Consistency Changes in Global Spread Caused by Tempering[1]

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THE present studies of tempering of global edible spread were undertaken to provide a better understanding of the process whereby tempering modifies spread consistency and improves the "mouth feel," causing it to become less waxy (7). Global edible spread is a plastic mixture of saturated monoglycerides and oil which maintains its consistency and hence remains spreadable over a wide temperature range (5).

It is customary to temper commercial shortenings to improve their consistency as well as to obtain other desirable changes in the character of their crystals. The cause of consistency changes with tempering is somewhat obscure. Bailey (1) reviewed the phenomena associated with tempering and characterized them variously as a) an homogenization of non-uniform intra-crystal composition occurring during rapid solidification of fat, b) preferential solution of lower melting components as evidenced by a decrease in amount of solids dilatometrically determined, c) an increase in stiffness of crystals which the fat contains as shown by improved creaming quality, and d) removal of supersaturation accompanying supercooling by elevation of temperature, allowing nucleation and crystal growth with resulting hardening. In general, polymorphism is considered to play only a secondary role in consistency changes caused by tempering. Similarly there is little evidence that crystal size is altered appreciably by tempering fats.

Experimental Materials and Methods

Global edible spreads used in this study were prepared from winterized cottonseed oil and commercial, molecularly distilled monoglyceride which had been prepared from a completely hydrogenated lard. Most of the spreads studied contained 18% monoglyceride. Other components included salt, coloring, flavoring agents, and antioxidants customarily used in formulation of edible spreads. The addition of phosphatides as recommended recently (7) retards some of the consistency changes we were interested in studying; hence spreads used in this investigation did not contain added phosphatides. The spreads were produced in a laboratory-size Votator [3] as described elsewhere (7).

Micropenetrations (3) determined with a needle penetrometer in a constant-temperature room at 77°F. (25°C.) were used as a measure of consistency. Measurements were made on samples tempered in 1-oz. vials. All treatments in which samples were held at some specified temperature prior to consistency measurements will be called "tempering." Other techniques for examination of spreads included microscopy, X-ray diffraction, and ultracentrifugation.

Ultracentrifugal sedimentation of global spreads was conducted as described elsewhere (4). Solids content of global spread was determined by adding a known quantity of oil-soluble dye (1,4-bis-dimethylamino anthraquinone) to the global spread, separating a portion of the oil phase by ultracentrifugation at 85,000 × gravity for 60 min. at 77°F.(25°C.) and measuring the intensity of dye color. The reduction in dye color intensity caused by dilution in the oil phase of the spread permitted calculation of solids content (9). After ultracentrifugation the amount of solid residue remaining was determined by weighing after decantation of supernatant oil. X-ray diffraction patterns of spreads and solid residues obtained by ultracentrifugation were made by using copper K_α radiation and recorded either on photographic film in circular cassettes of 143.3-mm. diameter or on strip charts as the output of a Geiger-Muller diffractometer.

Results

Consistency Changes in Spreads Caused by Tempering. As it emerged from the Votator, global edible spread was semifluid, gradually setting up to a more rigid body. Spreads became sufficiently firm so that their penetration could be measured in 15-30 minutes. Changes in consistency were found to extend beyond 200 hrs. Effect of tempering a semifluid spread containing 18% monoglyceride and 82% cottonseed oil at 112°F.(44°C.) for 1, 8, or 48 hrs. is shown in Table I. Consistencies are reported after subsequent holding at 77°F.(25°C.) for 3 hrs., 24 hrs., and 1 wk. If duration of tempering was insufficient, *e.g.,* 1 hr., the spread became firmer during the 1-wk. period. A sample tempered for 1 hr. was harder than an untempered control in the period shortly after treatment, but since the untempered sample continued to harden at a more rapid rate, the tempered spread ultimately was the softer. The sample which had been tempered for 48 hr. at 112°F.(44°C.) maintained a constant consistency upon subsequent storage at 77°F.(25°C.). This stable consistency was softer than that found for untreated spreads after they had been stored for comparable periods.

TABLE I

Influence of Tempering on Consistency of Global Edible Spread

Duration of tempering at 112°F. (44°C.), control at 77°F.(25°C.)	Penetration, mm./10, after storage at 77°F.(25°C.) for					
	3 hr.		24 hr.		1 wk.	
Hours	Tempered	Control	Tempered	Control	Tempered	Control
1	150	190	140	125	110	105
8	145	170	135	120	140	105
48	145	120	155	120	155	105

Heat treatments of a spread containing 18% monoglyceride at temperatures other than 112°F.(44°C.), followed by consistency measurements after storage at 77°F.(25°C.) subsequent to tempering, resulted in penetrations shown in Table II. Compared to storage at 77°F.(25°C.), tempering at 34°F.(1°C.) produced a softer but equally unstable spread. Tempering considerably above room temperature resulted in a rapid stabilization of spread consistency. Also it would ap-

[1] Presented at the meeting of the American Oil Chemists' Society in Chicago, Ill., November 2-4, 1953.
[2] One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.
[3] The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

TABLE II

Effect of Temperature of Tempering on Consistency of Global Edible Spread

Tempered for 8½ hr. at	Penetration, mm./10, after storage at 77°F.(25°C.) for		
	3 hr.	24 hr.	1 wk.
34°F.(1°C.)	207	147	115
77°F.(25°C.)	170	120	105
95°F.(35°C.)	130	130	127
112°F.(44°C.)	145	135	140
130°F.(54°C.)	167	155	147

pear from these data that the higher the temperature of tempering above 77°F.(25°C.), the softer the consistency at which the spread was stabilized.

TABLE III

Stabilization of the Consistency of Global Edible Spread by Tempering

Duration of tempering	Change in penetration,[a] mm./10, on storage at 77°F.(25°C.), after tempering at				
	34°F. (1°C.)	65°F. (18°C.)	95°F. (35°C.)	112°F. (44°C.)	130°F. (54°C.)
Hours					
1	−100	−85	−70	−35	−20
3	− 95	−85	−25	−20	0
8½	− 92	−80	− 3	− 5	−20
24	− 95	−70	−15	−12	− 5
Days					
2	−105	−45	− 5	− 5	0
5	−110	−27	− 5	0	−10
7	−110	− 5	−10	+10	0
14	− 85	0	− 5	− 5	....
30	− 65	+ 5	0	0	0

[a] Difference in penetration of the sample 3 hrs. after tempering, as compared to 1 wk. after tempering. Negative values indicate hardening; positive, softening.

The relation between temperature, time of tempering, and extent of stabilization accomplished is shown in Table III. After tempering for periods indicated, at temperatures shown as column heads, samples were stored at 77°F.(25°C.). After 1 week's storage, penetration generally was stabilized at a minimum value. Change in penetration, during storage, as expressed by the difference between 3-hr. and 1-wk. penetration values, was very small if tempering occurred at an elevated temperature or for a prolonged period at lower temperatures. Tempering at a sufficiently low temperature caused practically no stabilization of spread consistency toward 77°F.(25°C.) storage.

Figure 1 presents graphically the consistency of spreads which had been tempered at 34°, 95°, 112°, and 130°F.(1°, 35°, 44°, and 54°C.) for various periods of time, and then stored at 77°F. (25°C.) for 1 wk. The general course of tempering and the typical curve obtained when penetration was plotted against

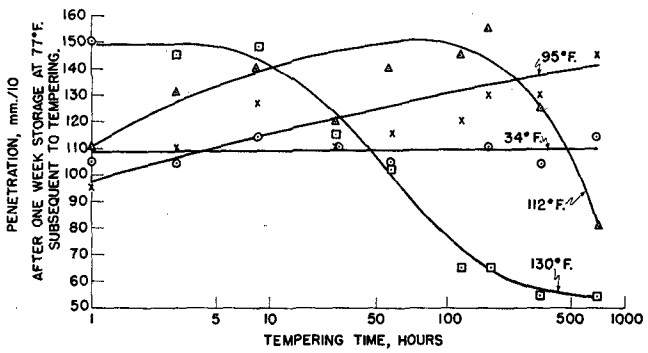

FIG. 1. Consistency of spreads tempered at various temperatures for various times.

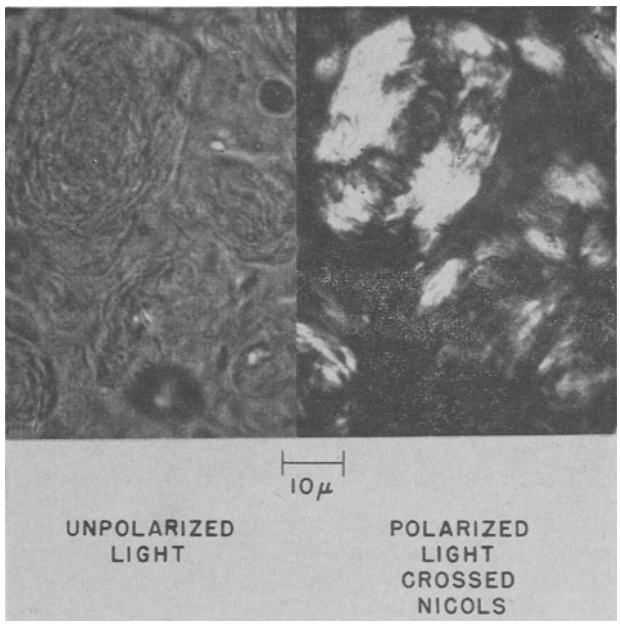

FIG. 2. Photomicrographs of untempered global edible spread.

time of tempering showed an approach to maximum softness, followed by terminal hardening. It appeared again that the function of increasing temperature was to accelerate changes in spread consistency. Spreads tempered at 95°F.(35°C.) had not reached maximum softness even after 1 mo. However spread stored at 130°F.(54°C.) had softened and hardened in this period of time.

Evidence that the hardening process in untempered spreads was quite different from the hardening process occurring in tempered spreads is presented in Table IV. These data show consistency changes occurring when spreads were tempered successively under two different conditions. Aliquots of spreads containing 18% monoglyceride were held at 77°F.(25°C.) until they attained various consistencies and then were transferred to 112°F.(44°C.) and held for 24 hours. Upon cooling, all aliquots had changed to a uniform soft consistency irrespective of previous consistencies at 77°F.(25°C.). However aliquots which had been brought to various consistencies by tempering at 130°F.(54°C.) and then retempered for 24 hrs. at 112°F.(44°C.) were not altered in consistency by additional tempering.

All experiments reported above were conducted on spread containing 18% monoglyceride. Spreads con-

TABLE IV

Influence of Changing Tempering Conditions on Consistency of Global Edible Spread

Time of initial storage or tempering	Penetrations, mm./10			
	Initial storage at 77°F. (25°C.)	Subsequent[a] tempering 24 hours at 112°F. (44°C.)	Initial[a] tempering at 130°F. (54°C.)	Subsequent[a] tempering 24 hours at 112°F. (44°C.)
Hours				
1	200	145	155	160
3	175	130	125	130
8½	155	130	120	130
24	135	150	135	135
Days				
2	115	125	120	105
5	100	125	65	65
7	105	130	55	65
14	85	115	60	65
30	90	140	55	60

[a] Penetrations determined after 1 week's storage at 77°F.(25°C.) subsequent to designated treatment.

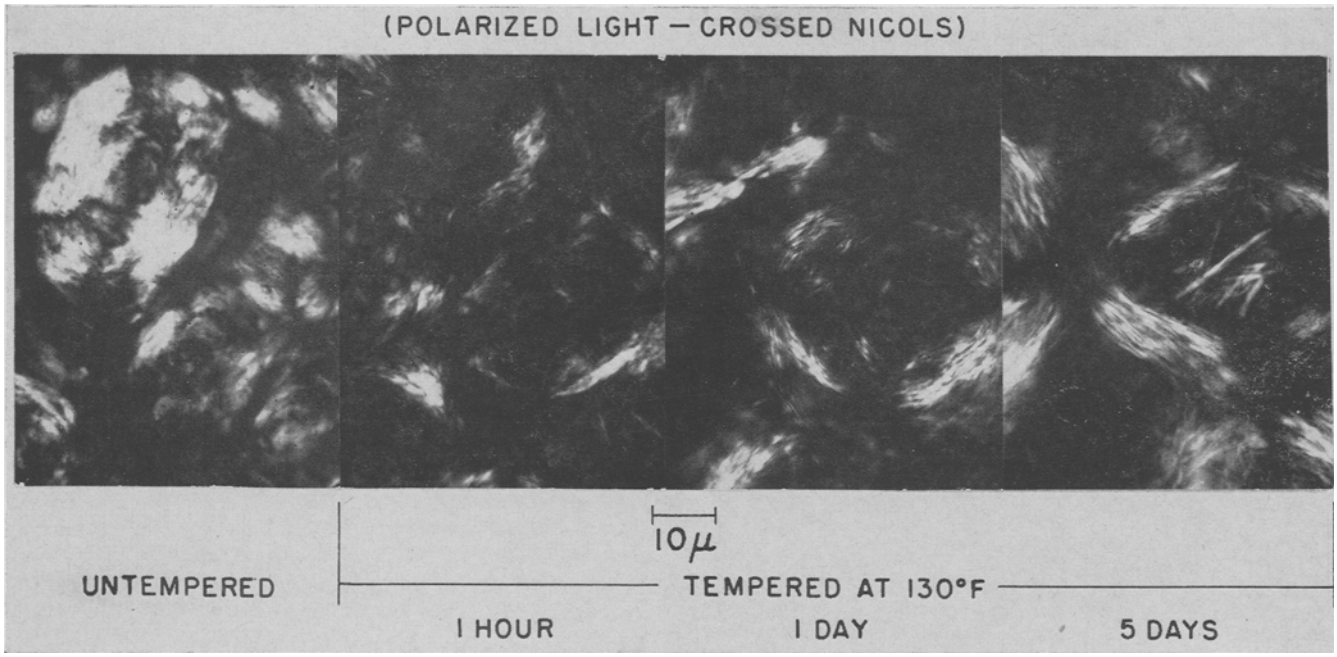

FIG. 3. Photomicrographs of tempered global edible spread.

taining 30 or 13% monoglyceride showed, respectively, lesser and greater consistency changes on tempering. Since the consistency of firmer spreads would show less sensitivity to changes in size, shape, or amount of component solids, the above results might be anticipated.

Microscopy of Spreads

Microscopic examination of global spread, within one-half hour after it had been prepared, showed that the Votator imparted to the spread a characteristic aggregate structure. Figure 2 shows photomicrographs of global spread under normal illumination and in polarized light. Crystalline material composed of insoluble monoglyceride was largely aggregated into ellipsoidal or ball-shaped aggregates 20-50 microns in dimension. Examined between crossed Nicol prisms, crystalline material in the aggregates was observed to possess a tangential orientation rather than radial orientation of spherocrystals. Component crystals which could be distinguished appeared to be only a few microns in dimension. On tempering spreads, the ball-like aggregates weakened and, in mounting for microscopic examination, frequently were completely destroyed. Careful examination showed that opaque areas of the ball-like aggregates in untempered spread disaggregated during tempering into component crystals. Because of the small size of crystals and indistinctness of their boundaries, it was difficult to ascertain whether changes in crystal dimensions occurred during tempering. There was certainly no marked change observed in crystal size in early stages of tempering (Figure 3a, 3b). With increasing intensity of tempering treatment a fibrous character developed in organization of crystals, and crystals appeared to elongate (Figure 3c). This was associated with development of a faintly birefringent background which could be seen in some mounts to arise from a platelike crystalline component. As this development of needlelike and platelike crystals occurred, hardness of spread increased. With prolonged holding at higher temperature, such as for 1 wk. at 130°F.(54°C.), needles of considerable length appeared (Figure 3d). Obviously a marked recrystallization of solid constituents occurred as a result of tempering at this temperature.

X-ray Diffraction Patterns of Spreads. To determine if structural changes occurred in the crystalline components during tempering, spreads were examined by X-ray diffraction. It was found that monoglycerides of spreads, as they emerged from the Votator, were crystallized in the β-structure of glyceryl monostearate (8). A single line suggestive of the α-structure was present in patterns of laboratory preparations obtained by extremely rapid chilling, but diffraction patterns taken after a few hours' standing at room temperature no longer showed this line. Throughout the course of the tempering process there was no evidence to show that a polymorphic transformation had occurred. It appeared however that there was an increase in sharpness of diffraction lines as tempering proceeded. This can be seen in Figure 4, which shows the diffraction pattern of an untempered global spread and the same spread after tempering for 24 hr. at 112°F.(44°C.). Although many of the side spacings in the range of 20°-30° diffraction angle were intensified, the most marked effect was intensification of diffraction from long spacings in the region of less than 15° diffraction angle. These results could be interpreted to indicate an increase in perfection or size of crystals without occurrence of a crystal structure change.

Ultracentrifugation of Spreads. The technique of ultracentrifuging plastic spreads permits estimation of proportion of solids in a spread and amount of solid residue obtained from centrifugation. The ratio of these two determinations furnishes a measure of compactness of packing of solid components of a spread. Table V shows the ratio of residue weights and solids content of spreads of different monoglyceride content as determined untempered and after tempering for 24 hr. at 112°F.(44°C.). Untempered spreads had 14% more centrifuge residue on the av-

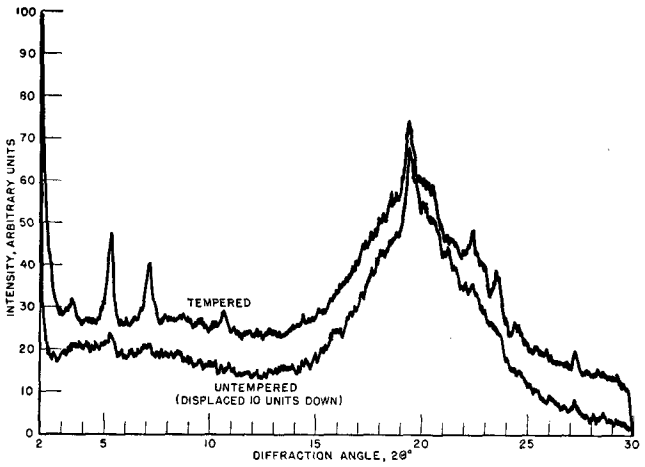

FIG. 4. X-ray diffraction patterns of untempered and tempered global edible spreads containing 18% monoglyceride (taken with Geiger-Muller spectrogoniometer).

erage than tempered spreads. On the other hand, untempered spreads averaged 6% less true solids than tempered spreads. These results indicated that crystallization of monoglycerides was not complete in untempered spreads. Nevertheless crystals of untempered spread had such shape as to entrap more oil.

TABLE V
Effect of Tempering on Solids of Global Spreads

Monoglyceride content	Ultracentrifuge residue			Solids content		
	Untempered	Tempered	Untemp'd / Tempered	Untempered	Tempered	Untemp'd / Tempered
%	%	%		%	%	
9	23.8	20.5	1.17	8.3	8.8	0.94
13	35.4	31.7	1.12	10.9	12.0	0.91
17	44.8	40.6	1.11	15.0	16.2	0.92
21	52.6	50.0	1.05	19.2	20.6	0.93
29	77.5	62.3	1.24	25.4	25.4	1.00
	Average		1.14	Average		0.94

Discussion

Consistency changes which require explanation in this study of tempering of global spread are as follows: a) fluid spread as it emerged from the Votator hardened slowly at room temperature; b) tempering at elevated temperature for moderate periods caused softening; c) irrespective of initial consistency of a given untempered global spread, tempering reduced consistency to a uniform level; and d) prolonged storage at an elevated temperature ultimately led to hardening.

Hardening of spreads at room temperature after emergence from the Votator probably was caused by slow deposition of a small amount of material which cemented existing aggregates together. It has been shown by Kolthoff, in a study of aging of crystalline precipitates (6), that cementing together of particles into agglomerates is a normal aging phenomenon. Monoglycerides which deposited may have constituted supersaturation in the oil phase subsequent to its rapid chilling. That such precipitation occurred was shown experimentally by centrifuging a freshly prepared global spread. Although the supernatants were clear after ultracentrifugation, after 12 hours a small amount of solid had deposited from the oil.

Observations that spreads did not become hard when stored at 34°F.(1°C.) are in agreement with observations reported by Bailey on blended shortenings (2). Explanation for maintenance of soft consistency was that at this temperature shortenings were supercooled and maintained a state of supersaturation indefinitely. It is interesting to note that there appeared to be a slight increase in amount of solids in global spread as a result of tempering. This may indicate that supersaturation had been maintained in global spreads until temperature was made more favorable to crystal deposition.

Softening of spreads caused by tempering at elevated temperatures may be attributed to recrystallization of primary particles, causing aggregates to lose their strength and spreads to become more fluid. Sharpening of reflections in the diffraction spectrum on tempering a spread could arise from development of more perfect or larger monoglyceride crystals. Rapid crystallization of monoglyceride in the Votator may have given rise to many imperfect or small crystals, and recrystallization during tempering provided a means of reaching a lower energy state. Transformations in shape involved in recrystallizations during short periods of tempering were not made clear by microscopic examination. Perhaps because of extreme smallness of crystallites involved, the only change observed was transition of relatively opaque aggregates to aggregates which contained many fine but distinct primary particles.

Kolthoff (6) found that lead sulphate crystals which were rapidly precipitated showed a feathery appearance, presumably from overgrowths. Upon aging, these feathery overgrowths disappeared to leave crystallites of approximately the same size, but with much more sharply defined faces. If recrystallization of monoglyceride in these global spreads parallels that in precipitates which Kolthoff studied, feathery overgrowths are responsible for the observed unresolved opacity of aggregates and, by virtue of their greater ability to entrap oil, contribute to higher residue volume as obtained upon ultracentrifugation of untempered spreads. Greater mobility of oil in tempered spread which has better defined crystals might cause the improvement in "mouth feel" found on tempering.

Uniform soft consistency to which aliquots of a spread could be tempered, regardless of hardness attained on previous storage at 77°F.(25°C.), indicates the greater importance of production conditions in determining the consistency of tempered spreads than storage prior to tempering. Whereas changes in primary particles caused by variations in Votator operation might be obscured in untempered spreads as a result of hardening which they undergo in normal storage, tempered spreads might show a much more diverse character.

Microscopic examination clearly showed changes occurred in crystal size and shape in those spreads which had been overtempered or held for a prolonged period at elevated temperatures. Both long needlelike crystals and thin platelike crystals appeared. Marked growth in crystal size which occurred during the course of aging suggested the process of solution of smaller crystals and growth of larger ones known as "Ostwald ripening." Asymmetric crystal habits probably caused extreme hardening of these spreads. Normally it would be anticipated that increased crystal size which was observed would cause softening of a spread. Hardening which was observed would indi-

cate that shape changes were more than sufficient to compensate for size changes.

It would be desirable to control recrystallizations which apparently occurred in these spreads during the course of tempering. Kolthoff observed that dyes which were absorbed on the surface of crystalline precipitates prevented recrystallization. As reported by Lancaster *et al.* (7), phosphatides added to global spread formulations retarded hardening on prolonged storage and enhanced softening under mild tempering treatments. Phosphatides may function by hindering one type of recrystallization and assisting the other.

Although these studies were conducted to clarify changes associated with improvement in palatability of spread, they have a strong bearing also on storage properties of spreads. Global spread is designed for use under diverse climatic conditions. Shipping to tropical regions could possibly involve prolonged storage at temperatures in the neighborhood of 112°F. (44°C.). Need for stabilizers to prevent spreads from becoming hard is quite apparent.

Summary

Global edible spreads became firmer in consistency subsequent to their manufacture probably because slow deposition of monoglyceride in the supercooled mixture cemented existing aggregates together. Tempering global edible spread at 95°F.(35°C.) or above caused softening initially, followed by hardening on prolonged tempering. The higher the temperature in the range, 95°-130°F.(35°-54°C.), the more rapid was the rate at which consistency changes occurred. Physical studies of spreads led to the conclusion that consistency changes were a consequence of recrystallization of solid components. Softening occurring in initial stages of tempering resulted from a) weakening of aggregate structure present in untempered spread and b) recrystallization of solids into more perfectly ordered and sharply defined crystals. Hardening after prolonged tempering resulted from further recrystallization of solids into needlelike and platelike forms.

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ABSTRACTS . . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor

Processing fatty oils. A. D. Rich(Filtrol Corp., Los Angeles 17, Calif.). *Ind. Eng. Chem.* 46, 2272-77(1954). Work was undertaken in the pilot plant to substantiate the laboratory findings. Lots of vacuum, dry rendered fancy and special tallow were dried and clarified by mixing 0.5% diatomaceous earth with the fat in the bleacher at 160°F. under 7 mm. of mercury pressure for 30 minutes and filtering. The two fats were bleached with activated and natural clay adsorbents. Each run was repeated except that 1% of water was added with the adsorbent. The tests confirmed that the bleached color of the fat was markedly lower when the water was used and the activated clay adsorbent was employed.

Positional asymmetry of fatty acids on lecithin. D. J. Hanahan(Dept. of Biochem., Univ. of Washington, Seattle). *J. Biol. Chem.* 211, 313-19(1954). A positional asymmetry for the fatty acids of some of the naturally occurring lecithins from liver has been established. It has been shown that the lecithins of beef, rabbit, dog, guinea pig, and rat livers have only unsaturated fatty acids on the α'-ester position and only saturated fatty acids on the β-ester position.

A convenient route to (distearoyl)-L-α- and β-monostearoyllecithin. Position of fatty acids on the lecithins of egg. D. J. Hanahan(Dept. of Biochem., Univ. of Washington, Seattle). *J. Biol. Chem.* 211, 321-25(1954). (Distearoyl)-L-α-lecithin may be conveniently prepared in good yields by hydrogenation of the chromatographically purified lecithins of chicken egg. An individual lysolecithin, β-monostearoylglycerylphosphorylcholine (β-monostearoyllecithin), may be obtained by the action of lecithinase A on the purified lecithins. The fatty acids of the lecithins of egg have been found to be "asymmetrically" located; i.e., only unsaturated fatty acids on the α'-ester position and saturated fatty acids on the β-ester position.

Oil extraction and drying process. R. W. Barns(French Oil Mill Machinery Co.). *U. S. 2,695,304.* An oil, containing water, is dried by sparging with hot vapors of a dry, water-immiscible solvent which forms an azeotrope with water. The process is continuous.

Process for recovery of resins, waxes, and oils from peat. E. J. Schabelitz(Schabelitz Biochemical Corp.). *U. S. 2,695,838.* Pulverized peat is leached with ethylene dichloride at atmospheric temperature and pressure for 2 to 3 hrs. to remove soluble oil, wax, and resinous constituents. The extract is drawn off, and these constituents are recovered by removal of the solvent. The dried peat is compressed into briquette form.

Stabilization of fats and oils with tetraoxy derivatives of biphenyl. A. Bell and M. B. Knowles(Eastman Kodak Co.). *U. S. 2,697,111.* Fats and fatty oils are stabilized by the addition of 0.001 to 1.0% by wt. of 2,2',5,5'-tetrahydroxy-4,4'-di-*tert*-butyl biphenyl.

Rendering fat. A. J. Kramer. *U. S. 2,697,112.* Fatty tissue is comminuted to a particle size of 0.25 to 1 inch and heated to a temperature between 140° and 212°F. The hot tissue is pulped mechanically to a non-cellular fibrous state and the fat is immediately separated.

Method of removing protein from fatty tissue. A. J. Kramer. *U. S. 2,697,113.* Fatty tissue is comminuted, heated to 140° to 212°F., and pulped to a non-cellular fibrous state. Hot water is added. The pulp is allowed to separate and the fat is skimmed off.

The determination of percentage fat and water in milk powder. W. Mohr and D. Merten(Anstalt Milchwirtschaft, Kiel, Germany). *Milchwissenschaft* 9, 153-8(1954). Six methods, each considered a standard in one country or another, were compared in the determination of moisture in milk powder and