Changing the Molecular Structure of Milk Fat as a Means of Improving THE SPREADABILITY OF BUTTER

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Butter often is too hard to spread easily at refrigerator temperatures. The need for improving spreadability is recognized; but, as yet, methods of controlling this property of butter have not been developed.

A survey of published research indicates most of the steps in the process of churning butter have only minor influence on the hardness and spreadability of the final product. Data of Dolby indicate that the churning process itself accounts for only 26.5 percent of the total variation in butter hardness (7). The rest of the variation in butter hardness, and spreadability, is due to seasonal changes in the chemical composition of milk fat and differences in the temperature treatment of the cream prior to churning (4, 11). These two factors apparently act through their effect on the ratio of solid to liquid fat in the butter. It is thought that changes in this ratio cause proportional changes in the hardness of butter.

In view of these facts it seemed a logical approach to the problem of controlling the spreadability of butter would be to find ways of changing the composition of milk fat. This publication reports the results of a two-part study of the problem. The first part concerns the rearrangement of triglyceride molecules in milk fat by means of a "directed interesterification" reaction. The second part deals with the flavor problems of butter resulting from the molecular rearrangement.

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Part 1. Changing the Molecular Structure of Milk Fat

Theoretical Basis for the Study

At ordinary temperatures butter is composed of both crystalline and liquid fat. The lattice formed by the crystalline fat gives butter its form, and it appears that about 15 to 25 percent of the fat should be crystalline in order for it to hold its shape while being handled (13). More than 25 percent of solid fat often makes the product too hard to spread. Since butter contains 40 percent or more of solid fat in many cases (3), reducing the amount of crystalline fat it contains should improve its spreadability. It was thought that a "directed interesterification" reaction would do this.

The term "interesterification" (also called rearrangement) refers to a reaction in which a mixture of glyceride molecules under proper conditions are caused to exchange fatty acid radicals (8). This results in a redistribution of the fatty acids among the different glyceride molecules. Sodium methoxide is ordinarily used as a catalyst (1). If the temperature of the reaction is high enough so that all of the glycerides will be liquid when they are formed, the fatty acid exchange will proceed until an equilibrium composition representing a completely random arrangement is obtained. However, if the temperature of the reaction is controlled so that some of the glycerides are solid when formed, these glycerides can be removed from the reaction by precipitation. Thus the direction of the reaction can be controlled. This reaction is illustrated in Figure 1.

The application of the reaction to milk fat can best be illustrated with the graphs in Figures 2 and 3. The pattern of fatty acid arrangement on the glycerides of milk fat is not fully understood. However, if one assumes a random distribution of fatty acids in the glyceride molecules of untreated milk fat, the calculated distribution of melting points for these glycerides will be skewed toward the higher temperatures, as shown in Figure 2. After directed interesterification, the distribution of melting points will shift, as shown in Figure 3. Some of the glyceride molecules will have higher melting points than before, and many will have lower melting points. The net result, however, will be fewer tri-

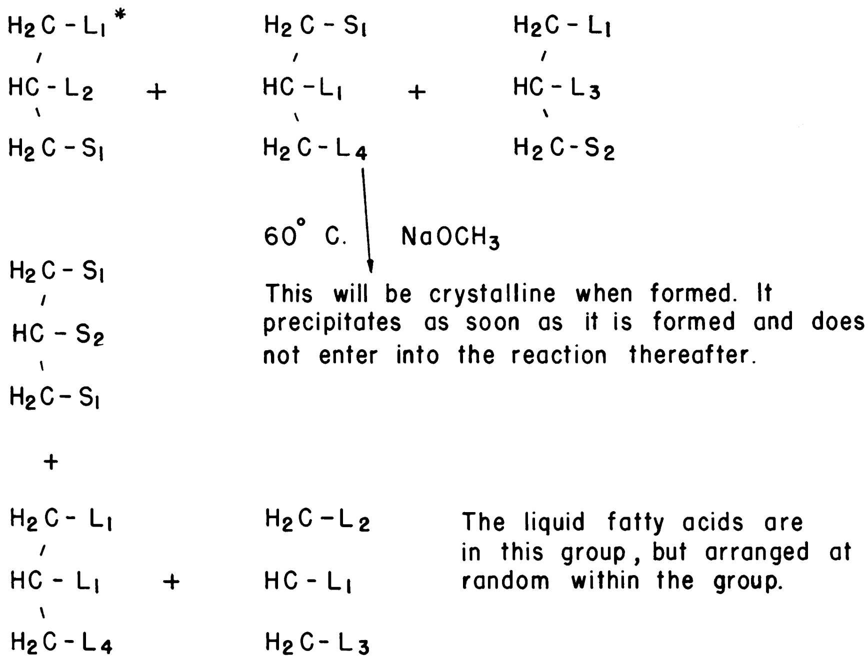

Figure 1. Illustration of a directed interesterification reaction. *L_1=a fatty acid which is liquid at 60° C.; **i.e.**, straight chain compounds of 12 carbon atoms or less, and unsaturated compounds. L_1, L_2, L_3, etc. indicate different liquid fatty acids. S_1=a fatty acid which is solid at 60° C.; **i.e.**, straight chain compounds or more carbon atoms.

glyceride molecules with melting points above 20° C. and more with melting points of less than 20° C. In theory this decreased proportion of high melting point glycerides should influence the body of the finished butter and make it more spreadable.

Methods Employed

The milk fat for these experiments was obtained from fresh sweet cream butter by melting it, then decanting and filtering the fat. This fat was divided into two or more portions of 300 to 350 ml. each. One portion served as an untreated control, and the others were experimental samples. The molecules of the experimental fat were rearranged by directed interesterification, and both the experimental and control fats were rechurned into butter.

The interesterification reaction was carried out at 45° C. using 0.5 percent of sodium methoxide as the catalyst. The reaction was allowed

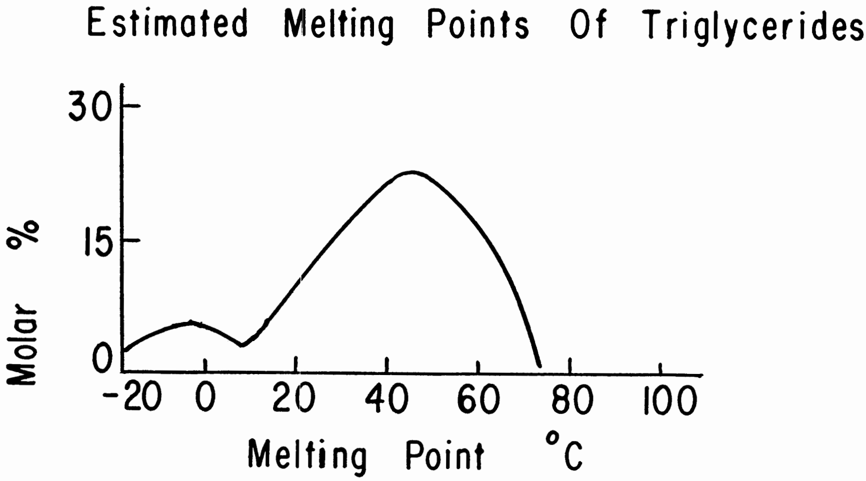

Figure 2. Normal milk fat calculated from data of Bailey (2). Assuming a normal distribution of fatty acids on the glyceride molecules.

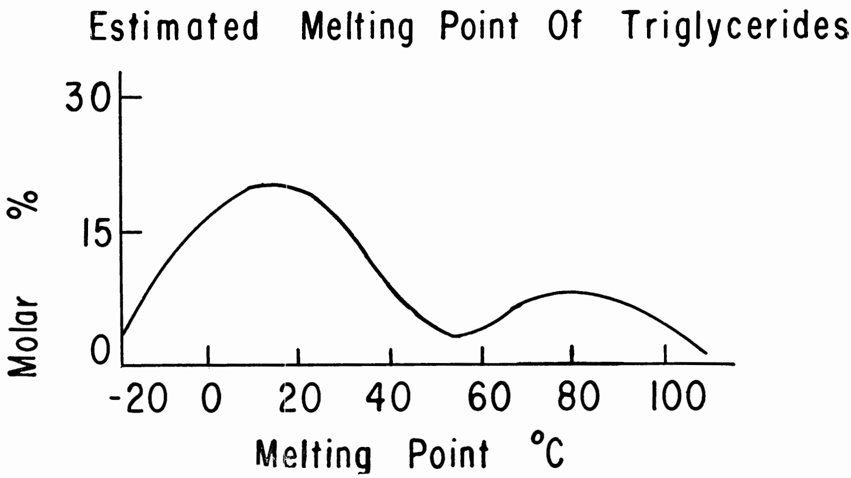

Figure 3. Milk fat after directed interesterification.

to proceed for 30 minutes (8). Churning was accomplished in an apparatus resembling a miniature ice cream freezer (Figure 4). The dasher of this apparatus was driven by a laboratory motor. The cylinder was 7.0 inches high and 3.5 inches in diameter with a capacity of 500 g. of butter. Both the dasher and the cylinder were made of tinned bronze. This apparatus was especially designed for this work and was intended to duplicate the conditions encountered in churning butter by a continuous process.* After interesterification, 2 percent salt and 18 percent

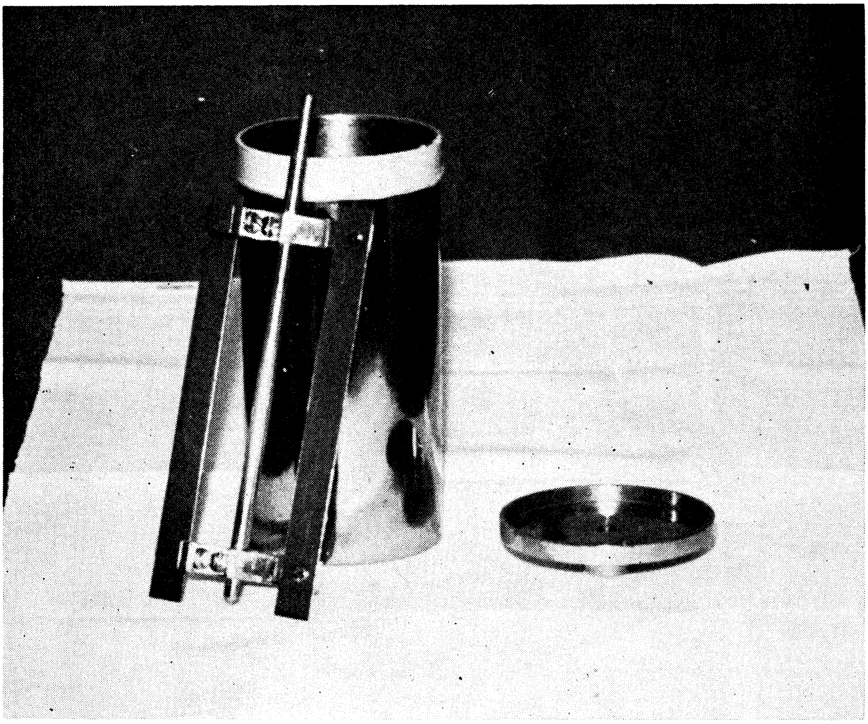

Figure 4. The churning apparatus used in the experiments. Both the dasher and cylinder are made of tinned bronze. Capacity was 500 grams of butter.

water were added to the fat samples. The salt was dissolved in water and these were mixed with the fat by stirring them in the apparatus for two minutes. The churn was then set in an ice bath at 40° F. where butter was churned in approximately three minutes.

After churning, the composition of the butter samples was checked using the Kohman Analysis, and the hardness of the butter was determined. For purposes of this work, hardness was defined as the weight of mercury required to push a sharp metal rod through a pat of butter 3/8 inches thick and about 2 inches in diameter. This property was measured with an apparatus patterned after that described by Gallup (9). Calculations from data of preliminary work showed a correlation coefficient of 0.933 for hardness, as measured by this apparatus, and

*Rearranging milk fat was not practical when butter was churned in batches from cream. However, the reaction could easily fit into many continuous buttermaking operations where practically pure fat is obtained during the processing.

spreadability, as determined by a panel of judges. This figure was similar to the value of 0.95 obtained by Huebner and Thomsen (10). On this basis hardness was used as an indication of spreadability.

An effort was made to determine the amount of liquid fat in the butter obtained in this study. The principle of this procedure was similar to the one used by Dolby (6), and later by DeMan and Wood (5). Liquid fat from a cut surface of butter was allowed to soak into Whatman No. 42 filter paper for 24 hours at a temperature of 46° F. The butter was then removed from the paper, and the fat which had soaked into it was extracted with a Soxhlet apparatus. The values obtained were recorded as grams of fat per square centimeter of butter surface.

Results and Discussion

Rearranging the triglyceride molecules of milk fat by a directed interesterification reaction caused a marked change in the hardness of the resulting butter. In all of the ten batches, shown in Table I, the hardness of the butter made from rearranged fat was less than that of its control made from untreated fat. This decrease in hardness was statistically significant at the 1 percent level of probability.

Table 1.—Hardness of Butter Treated by Directed Interesterification.[1]

Batch No.	Control Butter	Interesterified Butter	Decrease
1	567	277	290
2	653	260	393
3	443	<180	263
4	600	<180	420
5	630	416	214
6	570	<180	390
7	550	265	285
8	476	<180	296
9	532	377	155
10	536	422	114
Average	555.7	273.7	282[2]

[1] Hardness expressed as grams of mercury required to push a sharp metal rod through a pat of butter 3/8-inch thick.
[2] $P<0.01$

The metal rod and the mercury container in the apparatus used to measure hardness weighed 180 grams. Thus, values of less than 180 grams could not be measured with this instrument. Several of the butter samples made from the rearranged fat in this work did have hardness values of less than 180 grams. These had to be recorded as "less than (<) 180 grams."

The reduction in butter hardness appeared to be directly, but not perfectly, related to the proportion of liquid fat in the butter. These data are shown in Table II. The amount of liquid fat increased in eight of the ten batches, and this increase was statistically significant at the 5 percent level of probability. The correlation between hardness and the amount of liquid fat in this butter was —0.675.

Table II.—Liquid Fat in Butter Treated by Directed Interesterification.[1]

Batch No.	Control Butter	Interesterified Butter	Increase
1	52	73	21
2	37	104	67
3	45	222	177
4	15	194	179
5	22	18	— .4
6	13	32	19
7	16	34	18
8	13	142	129
9	58	18	—.40
10	5	14	9
Average	27.6	85.1	57.5[2]

[1] mg./cm.^{2} Mg. of fat absorbed by filter paper at 46° F. in relation to the cross sectional area of the butter cube.
[2] $P < 0.05$

The rather large variations between replicate batches in this work would undoubtedly have been smaller had more precise measuring techniques been available. Even with these variations, however, statistical analysis left no doubt that rearranging the molecules of milk fat by a directed interesterification reaction reduced the hardness of the resulting butter by more than half. This reduction in hardness was accompanied by a corresponding increase of over 200 percent in the amount of liquid fat in the butter.

Part 2. Eliminating Disagreeable Flavor in Rearranged Milk Fat

The Problem

Rearranging the fatty acids in milk fat molecules brought about a marked reduction in the hardness of the final butter. One problem which was immediately obvious, however, was the disagreeable flavor which appeared in the butter. If nothing were done to counteract it, this flavor appeared almost immediately in the fat and the butter, and became progressively worse until the product usually was judged unfit for consumption after three or four days of storage at 44° to 48° F.

After reviewing the literature it appeared that this flavor might be similar to the "rancid-like" flavor described by Josephson and Dahle (12) and more recently by Smith *et. al.* (14). This flavor results from heating milk fat which contains none of its natural antioxidants. The natural antioxidants are thought to be mostly in the so called "phospholipid" fraction of milk fat. Much of the phospholipid material is lost in the process of churning butter from cream in a conventional barrel churn, and butter churned in this manner was the raw material from which the fat for this work was obtained. What phospholipid the butter did contain was probably lost when it was melted and the water portion of it discarded to obtain the pure fat used for this work.

Methods Employed

It was thought that this "rancid-like" flavor could be removed from the fat by refining it, after rearrangement, in a manner similar to that used in removing foreign flavors from other types of fat. Accordingly, a "refining" procedure was adopted which was patterned after certain of the processes described by Bailey in his book on *Industrial Oil and Fat Products* (1). In general, the refining process consisted of "neutrallizing" the fat and then "steaming" it.

The free fatty acids in the fat were neutralized with a sodium hydroxide solution to a phenolphthalein end-point. In addition, an excess which equaled 0.48 percent of dry NaOH in relation to the weight of the fat was added. The alkali solution was added to the fat, and the mixture was heated to a temperature of 120° to 130° C. and stirred slowly for 30 to 45 minutes. During this time a precipitate formed in the mixture. The fat then was separated from the water, and the precipitate was removed by filtering through a pad of "Fuller's Earth". After this, the fat was steamed. This consisted of bubbling steam through the fat, under a vacuum of 25 to 27 inches, for a period of four to six hours. During this time the fat remained at a temperature of 90 to 100° C.

After the rearranged milk fat had been "refined" by the processes just described (or some modification thereof), 18 percent water and 2 percent salt were added. The mixture then was churned into butter, using the apparatus described previously.

Trial 1

The first flavor removal trial was an effort to remove the undesirable flavor found in rearranged fat by "refining" it. The refining process described above was the starting point in the design of these experiments. It was the so called "normal" procedure, the variations of which are shown in Table III. These variations were introduced in the refining procedure in an effort to learn more about the cause of the undesirable flavor found in rearranged fat. These variations included: conducting the rearrangement reaction in a nitrogen atmosphere rather than in air; eliminating the neutralization or steaming operation; and increasing the temperature of neutralization from 100° to 180° C.

After the butter was rearranged, refined and churned, its flavor was evaluated by a panel of three trained judges, who used the following rating system to describe the "rancid-like" flavor of this butter: 4 = no criticism; 3 = slight off-flavor, 2 = definite off-flavor, 1 = pronounced off-flavor, and 0 = unfit for consumption.

The flavor evaluations in this first trial were conducted over a 12-day period. During this time the flavor of the butter was evaluated six times by each of the three judges. Thus, the flavor ratings in Table III represent an average of 18 observations. In this trial, the keeping quality was expressed as the number of days which elapsed before the butter developed a definite off-flavor—a flavor rating of 2.0 or less.

Trial 2

The average flavor ratings in the first trial were misleadingly low, since by the end of the 12-day period nearly all of the samples had de-

Table III.—Effect of Variations in Rearranging and Refiniing Milk Fat on the Keeping Quality of Butter Made from that Fat—Trials 1 and 2.

Sample		Processing Steps			Keeping Quality	Days that flavor rating was 2.0 or more
No.	Treatment	Rearrangement	Neutralization	Steaming	Ave. Flavor Rating	
		(Atmosphere)	(Temperature °C.)			
Trial 1						
1	Control—No Treatment	---[1]	---	-----	1.5	4
2.	Normal Treatment	(air)[2]	100	90-100	2.2	7
3	Rearranged in a Nitrogen Atmosphere	(N_2)	100	90-100	3.0	12
4	High Heat Treatment during Neutralization	(air)	180	90-100	0.2	0
5	Steamed but not Neutralized	(air)	---	90-100	2.7	12
6	Neutralized but not Steamed	(air)	100	-----	1.3	1
Trial 2						
7	Control—No Treatment	----	---	-----	2.8	--
8	Normal Treatment	(air)	100	90-100	2.4	--
9	Steamed but not neutralized	(air)	---	90-100	0.1	--

[1] Sample not given this treatment.
[2] The variations indicated are the atmosphere (air or nitrogen) for the rearrangement reaction and the temperature (°C.) at which neutralization or steaming was conducted.

veloped some degree of undesirable flavor. Portions of the trial were repeated in an effort to demonstrate more conclusively that the refining processes removed most of the undesirable flavor in the butter, and that steaming was a critical step in the process. This second trial was conducted over a period of five days, during which the flavor of each sample was evaluated four times by each of the three judges.

Results and Discussion

The procedures used for "refining" the fat before churning helped remove the undesirable flavor of butter which resulted from rearranging the molecules of the milk fat. Results are shown in Table II. Samples 2 and 8, which were refined following rearrangement, had flavor scores that were similar to those of samples 1 and 7, which were the unrearranged or control samples.

Steaming seemed to have had more influence in preventing the off-flavor than did the neutralization process. When the fat was not steamed, as in samples 6 and 9, the resulting butter had very low flavor scores. This butter was judged unfit for consumption the day after it was churned. On the other hand, the results obtained from sample 5 indicate that the neutralization process could probably be eliminated without damaging the flavor of the fat, providing that an excessive quantity of free fatty acids was not produced as a result of the interesterification reaction.

The flavor of the butter in this work probably was similar to the rancid flavor in milk fat described in the literature (12, 14), since excessive heat treatments, as in Sample 4, appeared to make the flavor more pronounced. Conducting the interesterification reaction in a nitrogen atmosphere (sample 3) appeared either to improve the flavor of the resulting butter or prevent the flavor from appearing.

Salt appeared to enhance both the desirable and undesirable flavors of the butter in this work. The unsalted butter had a bland taste and lacked the desirable flavor usually associated with good butter. However, it did not develop the undesirable rancid flavor associated with much of the other butter in the study.

Summary

The objectives of this work were: a) to determine the influence of rearranging milk fat molecules on the hardness of the resulting butter (hardness was used as an indication of spreadability), b) to determine if the refining process used in this work would counteract the rancid flavor which usually was present in the butter made from this rearranged fat.

Milk fat was obtained from fresh sweet cream butter by melting it, then decanting and filtering the fat. The fatty acids on the triglyceride molecules of this fat were rearranged with a directed interesterification reaction. The rearranged fat was then refined. Refining consisted of neutralizing the free fatty acids in the fat, then bubbling steam through the fat under vacuum for 4 to 6 hours. After being refined the fat was churned into butter.

The data obtained in this study indicate that rearrangement reduced the hardness of butter an average of about 50 percent. A correlation coefficient of —0.675 was calculated for this decreased hardness and the corresponding increase in the liquid fat present in the butter.

Although the rearranged fat often had a rancid flavor, this could be removed by the refining processes used in this work. The data obtained in this study indicate that the flavor of the butter was improved if the interesterification reaction was conducted in a nitrogen atmosphere rather than in air. High heat treatment appeared to intensify the flavor in the fat, and these data, together with those in the literature, seem to indicate that heat may be the cause of the rancid flavors encountered in this type of fat. Of the two steps involved in the refining the fat, neutralization and steaming, steaming appeared to have the most influence in counteracting undesirable flavors. It may be that neutralization can be eliminated as a refining process without materially affecting the flavor of the fat and the resulting butter.

Literature Cited

1. Bailey, A. E. *Industrial Oil and Fat Products.* 2nd Ed. Interscience Publishers, Inc. New York. 1951.
2. Bailey, A. E. *Melting and Soldification of Fats.* Intersicence Publishers, Inc. New York. 1950.
3. Brunner, J. R., and E. L. Jack. The relation between the degree of solidification of fat in cream and its churning time. II. The physical distribution of the liquid solid phases within the globule. *J. Dairy Sci. 33*: 267. 1950.
4. Deman, J. M. and F. W. Wood. Influence of Temperature Treatment and Season on the Dilatometric Behavior of Butterfat. *J. Dairy Res., 26:* 17, 1959.
5. Deman, J. M. and F. W. Wood. Oiling—off Properties of Butter. *J. Dairy Sci., 41:* 369. 1958.
6. Dolby, R. M. The Effect of Temperature of Cream Before Churning on the Consistencyy of Butter. *J. Dairy Res., 21:* 67. 1954.
7. Dolby, R. M. The Properties of New Zealand Butters and Butterfat. II. The Relation of Hardness of New Zealand Commercial Butter and Composition of the Butterfat. *J. Dairy Res., 16:* 336. 1949.
8 Eckey, W. E. and M. W. Formo. Directed Interesterification in Glycerides. Reaction in Presence of Added Glycerol. *J. Amer. Oil Chem. Soc. 26:* 207. 1949.
9. Gallup, W. D. Jr. Studying the Hardness of Butterfat. *J. Ind. Eng. Chem. Anal. Ed., 8:* 123. 1936.
10. Huebner, V. R. and L. C. Thomsen. Spreadability and Hardness of Butter. I. Development of an Instrument for Measuring Spreadability. *J. Dairy Sci., 40:* 839, 1957.
11. Huebner, V. R. and L. C. Thomsen. Spreadability and Hardness of Butter. II. Some Factors Affecting Spreadability and Hardness. *J. Dairy Sci., 40:* 839. 1957.
12. Josephson, D. V. and C. D. Dable. Heating Makes Butter Keep. *Food Ind. 17:* 630. 1945.
13. McMichael, C. E. Finishing and Packaging of Edible Fats. *J. Amer. Oil Chem. Soc. 33:* 512. 1956.
14. Smith, L. M., E. N. Frankel, W. Haab, and E. L. Jack. Effect of Phospholipids and Unsaponifiable Matter on Oxidative Stability of Milk Fat, *J. Dairy Sci., 41*: 473. 1958.

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