• *Technical*

A Comparison of Sodium Methoxide-Treated Lards[1]

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The treatment of lard with interesterification catalysts can give a variety of products, depending on the time and temperature relationships used in the treatment. These products are distinguished from each other by several means; x-ray diffraction analysis, cooling curves, dilatometric analysis, photomicrographic analysis, and glyceride composition.

A correlation of the physical and functional properties of these treated lards has been made, showing that a stable shortening with good baking characteristics is associated with complete and permanent alteration in lard crystal structure, that is, crystal modification. Shortenings from those lards which exhibit some *beta* crystal properties either initially or on subsequent storage do not retain these desirable characteristics.

SHORTENINGS made from natural lard characteristically have a waxy or grainy texture and exhibit unsatisfactory cake-baking qualities. Much attention has been given (1,2,3,4,5) to the improvement with interesterification catalysts under a variety of conditions.

The purpose of this paper is to compare lard products obtained from several different conditions of treatment. Specifically the products compared are a) untreated lard, b) crystal-modified lard (CML), c) partially-modified lard (PML), and d) lard treated by directed interesterification (DIL). The term crystal-modified is used since it represents the minimum treatment required to effect in lard a permanent and stable change in its crystal structure. A relationship between the various types of products is represented schematically in Figure 1.

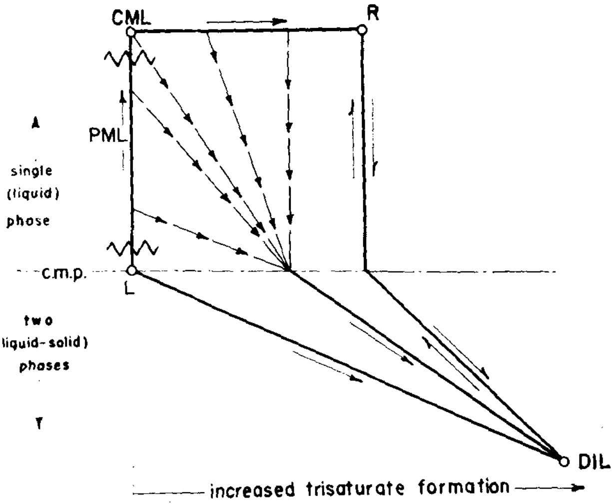

FIG. 1. Products from the treatment of lard. Legend: c.m.p.—complete melting point of lard. L—lard. PML—partially-modified lard. CML—crystal-modified lard. R—randomized lard. DIL—directed interesterified lard. When lard is treated at temperatures above its c.m.p., the products formed will follow the sequence PML, CML, and R; the latter represent maximum trisaturate formation in the liquid state. Treating lard below its c.m.p. results in a DIL product, which can be obtained from any point along the line L-CML-R. Reversibility is only possible between the DIL and R products.

Experimental

Crystal-modified lard was prepared by treating lard, which had been previously filtered and dried, with 0.5% sodium methoxide, under different sets of time and temperature conditions; the reaction was terminated by the addition of water. The time and temperature relationships for obtaining crystal modification is shown in Figure 2. Partially-modified lard must be described by time-temperature relationships which were not sufficient completely to modify the lard. The manner of determining the extent of partial modification will be discussed at a later time. In general, the directed interesterification process was carried out by treating the lard with 0.5% catalyst (usually sodium metal or sodium methoxide) at 75°F. In certain preparations the lard was first treated with catalyst at 195°F. for 20 min. prior to cooling the resulting modified lard to 75°F. for precipitation of the trisaturates. In other instances a 10% catalyst suspension in lard was preactivated at 110°F. for 10 min. and was added to lard. The directed rearrangement then took place with lard as the starting material rather than with crystal-modified lard as in the previous case. Directed interesterification was also conducted from 40 to 98°F.

Methods of Analysis

X-Ray Diffraction Analysis. Samples for x-ray diffraction analysis were prepared by quick chilling the melted fats on dry ice and tempering them at 75°F. for 48 hrs. Sample thickness was 0.082 in. Diffraction patterns were taken on flat film with film-to-sample distances of 7.5 cm. for short- and 20.0 cm. for long-spacing patterns. Diffraction patterns of aged samples were made at the same temperatures as used for incubation.

X-ray diffraction was done on a standard General Electric XRD-1 unit, using copper radiation with a nickel filter in a 0.025-in. slit system.

Cooling Curves. Cooling curves were determined by the differential technique described in another paper (6).

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Dilatometric Data. Dilatometric data were obtained by using the method of Fulton *et al.* (7)

Photomicrographs. Photomicrograph samples were prepared by placing a drop of melted sample on a microscope slide and covering with a cover slip. The fats were allowed to crystallize for 48 hrs. at 75°F. before photographing. Photographs were made at 400 × under polarized light. (Engraving printed at 290 ×.)

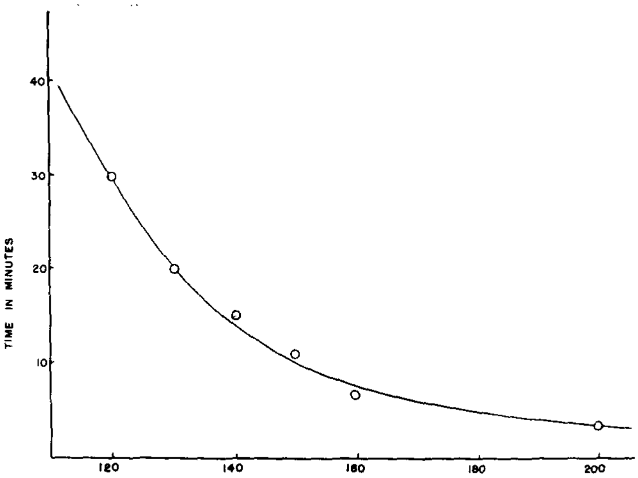

FIG. 2. Minimum time required for crystal modification of lard in relation to reaction temperature.

Glyceride Composition. Fractionation of samples were carried out from acetone solvent, according to the method of Riemenschneider (8). The trisaturated triglycerides were crystallized at 75°F. while the disaturated were removed from the solvent at 45°F.

Products for Bakery Performance Tests. A home type of power ice cream freezer, using crushed ice in water as the chilling agent, was used to plasticize the shortenings. Eight per cent hard fat was added to the various products as a firming agent. The prepared shortenings were tempered at 85°F. for at least 48 hrs. Consistencies were determined by using the Bloom consistency tester (9). The pound cake baking test was used exclusively to evaluate performance.

Results and Discussion

X-Rays. X-ray diffraction characteristics have had little mention in the literature as a means of describing the physical properties and behavior of natural fats. In one instance (10) crystal characteristics of a few natural fats have been described in terms of a) their tendency to erupt on slow solidification or b) the relative coarseness of their crystal structure. A more exact and significant way of characterizing the crystal structure of natural triglyceride mixtures would be through the use of x-ray diffraction analysis.

In this discussion we shall restrict the classification of lard and treated lards to their most stable crystal form under the conditions normally encountered in the handling, shipping, and storage of shortenings prepared from such products. Temperature is an important factor and it is essential that the samples under investigation not be mistreated. Extremes in temperature will cause abnormal polymorphic transitions.

Table I cites the diffraction patterns exhibited by lard and the lard products resulting from treatment by the various methods described above. These patterns are compared with that of partially hydrogenated cottonseed oil.

Lard in its stable form exhibits a mixed *beta,beta-prime* pattern as characterized by its short-spacing measurements. Line spacings of triglycerides have been given as 3.7, 3.9, 4.6, 5.3 for the *beta* form and 3.8 and 4.2 Å for the *beta-prime* (10). The most prominent lines in lard are those spacings which are characteristic of the *beta* form.

It should be pointed out that it is possible to obtain a plasticized lard in the *beta-prime* form. This however is an unstable condition, and after a short time a transition to the stable predominately *beta* product will take place. Visual evidence for this is well known in that lard can be chilled to a smooth-textured product only to become coarse and grainy soon afterwards.

TABLE I

Typical Diffraction Patterns of Lard Products from Various Processes

	No treatment		Directed interesterification		Partial crystal modification[a]		Full crystal modification		Hydrogenated CSO[c]	
	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
S.S.	3.76	M–	3.79	M	3.77	M	3.81	M	3.79	S–
	4.12	M	4.18	S	4.13	M	4.19	S	4.17	S
	4.52	S	4.58	M	4.56	S	4.61	VVW[b]	4.55	VVW[b]
	5.32	W	......	....	......	....	......	....	......	....
L.S.	13.7	W	14.3	M–	14.5	M–	14.4	M–	14.4	M
	22.9	M	......	....	......	....	......	....	22.2	W
	44.5	S	44.1	S	43.9	S	44.05	S	43.3	S
Avg. d	43.8	....	43.5	....	43.7	....	43.7	....	43.9	....

[a] Prepared by treatment at 65°C. for 10 min.
[b] Very weak and diffuse background area.
[c] Hydrogenated to an I.V. of 59.4.

TABLE II

Progressive Change in X-ray Diffraction Patterns of Treatment of Lard in the Liquid State

	Increased Treatment												Randomized lard[b]	
	Lard		1		2		3		4		CM Lard			
	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
S.S.	3.76	M–	3.75	M	3.8	M	3.77	M	3.8	M	3.81	M	3.77	M-
	4.12	M	4.1	S–	4.11	S-	4.13	M	4.13	S	4.19	S	4.16	S–
	4.52	S	4.56	S	4.62	S	4.6	S	4.56	W	4.6	VVW[a]	4.6	VVW[a]
	5.32	W	5.4	VW	......	....	......	....	......	....	......	....	......	....
L.S.	13.7	W	13.56	W	13.98	W	14.45	W	14.5	M–	14.4	M–	14.26	M
	22.9	W	22.03	W	22.03	W	......	....	......	....	......	....	......	....
	33.9	M	33.87	M	33.42	M	33.8	M	......	....	......	....	......	....
	38.6	M	......	....	......	....	......	....	......	....	......	....	......	....
	43.5	S	43.71	S	43.9	S	43.8	S	43.7	S	44.05	S	44.12	S
Avg. d.	43.6	....	43.3	....	42.3	....	43.6	....	43.6	....	43.7	....	43.7	....

[a] Very weak and diffuse background. [b] Treated at 90°C. for 2 hrs.

Crystal-modified lard is the only nonrandom lard product covered by this investigation which exhibits a *beta-prime* pattern similar to that of hydrogenated cottonseed oil. All of the other treated lards, partially-modified lard and lard prepared by directed interesterification, have some *beta* characteristics which, as will be shown later, correlate with their poorer functional properties.

Table II shows the observed progressive change in x-ray diffraction patterns with continued treatment of lard in the liquid state. These examples were chosen from the time-temperature series, used to make up Figure 2, and illustrate the basic line-spacing changes observed during progression of the reaction, from lard to the stable form, *i.e.*, crystal-modified lard, after which there is no further change in the x-ray pattern with continued treatment toward randomization.

As previously reported by Hoerr and Waugh (12), some changes in long spacings are observed. A shift from 13.5 Å to 14.5 Å and disappearance of the 22.5 Å line occur very early in the modification reaction. At this time the short spacings are still essentially those of the *beta* form, as shown by the strong 4.6 Å line.

Even when the 4.6 Å line is weak but definite, full crystal modification has not really been attained. Sample 4 in Tables II and III is an excellent example of this. Table II shows this sample to have a weak 4.6 Å line and completely altered long spacings. On aging, the sample reverts to a stronger *beta*, structure, shown in Table III as having a strong 4.6 Å line. The long spacings do not however demonstrate such reversion.

TABLE III

Typical Diffraction Patterns of Aged Samples Shown in Table II

	Lard		Samples 1 and 2		Samples 3 and 4		CML and randomized lard	
	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
S.S.	3.69	M	3.75	M	3.8	M	3.8	M
	3.87	M	4.2	W	4.16	M	4.18	S
	4.2	W	......	....	......	....	......	....
	4.6	VS	4.6	S	4.6	S–	4.6	VVW[a]
	5.3	W	5.3	VW	......	....	......	....
L.S.	13.4	W	13.7	W	14.5	M	14.4	M
	23.2	W	22.4	W	......	....	......	....
	43.8	VS	43.5	VS	43.5	VS	43.7	VS

[a] Diffuse background area; no definite line is discernible.

Table III also shows that the *beta-prime* structure of crystal-modified lard does not revert on aging but is actually a stable structure.

The lard products prepared by directed interesterification all exhibit some *beta* properties, as indicated by the presence of a line at 4.6 Å (Table I). This can be attributed to the formation of trisaturated triglycerides during progress of the reaction. However on aging a completely new and heretofore unreported stable diffraction pattern for treated lard was observed. The basic characteristics of this pattern are a very strong 4.6 Å line, which lies in the center of a shaded area with well-defined borders at 4.2 and 5.3 Å and will be designated by the symbol *Nu* (V). This pattern does not undergo further transition to the *beta* pattern, which is distinguished by having four definite and distinct lines. Figure 3 shows a comparison of this pattern with lard and crystal-modified lard. The long spacings for this form are similar to those of crystal-modified lard and do not change with aging or tempering at higher temperatures for long periods of time.

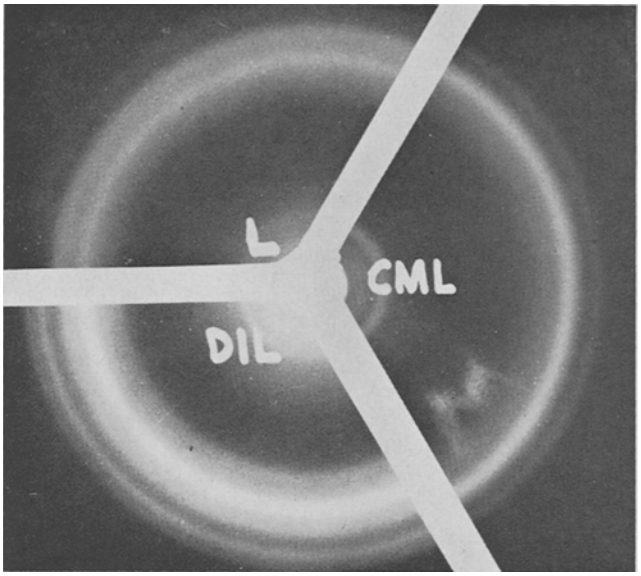

FIG. 3. Comparison of x-ray diffraction patterns of lard (L), completely-modified lard (CML), and directed interesterified lard (DIL). The latter exhibits the *Nu* diffraction pattern.

Table IV shows a series that illustrates the progressive change in x-ray pattern during the directed interesterification of lard. In the earlier stages of treatment a close approach to the *Nu* pattern is observed, which, as treatment progresses, develops into a pattern similar to that observed for partially-modified samples.

Table V, which cites the pattern changes encountered during the directed interesterification of crystal-modified lard, also illustrates the reversibility of these treatments, as shown earlier in Figure 1. In this case the pattern development is from a *beta-prime* type to one with strong *beta* characteristics. Unlike the directed interesterification of lard, these patterns do not show the *Nu* pattern. In each case however, whether lard or modified lard was used as a starting material, the samples upon aging will all develop the characteristic *Nu* pattern. Long-spacing arrangements for these treated lards follow much the same pattern established earlier for liquid-state, treated lards, as described in Table II.

TABLE IV

X-ray Diffraction Data on Lard Treated by Directed Interesterification

(Treated with 0.5% sodium methoxide at 110°F. for 10 min. prior to being held at 75°F. for the times indicated below)

	3 Hr.		1 Day		2 Days		10 Days		20 Days	
	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
S.S.	3.86	M	3.89	M	3.9	M–	3.86	S	3.86	S–
	4.21[a]	M	4.23[a]	S–	4.3	S	4.34	VS	4.32	S
	4.67	VS	4.71	VS	4.68	M	4.7	M	4.66	S
	5.4[a]	W	5.3[a]	VW	......	....	......	....	......	....
L.S.	13.6	W	13.9	W	14.51	M	14.37	M	14.4	M
	22.6	M	22.8	M	......	....	......	....	......	....
	33.77	M	33.67	M	......	....	......	....	......	....
	46.5	S	45.2	S	44.05	VS	43.3	S	44.05	VS
Avg. d	44.2	....	44.2	....	43.8	....	43.3	....	43.4	....

[a] Shaded area extending from 4.2 to 5.3 line. This resembles the *Nu* pattern with a more definite line formation at 4.2 Å. At 5.3 Å this is a border formation and not a discrete line.

TABLE V

X-ray Diffraction Data on Samples from the Directed Interesterification of Pre-activated Lard

(10% of lard to be treated was heated with catalyst at 90°C. for 20 min. and added to main body of lard held at 75°F. Samples were incubated at 75°F. for the periods cited below.)

	0 Hr.		1 Hr.		2 Hr.		3 Hr.		24 Hr.		4 Days	
	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
Short spacings	3.89	M+	3.9	M+	3.87	S—	3.88	M+	3.9	S	3.89	S—
	4.34	S	4.26	S	4.21	VS	4.21	S	4.27	VS	4.22	VS
	4.78	VD	4.69	VW+	4.63	M	4.65	M—	4.69	M+	4.64	M
Long spacings	14.29	M	14.37	M	14.43	M	14.43	M	14.29	M	14.37	M
	44.05	M	44.6	S	44.05	S	44.05	S	44.05	S	44.05	S
Avg. d	43.4	....	43.9	....	43.6	....	43.6	....	43.4	....	43.6	....

Differential Cooling Curves. The changes in glyceride structure, occurring at different stages of modification, are reflected by the series of differential cooling curves shown in Figure 4. Curve A, representing untreated lard, is characterized by a strong peak at 4 to 5 min., which can be attributed to the disaturated monounsaturated glycerides present (6). Curves B and C represent samples taken as the modification process progresses and show the "S_2U" peak diminishing to the point that it becomes indistinguishable as in Curve D, the curve for fully-modified lard. The disappearance of this peak has been found to parallel the gradual loss of the 4.6 Å line of the x-ray diffraction pattern as the modification reaction goes to completion.

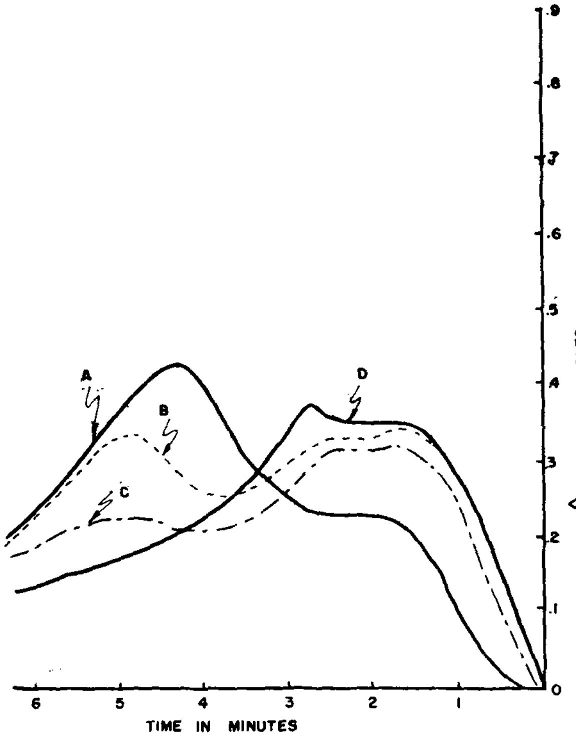

FIG. 4. Differential cooling curves of lard (Curve A), partially-modified lard (Curves B and C), and completely-modified lard (Curve D).

The increase in the trisaturated triglyceride content during the directed interesterification of lard is shown by the development of the peak at about 3 min. in the series of curves of Figure 5. The lowest curve is typical for crystal-modified lard. As the trisaturated triglycerides build up, the curves become more nearly like those of a modified shortening to which hard fat has been added.

Dilatometric Measurements. The dilatometric behavior of lard, randomized lard, and directed interesterified lard has been reported by Hawley and Holman (13). A more intensive study of the various treated-lard products shows some rather interesting phenomena. Figure 6 shows the relationship between lard, crystal-modified lard, and partially-modified lards. These curves exhibit a normal progression from the original lard through levels of partial modification to fully-modified lard. In the earliest stages of treatment the curve of partially-modified lard (PML-A) still retains the characteristic lard shape throughout. The typical lard pattern no longer appears as the product nears modification (PML-B). Both partially-modified lards show lower solids content than either lard or completely-modified lard in at least some portions of the curve. This is analogous to combining two different fats and is apparently caused by the intersolubility of the triglycerides of each fat.

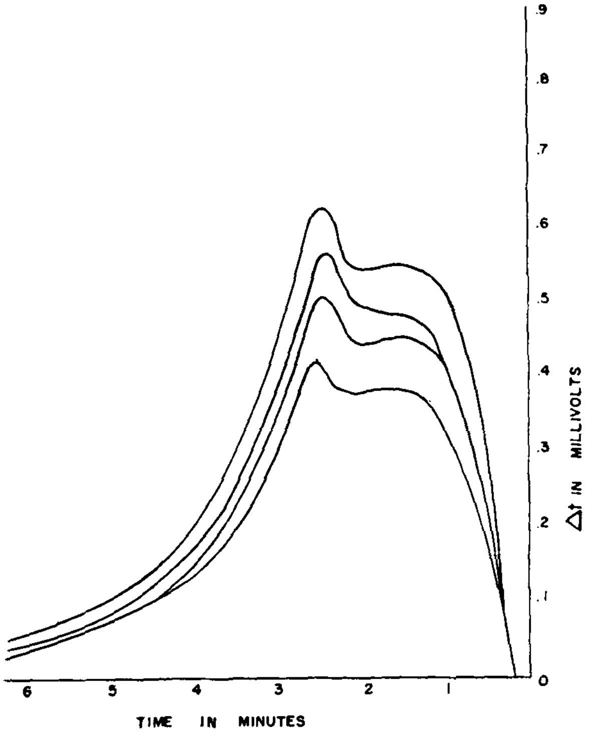

FIG. 5. Differential cooling curves of lard subjected to directed interesterification.

The step-by-step transition from lard and CML to the product of directed interesterification is given in

Figures 7 and 8. The final products, obtained at various reaction temperatures below the melting point of lard, are given in Figure 9. The normal progression of increased solids, as the temperature of treatment decreases, is apparently reversed between 60 and 40 degrees.

Typical commercial shortening products were duplicated by adding 12% hard fat to crystal-modified lard, and hardening the lard treated by directed interesterification to an iodine value 5 units below the original. The solid fat index curves of these products are given in Figure 10. While the original products have considerably different curves, those of the finished shortenings are almost identical. Since dilatometric measurements are usually compared with consistency and plastic range of the finished shortenings, the actual consistencies are included for comparison (Figure 11). The relationship between the

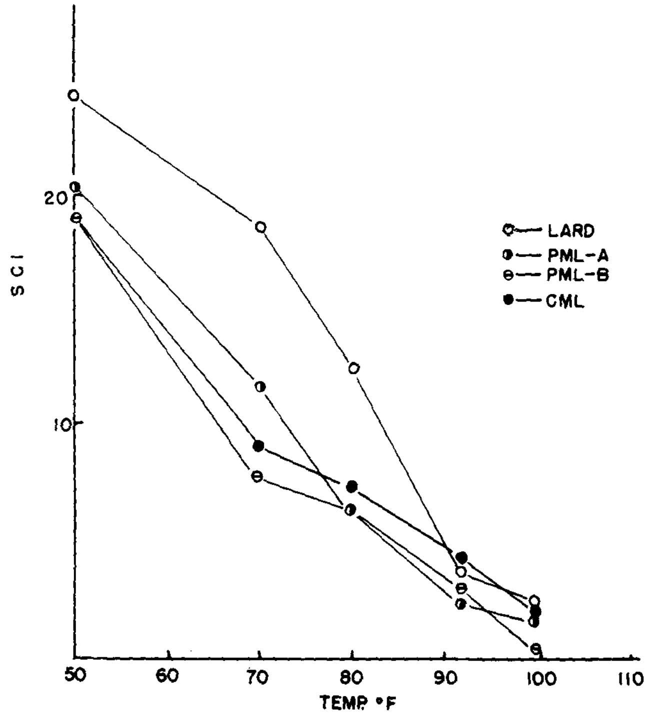

FIG. 6. Dilatometric curves of lard, partially-modified lard, and completely-modified lard.

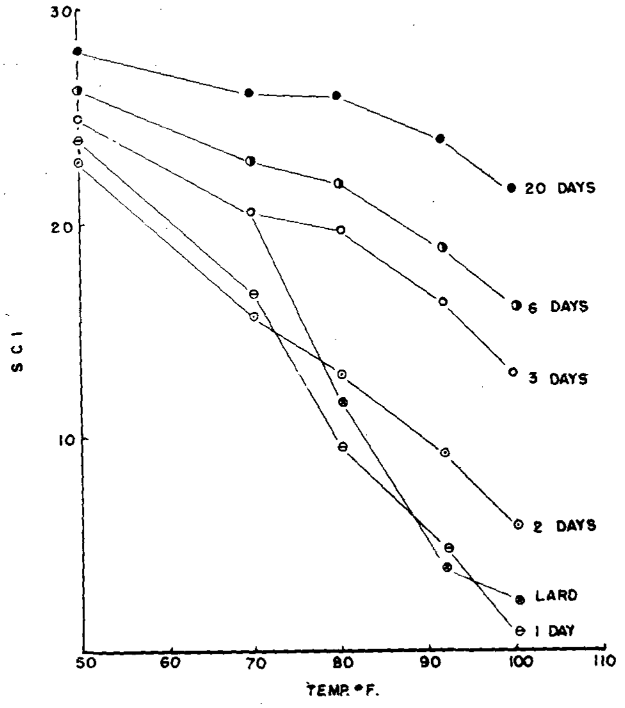

FIG. 7. Dilatometric curves of the progression of directed interesterified lard prepared from lard at 75°F. reaction temperature.

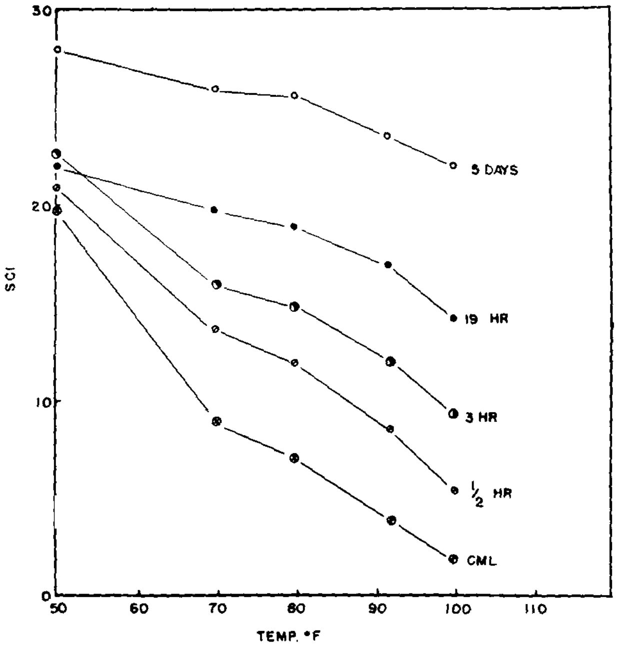

FIG. 8. Dilatometric curves of the progression of directed interesterified lard, prepared from crystal-modified lard at 75°F. reaction temperature.

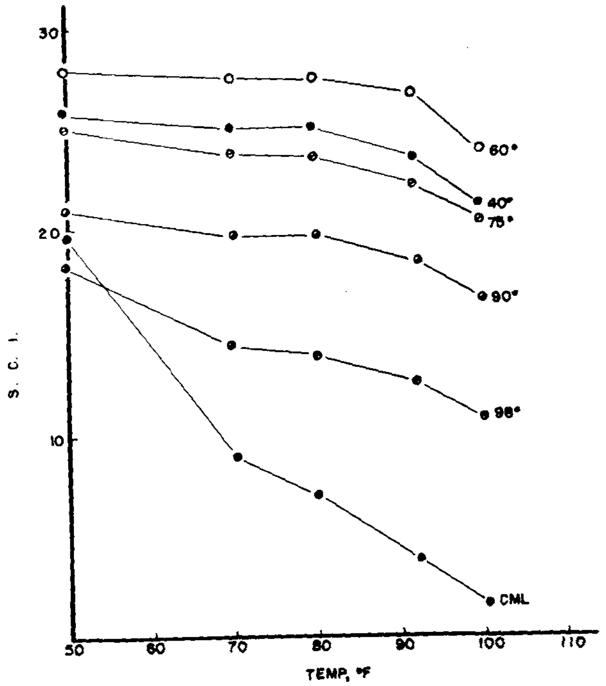

FIG. 9. Dilatometric curves of directed interesterified lard reacted at various temperatures.

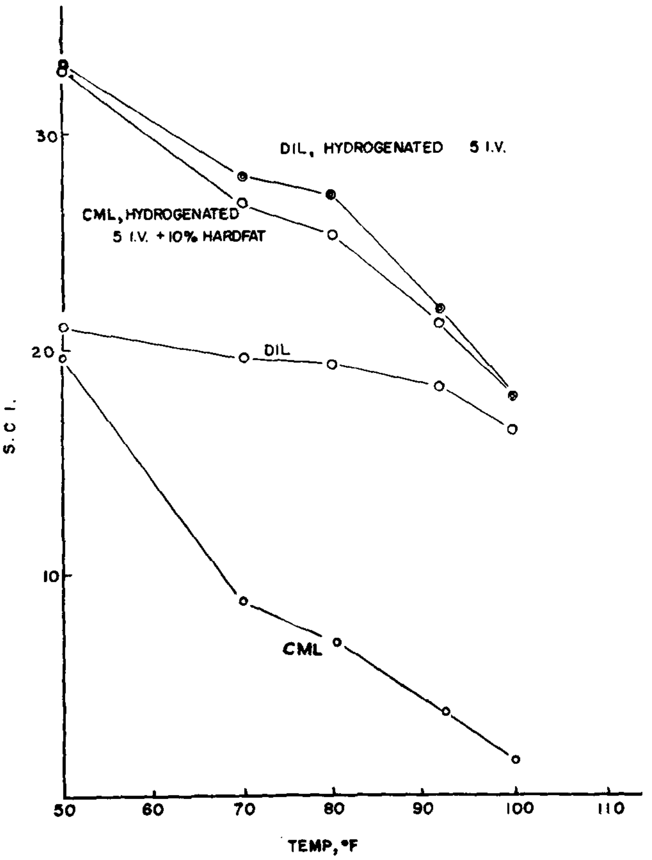

FIG. 10. Comparison of dilatometric curves of completely-modified lard and directed interesterified lard and their finished shortenings.

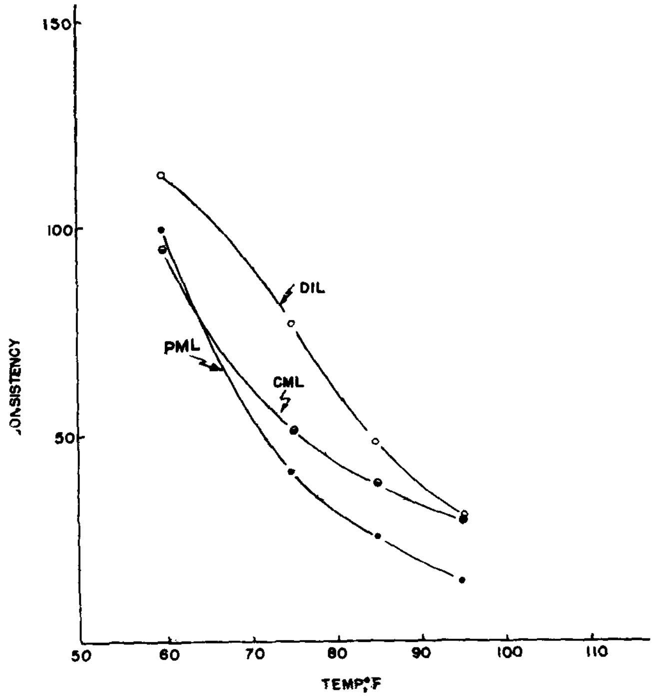

FIG. 11. Curves of Bloom consistency *versus* temperature for various treated lards.

consistency curves of the three shortenings is similar to the relationship between the solid fat index curves of the same products. The crystal-modified lard shortening had a broader plastic range than the other products in the comparison.

Photomicrographs. The effect of various treatments on lard in relation to finished shortenings can easily be visualized from the observation of photomicrographs of the treated lard (Figure 12). The clusters of fat crystals which cause graininess in shortenings are completely absent in the crystal-modified lard pictures even after aging for 60 days at 75°C. As was pointed out previously, freshly-plasticized lard and lard treated by directed interesterification can be obtained in the *beta-prime* form. This form however is not stable for these products and will soon revert to the typical aged forms, showing clusters of crystallized fats. The aged CML shows a coarsening of structure, but nowhere are seen the large granular clusters that are found in the other products.

TABLE VI

Triglyceride Distribution in Treated Lards

Product	M.P. (FAC)	% GS_3	% GS_2U	% GS_3 + GS_2U
	°*F*.			
Lard	110	0.8	16.9	17.6
CML	106	0.7	14.0	14.6
DIL				
98°F	118	9.0	7.0	16.0
90°F	121	13.2	8.2	21.3
75°F	122	15.6	9.1	24.7
70°F	122	16.2	10.0	26.1
60°F	122	18.6	10.1	28.7
40°F	122	15.4	12.1	27.5

Glyceride Composition. Table VI shows the trisaturated and disaturated triglycerides that are obtained from fractional crystallization of the lards from acetone. Those formed during directed interesterification at various temperatures are compared with values obtained from crystal-modified lard and untreated lard. The weights of material obtained from each fractionation have been corrected for the theoretical iodine value of the GS_2U portion of each fraction. The low values obtained from modified lard and lard show that a considerable percentage of the harder portions of these products is still dissolved in the more unsaturated fractions, and these were not subjected to exhaustive recrystallization. On the other hand, all of the values given show an empirical relationship. The trisaturated triglyceride fraction of directed interesterified lard increases regularly to a maximum at 60°F. The disaturated fraction has its maximum at 40°F.

It is interesting to note that the chief difference between treatment at 98°F., just below the melting point of lard, and lard modified wholly in the liquid state is in the shift of the saturated acids from occurring primarily in the disaturated triglycerides to increased formation of the trisaturated triglycerides. Meanwhile the total of these two fractions does not change markedly. As the temperature of treatment decreases from 98°F. however, the total increases with the major increase in the trisaturated fraction. It will be noted too that the capillary melting-points of the products follow to some extent the increase in trisaturated triglycerides.

Performance Evaluation: Baking Tests. One of the most critical evaluations for shortenings is the pound cake baking test. Table VII summarizes these results.

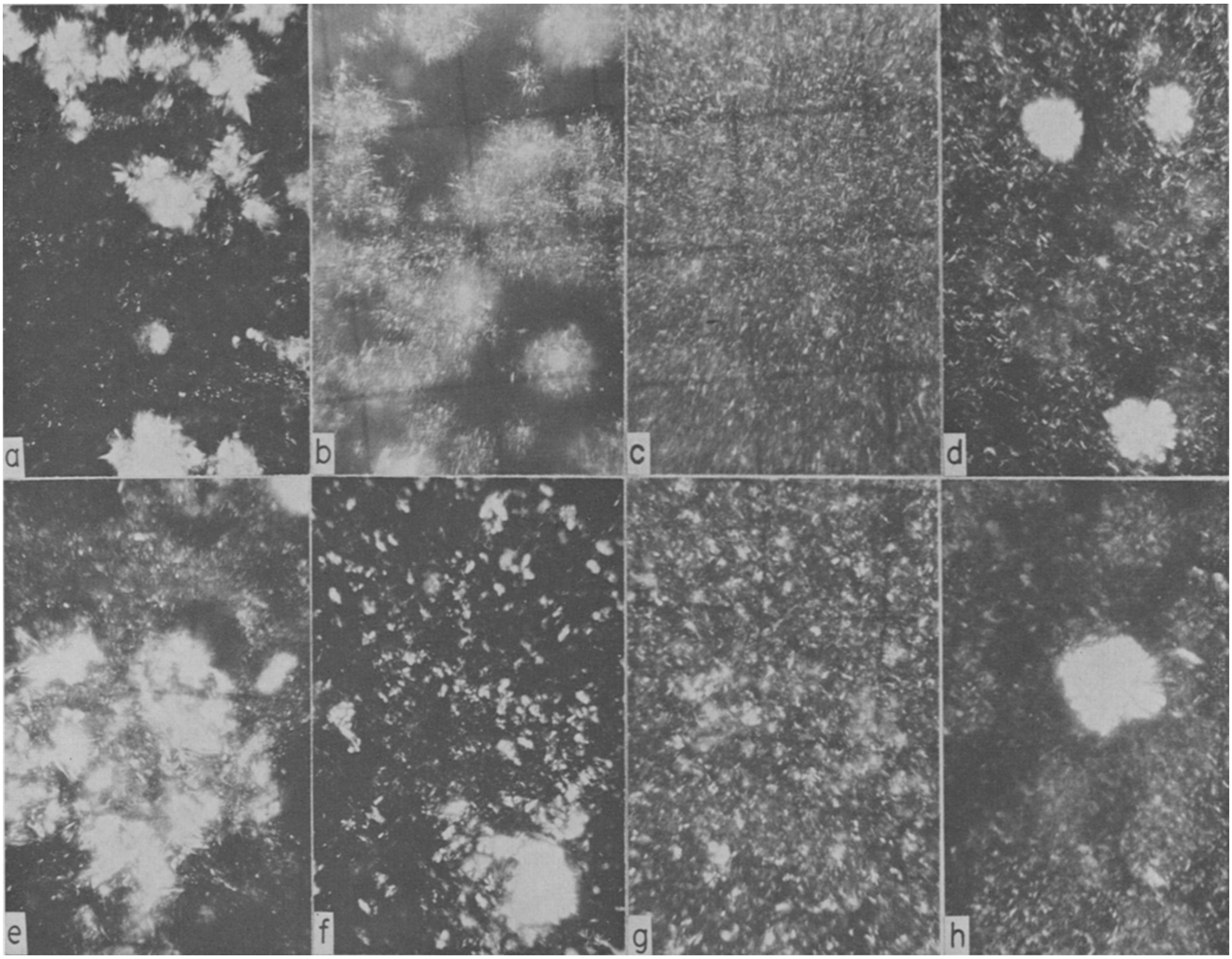

FIG. 12. Photomicrographs of treated lards, 290 ×. a—Lard, fresh. b—Partially-modified lard, fresh. c—Crystal-modified lard, fresh. d—Directed interesterified lard, fresh. e—Lard aged. f—Partially-modified lard, aged. g—Crystal-modified lard, aged. h—Directed interesterified lard, aged.

TABLE VII

Bakery Evaluation of Treated Lards Stored at Different Temperatures

Product	Pound cake volume in ml.							
	75°F.		85°F.		95°F.		100°F.	
	2 wks.	16 wks.	1 wk.	8 wks.	1 wk.	4 wks.	1 wk.	4 wks.
Lard	1475	1435	1400	1190	1260	1185	1400	1100
PML	1500	1445	1470	1335	1455	1245	1400	1295
CML	1525	1565	1535	1550	1520	1570	1510	1555
DIL	1505	1455	1595	1305	1445	1340	1440	1355

The cakes baked from lard shortening are poor after a one-week tempering period and worse after storage. Partially-modified lard produced cakes which were in some cases larger than those from crystal-modified lard when the tempering process was carried out for the short period. Longer storage however caused the breakdown of partially-modified lard shortenings; baking performance was considerably poorer than the original. Lard treated by directed rearrangement also showed this instability after storage. Crystal-modified lard however showed excellent stability in storage and, if anything, showed improved baking performance after storage.

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REFERENCES

1. Bailey, A.E., "Proceedings of the Fifth Research Conference," American Meat Institute, 1953, pp. 11–17.
2. Eckey, E.W. (to Procter and Gamble Company), U.S. Patents 2,442,531–2,442,532 (1948).
3. Vander Wal, R.J., and Van Akkeren, L.A. (to Armour and Company), U.S. Patent 2,571,315 (1951).
4. Mattil, K.F., and Norris, F.A. (to Swift and Company) U.S. Patent 2,625,478 (1953).
5. Armour and Company, Belgian Patent 529,164 (1954).
6. Jacobson, G.A., Tiemstra, P.J., and Pohle, W.D., J. Am. Oil Chemists' Soc., *in press.*
7. Fulton, N.D., Lutton, E.S., and Wille, R.L., J. Am. Oil Chemists' Soc., *31*, 98–103 (1954).
8. Riemenschneider, R.W., Luddy, F.E., Swain, M.L., and Ault, W.C., Oil and Soap, *23*, 276–282 (1946).
9. Bloom, O.T., U.S. Patent 2,119,699 (1938).
10. Bailey, A.E., Jefferson, M.E., Kreeger, F.B., and Bauer, S.T., Oil and Soap, *22*, 10–13 (1945).
11. Lutton, E.S., J. Am. Oil Chemists' Soc., *27*, 276 (1950).
12. Hoerr, C.W., Waugh, D.F., J. Am. Oil Chemists' Soc., *32*, 37–41 (1955).
13. Hawley, H.K., and Holman, G.W., J. Am. Oil Chemists' Soc., *33*, 29–35 (1956).

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