The Relationship of Polymorphism to the Texture of Margarine Containing Soybean and Cottonseed Oils

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It is well known that the physical structure of margarine and shortening is determined not only by the type of oil but also by the chilling, mixing, and tempering methods employed in manufacture. Thus the desired consistency, texture, or appearance of a product may be lost by altering any of the conditions that are known to affect these characteristics.

In many cases a change in physical properties has been traced to polymorphic transformation of the fat crystals. Hence, in order to be certain that the consumer will receive a product with the same desirable physical characteristics possessed at the time of its manufacture, it is important to ascertain the polymorphic behavior of the oils which are used in the formulation.

For several years it has been known that margarine formulated entirely from hydrogenated soybean oil has under certain conditions a tendency to lose its initial smooth texture and gradually become grainy (1). Margarine manufacturers have overcome this defect by incorporating 10% or more of cottonseed oil in the formulation. Bailey (2) has said that polymorphism occurs to a much greater degree in highly hydrogenated soybean oil than in a similarly hardened cottonseed oil but is not normally in evidence in partially hydrogenated vegetable oils. Struble (3) states that soybean oil shows more of a tendency towards graininess than does cottonseed oil and that, in general, sharp-melting hydrogenated oils will grain more easily than hydrogenated oils of wide plastic range.

The purpose of the work described in this paper was to study the nature of this transformation in texture, especially with respect to its relationship to polymorphism, and to ascertain how the development of grain can be eliminated. This was accomplished by comparing the organoleptic and physical properties of oils and margarines which were chilled, homogenized, and tempered under conditions designed both to prevent and accelerate any tendency toward graininess.

Experimental

Preparation of Samples. Refined, bleached soybean oil was hydrogenated at 200°C. and 5 lb. of hydrogen pressure to an iodine value of 74 in conventional laboratory apparatus. Flaked nickel catalyst containing 25% active metal was used at a level of 0.1%. The hydrogenated oil was filtered, bleached, and then steam-deodorized at 225°C. and 2-mm. vacuum for 4 hrs. Refined, bleached cottonseed oil was hydrogenated, filtered, and deodorized in a similar manner. Blends containing 10, 20, and 30% hydrogenated cottonseed oil with the hydrogenated soybean oil were prepared.

Margarine samples were prepared from hydrogenated soybean oil and from hydrogenated blends containing 25 and 50% cottonseed oil. The oils were emulsified with 0.6% of commercial mono- and diglycerides, 0.1% commercial lecithin, artificial color, and the normal amounts of cultured skim milk and salt. The emulsions were then chilled from 33°C. to 18°C. in a Votator.

Chilling and Tempering Procedures (4). Approximately 150 g. of each oil were liquefied at 50°C. and quickly chilled in a tray at —10°C. for 3 min. The partially solidified samples were stirred by hand with a rubber paddle until the texture of each was homogeneous and smooth. The temperature of the homogenized samples was approximately 18°C. Half of each sample was placed in a glass jar, tempered at 5°C. for 3 weeks, and then stored for 24 hrs. at 24°C. The remainder of the homogenized samples were tempered at 24°C. for 3 weeks.

The samples of margarine were tempered in a similar manner.

Sample Analyses. Complete melting points (F.A.C.) of the tempered oils were determined in thin glass tubes. The temperature of the water bath was raised approximately one degree per minute.

For microscopic study a small amount of sample was placed on a glass slide and pressed to a thin film with a cover slip. Photomicrographs were taken at 24°C.

X-ray diffraction patterns were produced on a standard General Electric XRD-1 unit, using copper (K-alpha) radiation with nickel-aluminum filtration and a slit width of 0.025 in. Samples were mounted in 0.082-in. brass discs and exposed to flat casette films for one hour at 24°C. The film to sample distance was 7.5 cm. for short spacing patterns and 20.0 cm. for long spacings.

Dilatometric data were obtained by using the method of Fulton *et al.* (5).

Results

The organoleptic and physical properties of the samples were found to be related to the oil composition as well as to the temperature at which the samples were tempered. All of the samples which were tempered for 3 weeks at 24°C. had smooth textures and showed no evidence of oil separation. The hydrogenated soybean oil tempered at 5°C. was very grainy and exceptionally soft and showed oil separation at 24°C. The sample containing 10% cottonseed oil had the same properties but to a lesser extent. The oil samples containing 20 and 30% cottonseed oil retained their original smooth texture and appearance. The margarine prepared from hydrogenated soybean oil and tempered at 5°C. was extremely soft and grainy whereas the margarines made from the blends containing 25 and 50% cottonseed oil retained a smooth and relatively firm texture.

X-ray diffraction patterns and photomicrographs of the oils and margarines tempered at 5°C. are shown in Figures 1 and 2, respectively. The results demonstrate in terms of physical properties the observed differences in texture.

The photomicrographs show marked gradations in the size and structure of the crystals. Clumps of large, elongated, branching crystals characterize the

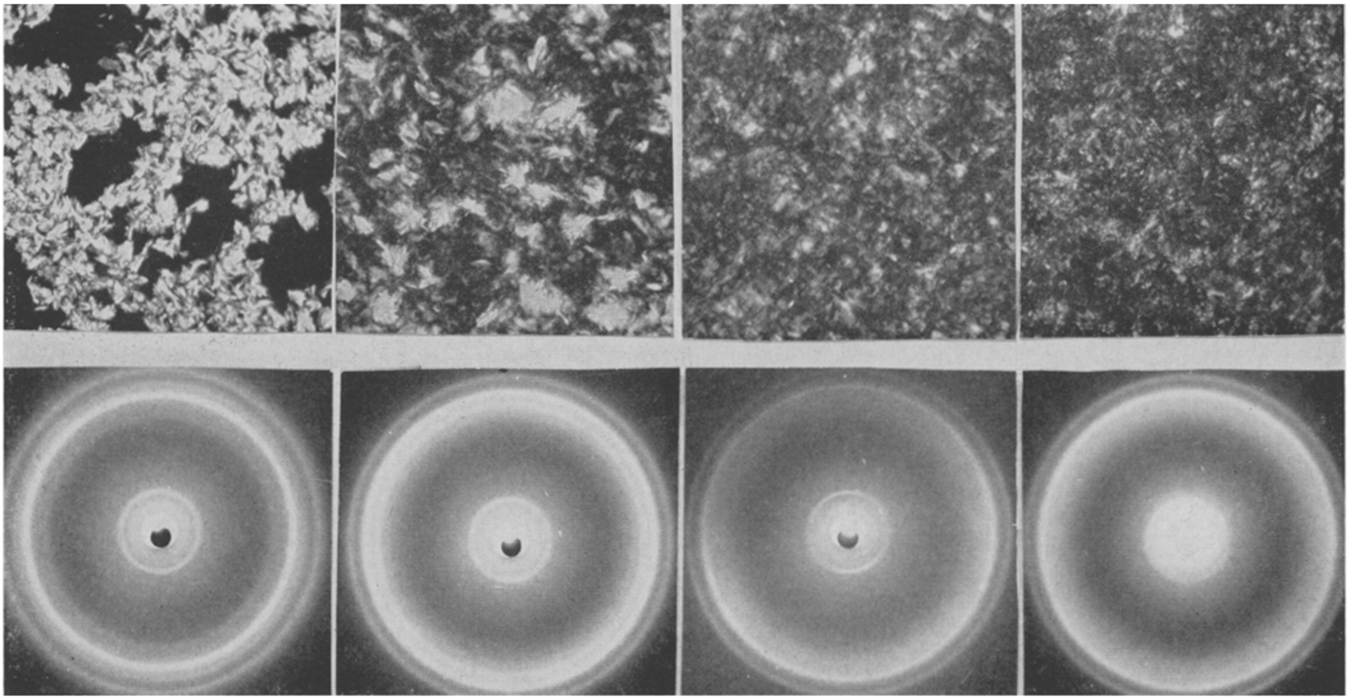

100% Soybean oil — 90% Soybean oil 10% Cottonseed oil — 80% Soybean oil 20% Cottonseed oil — 70% Soybean oil 30% Cottonseed oil

FIG. 1. Photomicrographs (100X) and X-ray patterns of margarine oils tempered at 5°C.

sample of hydrogenated soybean oil as well as the margarine prepared from this oil. This type of crystal is also present in the sample containing 10% cottonseed oil but to a lesser degree. It is practically nonexistent in the oils or margarine if the percentage of cottonseed oil is 20% or greater.

The X-ray diffraction patterns also reveal differences in the amount and type of crystals that are present. The hydrogenated soybean oil and its corresponding margarine exhibited the *beta* type of patterns whereas *beta prime* patterns were obtained for the samples containing 20% or more of hydrogenated cottonseed oil. A mixed *beta, beta prime* pattern was obtained for the sample of oil containing 10% hydrogenated cottonseed oil. The short spacings, long spacings, and relative intensities are given in Table I.

TABLE I

X-Ray Diffraction Patterns of Oils

% Soybean	100		90		80		70	
% Cottonseed	0		10		20		30	
	Å	I/Io	Å	I/Io	Å	I/Io	Å	I/Io
Short spacings	3.76	M	3.80	M	3.80	M	3.76	M
	4.18	W	4.15	VS	4.16	S	4.15	VS
	4.49	VS	4.49	M				
	5.3	W						
Avg. d	44.5		44.6		44.7		43.6	
Long spacings	14.62	M	14.85	M	14.92	M	14.62	M
	45.2	S	44.6	S	44.6	S	43.3	S

X-Ray Diffraction Patterns of Margarines

% Soybean	100		75		50	
% Cottonseed	0		25		50	
	Å	I/Io	Å	I/Io	Å	I/Io
Short spacings	3.83	M	3.81	M	3.82	M
	4.2	M–	4.22	VS	4.21	S
	4.56	S				
	5.3	W				

X-ray patterns as well as photomicrographs of the samples tempered at 24°C. for three weeks showed that the crystals were in all cases *beta prime.*

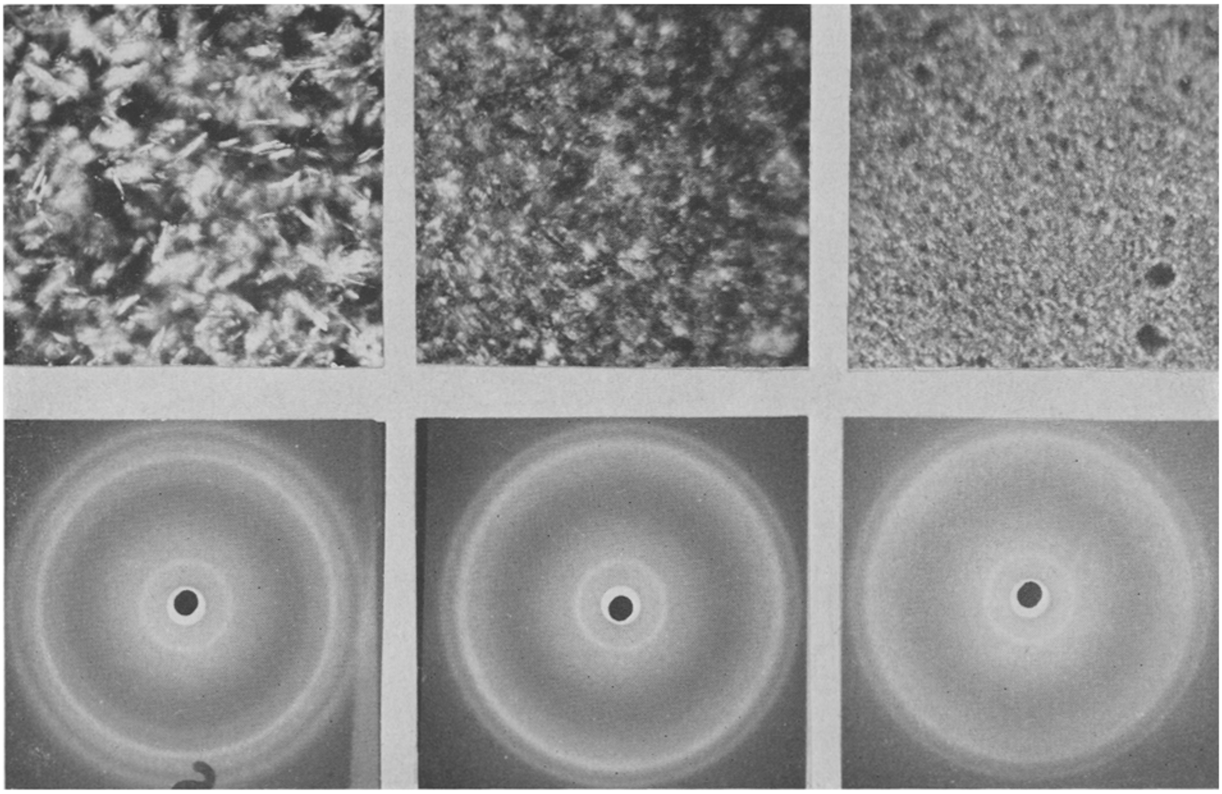
Complete melting points of the oils tempered at 5°C. and 24°C. are given in Table II. The 90 and 100% soybean oil samples, which were tempered at 5°C. and contained primarily *beta* crystals, melted slightly higher than the samples in which the crystals were solely *beta prime.*

The dilatometric curves shown in Figure 3 for the hydrogenated cottonseed and soybean oils give a relative index of their fat solids at 5°C. (extrapolated value) and 24°C. (experimental value). The difference at 5°C. is 13.3 units, but at 24°C. it is only 3.3 units, indicating a comparatively greater fat solids content in soybean oil at the lower temperature. Extrapolated values for the S.F.I. of the oil blends at 5°C. fall in the region between these two curves and are displaced slightly below the curve for soybean oil. The changes in fat solids at this temperature for blends containing 90, 80, and 70% hydrogenated soybean oil are approximately 1, 2½, and 3 units lower than that of 100% soybean oil. The actual percentage of solids in the samples stored at 5°C. are probably greater than that indicated by the S.F.I. curves because the curves represent the dilation or contraction of fully tempered oils.

TABLE II

Melting Points of Oils After Tempering for 3 Weeks

Oil		Complete Melting Point (°C.)	
% Soybean	% Cottonseed	Tempered at 5°C.	Tempered at 24°C.
100	—	40	38
90	10	40	37
80	20	38	37
70	30	37	37



100% Soybean oil

75% Soybean oil
25% Cottonseed oil

50% Soybean oil
50% Cottonseed oil

Fig. 2. Photomicrographs (200×) and X-ray patterns of margarine tempered at 5°C.

Discussion

The results clearly indicate that the graininess observed in the 90 and 100% soybean oils and 100% soybean oil margarine is caused by the presence of higher melting *beta* polymorphs. Since all of the samples were initially smooth in texture and only those having a high content of soybean oil and tempered at 5°C. exhibited *beta* characteristics, graininess or *beta* development must be primarily a function of crystal growth rather than polymorphic transition.

In the quick crystallization of fat or oleaginous mixtures a great many centers of crystallization or crystal nuclei are formed, upon which subsequent crystal growth and continued crystallization during tempering can take place. [Tempering has been described as an unmixing process in which melting and resolidification can produce a greater degree of homogeneity (2) (page 304).] The degree and rate of crystal growth, however, will depend upon the number of crystal nuclei, the tempering temperature, and also on the particular polymorphic form of the crystals or crystal nuclei which are present (6). For the samples under investigation the degree of crystal growth will also depend on the amount of solids present in both cottonseed and soybean oil at any one temperature (Figure 3).

The crystallization phenomenon of the hydrogenated sample of soybean oil illustrates the persistent supercooling theory cited by Bailey (2) and also advances the theory to include its effect on crystal growth during low and high temperature storage (tempering). As a result of rapid nucleation at —10°C. in the presence of considerable supercooling, the sample after homogenization at 18°C. was quite smooth in texture and possessed *beta prime* characteristics. Since crystal growth depends upon thermal energy, the sample held at 5°C. will undergo such growth very slowly. This condition for further crystallization and crystal growth is known to produce larger but fewer crystals and, with triglycerides, will favor crystallization in the *beta* form. This is especially true for soybean oil, which has the *beta* form as its most stable state. From the experimental data it is not possible to predict the proportion of crystal growth in the *beta* or *beta prime* forms as the sample is cooled and stored at 5°C. The high viscosity of the residual oil and the low thermal activity of the molecules at this temperature would account for the slow development of macro, *beta* crystals that results in grain. The hardness of the soybean oil sample at 5°C. can be attributed to a high solids content at this temperature as well as to the fact that considerable crystallization occurs from a quiescent, supercooled state.

Although the X-ray patterns of hydrogenated soybean oil and its corresponding margarine exhibit a weak *beta prime* line at 4.2 Å, it is obvious that these samples contain primarily *beta* crystals. Certain low melting *beta prime* polymorphs, which were formed initially during the process of chilling to —10°C. and homogenization at 18°C., probably disappear during tempering. These crystals would contain a high percentage of normally liquid oil, a condition that results in instability and low melting points. Although it is possible that melting and resolidification of these mixed crystals in the *beta* form occurs as the samples were cooled and stored for three weeks at 5°C. (the samples were removed

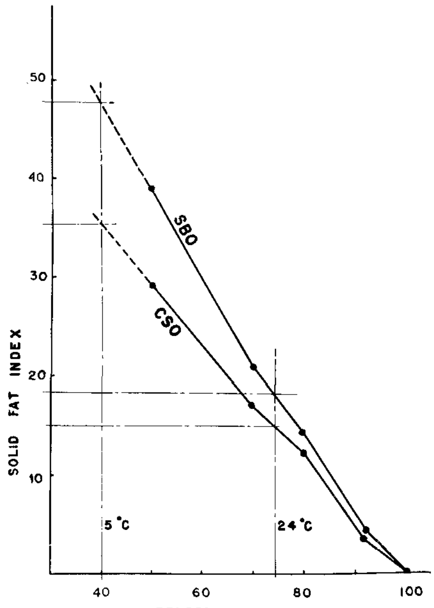


Fig. 3. Dilation curves of hydrogenated soybean and cottonseed oils.

periodically from the refrigerator for examination), the tempering process undoubtedly is complete after the samples were placed at 24°C. After a day at this temperature the samples were abnormally soft and very grainy and contained a high proportion of free oil.

In the case of the chilled and homogenized samples, which were stored for three weeks at 24°C., a more rapid rate of crystal growth can be expected. The stable polymorph in all cases is *beta prime* because the crystals are deposited under conditions favorable for the growth and stabilization of this form. The crystals were small, numerous, and enmeshed a considerable amount of free oil. The samples tempered in this way were observed to be much firmer at 24°C. than those tempered at the lower temperature.

It should be mentioned that margarine usually is handled in much the same manner as the samples tempered at 5°C. in this investigation. After margarine is votated, it is worked slightly and packaged at a temperature of about 18°C. It is then placed in storage at a lower temperature, and as it is moved in transit and awaits purchase, its temperature undoubtedly fluctuates above and below 5°C. The conditions are thus ideal for slow crystal growth and the development of considerable grain if the oils used in margarine manufacture are likely to develop this type of crystal structure.

Crystallization of the oils and margarine containing both hydrogenated cottonseed and soybean oil is influenced by the same factors discussed above. However as homogeneous mixtures they will behave differently than pure soybean or cottonseed oils. The extent to which one will influence the other will depend on such factors as intersolubility and the crystallization energy of the various triglycerides. Mixed crystals or solid solutions containing triglycerides contributed from each of the two oils will be formed. Although it is difficult to predict the effect that a given quantity of one oil will have on the other, a correlation of the data in Figures 1 and 2 with that in Figure 3 indicates that 10–20% hydrogenated cottonseed oil will sufficiently increase the intersolubility of soybean and cottonseed oil solids so that crystal growth and continued crystallization will be controlled by the cottonseed oil solids, which have the *beta prime* form as their stable state. Even though these percentages of hydrogenated cottonseed oil do not appreciably decrease the solids content from that of pure hydrogenated soybean oil, earlier work has shown that the incorporation of small quantities of certain triglycerides can control the type of crystallization produced in mixed crystals (7).

Summary

A correlation of the organoleptic and physical properties of hydrogenated soybean oil, blends of this oil with hydrogenated cottonseed oil, and their corresponding margarines has been made by comparing samples crystallized under tempered and essentially untempered conditions. Margarine, which is usually processed under the latter condition and which contains a high percentage of hydrogenated soybean oil, will at times show a strong tendency to develop grain. This graininess was characterized by the presence of high melting *beta* polymorphs, formed by a slow rate of crystal growth.

Thus the difference in the polymorphic behavior of highly hydrogenated cottonseed and soybean oil observed by Bailey still prevails in the partially hydrogenated oils but to a lesser extent. The tendency for hydrogenated soybean oil to form *beta* crystals can be reduced or eliminated by conditions which promote faster crystal growth and/or the incorporation of *beta prime* stable triglycerides, which control crystal growth through mixed crystal or solid solution formation.

Acknowledgment

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