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DSC AND EPR INVESTIGATION OF THE EFFECT OF FAT CRYSTALLIZATION ON THE CONSISTENCY OF BUTTER

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Abstract

It was possible to determine the liquid fat content and melting behaviour of butters unenriched and enriched in low melting point milk fat fraction (mp=10°C) made from traditionally (6–11–11°C) and heat step technology ripened (6–20–11°C) cream by using EPR spectroscopy and ultrasensitive DSC methods.

It was determined that

– butters made from heat step technology (H) ripened cream have smaller liquid fat content in the continuous fat phase than that of made from traditionally (K) ripened cream,

– there were different fat melting behaviours: the K-butter in temperature range of 0–20°C had one melting peak while H-butter had two ones, and

– the effect of enrichment is different in the fraction of low melting point: the melting temperature decreased in the case of K-butter, but the H-butter exhibited smaller enthalpy at the lower melting temperature having same melting temperatures.

Our experiments support the view that H-butter is much more structured than K-butter which is caused by fat fragments containing cubic crystals, developed during the ripening of heat step technology. With respect to the minimum liquid fat content of maximum fat fragments, and vice versa, the cream ripening temperature of solid and spreadable butter can be optimalized by determination of cream ripening temperature-liquid fat content function (min.–max. curve)

The experiments have proved without any doubt that butter of cold spreadable, not softening at room temerature, can be only produced by the combination of heat step cream ripening and enrichment with a low melting point fraction.

Keywords: butter, cream ripening, fat crystallization, heat step technology

Introduction

In recent decades, butter production has decreased, while margarine production has increased worldwide. The main reasons for this tendency are:

– nutritional propaganda
– shifting price ratios and
– the poorer spreadability of butters as compared with that of margarines.

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Table 1 Possible butter assortment in Hungary based in home research

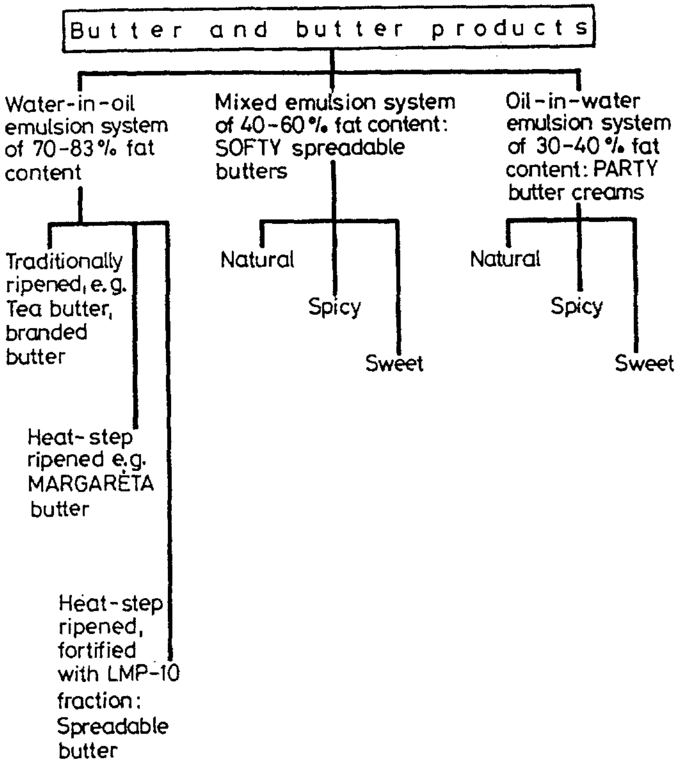
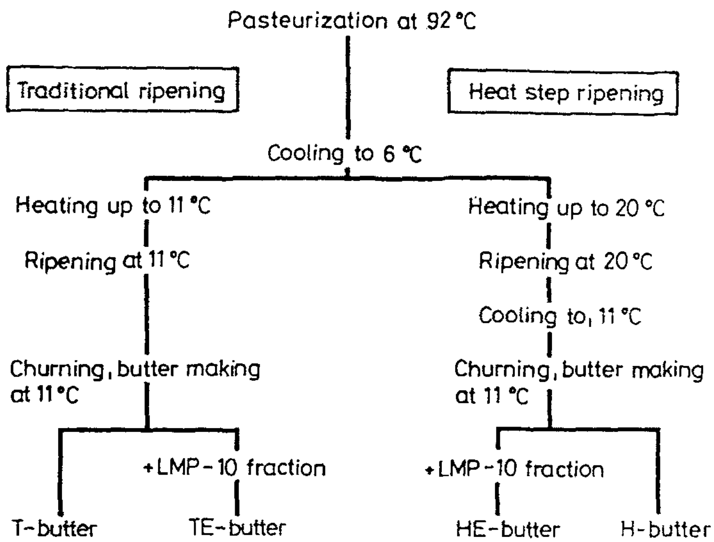


Table 2 Average fatty acid composition and standard deviation of the Hungarian winter milk fat

Denomination	Fatty acids Average ratio in milk fat/%	Average deviation
Capronic acid (C:6:0)	1.49	0.25
Caprylic acid (C:8:0)	0.97	0.17
Capric acid (C:10:1)	2.83	0.27
Caproleic acid (C:10:1)	0.26	0.07
Lauric acid (C:12:0)	3.44	0.41
Myristic acid (C:10:1)	12.53	0.59
Myristoleic acid (C:14:1)	1.72	0.32
Palmitic acid (C:16:0)	33.53	1.94
Palmitoleic acid (C:16:1)	1.92	0.62
Stearic acid (C:18:0)	10.77	0.49
Oleic acid (C:18:1)	28.28	1.33
Linoleic acid (C:18:2)	1.16	0.52
Arachidonic acid (C:20:0)	1.09	0.75

Table 3 Parameters of cream ripening



LMP-10: Anhydrous milkfat, 10 °C melting point, Corman, Belgium

T = traditionally ripened
TE = traditionally ripened enriched
H = heat step ripened
HE = heat step ripened enriched

The nutritional propaganda launched by the American Ancel Keys was based on the lipid theory, according to which the high cholesterol and saturated fatty acid contents of animal fats were responsible for arteriosclerosis and high blood pressure, and eventually for heart attacks [11]. Although, science has disproved the Keys theory and has given back to butter its real nutritional value as compared with the 'artificial fat' margarine [2, 3], advertisements in Hungary still suggest the opposite [12].

The price conditions of butter products have been steadily worsening in Hungary in the past 5 years. This process was even overstated by public opinion. In 1992, butter creams were cheaper than margarines, but our survey revealed that 80% of consumers thought them more expensive [1].

It is a real objection of consumers that butters can not be spread like margarines. Our research is therefore aimed at the development of butter products that can be well spread in the cold. We intend to establish the assortment of butter products shown in Table 1 in Hungary.

From among the products in the Table, Party butter creams of oil-in-water emulsion type which are well spreadable in the cold have been successfully marketed in Hungary for 10 years [9]. The well-spreadable Softy product family of mixed emulsion type is now being introduced. This paper summarizes the main results of our research to develop spreadable butter made of cream ripened by the heat step method and enriched with the low melting point milk fat fraction LMP-10.

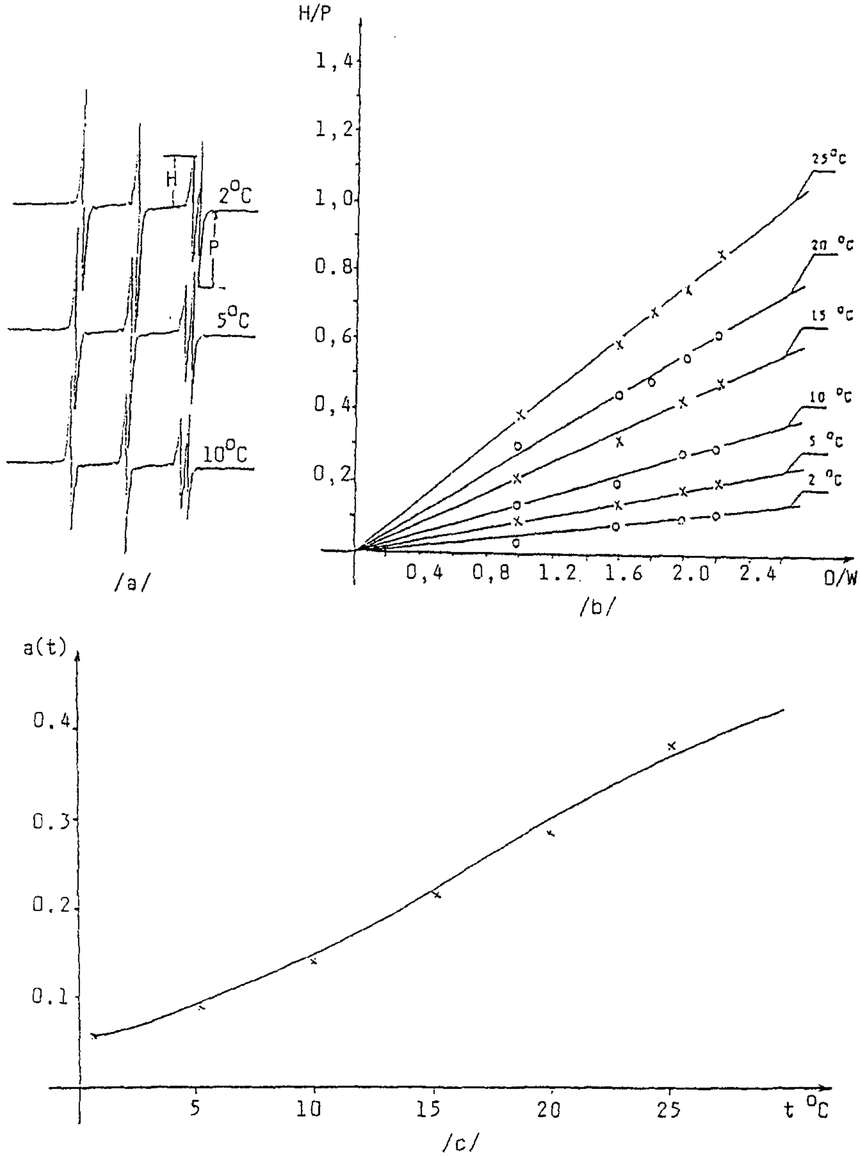


Fig. 1 EPR curves (a) of model emulsions, the parameters *H*/*P* measured from them as a function of the oil and water (O/W) contents (b), and the slopes of the straight lines ($a(t)$) as a function of temperature (t) (c)

Materials and methods

Cream obtained in the winter period was used in the experiments. The average fatty acid composition of the fat of the cream is given in Table 2.

The standard deviations of the relative quantities are also given in this Table.

The cream was pasteurized, and then ripened traditionally or by the heat step technology, as shown in Table 3.

To examine the effects of modification of the fatty acid composition, butters made from cream ripened traditionally or by the heat step procedure were enriched with a low melting point milk fat fraction.

For characterization of the spreadability of butters, the consistency firmness was measured with a penetrometer in the temperature range 5–25°C, and the reciprocal of the penetration values was then plotted as a function of temperature.

The crystallization and melting properties of milk fat in butters were examined with a SETARAM Micro DSC-11 ultra-sensitive scanning calorimeter. The butter sample mass was 700–900 mg and a traditional batch measuring 1 ml cell pair was used in the experiments. The measurements were carried out in the temperature range 0–50°C and at a heating and cooling rate of 0.3°C min^{-1} after adjustment of the thermal balance when the heat flow fluctuation was below 1 μW.

An EPR spectroscopic method has been elaborated for measurement of the percentage liquid fat content of butters in the continuous phase. The main point was to prepare model emulsions from water, palmitic acid and sunflower oil which were indicated with a Tempol free radical soluble both in water and in oil.

Table 4 Calculation of liquid fat content of butter being in continuous phase

$$\frac{H}{P} = a(t)\frac{F_1}{W}$$

$$a(t) = \frac{1}{1 + \exp(2.1453 - 0.1280\,t)}$$

$$F_1\% = \frac{F_1}{F_t}100 = \frac{F_1}{100 - W}100$$

$$F_1 = \frac{H}{P}\frac{W}{a(t)}$$

$$F_1\% = \frac{H}{P}W\frac{1 + \exp(2.1453 - 0.1280\,t)}{100 - W}100$$

H/P : Parameter measurable from EPR-spectrum
W : Water content of sample, g/100g
t : Temperature/°C
F_1 : Liquid fat content of sample, g/100g
F_t : Total fat content of sample, g/100g
$F_1\%$: Percental liquid fat content referred to total fat

Figure 1a depicts EPR curves of model emulsions at different temperatures. The parameter H/P, which is measurable from the curves, is proportional to the concentration of radical spin in oil/water. It is clear from Fig. 1b that the solubility depends on temperature, but H/P yields a linear function of the quotient of the oil and water contents at a given temperature. A plot of the slope of the straight lines as a function of temperature is demonstrated in Fig. 1c.

On the basis of the experiments and the simple mathematical deduction included in Table 4, a relationship has been elaborated, with the help of which the liquid fat content of a sample in the continuous phase can be determined.

Results and discussion

Figure 2 shows the liquid fat content of a butter made of cream ripened by the heat step and traditional methods and the standard deviations as a function of temperature.

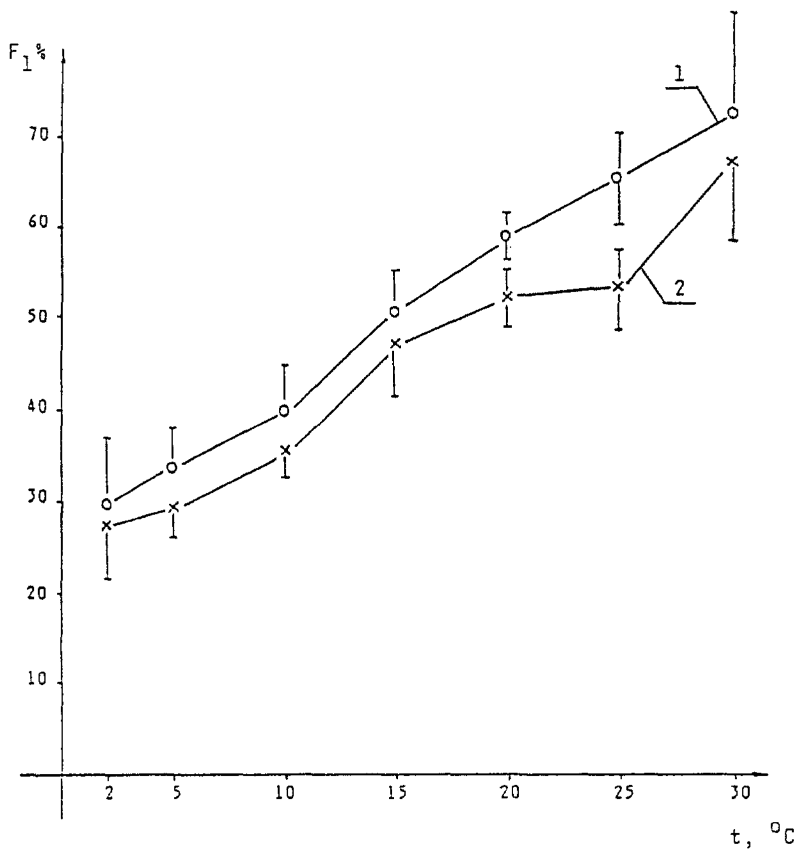


Fig. 2 Percentage liquid fat content (F_l%) of butters made from cream ripened by traditional (1) and heat step (2) methods as a function of temperature (t)

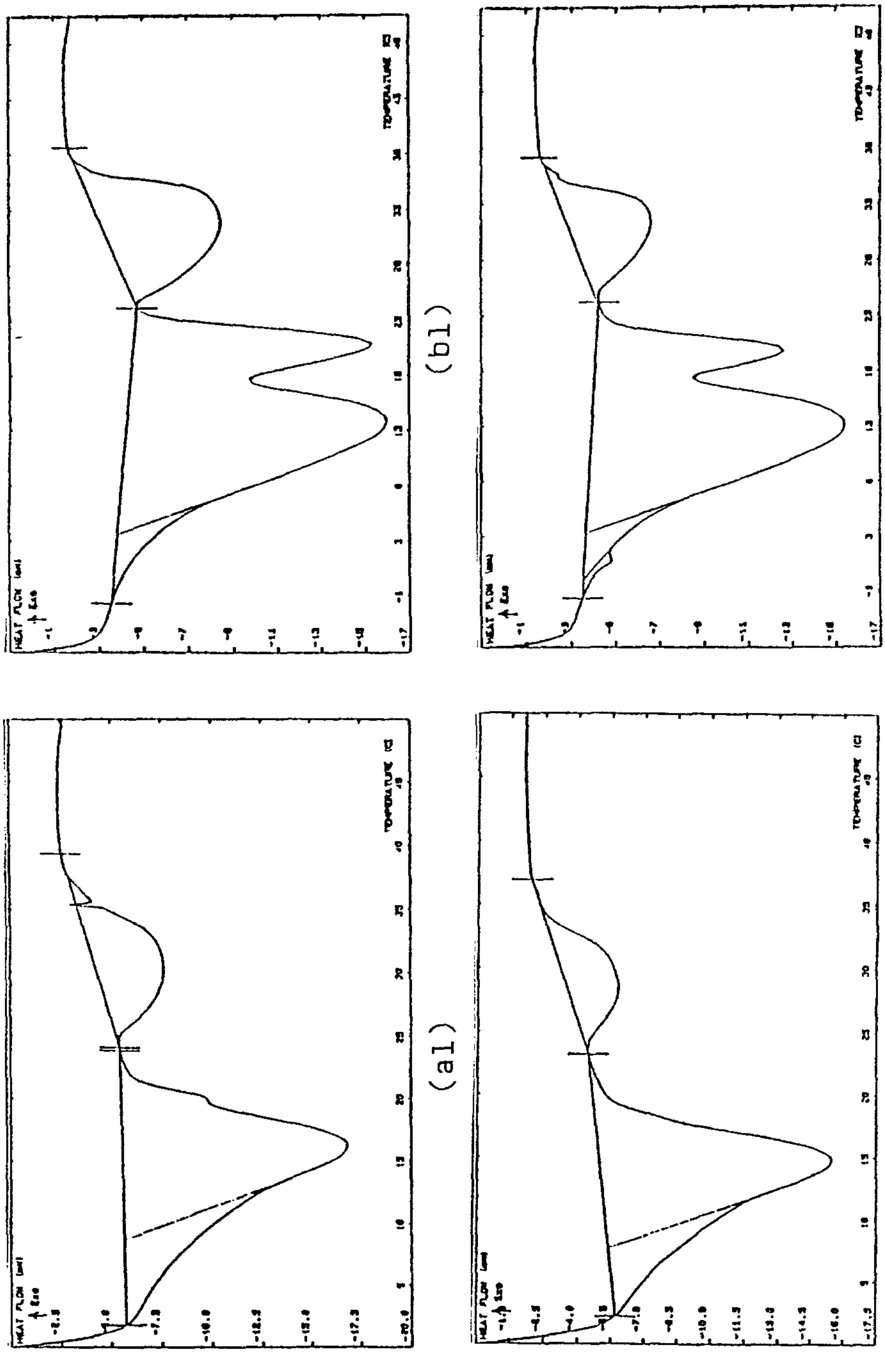


Fig. 3 DSC curves of butters made from cream ripened traditionally (a) or by the heat step method (b) and not enriched (1) or enriched with 25% milk fat fraction LMP-10 (2)

Figure 2 clearly reveals that the amount of liquid fat in the continuous phase is lower at every temperature in heat step-ripened butters than traditionally ripened butters. The differences in the temperature in range 5–25°C are significant. It is also obvious that the liquid fat content in heat step-ripened butter does not change in the interval 20–25°C.

The present experiments prove that the heat step method of cream ripening creates a particle structure consisting of triglycerides of different melting points in the butter [5, 6]. This structure provides a better spreadability of the butter at lower temperatures, in spite of the fact that in such a butter the amount of liquid fat in the continuous phase is lower than in a traditional one [4, 7].

Figure 3 contains DSC curves of butters made from traditionally (a) and heat step-ripened (b) cream not enriched [1] or enriched with 25% milk fat fraction LMP-10 [2].

Table 5 Effect of cream ripening and enriched with milk fat fraction of a low melting point on the melting and crystallization characteristics of butter fat

	Butter samples			
Ripening	Content of LMP-10	Melting temperature and range/°C		
method	fraction/%	T_{m1}	T_{m2}	T_{m3}–T_{m4}
Traditional	0.0	16.18±0.08		25–39
Traditional	25.0	14.60±0.10		23–37
Heat step	0.0	13.08±0.15	20.62±0.42	25–39
Heat step	25.0	13.32±0.26	20.12±0.34	22–37

	Butter samples		
Ripening	Content of LMP-10	Crystallization temperature/°C	
method	fraction/%	T_{c1}	T_{c2}
Traditional	0.0	15.18±0.08	9.58±0.13
Traditional	25.0	13.46±0.23	8.12±0.13
Heat step	0.0	15.16±0.15	9.68±0.19
Heat step	25.0	13.48±0.18	8.08±0.15

It is obvious that the effects of addition of the milk fat fraction LMP-10 on the melting properties differ for the two ripening methods. For butter made from traditionally ripened cream, the addition decreases the temperature of the first melting peak. However, in the heat step-ripening method, the temperatures of the double peak formed due to ripening remain unchanged. However, the enthalpy of the lower melting point part of the double peak is higher.

Table 5 lists the melting and crystallization temperatures.

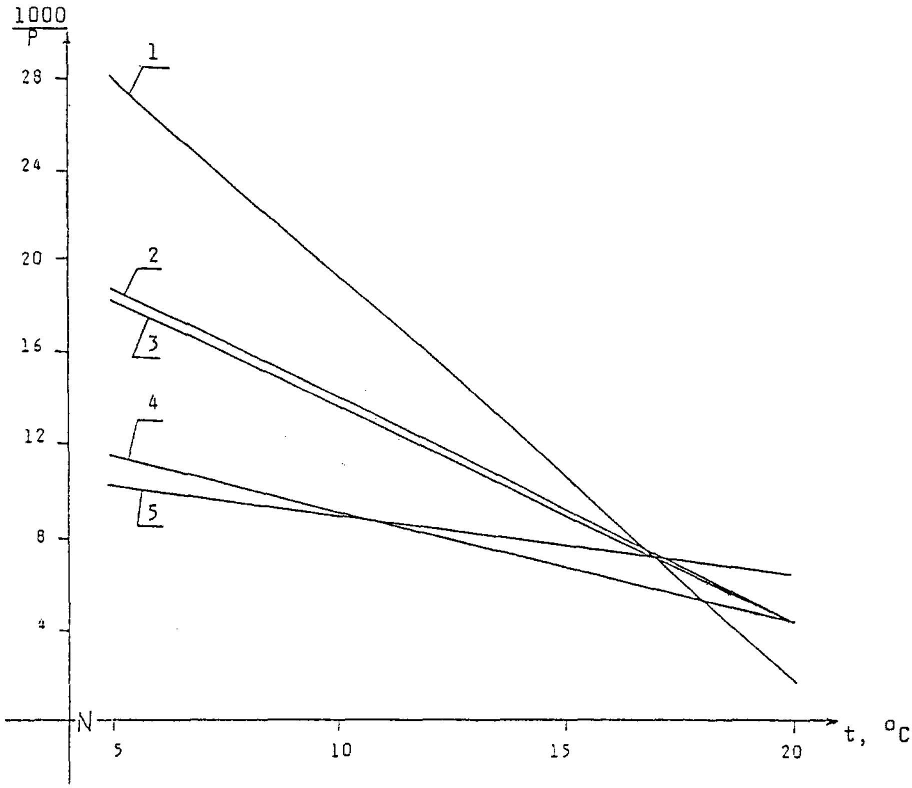


Fig. 4 Consistency firmness (1000/*P*) of butters made from cream traditionally (1) or heat step (2) ripened, and from cream containing 25% milk fat fraction LMP-10 traditionally (3) or heat step (4) ripened, and of a margarine (5) as a function of temperature (*t*)

The ripening leads to a significant difference in the melting temperatures in the case of traditional ripening and in the crystallization temperatures in the case of heat step ripening.

Figure 4 demonstrates consistency firmness of butters made from cream that is traditionally [1] or heat step [2] ripened and not enriched, and of cream containing 25% milk fat fraction LMP-10 traditionally [3] or heat step [4] ripened, and that of a spreadable margarine [5] as a function of temperature.

It is obvious that the heat step ripening of cream results in the cold spreadability of butter being better, and it improves still further if the LMP-10 fraction is added.

These experiments prove beyond doubt that cold-spreadable butter, like margarine, can only be produced through a combination of heat step cream ripening and enrichment with a low melting point fraction.

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