q3	Dmax	Dmin
medium nozzle(#3); 1atm; -15 to -10°C, 12l/hr; 50°C	24.44	15.56	28.89	60.00	8.89
medium nozzle; 2 atm; -15 to-10°C; 12l/hr; 50°C	18.89	13.33	25.00	202.22	8.89
medium nozzle; 2 atm; -15 to-10°C; 12 l/hr; 35°C	28.89	20.00	46.67	157.78	15.56
large nozzle(#2); 1atm, -15 to -10°C, 6l/hr; 50°C	28.89	20.00	40.00	204.44	4.44
large nozzle; 2 atm, -15 to -10°C, 6l/hr; 50°C	26.67	20.00	35.56	191.11	15.56
large nozzle; 2 atm, -15 to -10°C, 12l/hr; 50°C	25.56	17.78	35.56	153.33	8.89
large nozzle; 1 atm, -5°C to 0°C, 12l/hr; 50°C	22.22	17.78	42.22	215.56	8.89
large nozzle; 1 atm, -15°C to -10°C 12l/hr; 50°C	22.22	17.78	40.00	146.67	8.89
calcium caseinate	20.00	9.44	30.56	64.44	4.44
Skim milk powder	52.12	34.27	91.33	464.49	4.44

Dm = diameter below which 50 percent of the particles fall
Q1 = first quartile diameter (25% of the particles below)
Q3 = third quartile diameter (75% of the particles)
Dmax = maximum diameter
Dmin = minimum diameter

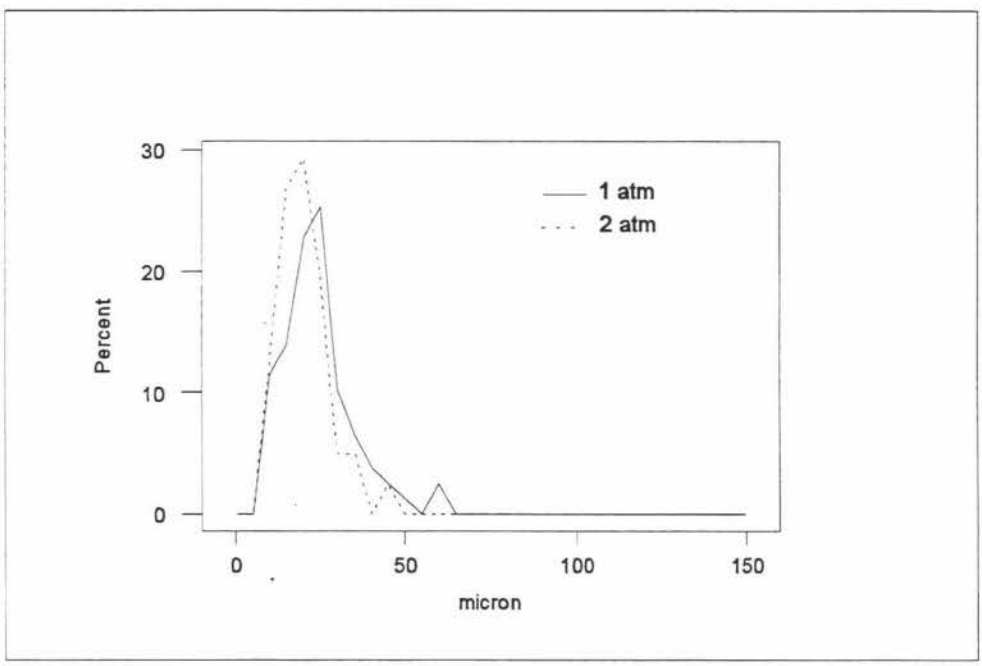


Fig. 5.4 The Particle Size Distribution of the SBF42 Powder. Chamber temperature = -15 to -10°C; feed flow rate = 12 l/hr; nozzle #3.

It is apparent from these results that the ability to change the particle size distribution by varying the atomising gas pressure provides a useful tool for modelling the process conditions to achieve particular powder characteristics. Using this tool, powders with particles ranging in size from fine to coarse may be tailored for specific purposes. There is, however, a limit for manipulating the atomising conditions. Masters (1991), commented that the ratio of the gas flow to the feed flow can be varied within the range of 0.1 to 10.0, to acheive different particle distributions. Outside this range, atomisation ceases to be effective in varying the size distribution.

Perhaps it should also be noted here that while the two fluid nozzles seem to offer the advantage of flexibility in varying the size distribution of the particles, they simultaneously run the risk of occluding gas in the particles (Masters, 1991). This could be a problem if the atomising gas is not strictly oxygen-free. The oxygen occluded would facilitate oxidation of the powder.

The effect of the nozzle orifice

The particle size distribution decreased with the decreasing nozzle orifice. Powders poduced using the large nozzle gave a mean size of 25.56 μm, while the medium size nozzle reduced the size to 18.89 μm. The influence of the small nozzle could not be assessed because it repeatedly blocked when the hard fraction was processed, and hence, the trials were abondoned. Despite this, the unmodified powders produced using the same nozzle looked very fine. In fact, during the trials, most of the powder was recovered from the filter, perhaps indicating that a lot of the particles were too fine to be separated in the cyclone.

The effect of the feed temperature

Holding the liquid hard fraction (SBF42) at 35°C gave a mean particle size of 28.89μm, as opposed to 18.89μm when the feed temperature was 50°C. The holding temperature directly affected the viscosity of the feed. At 35°C the hard fraction had started crystallizing and had become highly viscous, whereas at 50°C the liquid had a lower viscosity. When highly viscous materials are atomised, they give large spray droplets (Kessler, 1989;

Masters, 1991).

The effect of the crystallising temperature

It was found that the lower the temperature in the crystallizing chamber, the more solidified the particles were. The reverse was true when higher chilling temperatures were used, and moreover, a lot of the particles stuck to the walls of the chilling chamber. Beside the incomplete solidification, the crystallising temperature did not seem to have any influence on the mean particle size, which was 22.22 μm for the two chilling temperatures tried. However, there was a variation in the overall particle size range. A range of 8.89μm to 215.56μm was recorded for 0 to -5°C, while a range of 8.89 to 146.67μm was noted for -15 to -10°C. This trend may be attributed to agglomeration of the particles when a higher chilling temperature was used. That is, the particles managed to stick together while they were in a spray form, before they solidified.

Interactions of the operating variables

The crystallizing temperature of -15 to -10°C, the atomising gas pressure of 2 atmospheres, and the feed flow rate of 12 l/hr seemed to produce good powders of the unmodified AMF and the SBF42, using the medium size and the large nozzles. Reducing the atomising gas pressure to 1 atm, using the large nozzle seemed to produce less solidified particles. For the softer fractions, SBF23 and SBF27, it appeared the best processing conditions were 2 atm, -15 to -10°C and 6 l/hr, using the medium sized nozzle.

In view of the effects discussed above, it seems logical to assume that the exact optimum operating conditions for the spray chilling process can be fine tuned for a particular crystallising vessel, and for a specific fat composition, by careful manipulation of the four operating factors detailed above.

5.2.3. The Physical Stability of the Powders

It came as no surprise that the powders produced from the different fat fractions displayed varying degrees of sensitivity to temperature. All the powders were satisfactorily stable at 5°C. When exposed to ambient temperature (20-23°C), varying degrees of tolerances were

noticed. The SBF23 and SBF27 started melting as early as five minutes after exposure. The unmodified AMF became cohesive ten minutes following the onset of exposure. On the other hand, the SBF42 managed to stay flowable for up to 15 minutes, before becoming prominently cohesive. Teo (1993) perfomed similar stability tests on powdered fats and concluded that the FFMR and hard fraction powders remained unchanged at 9°C and 15°C even after one hour of exposure. All the powders he studied were sticky after one hour at 20°C. It seemed sensitivity of the powders to temperature was also dependent on the size of the powder particles. Powders produced using the fine nozzle were found to be much more sensitive than the powders from other nozzles. This difference is believed to be related to the differences in the surface area to volume ratios of the particles. The smaller particles from the fine nozzle had a larger surface area to volume ratio, and as such, heat transfer to the interior of the particles was faster. The reverse was probably true for the particles produced using the other nozzles. What these findings imply is that in order to preserve the powdery structure of the these fat products, it would be necessary to condition the mixing, packaging and storage rooms, so as to achieve suitable processing environments.

No compressive studies were performed on the powdered fats, but it may be deduced from the observations of the vacuum packed powders in section 7.4.2 that these powders are easily compressed. A vacuum packing pressure of 700 mbars compacted the powder of FFMR into a hard solid mass. Consequently, rigidly constructed packaging units may be neccessary if hard lumping of the powders during storage is to be avoided.

5.2.4. The Improvement of the powders' physical stability through polymorphism

An attempt was made to improve the stability of the powders at ambient temperatures by manipulating the structural formations of the triglycerides crystals during crystallization. That is, it was attempted to take advantage of the ability of milk fat to exist in more than one structural forms, a phenomenon termed polymorphism, to produce the most stable powders. The objective was based on the crystal transformations diagramatically represented in figure 5.5.

As the figure shows, three principal polymorphic forms, α, β´ and β, are known to exist in milk fat (Nawar, 1985; Wilbey, 1991). Rapid cooling of liquid AMF gives rise to the simplest and least stable α-polymorph. When the formed α-form is heated to its melting point, rapid transformation to the more stable β´ form, and subsequently to the most stable and closely packed β-polymorph, occurs (Nawar,1985). It is also known that further cooling of α-polymorph causes tight packing of the triglyceride chains, and a gradual transition into the β-form.

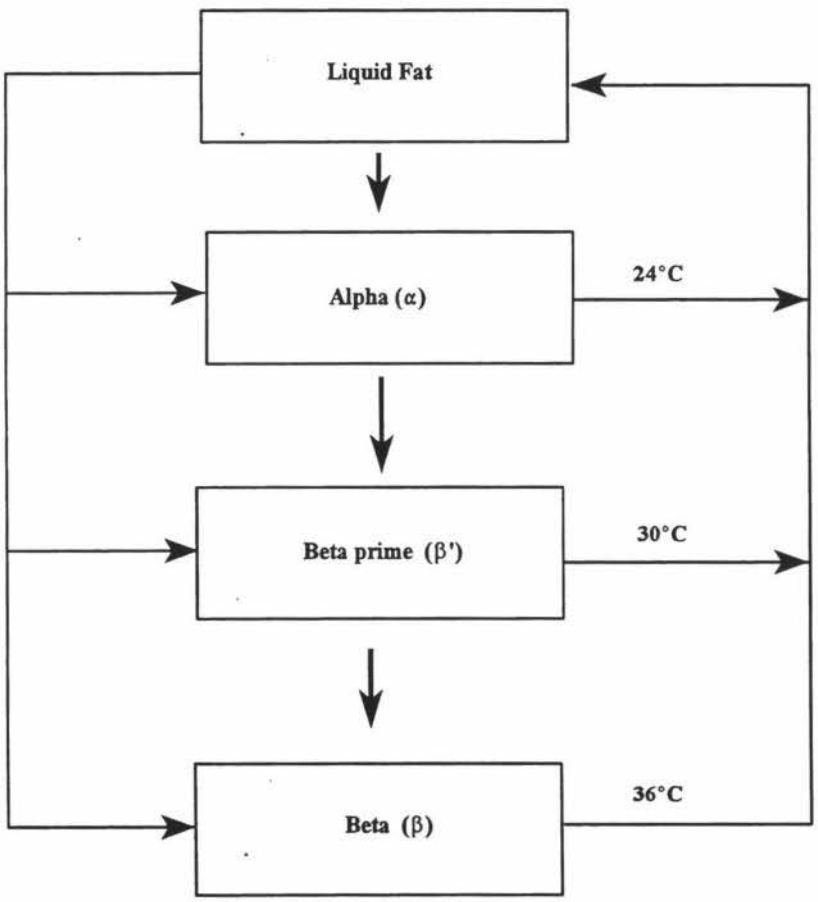


Fig. 5.5 Polymorphism in Milk Fat; This refers to the packing of the triglycerides molecules in the solid state. The temperatures represent the final melting points of the crystals.

Cooling rates tried; 42°C/hr (fast cooling) and 19°C/hr (slow cooling)

The stabilization of the powders by the polymorphic phenomenon was not deeply investigated, but a few trials for seeding β' crystals in the melt before spray chilling, were executed. These involved cooling the melt at the rates of 19°C/hr and 42°C/hr, to about 23°C, and holding the melt at this temperature for ten minutes. The temperature was then raised to 28°C and held for fifteen minutes, which was the time required for transforming α to β' (Wilbey, 1991). The melt, containing the nuclei, was then spray chilled using the large nozzle (nozzle 2).

When observed under the microscope, the particles of the powders from this process were found to have clusters of nuclei in the centre and softer fat on the outside (see figure 5.6). This was interpreted to be indicative of not rapid enough cooling rates of the melt. Slow cooling allows preferential crystallization of the high melting triglycerides, such that the crystals would have high melting triglycerides forming the core and low melting triglycerides depositing on the outside (Wilbey, 1991). This is not desirable if more stable powders are required.

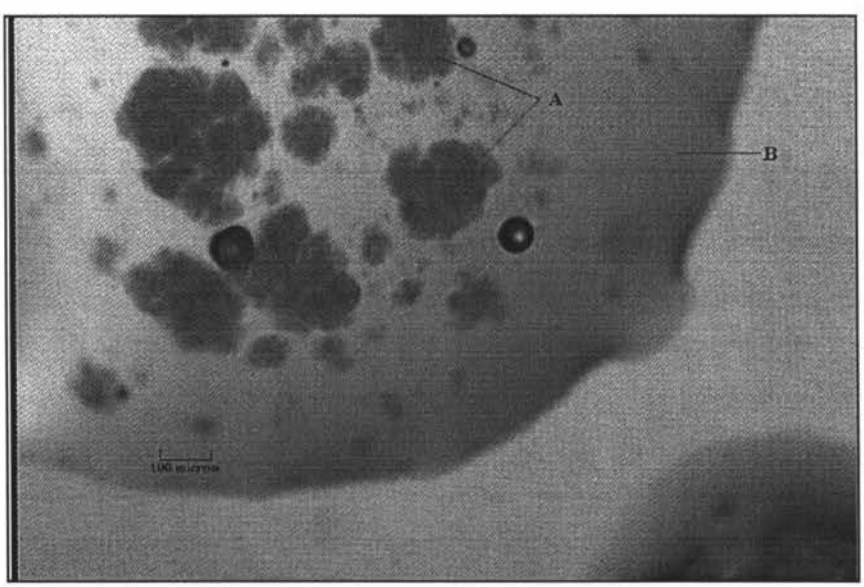


Fig. 5.6 The melted particles of AMF powder which was pre-seeded for β' crystals at a cooling rate of 42°C/hr. A = the high melting triglycerides which formed the core of the particles; B = the low melting triglycerides. Mag; x100.

It was also noted that the powders manufactured from the seeded melts were very coarse and seemed to be more sensitive to temperature than the non-seeded powders. The coarseness was attributed to the formed clusters of the nuclei in the particles, while the temperature sensitivity was related to the low melting glycerides deposited on the outer regions of the particles.

5.2.5 Nitrogen Usage

Figure 5.7 relates the amount of liquid nitrogen used in each run to the crystallising and the cyclone temperatures. The figure summarises the results of three runs for AMF processing. Each run was based on about 6 kilograms of liquid fat, originally held at 50°C. The atomising gas pressure was fixed at 2 atmospheres, and the crystallising temperature regulated at -15°C to -10°C. The feed flow rate was maintained at 12 litres per hour, and a medium size nozzle was used for atomising.

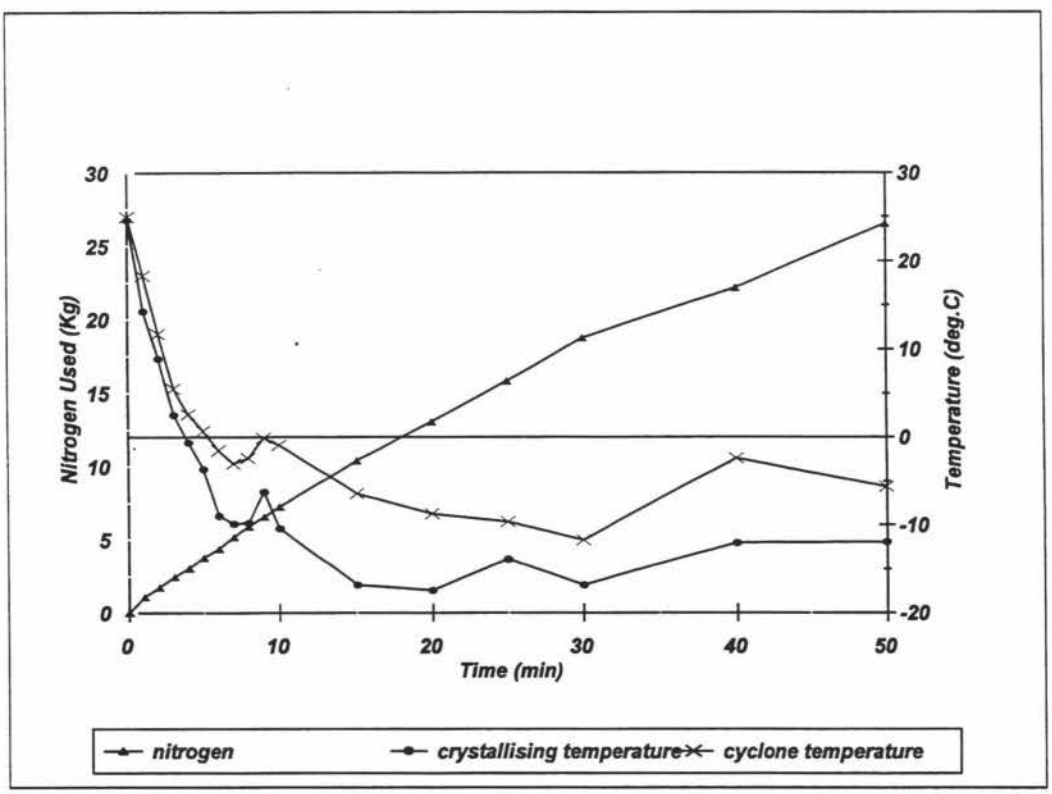


Fig. 5.7 Nitrogen usage versus the crystallising and the cyclone temperatures

On average, 3.84 ± 1.09 kilograms of liquid nitrogen was used to yield one kilogram of AMF powder. This figure did not compare favourably with the calculated theoretical value of 2.3 kilogrames nitrogen per kilogram of fat (see appendix 1). Coincidentally, the British Oxygen Company (BOC) has just released a specially designed spray crystalliser which is claimed to use 1 kilogram of nitrogen for every kilogram of the fat powder (BOC Gases, 1995). The explanation for the descrepency in the nitrogen consumption by the two crystallizers undoubtfully lies in the different structural designs of the crystallizers. It was evident that for the converted spray drier used in this project there were a lot of weak points in the design for heat gain, which contributed to excessive nitrogen usage. The presence of the motor fan, which generated some heat, and the large amount of nitrogen originally required to cool the vessel to the required temperatures are a few examples of the shortfalls of this crystallizer. It is believed that on large scale production the amount of nitrogen lost due to heat gain would be infinitely small, and hence, the quantity of nitrogen required per 1 kilogram of fat would be significantly reduced.

5.2.6 Conclusions

Powdered AMF can be manufactured by spray-chilling of the liquid fat. The physical properties of the powder can be varied by careful control of the operating parameters, notably, the atomising gas pressure, the size of the atomizer, and the feed flow rate. At the feed flow rates of 6 l/hr and above, it is ideal to atomise at 2 atmospheres and crystallize at below -10°C. A particle size range of 4.44 to 215.56 μm, and a mean particle size ranging from 18.89 to 28.89μm were achieved using the pneumatic nozzles described.

The very fine powders were very unstable at room temperature, while the powders produced using the nozzles of apertures of 1.0 mm and 1.5 mm were fairly stable. Exposing the powders to ambient temperature for over five minutes made the powders cohesive. The hard fraction powders were less cohesive than the rest of the fractions. All the powders were physically stable at 5°C.

About 3.84 kilograms of nitrogen was required to crystallise one kilogram of fat.

6 THE DRY-BLENDING QUALITIES OF THE POWDERED FATS AND SOME PHYSICAL PROPERTIES OF THE BLENDS PRODUCED

The blending of substances in powder form is the most efficient, convenient and often easiest of most mixing operations. Moreover, it is perhaps the most hygienic. The success of blending powders depends primarily on the physical properties of the powders mixed. Such physical properties have been reviewed by Schubert (1987) and Peleg (1978). Several methods for evaluating the same are extensively outlined by Peleg (1978).

Of interest in this work was the ability of the powdered fats to blend with other dry non-fatty powders, notably, skim milk powder and calcium caseinate. It was also desired to evaluate the physical properties of the produced blends, particularly their flowability and bulk density.

A knowledge of the flow properties of the powders is essential for the design and specification of conveying and metering equipment (Tuohy, 1989). Likewise, the bulk density of a powder is important for the sizing of storage silos, powder handling equipment and packaging (Peleg, 1978).

6.1. Procedure

The powdered fat previously stored at 5°C was weighed and blended with skim milk powder and calcium caseinate to yield blends containing 10 to 70 percent fat powder. In the preliminary trials the effect of storing all the powders at 5°C before mixing was investigated. All the mixings were performed at room temperature. Immediately after production, the flowability and the bulk density of the powders were determined.

6.2. Results and Discussions

Mixing qualities

Big differences in the ability of the skim milk and calcium caseinate powders to support high quantities of fat are apparent from table 6.1. A maximum of 30 percent fat content could be achieved when AMF and SBF23 were mixed with skim milk powder. Furthermore, 50 percent of the fat was successfully blended when SBF42 was the substitute. Beyond these limits the blends compacted into solid lumps. Incidentally, mixing the powders previously stored at 5°C did not improve the situation as was anticipated. For the calcium caseinate, comparatively higher amounts of fat could be blended. A maximum of 70 percent fat content was achievable with SBF42 and AMF, and a relatively lesser value of 60 percent was attained using SBF23.

The observed discrepancies in the fat loads of the blends may be attributed to the differences in the particle sizes of the skim milk and calcium caseinate powders. The calcium caseinate having smaller particles was able to coat around the fat powder particles, and in so doing, providing a lubricative effect which allowed smooth slipping of the blend particles against each other. As a result there was minimum friction between the particles, and hence, less agglomeration of the fatty particles. It is believed that this coating effect by the caseinate accounted for the incorporation of higher fat quantities. In contrast, the skim milk powder which had larger particles could have promoted friction between the particles, causing heightened agglomeration of the fat particles, and consequently, the compaction of the blended powder. Beside the effect of the particle sizes, it is highly probable that mixing the powders at room temperature may have resulted in the melting of some fat, which then deteriorated the mixing process. It should be noted that it was deliberately designed to mix the powders at room temperature to fully explore the viability of such an arrangement for the powdered fats manufactured. Otherwise, it is surmised that cold mixing of the powders would reasonably improve this blending process.

Table 6.1. The angle of repose of the blended powders

Powder	Type of fat	Mean values for the blends containing fat content of													
		10%	SD	20%	SD	30%	SD	40%	SD	50%	SD	60%	SD	70%	SD
Skim milk	AMF	34.27°	2.33	39.59°	2.59	46.48°	0.53	-	-	-	-	-	-	-	-
	SBF42	29.27°	1.78	37.24°	2.5	45.18°	0.66	41.50°	2.01	45.33°	1.01	-	-	-	-
	SBF23	28.94°	1.81	42.97°	2.79	43.23°	0.00	-	-	-	-	-	-	-	-
Calcium caseinate	AMF	51.97°	2.19	51.02°	1.96	49.62°	2.05	46.46°	1.29	45.28°	0.96	42.95°	0.81	43.80°	1.97
	SBF42	52.17°	1.49	50.18°	2.75	48.39°	1.03	47.24°	0.39	46.57°	0.48	43.94°	2.41	46.52°	0.78
	SBF23	52.51°	1.27	50.69°	0.77	49.51°	2.25	45.93°	2.14	46.28°	0.81	44.49°	1.79	-	-

SD = standard deviation

Calcium caseinate: 52.64° ± 1.83

Skim milk powder: 21.56° ± 1.72

Commercial spray dried high fat powders; Naturlok vegefat 80 powder (78% fat): 26.49° ± 3.25

Cano (53% fat): 36.68° ± 3.67

Table 6.2. The bulk density, measured as poured density, of the blends

Powder	Type of fat	Mean values for the blends containing the fat content of													
		10%	SD	20%	SD	30%	SD	40%	SD	50%	SD	60%	SD	70%	SD
Skim milk	AMF	0.433	0.015	0.313	0.015	0.279	0.008	-	-	-	-	-	-	-	-
	SBF42	0.457	0.003	0.371	0.008	0.308	0.011	0.282	0.001	0.287	0.004	0.280	0.007	-	-
	SBF23	0.434	0.001	0.331	0.009	0.265	0.001	-	-	-	-	-	-	-	-
Calcium caseinate	AMF	0.234	0.005	0.247	0.003	0.253	0.009	0.258	0.004	0.269	0.003	0.278	0.001	-	-
	SBF42	0.209	0.004	0.213	0.001	0.218	0.002	0.184	0.002	0.229	0.001	0.206	0.002	0.218	0.002
	SBF23	0.217	0.002	0.232	0.003	0.239	0.008	0.247	0.003	0.251	0.005	-	-	-	-

SD = Standard deviation

Calcium caseinate: 0.215 ± 0.003 g/cm^3

Skim milk powder: 0.453 ± 0.009 g/cm^3

Angle of repose

The angle of repose is commonly quoted as an index of flowability of the powder. The lower the angle, the more flowable the powder (Peleg, 1978; Tuohy, 1989). Considerable variations in the angle of repose between the blends are evident from table 6.1. Generally, increasing the fat content in skim milk caused an increase in the angle of repose, reflecting gradual loss of flowability. Overall, angles ranging from 29.27° to 46.48° were recorded for skim milk blends, with correspondingly lesser angles obtained when SBF42 was used than when SBF23 and unmodified AMF were substitutes. The loss in flowability may be linked to the increasing bridging effect caused by the friction-generated viscous liquid fat (Peleg, 1978) between the particles. As was expected, the angles of repose reported here for the skim milk blends exceed those determined for skim milk powder (21.56°) and the commercial spray dried high fat powders (26.49° for N. vegefat and 36.68° for Cano). This variation could be associated with, among other factors, the shapes and the size distribution of the particles. It is known that the more uniform a mass of particles is in size and shape, the more flowable it is likely to be (Tuohy, 1989). Based on this argument, it is believed that irregular shapes and sizes, which emanated from non-ordered agglomeration of the fat and skim milk particles, were prevalent in the skim milk - fat blends, and that these irregular particles caused the observed minimised flow of the blends. The reverse was true for the skim milk and the other commercial high fat powders. The results obtained for skim milk powder here were lower than those reported by Sjollema (1963) and Tuohy (1989). The two reported 53 - 65° and 33 - 38° respectively. However, these results were obtained under different experimental conditions, and so may not be compared directly.

Unlike for skim milk powder, increasing the amount of the powdered fat in the calcium caseinate blends produced a drop in the angle of repose. Angles ranging from 42.95° to 52.51° were recorded, and practically, these blends did not flow as well as the skim milk blends. Surprisingly, there was no significant difference between the repose angles for the blends of SBF42 and those of the softer fractions. The repose angle of the calcium caseinate alone was 52.64°, which was in agreement with the observed resistance to flow of the powder. The limited flow characteristics of the calcium caseinate and its blends

may be linked to the highly probable chemical interactions between the particle surfaces. Such chemical interactions are often significant in very fine powders (Peleg, 1978), a class under which calcium caseinate may be categorized.

An angle of repose of 41 to 45° has been cited by some workers as a cut-off point for the flowability of powders (Tuohy, 1989). However, because the repose angle varies significantly depending on the test method used (Peleg, 1978), it would be inappropriate to directly adopt the cited angle as a reference mark for the work discussed here. Nonetheless, Peleg (1978) advised that irrespective of the test method, as a rule of thumb, powders which have an angle of repose of less than 40° are free flowing, and that those exhibiting repose angles of 50° and above are likely to cause flow problems. Therefore, based on the latter, it follows that the calcium caseinate mixtures and the skim milk blend with 30 percent fat were not free flowing. Because of this, a carefully designed conveying and discharging system which could aid the flow of these powders would be necessary in a production line.

Bulk density

Contrasting trends for the bulk densities of the skim milk and calcium caseinate blends are also overt from the results. As table 6.2 displays, the bulk density of the skim milk blends decreased with the increasing fat content. In contrast, bulk densities of the calcium caseinate blends increased with the increasing fat content. Bulk densities ranging from 0.265 to 0.457 g/cm^3 were recorded for the skim milk mixtures, with higher values observed for the SBF42 blends. The least densities were noted for the SBF23 blends. The bulk density of the skim milk alone was 0.453g/cm^3, which was comparable to the values reported by Tuohy and Fowler (1984) of 0.42 to 0.45g/cm^3. Values obtained for calcium caseinate blends ranged from 0.206 to 0.278 g/cm^3, while a value of 0.215 g/cm^3 was recorded for calcium caseinate.

Explanations for the observed trends may be based on the bulk densities of the individual components of the mixtures. As more and more light-weight fat replaced the relatively dense skim milk powder, a net decrease in the bulk density of the mixture resulted. For

the calcium caseinate mixtures, the fat was more dense than the calcium caseinate, and as a result the increasing amount of fat caused a net increase in the net weight of the blends.

6.3 Conclusions

The hard fat fraction powder mixed better with other powders than the softer fat fractions. A maximum of 30 percent unmodified AMF and the soft fraction were blended with skim milk powder. For the hard fraction, 50 percent fat was blended. The powder mixtures containing 20 percent fat were flowable (repose angles up to 40°), whereas the blends containing 30 percent fat were not free-flowing (repose angles more than 40°). The bulk densities of the skim milk blends decreased with the increasing fat content, and the density ranged from 0.279 to 0.457g/cm^3.

An upper limit of 70 percent fat content was mixed with calcium caseinate. All the calcium caseinate blends were not free-flowing. Their bulk densities increased with the increasing fat content. This ranged from 0.209 to 0.278g/cm^3.

7 Oxidation Studies of the Milk Fat Powders

Most information available concerning oxidation studies of pure milk fat is based either on liquid fat or solid fat which is not in the form of powder. Therefore, oxidation studies of the powders produced from milk fat, using the spray chilling technique, were carried out to ascertain the rate at which the powders deteriorated, when stored at different temperatures. Also, the potential for retarding this oxidative spoilage by flushing the sample bags with nitrogen gas, thus displacing the packages' head-space oxygen, was investigated.

7.1 Materials and Methods

7.1.1 Materials

Type of milk fat used

Fresh Frozen Milk fat for Recombining (FFMR) was used for the oxidation studies. This fat is manufactured from fresh cream by an Anhydrous Milk fat (AMF) process which has been modified to maximise the retention of buttery flavour (Banks, 1991). In other words, FFMR is AMF which is rich in flavour, and as such, the conclusions drawn from this study may be safely inferred on conventional AMF. The fat had been stored at -18°C for about four months, contained in 25 Kg packs, which were comprised of a card board box lined inside with a thick pigmented polypropylene sheet. At the time of use the FFMR had a peroxide value of 0.12 mEq O_2/kg. It also had a FFA content of about 0.3% oleic acid.

A detailed compositional analysis of the FFMR was not carried prior to the study, but it is known that at the time of manufacture the typical composition is as shown in table 7.1 (Rajah, 1991), and this composition complied with the New Zealand Dairy Board specifications for FFMR.

Table 7.1 The Typical Composition of Commercial FFMR

Component	Amount present
Milk fat	99.9%
Water	0.1%
Free Fatty Acids	≤0.3%
Peroxide Value	<0.3 meqv O_2/kg
Copper	0.05 mg/kg
Iron	0.2 mg/kg

Type of milk fat powder studied

Two types of powder were produced for this study. The first type, which shall be referred to as *air material* throughout this discussion, was manufactured as described in section 5.1.1. The second type, denoted as *nitrogen material*, was processed as outlined in chapter 5.1.2.

7.2 Packaging and Treatment of the Samples

About 150 - 200 grammes of the powder samples were packed in aluminium laminated bags (220 x 260 mm sample bags of the NZ Dairy Board), which were heat sealed. Half the bags of *air material* were purged with nitrogen gas before sealing. In this nitrogen-flushing process, the filled bag was first flattened out gently to expell air, and was loosely heat sealed. The seal formed was then gently pulled apart at one corner and nitrogen gas injected in under low pressure (using a nozzle gun) until the bag was fully inflated. The gas was gently expelled and the bag re-inflated. The inflated bag was left to stand for a few minutes (5 to 10 minutes) to allow the nitrogen to diffuse into the powder, then flattened out again and a new tight heat-seal made just above the initial one. However, during the later stages of the study, a vacuum sealer was made available. This sealer was able to flush the bags with nitrogen better, create a light vacuum within the bag, and make

a firm seal thereafter.

The samples were then stored at three different temperatures, modelled to represent the commonly used commercial storage environments. These were;

a) - 10°C - normal frozen storage temperature for FFMR

b) 5°C - normal refrigeration temperature for the fat

c) and 20°C - ambient storage temperature

For each temperature and every test interval, eight samples of each treatment (four of those flushed with nitrogen and four of those sealed without nitrogen purging) were stored. These samples were produced on two batch runs. For the *nitrogen material*, all the samples were flushed with nitrogen. The samples were analysed for oxidation at intervals of one day, one month, and four months. Three of the four samples were tested during each analysis. The forth sample was tested only when the results of the other three were inconsistant. The FFMR stored at -18°C was also analysed to serve as a control. This was tested at the 24 hours and one month intervals.

7.3 Measurement of The Oxidation Related Factors

7.3.1 Oxygen Dissolved in the Fat

The amount of oxygen dissolved in the fat at the beginning and after the spray crystallising process, and also, in the head-space of the sample bags was determined using an oxygen meter. The meter was calibrated in air, and was tested for accuracy by analysing air-saturated water at 20°C and 45°C, comparing the values obtained with the figures supplied in the calibration table. Moreover, the oxygen content of air-saturated FFMR was determined at 45°C. This was found to be 10.8 ppm, which tied very well with the oxygen content recorded for the environment (10.2 - 12.5 ppm). For the feed, measurements were carried in the melt at 40°C to 45°C. While readings were taken, the

electrode was stirred continuously to ensure that there was no deposit of fat adjacent to the oxygen membrane with an oxygen concentration less than that of the bulk sample. For the analysis of oxygen in the powders, the sample was filled into a tightly closed 250 ml glass jar, which was wrapped with aluminium foil, then placed in an oven at about 50°C to melt the powder. The melting process took about 1½ to 2 hours to complete. The temperature of the melt was allowed to drop to about 45°C, before opening the jar, and the oxygen content quickly measured. The time required for this temperature adjustment was determined to be 5 - 8 minutes.

The oxygen contained in the sample bags' head-space was estimated by making a hole at one corner of the bag, which was large enough to just insert the meter's electrode. The measurement was effected by carefully, but rapidly, stirring the air in the head-space with the electrode, whilst the bag's entrance was tightly sealed to minimize exchange of air with the environment. This whole exercise was completed in one minute.

7.3.2 Peroxide Value

Glassware preparation

All the glassware used for this test were soaked overnight in 50 percent hydrochloric acid solution, then rinsed thoroughly with deionised water, and dried.

Spectrophotometer

The spectrophotometer was started and adjusted for the test wavelength (505 nm) at least 20 minutes before commencing the measurements. This was done to stabilise the wavelength.

Test Solutions

The solutions were prepared as follows:

1. Chloroform - methanol mixture of 70 parts by volume of chloroform and 30 parts by volume of anhydrous methanol.

2. Ferrous chloride solution; prepared in indirect dimmed light. About 0.4 g barium chloride ($BaCl_2.2H_2O$) was dissolved in 50 ml of deionised water. Again, about 0.5 g ferrous sulphate ($FeSO_4.7H_2O$) was dissolved in 50 ml water. Slowly, the barrium chloride solution was poured, with constant stirring, into the ferrous sulphate solution. About 2 ml of 10 M hydrochloric acid was added to the mixture. The mixture container was placed in the dark to allow the precipitate to settle, and the clear solution was decanted into an amber bottle thereafter.

   NOTE: Absorbance of reagent blank had to be below 0.05 at 505 nm.

3. Ammonium thiocyanate solution; About 15 g of the solute was dissolved in 50 ml deionised water to make a 30% (m/v) colourless solution.

4. Standard solutions of ferric chloride; About 1.079 g ammonium ferric sulphate was dissolved in 70 ml water mixed with 5 ml conc. HCl. This was diluted to 100 ml to make solution A. From solution A, 10 ml was diluted to 100 ml with water to make solution B. 2 ml of dilution B was diluted with chloroform-methanol mixture (70:30) to 100 ml to give solution C. Solutions for a reference curve were prepared by measuring 2 ml, 4 ml, 6 ml, and 8 ml of solution C into test tubes. These were then diluted with 8 ml, 6 ml, 4 ml, and 2 ml of chloroform-methanol, in that order, to give a series containing 5, 10, 15, and 20μm ferric ion. 0.5 ml ammonium thiocyanate solution and 0.5 ml of 0.2 M HCL were added to each tube and mixed. The solutions were allowed to stand at ambient temperature for 5 minutes, after which their absorbance was measured at 505 nm. These were measured against the absorbance of the chloroform-methanol mixture. A reference curve was constructed by plotting ferric ion concentration against the absorbance.

Analysis of the Samples

The samples were tested by dissolving 1.0 gram (accurately weighed) of the melted fat (as described in section 7.3.1) in 8.9 ml of chloroform and methanol mixture (70:30),

contained in a test-tube. Then 0.5 ml of iron (II) chloride and 0.5 ml of ammonium thiocyanate were added and mixed thoroughly. The mixture was allowed to react in the dark, at ambient temperature, for five minutes. The absorbance of the samples was immediately determined at 505 nm in a 1.0 cm path-length cell. These were measured against a methanol-chloroform blank. Also, a fat blank was prapared by dissolving about 1.0 gram of the fat in methanol-chloroform, and was read under the same conditions as the samples. The resulting reading was used to correct the samples' readings as described by the equation below.

$$Nett\ absorbance = [\frac{Abs}{W_s}(sample)] - [\frac{Abs}{W_b}(fat\ \ blank) + Abs(reagent\ \ blank)] \qquad (7.1)$$

Where W_s = weight of sample in grams

W_b = weight of sample in the fat blank in grams

The entire duration of the test for each batch of samples, from the time they were weighed until they were read for absorbance, was restricted to below 15 minutes. Each sample was analysed in triplicate, and each repeat was done in duplicate.

The amount of the iron (III) in the samples was read from the reference curve, and the peroxide values were calculated from the ferric ions concentrations using the relationship

$$Peroxide\ Value\ (meq\ O_2/kg) = a \div 55.84 \qquad (7.2)$$

Where a = content of ferric ion in μg

7.3.3 Free Fatty Acids

Solutions

1. 0.1 M Sodium Hydroxide solution; About 0.5138 g NaOH pellets were dissolved in 200 ml of deionised water.
2. Neutralised 95% ethanol
3. 2% phenolphthalein indicator.

Analysis

About 10 grams of the molten sample was dispersed in 50 ml of ethanol, and 1 ml of phenolphthalein indicator solution was added. The mixture was boiled for 1 minute and was immediately titrated with 0.1 M sodium hydroxide solution to the phenolphthalein end-point. The acidity was calculated as oleic acid through the following expression;

$$Free\ Fatty\ Acid\ (as\ oleic)\ \% = \frac{Titre \times M \times 28.2}{W} \qquad (7.3)$$

Where M = molarity of NaOH

W = weight of sample (g)

7.3.4 Moisture Content

The moisture content of the powder was determined as the percentage loss in weight when 5.0 g fat powder, contained in aluminium dishes, was dried at 120-150°C on a hotplate.

7.4 Results and Discussions

7.4.1 The Physical State of the Powders

No significant changes were noted in the samples after the first day of storage, but after one month, the samples which had been stored at 20°C had melted, and smelled rancid. The rest of the samples, stored at 5°C and -10°C, were still in powder form, and smelled fresh. After four months all the samples had developed rancid smell.

7.4.2 The Peroxide Value (PV)

Air material

The peroxide values for the air material are summarised in table 7.2 below. These values are average results for three sample bags.

Figure 7.1 shows that in all the air material samples tested there was a significant increase ($P<0.05$) in the peroxide value after one month of storage. The PV doubled for all the samples stored at 20°C, and increased by up to half the original amount for the samples stored at 5°C and -10°C. The above trends were observed for both nitrogen flushed and non flushed samples, indicating that nitrogen-flushing did not suppress the progression of oxidation. The latter outcome was unexpected because nitrogen is known to be a good deterent for oxidation, especially for packed foods. Nonetheless, this eventuality may be explained as follows. First, it is likely that by the time the powder was bagged it had already absorbed sufficient amount of oxygen to cause the observed PV increase. In support for this argument, Jebson *et al* (1973) stated that if all the oxygen dissolved in the fat reacted during storage, to solely give peroxides, then by equivalence, every one ppm of oxygen would yield 0.125 meq, which is a significantly high yield. Second, it is probable that the method employed for injecting nitrogen into the sample bags was not very effective. This could not be helped at the time because no other better method was available. The latter possibility is very likely, considering the lower peroxide values obtained for the vacuum packed samples at the end of the study. Also, although precautions were exercised to minimise exposure of the fat to light, the contribution

Table 7.2 **The Peroxide Values of the Air Material Stored under Different Temperature Conditions.**

Temperature of storage	Cooled with Air and Packed in air (mEqvO_2/kg of sample)			Cooled in Air and flushed with nitrogen (mEqv O_2/kg of sample)		
	24 hrs	1 month	4 months	24hrs	1 month	4 months
-10°C	0.23±0.01	0.35±0.01	0.31±0.02	0.24±0.01	0.35±0.01	-
5°C	0.22±0.02	0.28±0.01	0.34±0.01	0.25±0.02	0.36±0.01	-
20°C	0.23±0.01	0.56±0.01	0.73±0.05	0.25±0.02	0.53±0.04	0.61±0.05

$P< 0.05$

FFMR; After 24 hrs = 0.12±0.01 mEqv O_2/kg sample

After 1 month = 0.21±0.03 mEqv O_2/kg sample

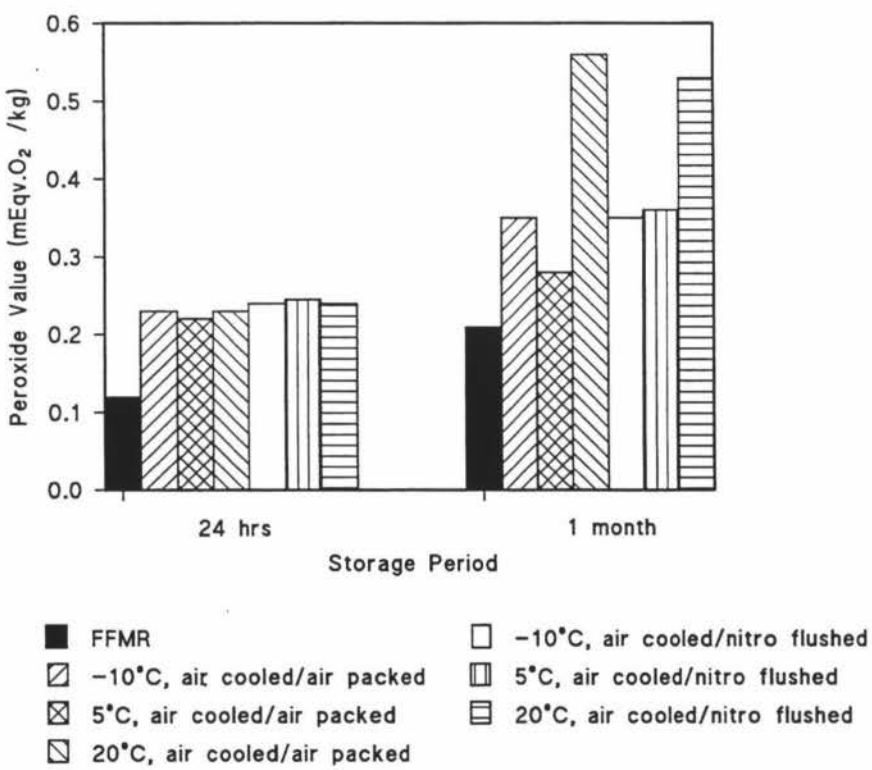


Fig. 7.1 The Peroxide Values of the Air Material After 24hrs and 1 Month of Storage at Different Temperatures.

of light to the PV results may have been significant during the various transfer stages of the samples. This could be expected since light has been shown to have very strong influence on the rate of lipid oxidation. For example, Keogh *et al* (1986) found that when liquid fat was exposed to fluorescent light for a quarter of an hour, an increase in the PV of up to 29% resulted. Nawar (1985) contended that under normal circumstances the initiation of the oxidation chain reaction is thermodynamically difficult (activation energy of about 35 kcal/mol), but with exposure to light the initial reaction step is booted, giving rise to reactive radicals. In brief, it is likely that by the time the samples were bagged, the oxidation reaction was already entering the most rapid *propagation* step. Whatever the exact reasons may be, it can be deduced from the FFMR's (control) peroxide values that the rise in the peroxide values of the powdered fats was not caused solely by processing with air.

There seemed to be an identical pattern in the variation of the oxygen concentration in the bags' head-space and in the molten samples, for most of the samples analysed. This pattern was more pronounced for the samples stored at 20°C, and is graphically demonstrated in figure 7.2.

The general trend was a slight increase, with time, of the head-space oxygen, followed by a decrease. The observed increase could have been caused by the release of residual oxygen from the intra and inter particles' voids when the powder melted, or equilibration of the dissolved oxygen. The oxygen in the samples increased for 20°C samples and was coupled by an abrupt PV increase. This rise may have been caused by, among other factors, the head space oxygen dissolving in the sample, moreso that the sample had a high proportion of liquid fat. Timms *et al* (1982) and Jebson et al (1973) demonstrated that the amount of oxygen that can dissolve in milk fat varies with the proportion of the liquid fat and the temperature. The more the liquid fat the higher the amount of oxygen that can dissolve, and vice versa. For the samples stored at 5°C and -10°C, which were predominantly in the solid phase, the oxygen in the samples remained constant for a few months.

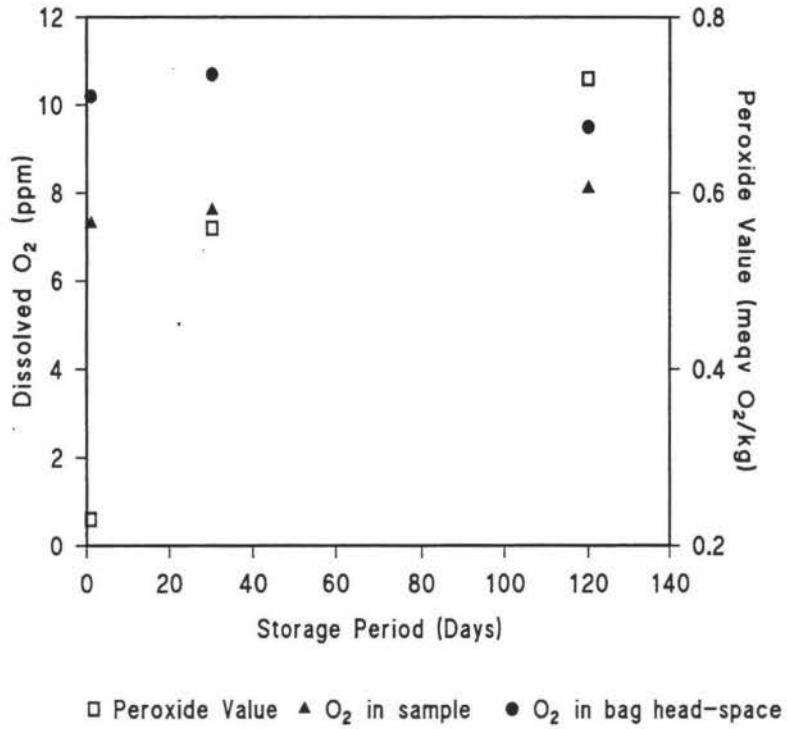


Fig. 7.2 Variation of head-space oxygen, oxygen in the molten sample and the peroxide value for the air material samples stored at 20°C.

Table 7.3 The estimated weight of the oxygen dissolved in fat, and the amount present in the head space.

Storage period	Oxygen dissolved in fat (mg)	Oxygen in head space (mg)
24 hrs	1.30	10.43
1 month	1.35	10.94
4 months	1.44	9.71

However, this oxygen concentration dropped during the fourth month, possibly reflecting an uptake of oxygen by the oxidation reaction. The latter observation was not obvious for the 20°C samples, and was suspected to be shadowed by the high dissolution of the

headspace oxygen into the sample.

The results for the head-space oxygen in the bags should be treated with caution, owing to the crudeness of the technique employed. A more accurate analysis of this parameter could be achieved using the gas chromatographic method. Perhaps it should be stated here that while the trends of the oxygen concentrations within the sealed bags are explained above, and seemed to display a logical pattern for the oxidation transformation steps, these trends did not form an important part of this study. The main emphasis was centred on the changes of the peroxide value *per se,* and hence, extra care was exercised in assessing the latter rather than the former.

Table 7.4 **The oxygen content in the air material sample bags' head-space and the molten samples measured using an oxygen meter**

Storage Temperature	Cooled with air & packed in air						Cooled in air & flushed with nitrogen					
	O_2 content in the bag (ppm) *			O_2 content in sample (ppm) **			O_2 content in the bag (ppm) *			O_2 content in sample (ppm) **		
	24hrs	1 Mo	4 Mo	24hr	1 Mo	4 Mo	24hr	1 Mo	4 Mo	24h	1M	4Mo
-10°C	10.7	10.7	10.6	10.6	10.7	10.1	8.3	9.4	9.4	4.4	8.5	8.2
5°C	10.1	10.2	10.0	7.2	7.2	7.0	8.2	7.2	7.0	4.2	8.5	8.1
20°C	10.2	10.7	9.5	7.3	7.6	8.1	8.3	9.3	7.6	4.3	8.7	7.3

P <0.05 hrs/hr = hours ppm = parts per million

Mo = month * Std. dev.= ±1.3 to 2.2 ** Std. dev. = ± 0.7 to 0.9

The oxygen content in the molten fat before spray cooling ranged from 4.2 ppm to 4.4 ppm for the different batches processed. This concentration was determined at the begining of each run. Although some measures were taken to minimise contact of the liquid fat with the environmental air while the production was in progress, the possibility of more dissolution of air in the fat could not be ruled out. More so that it took up to as long as 30 minutes to complete each production run. The oxygen in the environment ranged from 10.2 ppm to 12.5 ppm, measured at 9 to 17°C.

In general, all the samples were considered spoiled after one month. This conclusion was based on the fact that at the peroxide values of 3 to 4 meqvO_2/kg, AMF is not suitable for most applications (CSIRO, 1945). It was obvious from these results that an improved process which did not expose the fat to oxygen was necessary, if low peroxide values were to be maintained in the samples.

Nitrogen material

In comparison with the air material, a slow down in the rate of oxidation for the nitrogen material was observed. The one month storage period produced an increase by 27.7% and 44.4% of the peroxide values for the samples stored at -10°C and 5°C respectively. On the other hand, a high rise of the PV by 85.7% was recorded for the samples stored at 20°C, for the same storage period. After four months the peroxide values had doubled for all the samples, disqualifying the powder for most applications. The average results for these nitrogen materials are tabled below.

Table 7.5 The Peroxide Values of the Powder Samples Manufactured Using Nitrogen as the Chilling Medium.

Temperature of Storage	Peroxide Values (meq O_2/kg)		
	24 hrs	1 month	4 months
-10°C	0.18±0.02	0.23±0.02	0.49±0.03
5°C	0.18±0.01	0.26±0.02	0.51±0.02
20°C	0.21±0.01	0.39±0.03	-

$P < 0.05$

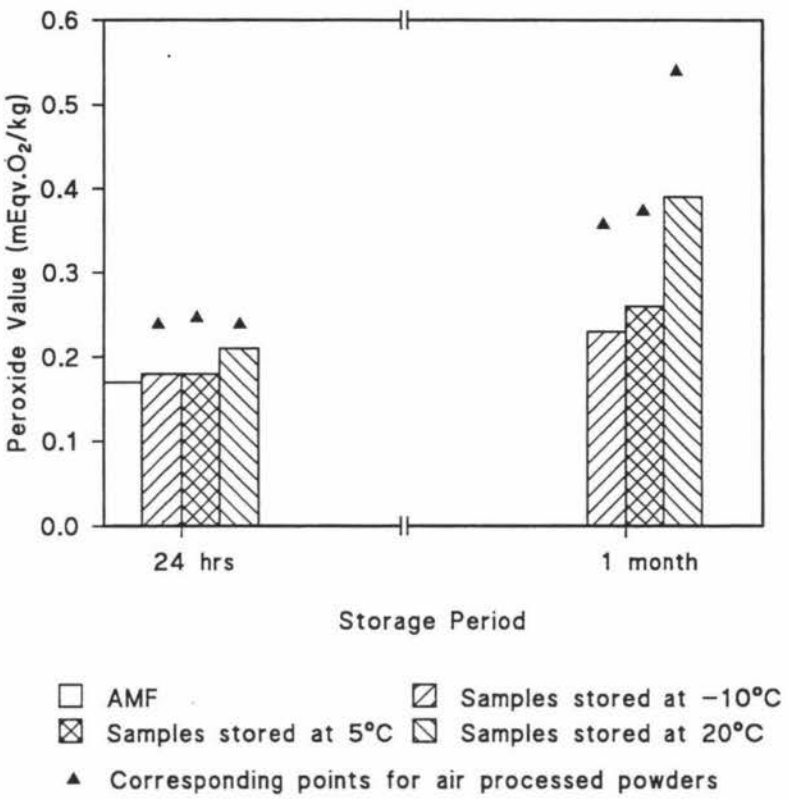


Fig. 7.3 The Peroxide Values of the Nitrogen Material After 24hours and 1 month of Storage at Different Temperatures.

The samples which had been vacuum packed were still usable after three months. However, these were compacted into solid lumps, thus limiting the chances of adopting this packaging method as a potential technique for handling these powders. Nevertheless, it is obvious from the vacuum packed samples' results that elimination of the oxygen in the package is crucial for arresting the rate of oxidation of the powder.

Table. 7.6 The Peroxide Values of the Vacuum Packed Nitrogen Processed Fat Powders.

Storage Temperature	Peroxide Value (meq O_2 /kg)	
	24 hours	3 months
-10°C	0.18±0.01	0.28±0.01
5°C	0.18±0.01	0.29±0.01
20°C	0.19±0.02	0.33±0.03

P <0.05

The foregoing results demonstrated that a relationship exists between the rate of oxidation of the fat powders and the degree of protection against the oxidation agents. It was shown that a longer shelf life can be achieved if the powders are processed under a nitrogen environment. It is envisaged that under full scale production, and with the better melting and liquid fat holding vessels, like those already in place for most modern milk fat plants, much longer shelf lives for the powders would be obtainable. It is also believed that proper protective packaging for these powders would not be a problem. Appropriate gas flushing techniques for packaging highly oxidation-susceptible powders have already been developed, and coincidentally, New Zealand is ahead the world in this packaging technology (Rockell, 1994).

7.3 Conclusions

The fat powders produced were found to be physically and oxidatively unstable at 20°C, but remained reasonably stable at 5°C and -10°C. Hence, 20°C was not a suitable temperature for storing these samples. Storage at -10°C would sustain the powders longer, but storage at 5°C could turn out to be more economical.

Processing of the powders under the conditions which exposed the fat to oxidation resulted in high peroxide values. Also, flushing of the sample bags with nitrogen by the method outlined did not give any protection to the samples against oxidation.

Processing of the powders under the nitrogen environment gave longer shelf lives than when no protection was accorded.

8 THE POTENTIAL FOR SPRAY CHILLING

8.1 Applications

It has been demonstrated that milk fat and/or milk fat fractions can be converted into powder by spray chilling. Infact, any material that can undergo phase changes from liquid to solid under the conditions of spray chilling may be handled as powder. The list may include cocoa butter, shortenings, emulsifiers, hydrogenated vegetable fats, pastry fats, bakery improvers, stabilizers, cheese and others. For example, at an early stage in this project phospholipids were successfully converted into powder, except that under the processing conditions used then, oxidation could not be avoided.

Having the fat in powder form offers a convenient way of blending it with other powdery materials. From the mixing trials reported in chapter 6, a good degree of uniformity could be achieved in the blends. In this respect, this dry blending process outweighed the traditional method of spraying liquid fat into powders. It may also be deduced from chapter 6 that once in powder form, the fat can be mixed with any carrier powder. The maximum amount of fat that can be incorporated in the mixture will depend on the physical properties of the carrier. This versatility in the application of the powdered fat could be a key to other product opportunities. New products such as ice cream powder, and premixes of butter cream powder, which would require only the addition of water for preparation, are some of the products which can be imagined.

The ability to manufacture powders of the milk fat fractions separately may provide a wider choice of AMF powder. This may also avail the advantage of standardising the physical properties of the formulated mixtures through selection and calculated gauging

of the component fat fractions.

8.2 Limitations

Processing of the fats into powder may require that chilling be done with nitrogen only, in order to minimise oxidation of the powders. Under such circumstances, the cost of nitrogen alone may elevate the overall production costs, rendering the technology less suitable for the intended purpose. Fortunately, some suppliers of nitrogen cost their supplies based on cost-reduction curves, which decreases the cost as the amount of nitrogen supplied increases. For example, figure 8.1 demonstrates a typical cost-reduction curve used by BOC Gases New Zealand Limited for the supply of food grade liquid nitrogen.

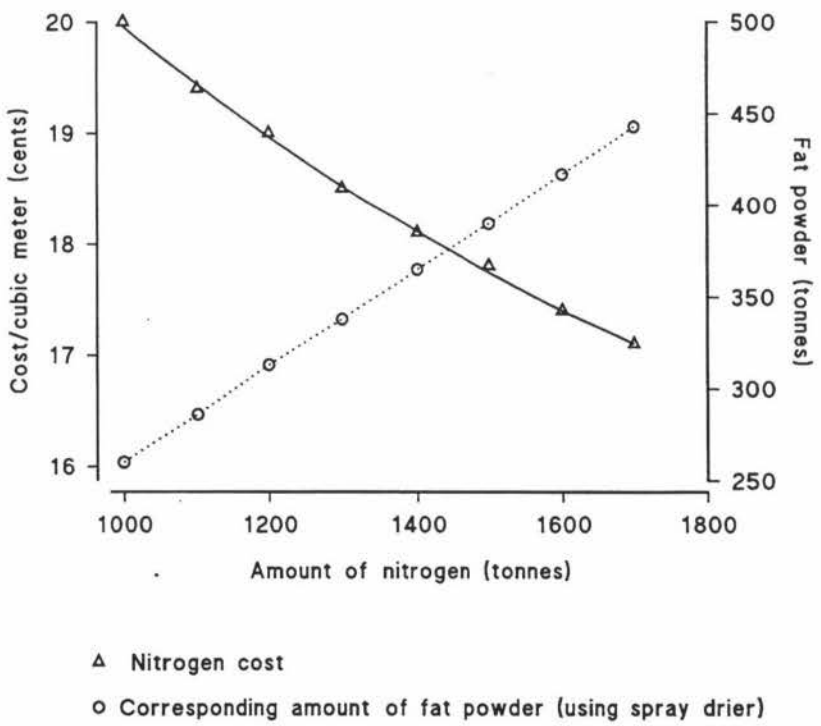


Fig. 8.1 A typical cost reduction curve for the supply of liquid nitrogen (courtesy of BOC Gases New Zealand Limited).

Note: The prices furnished are just estimates and are subject to change at any time.

Keeping the powders at room temperature was found to be detrimental to the powders, hence, it would be necessary to air condition the packaging and storage rooms so as to maintain the product in good condition.

8.3 Equipment

Since spray chilling shares similarities with spray drying, most of the engineering inventions applied in spray drying may be adopted directly, or with little modifications, in spray chilling. This could significantly reduce the costs of designing the necessary equipment for the spray chilling process. In the case where nitrogen would be required, nitrogen suppliers can provide the appropriate equipment and the necessary technological know-how for handling the cryogenic.

9 RECOMMENDATIONS FOR FURTHER WORK

The following are the possible areas which may be explored further to improve, and/or gain more insight into the processing of fat powders by the spray chilling technology.

9.1 Exploration of Polymorphism.

A brief explanation of polymorphism is furnished elsewhere in this report, and in addition, there is a wealth of text-books which cover this topic extensively.

The fact that milk fat can exist in several structural configurations, and that it is possible to influence the fat to assume the structure of choice by purely physical treatment, offers an ideal tool for bettering the physical stability of the powdered milk fat. It is therefore recommended that further investigations involving manipulation of the polymorphic structures of milk fat be carried. Seeding of more stable glyceride nuclei in the melt before spray chilling, and post-production tempering of the powders, should be attempted.

9.2 Chilling with a mixture of nitrogen and cold air

Chilling with nitrogen undoubtfully reduced the rate of oxidation in the powdered fats, and as such, liquid nitrogen appeared to be a very ideal chilling medium. However, it is suspected that nitrogen may turn out to be the most costly entity for the production. Hence, it may be desirable to investigate the effects of chilling with a mixture of nitrogen and air, then gauging the advantages of such a system against those of liquid nitrogen. An experiment imagined is one in which several ratios of air to nitrogen are tested against the peroxide value of the powder, then selecting the ratio which gives a satisfactory lower peroxide value. The chilling mixture could be re-cooled in the blast freezer.

The idea of chilling with a mixture of air and nitrogen was prompted by the following arguments;

i) It is believed that the solidification of the fat droplets in the chilling chamber takes place so rapidly such that the absorbtion of the environmental gases is very minimal. In support of this argument, Timms *et al* (1982) and Jebson *et al* (1974) concluded that very little oxygen dissolves in the solid fat such that it may be assumed that no oxygen dissolves at all.

ii) Mixing the air with nitrogen will dilute the oxygen in the air, such that very small amounts of oxygen may be present in the crystallising chamber.

9.3 Cold mixing of the powders

It is very likely that much higher fat content may be achieved in the blends of the powdered fats with other powders by mixing the powders at 5 - 10°C, instead of blending at ambient temperature. This could be verified experimentally.

Appendix 1

Theoretical amount of nitrogen required to cool the milk fat from 50°C to -18°C.

Assumption: there is no heat gain from the environment

1. Specific heat of nitrogen and milk fat

Nitrogen			Milk fat		
Temperature (°C)	Heat capacity (cp) (kcal/kg.K)	Specific energy (heat/kg)(kJ/kg)	Temperature (°C)	Heat capacity (kcal/kg.K)	Specific energy (cal/gm)
-196	0.2435		50	0.52	
-18	0.2482	183.0786	45	0.53	10.99088
			40	0.56	11.40958
	Latent heat	199.80	35	0.68	12.9797
			30	0.87	16.22463
			25	0.93	18.8415
			20	1.09	21.14435
			15	1.48	26.90148
			10	1.01	26.06408
			5	0.64	17.27138
			0	0.60	12.9797
			-5	0.55	12.03763
			-10	0.45	10.4675
			-15	0.42	9.106725
			-18	0.40	5.15001
	TOTAL .	382.8786 kJ/kg			211.569145 cal/gm 885.7977 kJ/kg

2. Ratio of specific heat of nitrogen to that of fat = $\frac{885.7977 \text{ kJ/kg}}{382.8786 \text{ kJ/kg}} = 2.31$

Therefore one kilogram of fat requires 2.3 kilograms of nitrogen to cool from 50°C to -18°C .

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