Morphology of Fats, Oils, and Shortenings

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THE TERM morphology is used to denote the general relation of the physical behavior and performance of fats, oils, and shortenings to their crystal structure and the molecular configuration of their triglyceride components. This report deals with the crystal transformations which occur in various common fats, the physical changes which take place during crystallization, tempering, and subsequent storage under different conditions, and the effects of this polymorphic behavior on the performance of commercial fats in certain shortening applications.

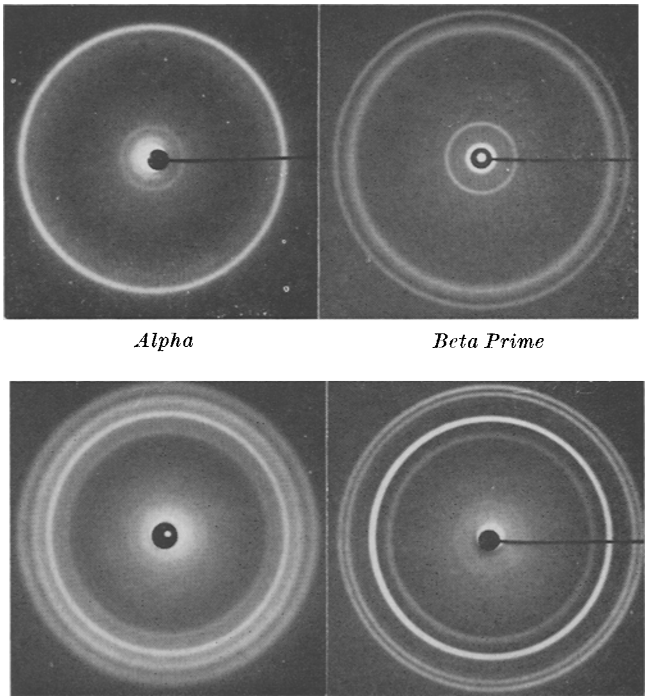
The subsequent discussion is based on the results of an extensive study of five individual triglycerides and numerous samples of common commercial fats, including various types of ordinary lard and hydrogenated lard, rearranged lard, tallow (beef), hydrogenated cottonseed and soybean oils of different iodine values, and the flakes of all these types of fats. The various crystal modifications in which fats exist and the sequence of polymorphic transformations which they undergo were determined by correlating their x-ray diffraction patterns with information obtained from cooling and heating curves under various experimental conditions, from solubility determinations in several organic solvents, and from observations by means of polarized-light microscopy under carefully-controlled conditions. The performance of shortenings is discussed in terms of the physical characteristics of the various crystal modifications in which they have been found to exist.

Polymorphic Transformations (1)

The interpretation of triglyceride polymorphism can be divided into two quite distinct schools of thought: the opinions supported by Malkin (2) and the concepts of Lutton (3). There has been considerable controversy between these two major view-points regarding the number of polymorphic forms which triglycerides exhibit, the names by which they should be designated, and the criteria by which the forms should be identified and differentiated. The writer has attempted to reconcile these conflicting interpretations and to explain more plausibly the effects of the polymorphic behavior on the performance of shortenings.

After examining more than 50 x-ray diffraction spectra of individual triglycerides and more than 300 spectra of a wide variety of common commercial fats, the writer has come to the conclusion that these materials exhibit the four types of x-ray diffraction patterns shown in Figure 1. Each of these spectra represents a specific crystal lattice which defines the molecular orientation in a definite and distinct polymorphic form. The writer has designated these forms *alpha, beta prime, intermediate,* and *beta.* Many fats and individual triglycerides exhibit all four polymorphic forms, but some tend to exhibit only two or three of the forms for certain definite reasons, which will be discussed subsequently.

The x-ray spacings which characterize the various polymorphic forms by defining the lateral arrangements of the molecules in the crystal lattices are listed in Table I. The spacings given are averages of all the spectra obtained for each crystal modification. Although there were minor deviations among the numerous spectra of each form, none of the observed spacings differed from the average by more than about 0.05 *Angstrom unit.* Included in this table are the average spacings for each of the polymorphic forms published by Lutton (3). There is essentially complete agreement between the results obtained by the writer and those of Lutton regarding the *alpha, beta prime,* and *beta* forms. It is to be noted that Lutton's β'-3 and β-3 forms differ from each other in only very minor respects and both agree quite closely with the writer's *intermediate* form.



Alpha *Beta Prime*

Intermediate *Beta*

FIG. 1. X-ray diffraction patterns of triglyceride polymorphs.

The order in which the triglyceride polymorphs are transformed successively from one to another has been established by study of the behavior of fats and their component triglycerides during cooling and heating. Typical cooling curves are shown in Figure 2. If liquefied fats or triglycerides are allowed to cool without any stirring, vibration, or other agitation, they will tend to exhibit cooling curves similar to the lower one in the diagram, indicating that the material has solidified completely in the *alpha* form. On the other hand, if liquefied samples are stirred or otherwise agitated during cooling, they will tend to exhibit behavior approximating that shown by the upper curve in the diagram, indicating that after initial crystallization in the *alpha* form the material has transformed more or less abruptly to the *beta prime* form, in which form the solidification was completed.

The relatively uniform behavior of fats and individual triglycerides during cooling is in contrast with

TABLE I
Characteristic Short Spacings of Triglyceride Polymorphs (in Angstrom units)

Alpha		Beta Prime			Intermediate	Beta		
This work	Lutton	This work	Lutton (β', β'–2)[a]	Lutton (β'–3)[a]	This work	Lutton (β'–3)[a]	This work	Lutton (β', β'–2)[a]
				4.61 M	4.62 S	4.60 S$^+$	4.57 VS	4.59 VS
		4.35 W	4.35 M$^-$	4.39 W$^+$		4.35 M	4.22 VW	4.20 W
		4.20 VS	4.19 VS	4.16 M$^+$	4.15 S	4.12 M$^+$		
						4.00 M$^-$	4.00 W$^+$	4.00 M
4.15 VS	4.15 VS	4.03 W	4.03 M	4.05 M$^-$				
						3.84 W	3.85 S	3.84 S
		3.80 S	3.80 S	3.78 S	3.75 S	3.77 S$^-$	3.65 S	3.66 S
				3.62 W$^+$	3.60 W$^+$	3.63 M	3.50 W	3.50 VW$^+$

Intensities of bands are indicated by the following: VS—very strong, S—strong, M—medium, W—weak, VW—very weak.
[a] Forms in parentheses are Lutton's designations.

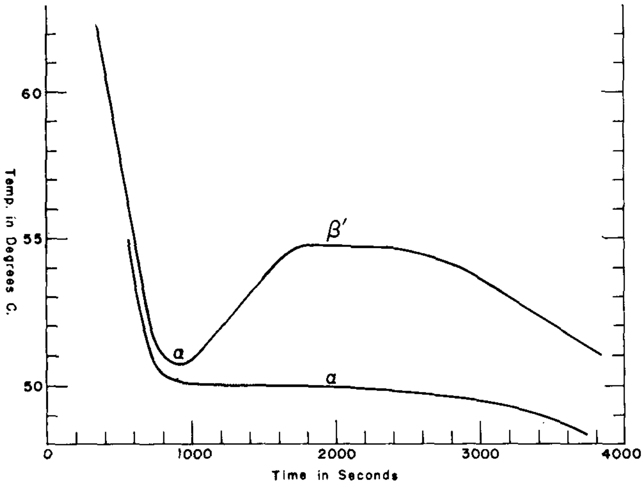


FIG. 2. Cooling curves of fats and individual triglycerides.

their variable behavior on heating, as is represented by the series of curves shown in Figure 3. The type of heating curve exhibited by a given sample at any particular time depends on the polymorphic form in which it completed crystallization, the temperature and duration of the holding (tempering) period, the rate of heating, and the molecular configuration of the components.

It is possible in some cases in which the sample has solidified in the *alpha* form to heat the sample sufficiently rapidly after crystallization to cause it to melt without transformation to a more stable form. Ordinarily however, even though samples are heated quite rapidly, they will exhibit the behavior shown by Curve I. In this case, shortly after the sample has reached its *alpha* melting-point and has begun to melt, transformation to the *beta prime* form occurs, the temperature rises relatively rapidly to the *beta prime* melting-point, and the sample completes its melting at this temperature without further transformation. If the samples have transformed to *beta prime* by the time they are reheated, they may exhibit a heating curve similar to Curve II, wherein the temperature rises directly to the *beta prime* melting-point and the samples simply proceed to melt. If the rate of heating is slightly less rapid than in the previous instance, a heating curve similar to Curve III will be obtained. As before, the temperature rises to the *beta prime* melting-point and the sample proceeds to melt. In this case however, before the sample melts completely, transformation to the *intermediate* form is initiated, the temperature rises again, and completion of melting occurs in the neighborhood of the *intermediate* melting-point. As the rate of heating is further decreased, heating curves like Curves IV and V will be obtained. In such cases transformation to the *intermediate* form occurs relatively sooner. As the duration of the *beta prime* form decreases, the greater will be the amount of material in the *intermediate form*, and consequently the longer will be the temperature halt at the *intermediate* melting-point. Some fats, held for a short time at room temperature, exhibit heating curves like Curve VI, in which the temperature rises initially to the *intermediate* melting-point; then, after more or less melting, transformation to *beta* occurs, the temperature rises to the *beta* melting point, and melting proceeds. Certain fats and most individual triglycerides transfor to the *beta* form during holding at room temperature or during extremely gradual heating. In this case they will exhibit heating curves like Curve VII, in which the temperature rises directly to the *beta* melting-point and melting proceeds.

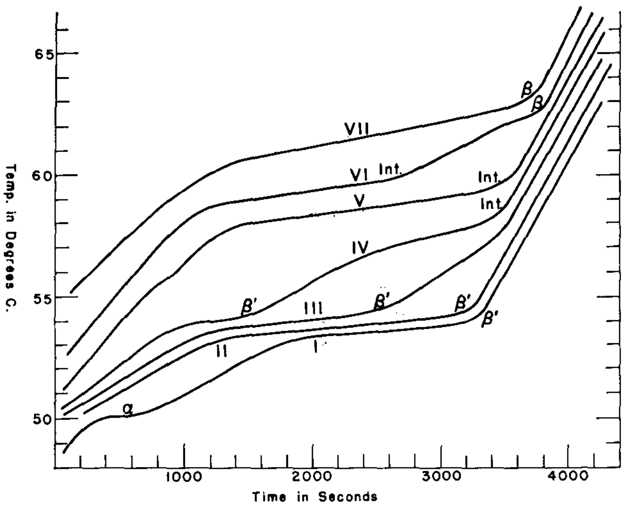


FIG. 3. Heating curves of fats and individual triglycerides.

Cooling and heating curves are thus interpreted to demonstrate that all fats and triglycerides crystallize from the liquid phase in the *alpha* form, transform more or less rapidly to *beta prime*, and subsequently to the *intermediate* and/or the *beta* modifications if they are likely to exhibit these higher polymorphs. This sequence is irreversible. Once transformation to the more stable forms has occurred, lower polymorphs can be obtained again only by melting the sample, crystallizing the *alpha* form, and repeating the sequence of transformations.

The order of the polymorphic transformations has also been confirmed by determination of the solubilities of several fats and triglycerides in hexane, chloroform, ethyl acetate, and acetone. The series of solubility curves of the polymorphic forms of lard flakes in hexane shown in Figure 4 is quite typical although the slopes of the curves differ somewhat

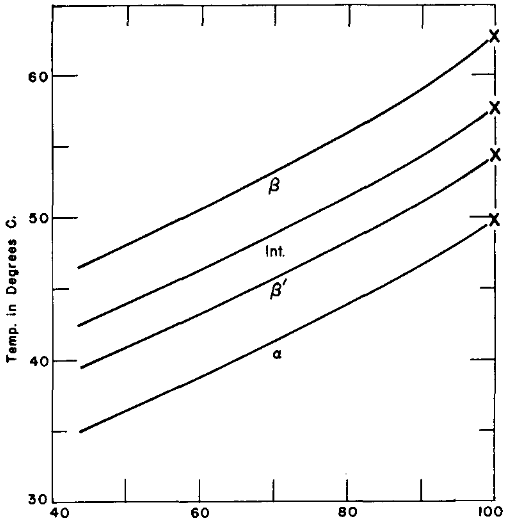


Fig. 4. Solubilities of polymorphic forms of lard flakes in hexane.

from solvent to solvent. When any of these solutions is cooled, precipitation of the solute always occurs at the *alpha* curve. On rapidly reheating the mixture, it usually redissolves at this temperature, but if the precipitated sample is held for a short time at temperatures just below the *alpha* curve, transformation to *beta prime* takes place, and the mixture must be heated to the *beta prime* curve to effect solution. Similar transformations to the *intermediate* and *beta* modifications can be brought about either by holding the samples at successively higher temperatures or by holding them at lower temperatures for longer periods of time. By carefully controlled heating, the entire sequence of solubility curves from *alpha* to *beta* can readily be obtained for certain fats and triglycerides.

The succession of polymorphic transformations was also demonstrated by observation of the visible changes which occur during the heating of fats and triglycerides in the polarized-light microscope. A typical series of observations on rearranged-lard flakes is listed in Table II. Such examinations furnish conclusive proof that each of the four polymorphic forms actually exists. The fact that crystals have been observed to grow in partially melted mixtures as the temperature is being increased removes all doubt that each polymorphic form is a separate and distinct crystalline phase. Polarized-light microscopy has also proved that, contrary to Malkin's contentions (2), the solid which first appears on cooling liquefied fats and triglycerides is crystalline instead of vitreous. The fact that the initial solid phase refracts polarized light, as do the other forms, is proof that such solid does indeed possess a definite molecular orientation.

TABLE II

Observations with Polarized-Light Microscopy
Rearranged Lard Flakes
(Sample Solidified with Dry Ice Prior to Microscopic Examination)

Time	Temperature	Observations	Remarks
min.	*° C.*		
0	49.8	Completely solid	α
3	49.8	Beginning to melt	
8	49.9	Partially melted	α m.p.
12	50.0	Crystals growing in melt	$\alpha \longrightarrow \beta'$
20	50.2	Abruptly solidified	β'
65	54.2	Beginning to melt	
75	54.4	Mostly melted	β' m.p.
80	54.5	Crystals growing in melt	$\beta' \longrightarrow$ int.
100	54.7	Completely solid	int.
125	58.0	Beginning to melt	
135	58.4	Partially melted	int. m.p.
140	58.5	Crystals growing in melt	int. $\longrightarrow \beta$
160	58.7	Crystals increasing	
180	59.0	Completely solid	β
210	60.2	Beginning to melt	
225	60.5	Partially melted	
240	60.8	Mostly melted	
260	61.1	Completely melted	β m.p.

TABLE III

Melting Points of Triglycerides (° C.)

Triglyceride	Alpha	Beta Prime	Intermediate	Beta
Tripalmitin	44.5	56.5	62	64.4
Recrystallized	46.0	57.1	....	66.4
Malkin (2)	45 (vit.)[a]	56.0 (α)[a]	63 (β')[a]	65.5
Lutton (3)	44.7	56.6	....	64.4
Tristearin (5)	53.5	64.5	69–70	73.0
Recrystallized	54.2	64.7	....	73.2
Malkin (2)	54.5 (vit.)[a]	65.0 (α)[a]	70.0 (β')[a]	71.5
Lutton (3)	54.0	64.5	....	73.0
Trielaidin (A)	15.8	....	....	42.5
Sample (B)	....	....	....	43.60 (f.p.)
Lutton (3)	15.5	....	....	42.4
Weygand and Grüntzig (4)	15	....	....	42.0
1-Oleoyl-2,3-Distearin	30.4	37.7	44.4	48.5
Lutton (3)	30.4	43.5 (β'–3)[b]	⟶ ?	....
2-Oleoyl-1,3-Distearin	26.3	36.7	45.0	50.7
Lutton (3)	22.4	35 (β'–3)[b]	? ⟵	44.3 (β–3)[b]

[a] Malkin's classification.
[b] Lutton's classification.

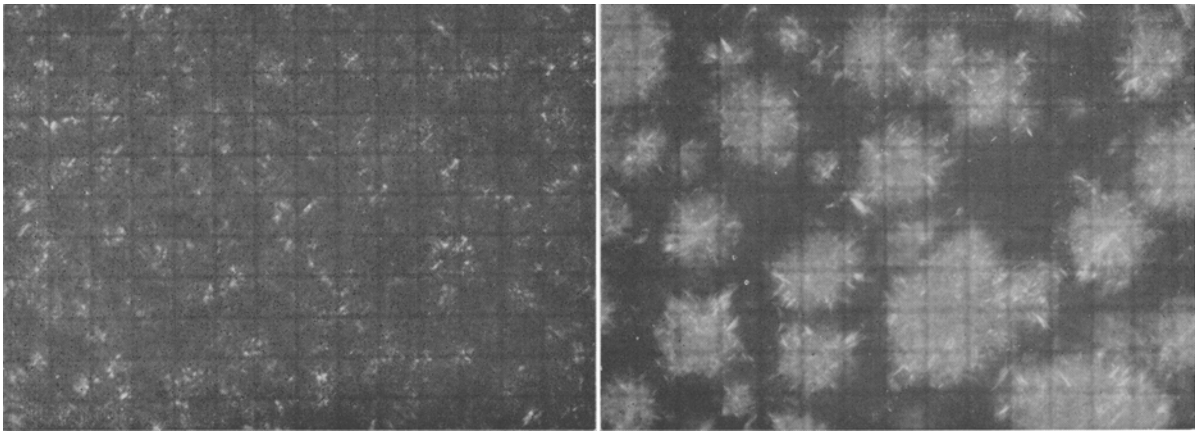
The solidification and melting points of the various polymorphs can be determined from the temperature halts in the cooling and heating curves, by extrapolation of the solubility curves to 100% solute, and by direct observation with polarized-light microscopy. The melting points of some individual triglycerides are listed in Table III. The more highly purified samples of tripalmitin and tristearin do not exhibit the *intermediate* form, and none of the samples of trielaidin seem to exhibit either the *beta prime* or *intermediate* forms. On the basis of melting points it appears that Lutton had actually observed the *intermediate* form of both the oleoyl-distearins rather than the forms which he reported.

Despite the fact that the completely hydrogenated fats are known to consist of different mixtures of triglyceride molecules, their melting points show a remarkable uniformity, as evidenced by Table IV. The effect of variations in composition is more pronounced in the case of the plastic fats, as shown by the melting points listed in Table V. The fats containing more randomized triglycerides do not transform to the higher-melting polymorphs. The effect of triglyceride composition is also indicated by the solidification points of hydrogenated cottonseed and soybean oils of different iodine values listed in Table VI. At iodine values above about 72 the oils tend to crystallize in the *alpha* form whereas those of lower iodine values tend to transform to *beta prime* during solidification. A similar effect is observed on the addition of flakes to the plastic fats, as shown by the behavior indicated in

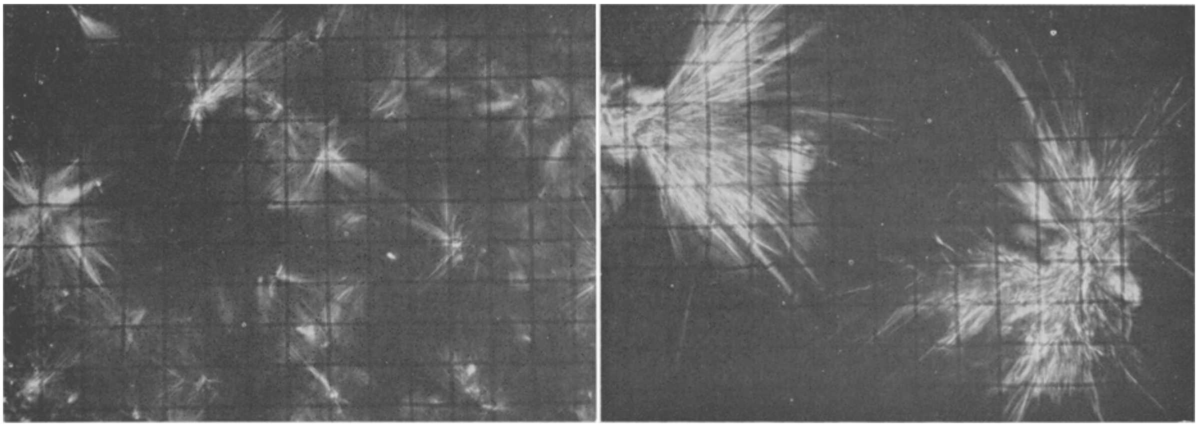
TABLE IV

Solidification and Melting Points of Completely Hydrogenated Fats (°C.)

	Alpha	Beta Prime	Intermediate	Beta
Lard flakes..............................	50.0	53.2	57.3	62.4
Rearranged-lard flakes............	49.8	54.5	58.5	61.1
Tallow flakes............................	50.0	54.3	58.0	60.0
Rearranged-tallow flakes.........	49.7	54.0	57.6	59.5
Cottonseed flakes......................	48.8	54.0	57.5	59.6
Soybean flakes..........................	50.3	55.0	59.4	62.7



Beta Prime *Intermediate*



Beta *Beta* (after long aging)

FIG. 5. Photomicrographs of fat crystals (In polarized light. Magnified about 200x. Grid lines represent 18 microns).

TABLE V

Solidification and Melting Points of Plastic Fats (°C.)

Plastic Fat	Alpha	Beta Prime	Intermediate	Beta
Ordinary lard	22.5–23.5	26–27	30–31	34–35
Hydrogenated lard	24–25	28–29	32–33	36–37
Cutting lard	19–21	23–24	27–28	......
Rearranged lard	20–21.5	23–24.5	27.5–28.5	......
Tallow	27.5–29	33–34	37–40	......
59 I.V. cottonseed oil	21–22	26–27	30–31	......
70 I.V. cottonseed oil	18.5–19.5	23.5–24.5	......	......
78 I.V. cottonseed oil	17–18	22–23	......	......
70 I.V. Soybean oil	19–20	24–25	28.5–29.5	......
92 I.V. soybean oil	15–16	20–21	......	......

Table VII. The percentage of flakes required to effect transformation appears to depend on the proportion of unsaturated fatty acid components in the fat. An increased proportion of higher melting triglycerides evidently enhances the transformation to more stable crystal forms.

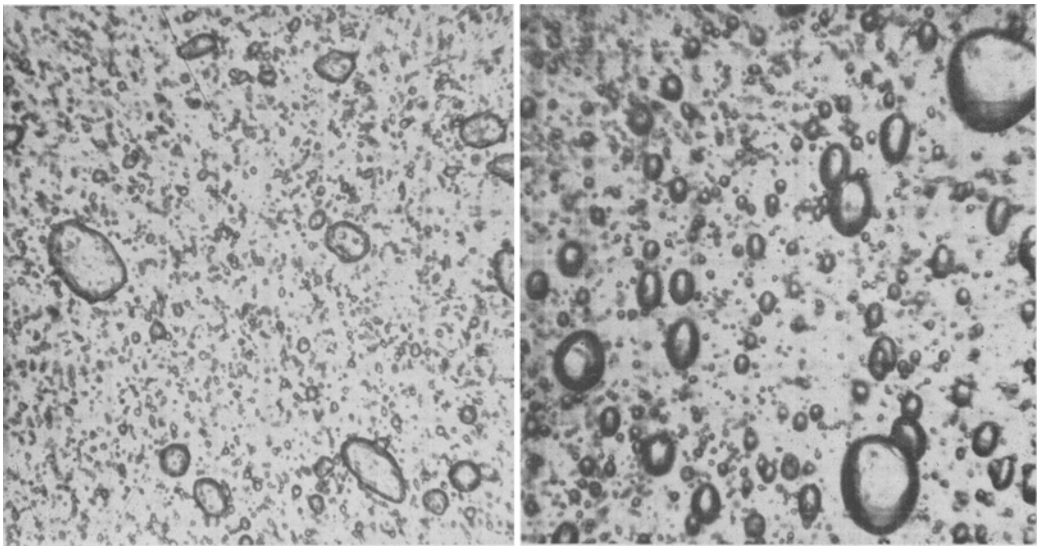
These studies of triglyceride polymorphism provide a basis for reconciling Malkin's and Lutton's divergent interpretations. Highly purified individual triglycerides which contain only one specific fatty acid group evidently exhibit only the *alpha, beta prime,* and *beta* forms, as Lutton reported. Less pure samples of these triglycerides and all those containing two or three different fatty acid groups exhibit all four crystal types, indicating that Malkin was generally correct, although his triglycerides are now known to have been relatively impure. Many of the fats (mixtures of triglycerides) also exhibit all four polymorphic forms, some exhibit only the *alpha, beta prime,* and *intermediate* forms, and others exhibit only the *alpha* and *beta prime* forms.

On the basis of the present investigation it has been deduced that the extent to which transformation of the fats proceeds depends on the ease with which the molecules can fit themselves together to form the successively more closely-packed crystal lattices of the higher polymorphs. Similar molecules, such as those of the individual triglycerides and the highly hydrogenated fats, are able to fit closely together, and their crystals readily transform to the compact *beta* lattice. The assorted molecules of many fats find it more difficult to pack together so readily, and transformation to the higher polymorphs is impeded. Thus fats consisting of quite randomized assortments of triglycerides tend to remain practically indefinitely in the *beta prime* form.

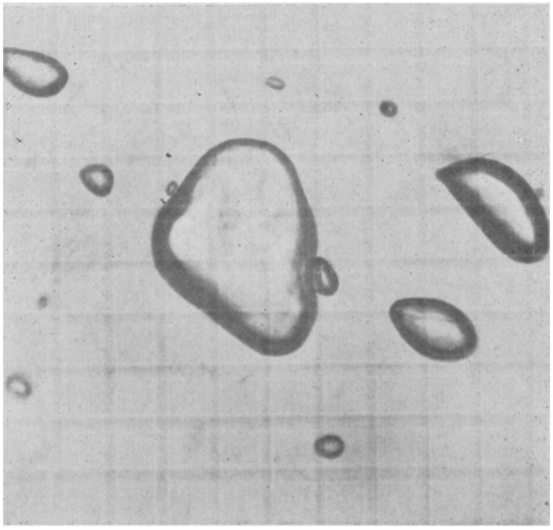
TABLE VI

Relation of Iodine Values to Solidification Points of Plastic Fats

Iodine value	Plastic fat	Solidification temperature, °C.	
		Alpha	Beta Prime
59	Cottonseed		26.4
67	Cottonseed		25.3
69	Cottonseed and soybean (50–50)		25.0
70	Soybean		24.1
70	Cottonseed		23.7
71	Soybean		23.5
71	Cottonseed		23.1
72	Cottonseed and soybean (50–50)		22.8
74	Cottonseed	18.3	
77	Soybean	18.0	
78	Cottonseed	17.3	
85	Cottonseed	16.8	
85	Soybean	16.6	
92	Soybean	15.5	



Beta Prime *Intermediate*



Beta

FIG. 6. Photomicrographs of plasticized fats (In ordinary light. Magnified about 200x. Grid lines represent 18 microns).

TABLE VII
Effect of Cottonseed Flakes on Solidification Points of Plastic Fats

Shortening	% Flakes	Solidification temperature, °C.	
		Alpha	Beta Prime
Rearranged lard	0	20.4	
Rearranged lard	4	21.2	
Rearranged lard	8		24.9
Rearranged lard	12		25.6
78 I.V. cutting lard	0	19.0	
78 I.V. cutting lard	4	20.3	
78 I.V. cutting lard	8		25.2
70 I.V. cottonseed oil	0		23.7
70 I.V. cottonseed oil	4		24.5
70 I.V. cottonseed oil	8		25.2
70 I.V. cottonseed oil	12		26.0
77 I.V. soybean oil	0	18.0	
77 I.V. soybean oil	4		24.2
77 I.V. soybean oil	8		25.5

It now appears that Lutton's and the writer's classifications of triglyceride polymorphs differ from each other and from Malkin's original categories chiefly with respect to the names by which the respective forms have been designated, as indicated in Table VIII.

Crystal Characteristics (6)

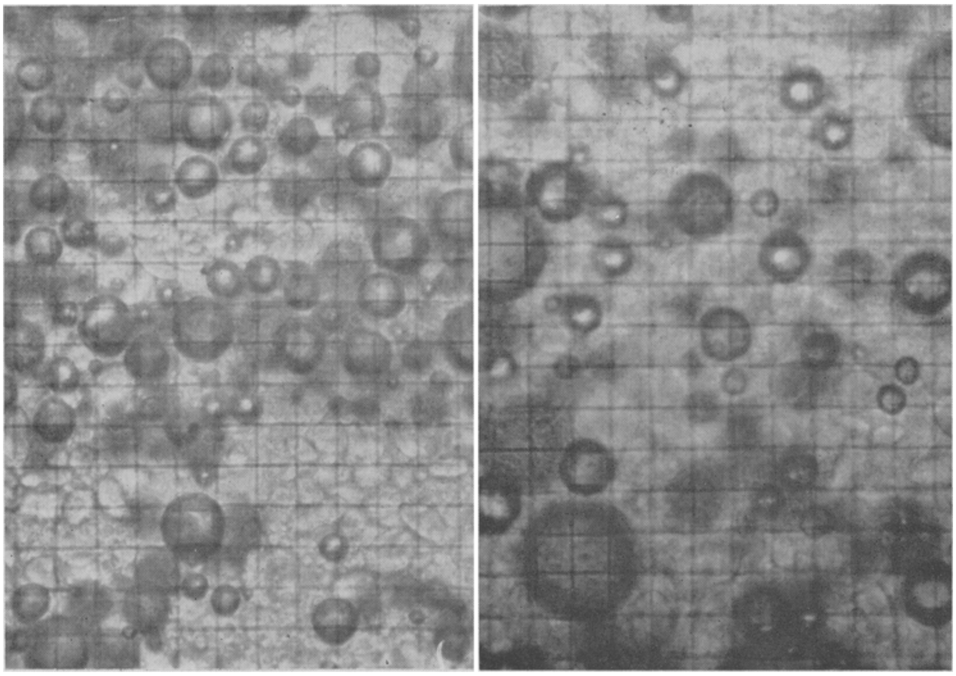
Each of the triglyceride polymorphs possesses specific crystal characteristics which are distinguishable under the microscope. These properties are largely responsible for the appearance and texture of fat products and exert a pronounced influence on the performance of shortenings in many applications.

The microscopic appearance of various types of fat crystals is shown in Figure 5. Crystals of the *alpha* form are fragile, transparent platelets about 5 microns in size. Since they are extremely transitory and require quite low temperatures to be kept long, they could not be photographed with the writer's equipment. The *beta prime* crystals are tiny, delicate needles which seldom grow to more than one micron in length. These are typical of the randomized fats, such as rearranged lard, tallow, and the hydrogenated cottonseed oils. Crystals of the *intermediate* form are somewhat coarser, tending to grow to about 3–5

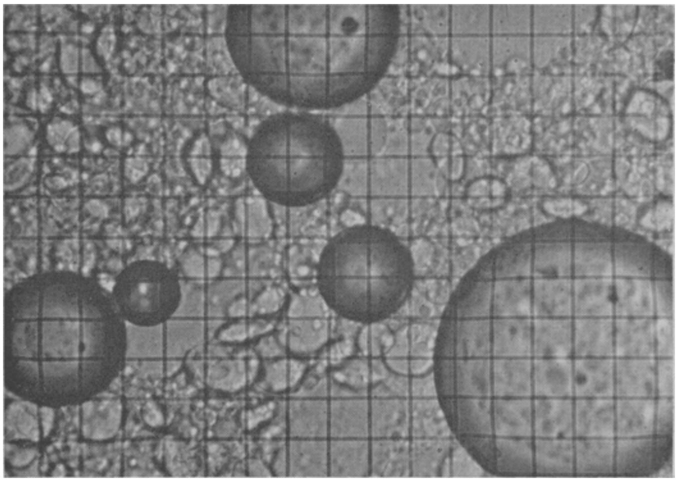
TABLE VIII
Classifications of Triglyceride Polymorphs

M. P.	Malkin	Lutton	This report
Highest	Beta	Beta	Beta
↑	Beta Prime	$[\beta'-3,\ \beta-3]$[a]	Intermediate
	Alpha	Beta Prime	Beta Prime
Lowest	Vitreous	Alpha	Alpha

[a] Inserted by the writer on the basis of his re-interpretation of Lutton's published data.



Beta Prime *Intermediate*



Beta

FIG. 7. Photomicrographs of cake batters (In ordinary light. Magnified about 200x. Grid lines represent 18 microns).

microns in length, and to aggregate in sizeable clumps which tend to get gradually larger with the passage of time. These are typical of many of the flaked shortenings, particularly those in which soybean flakes have been incorporated. The *beta* crystals are quite large and coarse, averaging 25–50 microns in length, and growing to more than 100 microns after extended periods of aging. Clumps of these *beta* crystals can be a millimeter or more in diameter. Such clumps are responsible for the appearance of visibly grainy shortenings.

If fats are allowed to crystallize without any special attention, a more or less heterogeneous semisolid slush is likely to result. It has long been common commercial practice to plasticize fats by whipping air into them during crystallization, thereby producing whiter, creamier, smoother, and more uniform shortenings. Fats existing in different polymorphic forms incorporate air somewhat differently during the plasticizing process, as shown by the photos in Figure 6. The tiny *beta prime* crystals incorporate a multitude of very small air bubbles about one micron or less in diameter. Air distribution in the *intermediate* fats presents a somewhat coarser pattern. *Beta* crystals are likely to incorporate relatively little air in the form of fairly large bubbles. The air-incorporating tendencies of fat crystals can be explained by analogy to the operation of the cutting blades of a meat chopper. As the crystals pass the air-fat interface during the agitation of the plasticizing process, they chop off pieces of air; the finer crystals produce the smaller air bubbles.

The air-incorporating capacity of fats has a direct bearing on their utility as shortenings, particularly in the applications which involve creaming. In Figure 7 are shown some photomicrographs of standard cake batters made with fats in different crystal modifications. The *beta prime* fats incorporate numerous relatively small air bubbles in the batter, the *intermediate* fats produce a somewhat coarser air-distribution pattern, and the *beta* fats produce relatively few, large air bubbles. Since the volume, texture, and tenderness of baked products are essentially a direct function of the number and size of the air bubbles in the batter, the fats in the *beta prime* crystal modification produce by far the most desirable cakes and likewise, by the same principle, the best icings. Fats in the *intermediate* form produce slightly inferior, but usually passable, creamed items whereas *beta* fats are totally unsatisfactory in any applications involving the creaming phenomenon.

Physical Behavior of Common Fats

The physical behavior of the various commercial fats can now be explained more plausibly on the basis of the occurrence of four crystalline forms than previously in terms of their existence in only three modifications. The subtle differences observed in the performance of various shortenings with the passage of time are not consistent with the pronounced physical changes required by the previous concept of the transformation from *beta prime* to *beta.* The gradual changes in the behavior of commercial fat products can now be shown to be associated with their transformation through the previously overlooked *intermediate* modification.

The relative rates of transformation of the polymorphic forms of various types of common fats are shown diagrammatically in Figure 8. This diagram indicates in a schematic way how the fats change to successively higher-melting forms with the passage of time under different conditions of treatment. The time scale is purely arbitrary, merely denoting the passage of time as it proceeds to the right. The behavior indicated is that which is usually observed in the normal course of ordinary commercial operations. It must be borne in mind that the rate of transformation depends on the rate at which the fats attain equilibrium with their environment, which in turn is influenced markedly by the size of the sample and the degree of agitation. Transformations which occur almost instantaneously in a few micrograms of fat on a microscope slide, and in a few hours in a test tube, may require several months in a 450-lb. drum of fat in a warehouse.

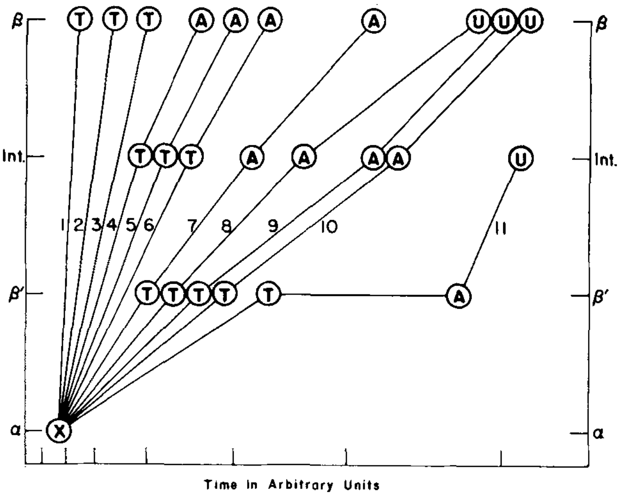


FIG. 8. Relative rates of transformation of fats.

Letters in the circles refer to the following: X—form during crystallization. T—form after normal tempering. A—form after aging during normal storage. U—form after storage under unusual conditions.

Numbers on the curves identify the following fats: 1—Lard flakes. 2—Soybean flakes. 3—Cocoa butter. 4—Killing lard. 5—Partially hydrogenated lard. 6—Ordinary lard. 7—High I. V. lard. 8—Rearranged-lard flakes. 9—Cutting lard, partially hydrogenated soybean oil (low I.V.). 10—Tallow flakes, cottonseed flakes. 11—Rearranged lard, ordinary tallow, partially hydrogenated soybean oil (high I.V.), partially hydrogenated cottonseed oil.

The fats at the left in the diagram, those which transform most readily to the *beta* form, are the fats which consist of relatively limited assortments of different triglyceride molecules. Proceeding to the right in the diagram, as transformation to the higher crystal forms is retarded, the fats contain greater assortments of triglycerides. The fats at the right, those which remain indefinitely in the lower forms, are the fats which contain the most randomly-distributed assortments of fatty acids in their molecules.

When flakes are blended into fats in the preparation of certain shortenings, the products generally tend to exhibit the polymorphic behavior of the flakes which have been incorporated rather than the normal behavior of the base stock. Thus ordinary hydrogenated cottonseed shortening flaked with lard flakes or soybean flakes, instead of remaining in the *beta prime* form, exists in the *intermediate* form after tempering and transforms gradually to *beta* during subsequent aging. On the other hand, when flaked with rearranged lard flakes, tallow flakes, or cottonseed flakes, ordinary cottonseed shortenings remain for long periods of time in the *beta prime* form, transforming very gradually to *intermediate* during aging; and occasionally, under very unusual storage conditions, some of these mixtures might transform to the *beta form.* The behavior of flaked soybean shortenings depends on the extent to which the oil has been hydrogenated as well as on the nature of the flakes. Soybean shortenings of higher iodine values exhibit behavior similar to that of the flaked cottonseed shortenings whereas those of lower iodine values tend to behave more like ordinary lard. The behavior of flaked rearranged lard shortenings is practically identical to that of the cottonseed shortenings. The addition of any kind of flakes to ordinary lard does little to modify its tendency to transform quite rapidly to the *beta* form. Rearranged lard flakes, tallow flakes, and cottonseed flakes tend to keep ordinary lard in the *intermediate* form for a little longer than normal, but it still transforms to *beta* fairly soon under normal storage conditions.

Commercial Processing of Shortenings

Since the most desirable shortenings for many purposes are those which exist in the *beta prime* form, it would seem to be a simple matter to choose the appropriate fat for processing. Unfortunately no natural fat or oil normally possesses all the required characteristics. Some commercial fats, such as the cottonseed and soybean oils and the tallows, contain sufficiently randomized triglyceride components, but the vegetable oils do not contain enough crystalline solids at ordinary temperatures, and the tallows contain too high a percentage of solids. Lard, on the other hand, contains far too great a homogeneity of triglyceride molecules for the desired purposes.

The vegetable oils can readily be hydrogenated to increase their proportion of solid triglycerides without destroying their desirable molecular heterogeneity. In this respect cottonseed oil can be hydrogenated to a greater extent than soybean oil. Some of the excess solids of tallow can be removed by fractional crystallization with or without solvents. The molecular heterogeneity of lard might be increased by partial hydrogenation, followed by removal of some higher-melting components by fractional crystallization. However the best method of increasing the molecular heterogeneity of lard is catalytic interesterification of its components.

Besides having long been standard practice in the production of shortenings, the incorporation of a certain percentage of flakes not only seems to help improve the properties of the products but is required for the proper performance of shortenings in creaming operations. From all considerations it is concluded that cottonseed flakes possess the most desirable characteristics for practically all shortening purposes. Tallow flakes and rearranged lard flakes can be used interchangeably with cottonseed flakes for most purposes. Soybean flakes exhibit far more undesirable properties, and lard flakes are quite objectionable from all considerations for use in any shortenings intended for creaming applications.

The rate of crystallization of fats has a pronounced influence on the ultimate texture of shortenings. It is imperative that crystallization be induced as suddenly as possible. When this is done, the molecules do not have sufficient time to form large aggregations, and consequently a multitude of very small crystals is formed throughout the solidifying mass. Such tiny crystals tend to incorporate innumerable, minute air bubbles during the plasticizing process, which is part of the chilling operation. The initial small size of the crystals and their separation by the air bubbles tend to prolong the time which must elapse before the crystals grow to undesirable size.

Tempering is the process whereby fats attain the physical state in which they are normally utilized. During tempering the crystals transform to the polymorphic form in which they normally exist under ordinary conditions. During this period the heat of transformation must be dissipated as rapidly as possible. If the fats are allowed to retain this heat by virtue of their normal thermal-insulating capacity, an appreciable portion of the crystals might be melted, and the subsequent gradual cooling under normal storage conditions will tend to promote transformation of the remaining crystals to the undesirable *beta* form.

Although small packages of shortening are undoubtedly tempered within the normal time, there is some question whether drum lots of all types of shortening are completely tempered under normal conditions in the time usually allowed. Many shortenings continue to change in structure over much longer periods. On the other hand, in the case of certain shortenings which exist apparently indefinitely in the *beta prime* form, normal tempering operations could be dispensed with. On occasion, some products are shipped immediately after filling without benefit of customary tempering, and frequently such products reach the consumer in perfectly satisfactory physical condition. Tempering merely involves a relationship between temperature and time. Elevated temperatures are not necessarily required for tempering still goes on at lower temperatures, albeit more slowly. Thus certain types of shortening will be tempered satisfactorily during the time which normally elapses while the products are being shipped and distributed to the ultimate consumers, provided that the temperature is not lowered too greatly during the period.

Even after careful tempering, reasonably conscientious care must be exercised during the subsequent storage of shortenings. Extreme variations in temperature must be avoided. Of course, certain fat products will withstand less careful treatment far better than others. The partially hydrogenated vegetable oils and the rearranged lard shortenings will retain their most desirable crystal form for many months at ordinary temperatures whereas at such temperatures ordinary lard transforms very rapidly to the undesirable *beta* form. Although vegetable oil and rearranged lard shortenings need not necessarily be refrigerated, their desirable crystal characteristics are undoubtedly preserved for longer periods at 16–18° C. (60–65° F.) Ordinary lard however must be refrigerated at perhaps 4–7° C. (40–45° F.) to increase the chances of retaining its *intermediate* form although it will probably transform to the *beta* form as soon as it is brought to room temperature.

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REFERENCES

1. Hoerr, C. W., and Scott, R. W., "Crystalline Forms of Commercial Fats and Oils," presented at the 48th annual meeting, American Oil Chemists' Society, New Orleans, La., April 29, 1957.

2. Malkin, T., "Glyceride Polymorphism," *Progress in the Chemistry of Fats and Other Lipids*, Vol. II, Academic Press Inc., New York, 1954. Contains references to all of Malkin's previous papers on the subject.

3. Lutton, E. S., *J. Am. Chem. Soc., 70,* 2441 (1948); *72,* 3254, 4519, 5064 (1950); *73,* 5595 (1951); *74,* 4827 (1952); and *75,* 2685 (1953).

4. Weygand and Grüntzig, *Z. Anorg. Allgem. Chem., 206,* 304, 313 (1932).

5. Hoerr, C. W., and Harwood, H. J., *J. Phys. Chem., 60,* 1265 (1956).

6. Hoerr, C. W., and Waugh, D. F., *J. Am. Oil Chemists' Soc., 32,* 37 (1955); Hoerr, C. W., *J. Am. Oil Chemists' Soc., 32,* 659 (1955); and Hoerr, C. W., and Kiess, A. A., *Proc. 8th Res. Conf.,* Am. Meat Inst., March 22, 1956.