Some Physical Characteristics of Rearranged Lard[1]

C. W. HOERR, Research Division, Armour and Company, Chicago, Illinois, and
D. F. WAUGH, Massachusetts Institute of Technology, Cambridge, Massachusetts

ORDINARY commercial lard has always been an excellent shortening for many purposes. The advent of the hydrogenated vegetable oils some years ago emphasized certain limitations of ordinary lard which have precluded its successful competition with the vegetable shortenings, particularly in certain cake-baking operations. Bailey (1) has described in detail the various methods of treatment which have been devised to overcome these defects by altering the natural properties of ordinary lard. Lard has been blended with other fats and oils; it has been refined, bleached, and deodorized; it has been hydrogenated; it has been fractionally crystallized, with and without organic solvents; it has been emulsified, homogenized, plasticized, and texturized. And it has been subjected to a wide variety of combinations and modifications of these procedures. Yet no really significant alterations in the fundamental characteristics of lard were brought about until lard was molecularly rearranged.

This relatively recent development (2), involving chemical treatment, effects certain changes in the basic nature of lard which dramatically alter its physical behavior, particularly its baking characteristics. For example, whereas ordinary lard produces substandard pound cakes, rearranged lard produces pound cakes whose volume is considerably in excess of the usual standard for good cake shortenings.

The current commercial process whereby lard is molecularly altered has been described elsewhere (3) in detail. Briefly, lard can readily be molecularly rearranged by heating it with a small amount of an alkali metal alcoholate, such as sodium methoxide, for periods of an hour or less at temperatures in a relatively short range above the melting point of the lard. After deactivation of the catalyst with water, extraneous reaction products are removed from the rearranged lard by water-washing and deodorizing. The product is then ready to be flaked, plasticized, and packaged in any desired manner.

This treatment has been described (4) as a shuffling process wherein the fatty-acid groups are redistributed among the triglyceride molecules in a more heterogeneous arrangement than that in the naturally occurring fat. Unfortunately no analytical technique is yet available for determining the exact composition and the relative proportions of the various triglyceride types with any degree of unquestionable reliability (5).
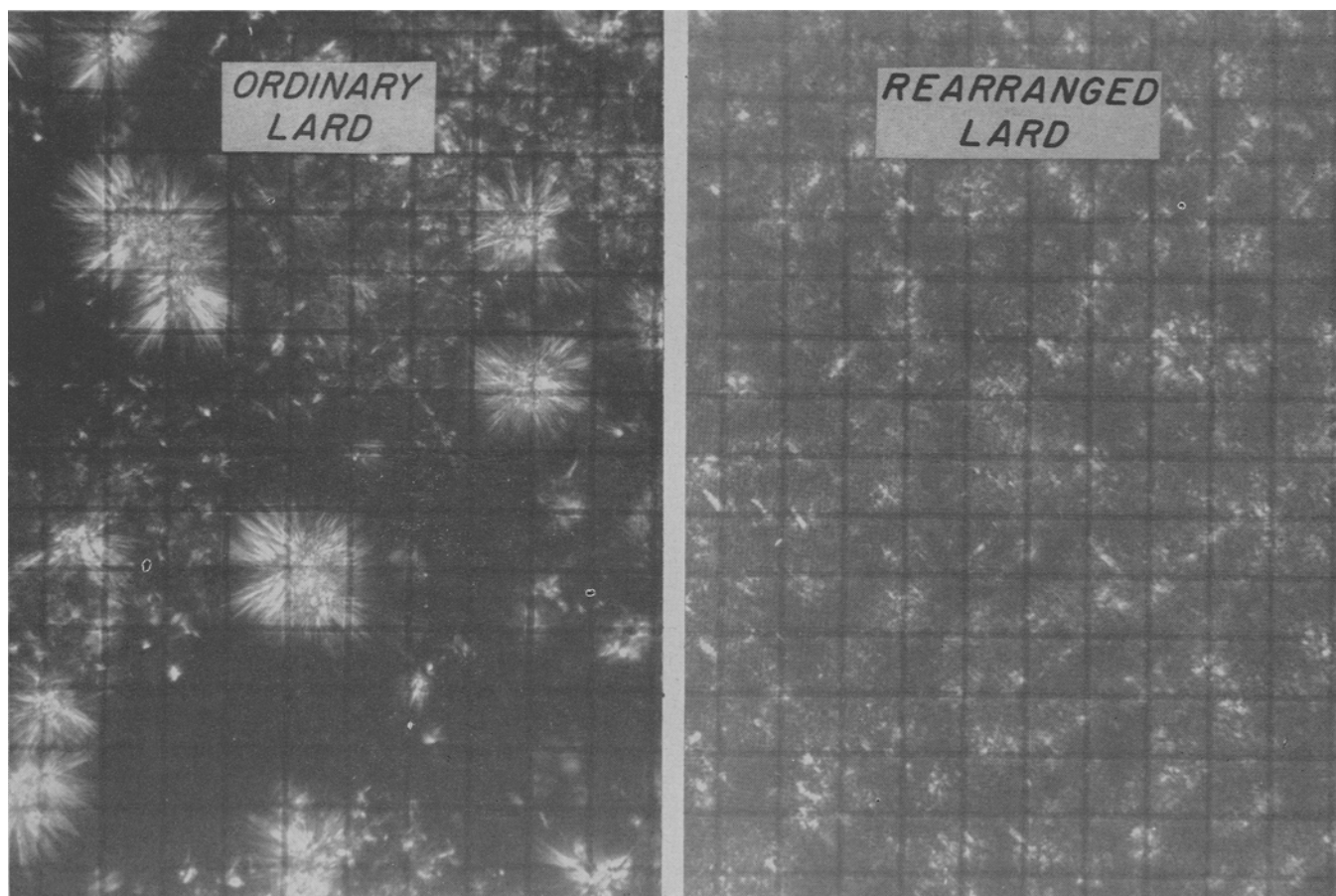
FIG. 1. Unplasticized fats allowed to crystallize on microscope slides. Tempered for 3 days at 25°C. Photographed with polarized light at 206.2 × magnification.
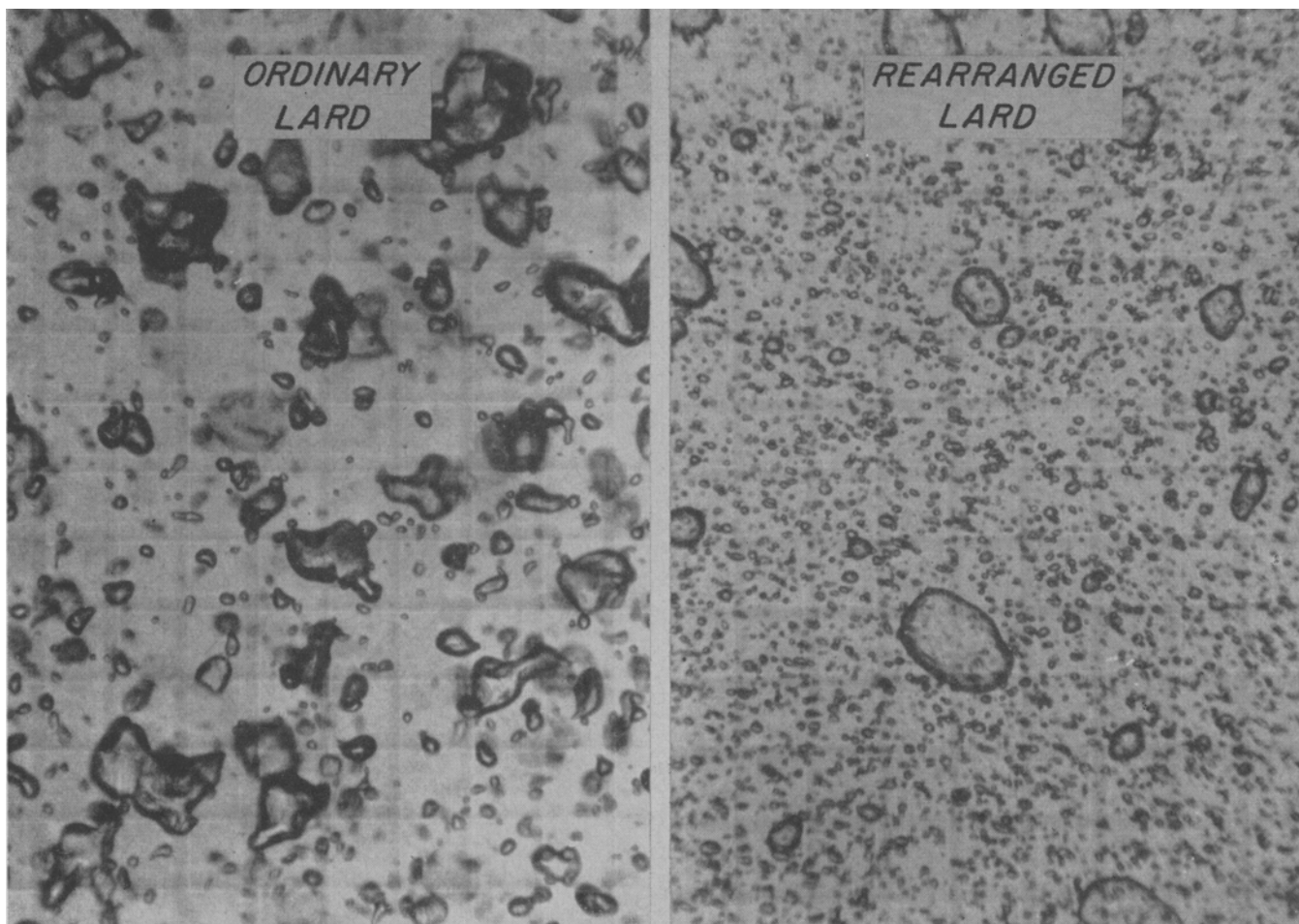
Fig. 2. Fats plasticized by means of Votators. Tempered for 3 days at 25°C. Photographed with ordinary light at 194 × magnification.

Experimental Observations

The usual analytical methods fail to show differences between ordinary lard and rearranged lard of such magnitude as to account for the remarkably enhanced baking characteristics of the latter. There is, for example, no change whatever in the iodine value, saponification number, or total fatty acid composition. The practically unaltered melting point of the treated lard fails to reflect the magnitude of change in baking behavior.

Certain differences between ordinary lard and rearranged lard are revealed by means of microscopic examination. The noticeably different crystal habits of these fats when crystallized directly on the microscope slide are shown in Figure 1. Whereas ordinary lard contains numerous clusters of relatively large, coarse, needle-like crystals, rearranged lard consists of a lacy network of uniformly delicate, almost submicroscopic, crystals.

Figure 2 illustrates the difference in microscopic appearance of these fats upon being plasticized by means of Votators. The incorporated air is dispersed in rearranged lard much more thoroughly than in ordinary lard.

The photomicrographs of pound-cake batters shown in Figure 3 further illustrate this comparison. The batter containing relatively little air dispersed in large bubbles characteristically produces a low-volume, coarse-grained cake, whereas the batter with a relatively greater number of smaller air bubbles produces a high-volume, fine-textured cake.

Whereas the foregoing illustrations demonstrate differences in behavior, clues to the fundamental divergence between ordinary lard and rearranged lard are found in x-ray spectra such as those shown in Figure 4. Interpretation of spectra such as these elicits the following observations:

1. The generally more diffuse pattern of rearranged lard indicates that this fat possesses a less well-ordered arrangement of its molecules.

2. Treatment of the lard increases the long spacings by about 20-25% (from 39Å to 48Å).

3. There is essentially no change in the short spacings upon rearrangement.

4. On the basis of the criteria recently published by Lutton (6) both ordinary lard and rearranged lard exist in the beta, or most stable, crystal modification by virtue of the fact that both fats exhibit a very strong, sharp spacing at 4.6Å.

Discussion

In speculating on what type of fundamental molecular structure would be consistent with the facts listed in Table I, we are faced with the problem of hypothesizing a molecular arrangement which involves no chemical change other than a redistribution of the fatty-acid components, and no change in the crystal lattice beyond a substantial expansion in a direction.

perpendicular to the successive planes of the glycerol groups.

TABLE I
Properties of Rearranged Lard Relative to
Untreated Lard

Property	After Rearrangement
Saponification number	No change
Iodine value	No change
Fatty-acid composition	No change
Melting point	Substantially unaltered
Triglyceride composition	More heterogeneous
Crystal habit	Smaller crystals
X-ray pattern	More diffuse
Long spacing	20-25% longer
Short spacings	Essentially unchanged
Crystal form	No change

The spatial arrangement of triglyceride molecules in their solid state has been deduced by means of x-ray measurements on highly purified, carefully identified samples (1, 6, 7). The schematic models shown in Figure 5 illustrate, within a fair degree of approximation, the manner in which various triglyceride molecules align themselves with one another. (The models are essentially to scale with respect to length of the glycerol group and over-all diameter of the carbon chains, but the carbon chains represented are only about half as long as those in lard. To be precisely to scale, such molecules would have been an impracticably cumbersome 5 ft. long.) It should be emphasized that the representation of a carbon chain by a cylinder is a schematic generaliza-

tion for it is well known from many precise measurements that carbon chains actually pack together more closely than the area of their over-all cross-section by intermeshing of their hydrogen atoms.

The models in Figure 5 illustrate the well-known manner in which triglyceride molecules are arranged as alternately overlapping tuning forks in the solid state. Actually, to depict the stable crystal form, these molecular models should be tilted some 30-40° from the vertical. For purposes of simplifying the present discussion, polymorphic complexities will be omitted, and the discussion will refer only to the stable crystal form.

Figure 5A represents the alignment of the molecules of a simple, saturated triglyceride such as tripalmitin. As these molecules solidify, they build up layers of these paired units, creating a well-ordered, stable, crystal lattice. In such a structure, wherein each molecule can come into the closest approximation with its neighbors, the Van der Waal's forces, which are effective only over these very short distances, exert a tremendous binding effect. Consequently a large amount of energy is required to separate these molecules, and for this reason such crystals possess relatively high melting points and high heats of fusion.

Triglycerides which contain oleic acid are shown in Figures 5B and 5C. The oleic acid chains are not linear in the solid state because of the angle introduced by the carbon-carbon double bond. Since such chains are not able to pack so closely as straight chains, the Van
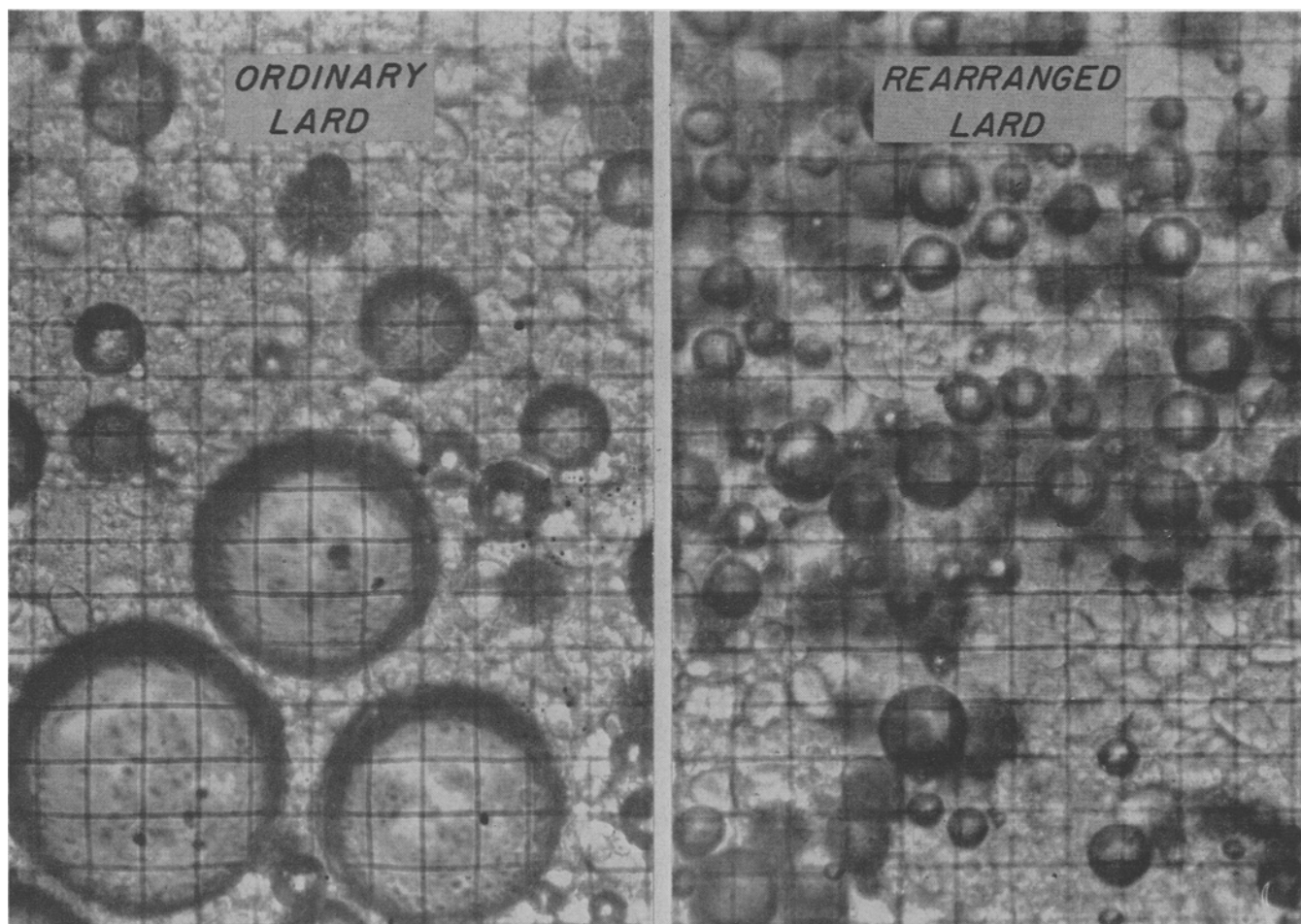

Fig. 3. Pound-cake batters mixed and photographed at 25°C. Ordinary light at 194 × magnification.
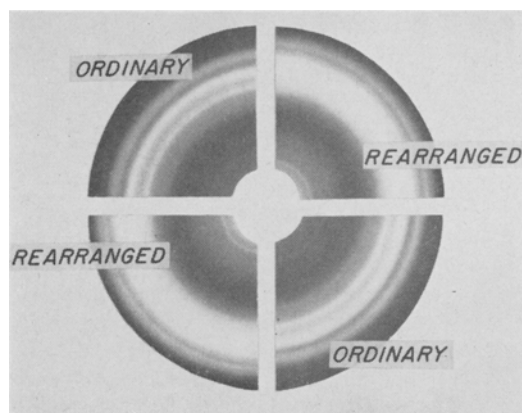
FIG. 4. X-ray diffraction patterns of fats tempered for about 2 weeks at 25°C. Specimen-to-film distance 5.0 cm. Exposure time 1.5 hours.

der Waal's forces are somewhat less effective, and consequently less energy is required to separate the molecules. The melting points and heats of fusion of such crystals are therefore relatively lower. This situation is exaggerated when the oleic acid group occurs on the terminal carbon atom of the glycerol.

Figure 5D represents a mixture of assorted triglyceride molecules. Close-ordered packing cannot be achieved by such heterogeneous molecules, and hence a relatively more disordered crystal lattice results.

The concept of molecular packing is illustrated further by Figure 6. Each of these models represents a section of a monomolecular layer of fat. The models in Figure 6A depict a fat consisting of only a few types of relatively simple, symmetrical triglycerides. In a layer of such a mixture the methyl end-groups of the paraffin chains will exhibit a series of high and low spots occasioned by the presence of longer and shorter chains. As the next layer of molecules begins to solidify on such a crystal, the chances are that the longer chains of this next layer will fit into the low spots of the previous layer, and the low spots of the new layer

will mesh with the high spots of the previous layer. There results a close-packed arrangement with a long spacing approximately twice the length of the average fatty acid present.

Figure 6B represents a fat consisting of a more heterogeneous assortment of triglyceride types. As

FIG. 6. Schematic illustration of packing of layers of triglyceride molecules. A. Close packing. B. Imperfect (extended) packing.

these molecules solidify upon cooling, the chances of a given molecule aligning itself with a similar molecule are considerably fewer than previously. The plane of the methyl groups of a given layer of these molecules will present a far more irregular surface than before. Then as successive layers solidify, there will be less chance that their molecules will be able to mesh neatly with the appropriate high and low spots of the preceding layers. Adjacent layers will thus tend to contact only at the high spots. The long spacing of the crystals will therefore be greater than before and will tend to approximate twice the length of the longest fatty acid in the mixture.

Although this suggested theory was deduced from a series of hypothetical suppositions, certain correlations between theory and fact present themselves. For instance, ordinary lard is generally considered to consist of a relatively simple assortment of fairly symmetrical triglycerides. Its long spacing is almost exactly twice that of palmitic acid, whose molecular dimensions represent the average molecule in lard. Rearranged lard, on the other hand, is generally considered to consist of a heterogeneous assortment of triglyceride types. Its long spacing is found to be
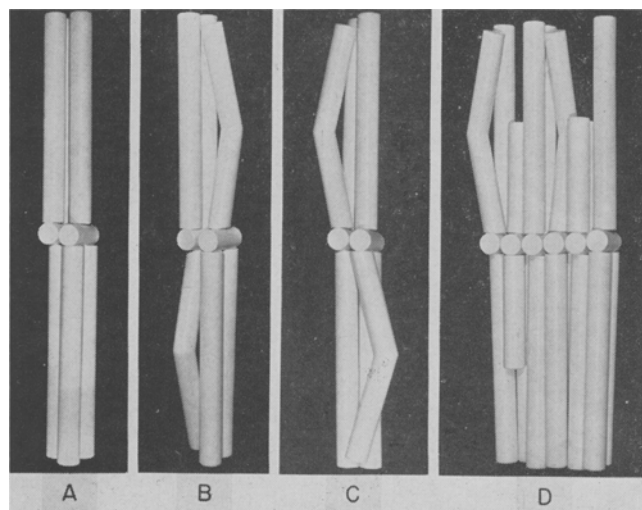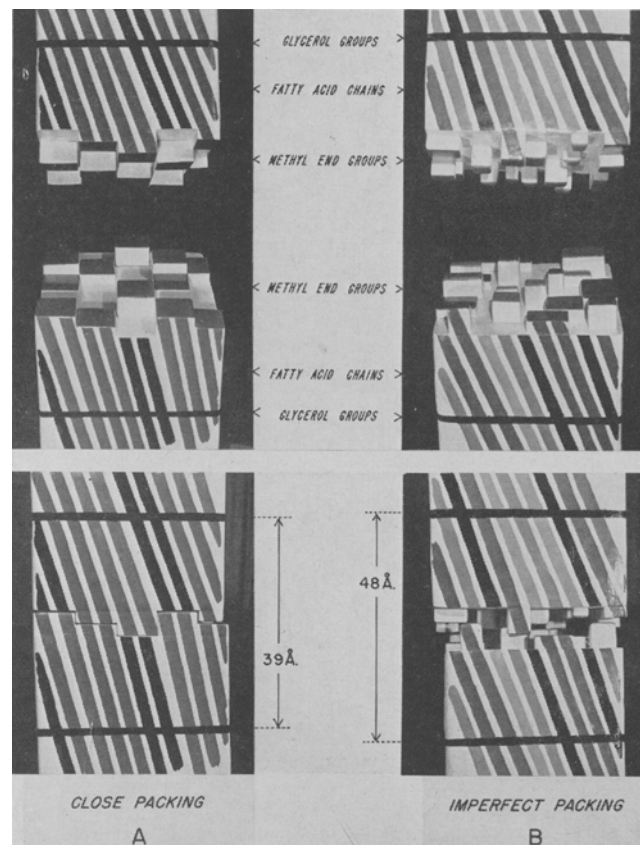

FIG. 5. Schematic arrangements of triglyceride molecules.
A. Monoacid saturated triglyceride such as palmitin.
B. Triglyceride containing unsaturated acid on the central glycerol carbon atom such as β-oleyl-dipalmitin.
C. Triglyceride containing unsaturated acid on a terminal glycerol carbon atom such as α-oleyl-dipalmitin.
D. Mixed triglycerides containing long and short saturated acids and unsaturated acids on central and terminal glycerol carbon atoms.

almost exactly twice that of the C_{20} chain, which is the longest fatty acid usually found in lard.

This packing theory suggests an explanation for the visible difference in the crystals of ordinary lard and rearranged lard. In general, the size of a crystal is related to its free surface energy, all other factors being equal. In a perfect crystal the free surface energy approximates zero. This value increases directly with the degree of imperfection of the molecular packing. Increased free surface energy decreases the ease with which a molecule can enter the crystal lattice. Therefore crystals which can attain the largest proportions possess relatively low free surface energy, and conversely those which grow with difficulty possess relatively higher free surface energy.

By inference, ordinary lard crystals must possess a relatively low free surface energy by virtue of their more homogenous close-packed structure. The

imperfect packing of the rearranged-lard crystals indicates that they possess a somewhat higher free surface energy. Consequently, as has been observed, ordinary lard crystals grow to relatively large proportions whereas the crystals of rearranged lard remain relatively much smaller.

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

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
R. L. Broadhead, Abstractor

The development of the European crushing industry since World War II. Anon. *Oils & Oilseeds J.* 7(1), 5-10(1954). A review showing that European oilseed imports (and crushing) have decreased since 1938 while oil imports have increased. Factors affecting the European oil industry are political controls, trade agreements, and increased crushing in Asiatic and African countries of the oilseeds produced in those countries.

Action of dry zinc chloride at elevated temperatures on cottonseed oil. E. P. Babin and V. G. Plyusnin. *Zhur. Priklad. Khim.* 27, 463-5(1954). $ZnCl_2$ acts as a catalyst for oxidation of the oil at elevated temperatures as indicated by a rise in the acetyl no. on heating the oil to 240° in the presence of 10% $ZnCl_2$. The iodine value declines sharply while the saponification no. drops slightly in the course of 21-hr. treatment. (*C. A.* 48, 7917)

Reconstructing glyceride oils. G. Barsky(E. F. Drew & Co., Inc.). *Brit. 706,562.* A mixture of glyceride oil, containing fatty acids of 6-10 C atoms, was allowed to react with fatty acids having 12-18 C atoms in the presence of 0.1-0.5% boric acid or Zn oxide under vacuum at temperatures ranging from 260-290°. The fatty acids, having 12-18 C atoms, displaced the fatty acids of the glyceride oils to yield products having properties similar to coconut oil and satisfactory for candy coatings and other confectionery uses. (*C. A.* 48, 11820)

High iodine value dehydrated castor oil. K. K. Dole and V. R. Kestar. *Paintindia* 2(1), 65(1952). Castor oil dehydrated in the presence of a specially active catalyst (unspecified), gave dehydrated castor oils with high molecular weight and iodine values of 172-175 as against the usual 148-153. (*C. A.* 48, 7917)

The fat and water content of the edible part of the herring. C. H. Branes and R. Dietrich(Inst. Meeresforschung, Bremerhaven, Germany). *Fette u. Seifen* 55, 533-541 (1953). After determining the water content, the fat content can be read from a graph.

Application of Neusal solution for the determination of fat in sweetened dairy products. Paul Demont(Sta. laitière, Grangeneuve-Fribourg, Switzerland). *Mitt. Lebensm. Hyg.* 45, 104-8 (1954)(in French). The determination of fat in sweetened dairy products by using Gerber van Gulik's butyrometer is described. The composition of Neusal solution is the same as the solution proposed by Schulz, et al., *C. A.* 46, 5218. (*C. A.* 48, 9576)

Wool grease and wool grease fatty acids, fatty alcohols, and soaps. Croda Ltd. and Edgar S. Lower. *Brit. 706,422.* Wool grease and wool grease fatty acids, fatty alcohols, and soaps, with a low color density were prepared by the addition of H_2O_2 (80-90% concentration by weight) to the wool grease products. The amounts of H_2O_2 used were about 5% by weight of the wool grease product. (*C. A.* 48, 11820)

Some characteristics of refining and hydrogenation of rape oil. A. A. Kaminskiĭ. *Masloboĭno-Zhirovaya Prom.* 19(3), 10-13 (1954). Refining of rapeseed oil by the use of acid-alkali and alkali methods is described. The procedures employed are essentially those of, resp., Zharski, et al. (*C. A.* 48, 388) and Z. and Romanova (*C. A.* 48, 8562). Owing to the moisture in rapeseed oil, the hydrogenation of oil refined by the acid-alkali method produces fat which is white in color, unless the sp. g. of the H_2SO_4 used is lowered to 1.76-1.64. This prevents the formation of a dark-green coloring matter from bound chlorophyll in rapeseed oil during its acid treatment. The hydrogenated fat becomes rose-colored. This color is readily removed, however, by active C introduced into the autoclave at 32-5° prior to completion of the process. With the alkali method the bound chlorophyll in rapeseed oil is subsequently absorbed by activated fuller's earth. (*C. A.* 48, 9721)

Improvement of cottonseed-oil quality. A. M. Goldovskiĭ. *Masloboĭno-Zhirovaya Prom.* 19(4), 8-10(1954). Certain factors (uniformly crushed-seed, particle size, moisture content during roasting, temperature and duration of roasting and pressing) which influence the formation and passage of bound and free gossypol, resp., into the oil are discussed. (*C. A.* 48, 11816)

Theory, computation, and design of apparatus for the process of deodorizing oils. N. I. Gel'perin and E. N. Gel'perin. *Masloboĭno-Zhirovaya Prom.* 19(4), 12-15(1954). Equations were developed to show the consumption of live steam by batch and continuous deodorizers. The latter have an economic advantage over the former and can be designed easily and efficiently. (*C. A.* 48, 11816)

Fats. Imhausen & C., G. m. b. H., and Karl H. Imhausen. *Brit. 694,670.* A process for preparing a hard, brittle fat of relatively low m.p. is claimed. Refined fatty acids of palm kernel or vegetable oils are steam-distilled at 3 mm., and then hydrogenated over Ni at 180° and 5 atm. to an iodine value of 0.8-3.0. The purified, hydrogenated acids are then esterified with approximately the theoretical amount of glycerol at 200° and 3 mm. in the presence of a Zn-dust catalyst. The product is refined with alkali, decolorized, and deodorized to a snow-white, hard, brittle solid m. 35-6° and showing a conchoidal surface of fracture. Ordinary hydrogenated fats also m. about 35°, but they lack hardness and brittleness. (*C. A.* 48, 9724)

Fats. Imhausen & Co., G. m. b. H. and Karl H. Imhausen. *Brit. 694,983.* An improvement of the process of *Brit. 694,970,* by which esterified material rather than free fatty acids are used in the hydrogenation step, affords better yields and reduces the loss of hydrogenation catalyst. In one example the original