Interesterification Products and Processes¹

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Abstract

Interesterification as applied to fats and oils is a process whereby the fatty acid molecules of glyceride molecules are rearranged in a random or directed manner. Either type of rearrangement may involve production of new triglyceride compositions in a predictable manner. A number of patented processes for accomplishing interesterification are discussed. Effective rearrangement catalysts are listed. Typical applications to commercial products are reviewed.

Introduction

LETRATURE REPRENCES on interesterification (1-6) gen-Lerally divide it into three classes of reactions: acidolysis, alcoholysis, and ester interchange.

Acidolysis involves the reaction of a fatty ester with an acid, usually a fatty acid (Figure 1). This reaction can produce an equilibrium mixture of reactants and reaction products, or it can be driven to completion by physically removing one of the reaction products. For example, coconut oil and stearic acid can be reacted so as partially to supplant the short-chain acids of the coconut oil with the higher melting stearic acid. The reaction can be carried out under temperature and vacuum conditions such that the C₁₄ acids volatilize as fast as they are freed from the triglyceride and are thereby removed from the reaction zone. Although a number of patents (7,8,9) have been issued which cover various methods for modifying fats by acidolysis, none are important in the edible oil industry today.

Alcoholysis (Figure 2), the reaction of fat and an alcohol, has several commercial implications. A triglyceride can be reacted with methyl or ethyl alcohol to produce the corresponding methyl or ethyl ester and free glycerine in virtually stoichemetric yields. Again, this reaction can be driven to completion by removal of the more volatile reaction product (10).

The production of mono- and diglycerides from fat is actually an alcoholysis reaction, with glycerine as the alcohol. Sorbitol and sucrose esters are also made by alcoholysis as well as by direct esterification with fatty acids. A mutual solvent for fat and alcohol, like dimethylsulfoxide, is frequently required for such reactions.

Ester interchange (Figure 3), the final class of inter-

³ Presented at the AOUS Short Course, East Lansing, Aug. 29-Sopt. 1, 1966.









esterification reactions, will be the chief subject of this paper. It involves the exchange of acid radicals from one ester to another. In other words, the fatty acids in a fat are "mixed up" or rearranged. Thus the derivation of the more common and descriptive name for ester interchange, rearrangement. When it pertains to triglycerides, ester interchange or rearrangement can be of two types, random or directed. In random rearrangement the fatty acid radicals freely move from one position to another in a single glyceride or from one glyceride to another.

As the fatty acids rearrange, they reach an equilibrium which is based on the composition of the starting material and is predictable from the laws of probability. Thus, when a mixture of tristearin and triolein is randomized, (Figure 4) six different glycerides are formed, thereby



(2) Intermolecular Rearrangement

FIG. 3. Ester interchange reaction.

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FIG. 4. Rearrangement of tristcarin and triolein.

leading to a marked change in melting point from 150F to 120F when equal weights of the two glycerides are used. Directed ester interchange, or directed rearrangement, refers to the modification of randomized glycerides by upsetting the equilibrium mixture, usually by crystallization of one or more of the higher melting components (11). For instance, if the randomized mixture in Figure 4 were cooled down so that the residual tristearin would crystallize, the liquid phase would no longer be random. More tristearin would form as the liquid components searched for the most thermodynamically stable composition. If tristearin continued to crystallize, the liquid phase would con-tinue to rerandomize. Theoretically all of the stearic acid would eventually be solidified as tristearin so that the composition would again be 50% tristearin, 50% triolein. As will be seen later, this process can be stopped at any intermediate stage by merely neutralizing the catalyst. Of course, if the tristearin were to be melted before the catalyst is neutralized, the mixture would revert to the random state.

Early Development of Interesterification

Interesterification reactions have been known for many years. In 1852 Duffy performed alcoholysis by using tristearin and ethanol (12). The ester interchange reaction was reported by Friedel and Crafts in 1865 (13). They recognized that heat alone would produce an equilibrium interchange between ethyl benzoate and anyl acetate. Distillation of ethyl acetate drove the reaction to completion. Glyceride rearrangement was reported by Van



FIG. 5. Solid-content index of cocoa butter and random rearranged cocoa butter.

TABLE I Cocoa Butter Triglycerides

	Natural	Randomized
Trisstarate (S_8) Disaturate (S_2U) Monosaturate (SU_2) Triumsaturate (U_3) Unidentified	2.2% 84.6 11.1 0.5 1.6	23.9% 43.8 26.8 5.5

Loon (14,15), Norman (16), and Grün (7) in the 1920's. At about the same time cach discovered that the melting point of various fats and fat mixtures could be changed by exposure to high temperatures and reduced pressures with or without the presence of various metals and metal salts. Actually the first fat rearrangement probably took place unknowingly when a small amount of soap was left in an oil which was being deolorized. Barsky patented the use of acidolysis to replace the lower molecular weight fatty acids in coconut oil with fatty acids from palm and cottonseed oils in 1939 (8).

The classical studies of Hilditch (17,18) on the fatty acid distribution in fats provided some understanding of the changes in physical properties associated with the ester interchange reaction. He observed that the saturated and unsaturated fatty acids were not randomly distributed in most naturally occurring glycerides. He also found that re-esterified or interesterified fat had a random distribution. This has since been confirmed by a number of other workers (19-22).

Random Distribution

The method of calculating the composition of glyceride types in a random distribution has been outlined by Feuge, Kraemer, and Bailey (23) and others (2,24). The calculation is simply a determination of the probable mole fraction of each of the constituent glycerides, based on the number and amount of particular fatty acids present.

If A, B, and C, are the molar percentages of fatty acids, a, b, and c, the molar percentage of a glyceride containing only one of the fatty acids will be the cube of the molar percentage of that fatty acid divided by 10,000.

$$-\% aaa = \Lambda^{s}/10,000$$
 (1)

The molar percentage of a glyceride containing two different fatty acids will be the square of the molar percentage of the fatty acid occurring twice times the molar percentage of the fatty acid occurring once times three, divided by 10,000.

$$\% aab = 3A^{2}B/10,000$$
(2)

The molar percentage of a glyceride containing three different fatty acids will be the product of the molar percentages of the three acids times six, divided by 10,000.

$$\%$$
 abc = 6ABC/10,000 (3)

The 3 is needed in Eqn. (2) because there can be 3 combinations of a, a, and b. Likewise there can be six combinations of a, b, and c.

Cocoa butter is a good example of a triglyceride with fatty acids distributed nonrandomly. Recent data (25), somewhat simplified in Table I, show that the saturated fatty acids of cocoa butter are found primarily in the oneand three-positions of disaturated-monounsaturated triglycerides. Very little trisaturate and monosaturate-diunsaturate are present. If the fatty acids were randomly distributed, the composition would approximate the second column of Table I. The marked changes in the physical characteristics made by randomizing are demonstrated by the differences

Composition of Lard				
	Natural	Randomized	Directed	
Sa	2%	5%	14%	
820	26	25	15	
803	24	44	32	

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FIG. 6. Solid-content index of natural lard, random rearranged lard, and directed rearranged lard.

in solid fat content of natural and random cocea butter (Figure 5). This graph, like others in this paper, relates solid fat content to temperature according to the method of Fulton, Lutton, and Wille (26). With a much lower disaturate content, randomized cocea butter has a much flatter SCI curve and a lower solids level at low temperatures. The higher trisaturate content is responsible for the increase in complete melting-point, from 94 to 126F.

Commercial Applications

Lard Shortenings. Rearrangement can be applied to a single fat or to a mixture of fats. The primary example of commercial application to a single fat is its use in modifying the physical characteristics of lard (27). This fat has an nunsual distribution of fatty acids (28), such that essentially all of the 27% palmitic acid in lard is found in the middle or 2-position. The 10% stearic acid



F16. 7. Consistency of plastic shortonings made from natural lard, random rearranged lard, and directed rearranged lard.

is all found in the end or 1/3-position. Unsaturated fatty acids fill up the remainder of the glyceride structures. One specific component, UPSt (U = unsaturated, P = palmitie, St = stearie), predominates the normally solid portion of lard. The 26% disaturates shown in Table II are all UPSt. This particular glyceride is responsible for the grainy, translucent appearance and stringy texture of natural lard (29). By randomizing lard, the UPSt content is reduced from 26% to 3.4% even though the total disaturate glyceride content is still 25%. The trisaturate content is increased from about 2.2% to 5%. All other possible combinations of unsaturated, palmitic, and stearic acid are created according to the laws of chance.

Randomization of lard manifests itself in radical changes in physical properties as well as composition. The intersolubility of the mixed disaturated glyceridos in random lard markedly changes its solids content (Figure 6). At 70F the solid fat content, as measured by solid content index, is almost cut in half. At 92F, where substantially all disaturates are liquid, randomized lard is higher in solids than natural lard. This is caused by the higher level of trisaturates in the randomized product.

Randomized lard is superior to natural lard as a shortening component (30). When 8-10% completely hydrogenated cottonseed hard flakes are added, it becomes a satisfactory shortening with a moderately good plastic range (Figure 7) and a good appearance. It can be partially hydrogenated (3-5 Iodine Value units) to improve oxidative stability without becoming too firm. Resistance to heat damage is also increased.

Directed rearrangement has also found application in the production of lard shortening (29). When lard is randomized, it has the composition shown on the vertical axis of Figure 8. By crystallizing trisaturates out of the random liquid phase, the composition begins to change according to the lines of the graph. Mono and disaturates decrease while trisaturates and triunsaturates increase. The process is normally stopped when about 14% trisaturates are formed. As a result, a shortening with a lower content of intermediate melting glycerides is finally obtained. This is graphically demonstrated by the flatter slope of the solids content index curve for directed lard in Figure 6. The lard is softer at low temperatures and firmer at high temperatures than either natural or random lard.



FIG. 8. Calculated change in lard glycoride composition with directed rearrangement.

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FIG. 9. Usage of lard in plastic shortenings in the United States.

Since directed lard has trisaturates formed in situ, there is no need to add hard flakes to make a shortening. Directed lard can be hydrogenated about twice as much as random lard for a given shortening consistency at 70F. Figure 7 shows that the consistency of a directed lard shortening is ideal over a wider temperature range than either natural or random lard. It is both softer at low temperatures and firmer at high temperatures.

Random and directed rearrangement have played a large role in the increased use of lard as a shortening ingredient during the last 10-15 years (Figure 9). Lard usage has stabilized at 400-500 million pounds per year although it was less than 100 million prior to the advent or rearrangement. Many of the household and bulk shortening brands marketed in the United States today contain rearranged lard as a primary ingredient (31).

Hard Butters. Random rearrangement of a single fat has another important commercial application, the production of hard butters or cocca butter substitutes, from palm kernel oil. This oil is made up of a wide range of fatty acids from C_n to C_{is} . Most of the C_{is} fatty acids are unsaturated. Figure 10 shows that palm kernel oil has a melting point of about 86F, too low to be used in candy coatings, coffee whiteners, and whipped toppings. When hydrogenated to increase its solids content at ambient temperatures, it contains a sizable fraction which does not



F16. 10. Solid-content index of palm kernel oil, hydrogenated palm kernel oil, and random rearranged, hydrogenated palm kernel oil.



F16. 11. Calculated composition in weight % of acctin fat with variable triacetin input (triacetin-free basis).

melt at body temperature. As a result, it has a waxy eating quality.

By randomizing palm kernel oil, its high melting fraction disappears without materially reducing its solids content at room temperature. By blending randomized and unrandomized hydrogenated palm kernel oil, any desired melting-point in between may be obtained. Many millions of pounds of palm kernel oil are processed in this manner each year in the United States.

Multifat Systems. Random and directed rearrangement can also be applied to a mixture of oils. Numerous patents (32-43) have been issued on edible fat products made by rearrangement of specific combinations of fats. Tallow can be made a more suitable component for shortening by rearranging it with 10-35% soft vegetable oil. Margarine oils and bard butters can be made by rearranging a lauric type of oil, like cocount oil, with hydrogenated domestic vegetable oils. Hydrogenated cocount oil can be used as an extender of palm kernel oil by corandomizing.

Acetin Fais. One specialty type of fat made by random rearrangement deserves mentioning. By substituting acetic acid for one or two of the long-chain fatty acids in a fat, large changes in melting point are achieved. This is done most conveniently by reacting a fat like lard or partially hydrogenated soybean oil with triacetin. Since fats and triacetin are not mutually soluble, the reaction must take place at the fat-triacetin interface, at least until the reaction has proceeded part way. In this respect, acetin fatproduction is similar to glycerolysis for production of monoglycerides. The reaction products include monoacetin and diacetin components at levels which depend on the proportion of starting materials. The distribution is a function of triacetin input (Figure L1). These are typical random-distribution curves, plotted on a weight basis for



FIG. 12. Solid-content index of hydrogenated vegetable basestock and acetin fat made from same basestock (acetic acid content 10%).

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TABLE 111

Interesterification Catalysts				
Type	Example	Required Level		
High Temperature (250)—500F)			
Metal salt Alkali metal hydroxide Alkali metal hydroxide	Zince chloride Sodium hydroxide Sodium hydroxide	$\begin{array}{cccc} 0.1-& 0.2\% \\ 0.5-& 1.0 \end{array}$		
Scap	Glycerine Sodium stearate	0.02~0.08		
	Olyceride	0.5 - 1.0		
Low Temperature (45-	-875F)			
Metal alcoholate Alkali metal	Sodium methylate Sodium Sodium/notassium alloy	$\begin{array}{cccc} 0.5-&1.0\\ 0.2-&0.5\\ 0.2-&0.5\end{array}$		
Alkali metal hydride Alkali metal amide	Sodium hydride Sodium amide	0.2 - 2.0 0.15 - 2.0		

triacetin-free material. Residual triacetins are normally removed by distillation. It is obvious that the relative contents of diacetins, monoacetins, and normal triglycerides may be readily varied by the triacetin input. Naturally the properties of the acetin fats become more or less fat-like as the acetie acid content is varied.

The solid-content index of a hydrogenated vegetable shortening base-stock and an acetin fat made from the same base-stock are shown in Figure 12. The acetin fat was made from a 17%, by weight, triacetin input and has an acetic acid content of 10%. Its glyceride composition is 26% diacetins, 48% monoacetins, and 26% normal triglycerides. The large difference in melting point is indicated by the temperatures at which the solid-content index is zero. When made into a shortening, the acetin fat will have a much flatter consistency/temperature curve than will the all-vegetable base-stock.

By varying the degree of hydrogenation and solids content of the vegetable component and the acetic acid content, a wide range of physical properties can be achieved. At a given level of oxidative stability an acetin fat has a much lower melting-point than its normal triglyceride equivalent. Likewise, at a given melting point, it has a much better oxidative stability. Acetin fats can be used in shortening, margarine, and salad oil formulations (44-50). However present commercial interest in acetin fats is largely in the coating area. This results primarily from the waxy translucent but flexible films which can be made from mixtures by molecular distillation. Direct acetylation of mono- and diglycerides with acetic anhydride will also yield acetin fats (51). Other short-chain acids can be substituted for acetic.

Rearrangement Catalysts

As has been mentioned earlier, rearrangement of triglycerides can occur without the aid of a catalyst. Very high temperatures, in the order of 450 500F, are required. Even then, the reaction proceeds to equilibrium very slowly; up to 24 hours are required (16). Under such conditions



FIG. 13. Phase diagram for sodium-potassium.



FIG. 14. Rearrangement catalyst neutralization reaction.

the glycerides will undergo some decomposition, and there will be development of free fatty acids.

It is generally more convenient to use a catalyst to speed the reaction and reduce the temperature require-ments. Many have been proposed (Table III). Rearrangement catalysts can be conveniently divided into two classes, those which will work only at high temperature and those which will work at both low and high temperature. The difference between the two types is a function of their ability to react with water. Under normal circumstances a triglyceride must be bone-dry before rearrangement will occur. This is true even though water itself has been shown to catalyze rearrangement under certain conditions (52). Metal alcoholates or alkaline metals and other lowtemperature catalysts will react with any water present in the system to provide the needed dry conditions. On the other hand, high-temperature catalysts require an outside energy source like temperature and/or high vacuum to remove the moisture from the system,

A number of high-temperature rearrangement catalysts have been patented. Among them are many metal salts such as the chlorides, carbonates, oxides, nitrates, and acctates of zine, lead, iron, tin, and cobalt (53). Alkali metal hydroxides, such as sodium, potassium, and lithium hydroxides (54), are probably the most commonly used high-temperature catalysts. These, along with soap, appear to work more effectively if used in conjunction with small amounts of glycerine or monoglyceride (1,2,32,55).

The alkali metal alcoholate, sodium methylate, is perhaps the most widely used, low-temperature rearrangement catalyst today (53,56). Along with the other lowtemperature catalysts it has the advantage of not requiring a closed system under high vacuum. It will rearrange triglyceride in an open tank. Sodium methylate also has advantages over the alkali metals (57,58) in that it can be easily dispersed in a fat. Sodium and potassium must first be finely dispersed in a solvent, such as toluene or xylene, before they can be safely incorporated into fat. Otherwise a violent reaction with residual moisture will take place on the catalyst surface, followed by splitting of

(Continued on page 454Λ)



FIG. 15. Effect of neutralizing reagent and time on refining loss of rearranged fat.

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FIG. 16. Batch random rearrangement vessel.

surrounding fat molecules to form a coating of soap. The heat generated by these reactions is sufficient to decompose and even char the glycerides in localized areas.

A sodium-potassium alloy has been used in the rearrangement process without requiring a dispersing solvent (59). As shown in the phase diagram for sodium and potassium in Figure 13, an alloy of these metals is liquid at temperatures as low as 10F. By selecting an appropriate composition, the alloy, commonly called NaK, can be dispersed directly in triglyceride by the use of a high shear agitator. It has been found that NaK particles less than 50 microns in diameter are most efficient. The alloy is more active than either of the metals by themselves. Apparently this results from the ability of liquid NaK particles to maintain unreacted metal on their surfaces while solid sodium or potassium particles become coated with oxides and hydroxides (29). Alkali metal hydrides and amides (60,61) also are reported to be effective at low temperatures. However neither has advantages which would make it economically attractive to use commercially.

It should be stated that it is doubtful that any of the above-mentioned materials is really the rearrangement catalyst. More probably intermediates like sodium glyeerate are formed in the fat and are the active catalysts,

Rearrangement catalysts must be removed from edible triglycerides at the end of the process. Several patents (62-64) have been issued on techniques for doing this while minimizing fat loss. Most catalysts can be removed by merely washing the fat with water to separate a salt or soap-rich aqueous phase. Or they can be reacted with phosphoric acid to be removed by filtration as a solid phosphate salt. Either technique results in a considerable loss of fat. Water added to a metal alcoholate like sodium methylate will yield sodium hydroxide and methyl alcohol. These, in turn, will react with neutral fat to produce soap and methyl ester. The soap is then removed by conventional



FIG. 17. Flow chart for continuous random rearrangement of lard, using sodium hydroxide catalyst.



FIG. 18. Lard random rearrangement reaction rate curves with variable catalyst usage.

refining techniques while the methyl ester will be stripped out in subsequent deodorization. Phosphoric acid neutralization will produce free fatty acids, which will also be lost in deodorization.

A technique has been developed which will minimize the loss of fat in the catalyst neutralization operation (29,65). By adding proper quantities of CO₂ along with the water (Figure 14), the system is buffered with sodium carbonate at a lower pH which will not split neutral fat. Figure 15 shows that the resulting refining loss is significantly reduced with this procedure. This is true especially if there is a time lag between catalyst neutralization and centrifugal separation of the fat and water phases.

Random Rearrangement Process

Random rearrangement can be accomplished either with a batch or a continuous process. For the batch process (Figure 16) a deodorizer can be used conveniently for high-temperature rearrangement. It will already have the sparging and vacuum equipment which are essential to the process. A mechanical agitator is optional.

Fat is heated to the desired reaction-temperature while being thoroughly dried under vacuum. In one patented process (55) a 50% solution of sodium hydroxide is then flashed into the hot fat. Another process (32) uses a slurry of sodium hydroxide in glycerine. There must be an excess of hydroxide above that needed to neutralize the free fatty acid in either process. One recent patent (64)



FIG. 19. Lard random rearrangement reaction rate curves with variable temperature.

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FIG. 20. Flow chart for continuous random rearrangement of lard, using sodium methylate catalyst.

demonstrates this quite clearly. If the free fatty acid in a fat is preneutralized, as little as 0.02% sodium hydroxide is all that is required for rearrangement.

Batch random rearrangement of triglycerides with lowtemperature catalysts does not normally require a closed vessel and a vacuum system. If enough sodium methylate or sodium is used, the free fatty acids will be neutralized and the moisture reacted so as to present the alkaline, bone-dry conditions necessary to accomplish rearrangement. Of course, the more catalyst used to offset free fatty acids and moisture, the higher will be the refining loss. Catalyst neutralization is normally carried on in the same vessel as the rearrangement reaction.

Figure 17 is a simplified flow chart of a continuous randomizing process, using sodium hydroxide as a catalyst. Crude lard has been selected as a representative triglyceride feed. Heated lard and sodium hydroxide are metered into the first of two vacuum driers. The mixture is sent through a short hold-coil which serves as a reactor and is then cooled to about 140F. The catalyst is neutralized with water or water and CO_s . The lard is then ready for refining and subsequent processing.

The rate of rearrangement for lard can be plotted as a function of the 70F solids content of the triglyceride. At this temperature, natural lard has an SCI of about 20; random lard has an SCI of about 10. Figure 18 is a plot of solids content against reaction time, with variable sodium hydroxide usage. With the particular crude lard used, 0.175% NaOII was the minimum required to reach equilibrium at 320F. This graph also demonstrates that, when reaction conditions are right, rearrangement occurs very quickly. When they are not right, the fat just will not rearrange no matter how long the reaction time is.

The effect of temperature on lard rate of rearrangement is shown in Figure 19. The lack of random equilibrium below 320F defines the minimum reaction temperature at this catalyst usage. At higher catalyst levels, or perhaps with better drying conditions, lower temperatures would be possible.

Figure 20 presents a flow chart for random rearrangement of lard by using a sodium methylate catalyst. It is similar to the previous sodium hydroxide process in many respects. However the lard is dried and cooled before the addition of the sodium methylate. Catalyst is normally added as a concentrated slurry in dry oil. Reaction temperatures as low as 120F are quite satisfactory with this system.

Directed Rearrangement Process

In directed rearrangement (66,67) only catalysts which are active at low temperatures are usable. Even so, the rate of random rearrangement is important since the trisaturated glycerides can precipitate only as fast as they are formed in the liquid phase. The greater activity of NaK makes it more suitable than either sodium or sodium methylate for this process.

Figure 21 is a flow chart of a patented process (68) for continuous directed rearrangement of lard. Vacuum

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F16. 21. Flow chart for directed rearrangement of lard.

drying is similar to that used in random rearrangement of lard. NaK is metered into the lard stream by means of a specially designed, variable-speed, positive-displacement pump. A high shear mixer is used to provide proper NaK particle size. At 120F the lard will be randomized in less than six minutes with as little as 0.2% NaK. Actually it is not necessary to reach random equilibrium before the directing process begins.

Lard-catalyst slurry is chilled to about 70F in a conventional shortening scraped wall freezer, cooled by direct expansion annonia. At this point many trisaturate crystal nuclei form. These nuclei are allowed to grow for about five minutes in a small crystallizer of a design similar to a shortening picker or work box. While crystallizing, the lard warms up to about 82F, as indicated in Figure 22. Another freezer recools the lard to 70F to renew the crystallization driving force. These things are happening simultaneously: any trisaturated glycerides are melting; and rearrangement of the liquid phase is forming trisaturates in an attempt to restore the equilibrium distribution.

Further precipitation, after the second cooling step, continues at a slower rate. Therefore relatively large crystallizers with carefully controlled agitation and about 1/2 hours of hold-time arc used to reach the endpoint. It has been found convenient to use four crystallizers in series to reduce end-for-end mixing and to provide simple endpoint control.

When directed rearrangement has reached the desired point, that is, when total trisaturate content is about 14%, the catalyst is neutralized. It is important to accomplish this neutralization before the trisaturates are remelted to prevent reaction backup. Thus water and CO_z are metered into the lard in a mixer before heating. The melted lard is pumped through a degasifier to release free hydrogen



FIG. 22. Temperature profile of lard directed rearrangement process.

prior to centrifuge separation of the foots. The directed rearranged lard is now ready for other processing such as hydrogenation or deodorization.

A variation on the directed rearrangement process which has been patented (69) would crystallize the disaturate glycerides in a fat before adding the rearrangement catalyst. Then as the liquid phase begins to randomize, more disaturates are formed. If the crystallization driving force is maintained, these disaturates will crystallize before they are converted to trisaturates. Thus a fat suitable for use in margarine with a melting point near body tem-perature can be obtained. Similarly, directed rearrangement can be carried out in the presence of a free alcohol. such as glycerine, in the reaction mixture (70). As the higher melting-point monoglycerides form, they will crystallize out of the liquid phase just as trisaturates do in the lard process.

REFERENCES

I. Eckey, E. W., "Vegetable Fats and Oils," Reinhold Publishing Corporation, New York, 1954, pp. 142-149.
2. Swern, Daniel, "Bailey's Industrial Oil and Fat Products," 3rd ed., Interscience Publishers Inc., Division of John Wiley and Sons, Inc., New York, 1964, pp. 946-972.
3. Markley, K. M., "Fatty Acids," Interscience Publishers Inc., Division of John Wiley and Sons Inc., 2nd ed., Part 2, New York, 1961, pp. 757-984.
4. Cowan, J. C. JACOE 27, 492-499 (1950).
5. Braun, W. Q., JACCE 37, 593-601 (1966).
6. Fouge, R. O., JACCE 38, 521-527 (1962).
7. Grön, A., U.S. Pat, JS06,560 (1924).
8. Barsky, G., Wecedine Products Inc. JUS, Pat, 2,182,832 (1989).
9. Eckey, E. W. (Procter and Gamble Company) U.S. Pat, 2,578,006 (1946).

- 9. Ackey, E. W. (Procter and Gamble Company) U.S. Pat. 2,378,006
 (1946).
 10. Wright, H. J., J. B. Segur, H. V. Clark, S. K. Cohara, E. E. Langdon and R. N. DuPbis, 611 and Scap 21, 145-148 (1944).
 11. Eckey, E. W. I & E.C. 40, 1183-00 (1948).
 12. Duffy, P. J. Chem, Soc. 5, 908-316 (1852).
 13. Friedel, O. and J. R. Craffs, Ann. 733, 207-211 (1865).
 14. Yon Loon, C., U.S. Pat. 1, 744-596 (1929).
 15. Frana Oelwerke Germania G.M.B.H. and W. Normann, German Pat. 417,215 (1920).
 17. Hildlich, T. P., "The Chemical Constitution of Natural Fats," 2nd ed., 9, 15, John Wiley and Sons Inc., New York (1049).
 14. Binstacharya, R., and T. P. Hildlich, Proc. Roy. Soc. (London) 4129, 468-476 (1930).
 19. Norris, F. A., and K. F. Mattil, Oil and Song 23, 289-291 (1936).
- 1943), (1943), 20. Desnuelle, P., and M. Nnudet, Bull. Soc. Chim. 13, 90-94

- (1953).
 (1940).
 (1943).
 (1943).
 (1943).
 (1943).
 (1943).
 (1943).
 (1944).
 (1944).
 (1944).
 (1944).
 (1944).
 (1944).
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New Literature

Applied Science Laboratories, Inc., have made available Catalogue No. 11, a 51-page indexed listing of their products for gas chromatography, thin-layer chromatography, lipids and calibration standards. They have also listed their custom syntheses and analytical services which now include lipid and nonlipid chemicals. (P.O. Box 440, State College, Pa. 16801.)

The 34-page "ASTM List of Publications" is now available upon request. It lists over 500 ASTM publications dealing with the knowledge of materials, materials evaluation, and the standardization of methods of test and specifications for materials. (Dept. HH, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103

The SOAP AND DETERGENT ASSOCIATION issues regularly its Periodical and Literature Digest, for Soap and Detergent Executives. Topics covered are Household and Genral, Industrial and Institutional, Research and Technical, Raw Materials and Processing, Glycerine, and General Business Management. This summary of current literature is sent as a service to Association members, and is available to nonmembers at \$12 per year. (Soap and Detergent Association, 485 Madison Ave., New York, N.Y. 10022.)

(Continued on page 466A)

Vander Wal, R. J., and L. A. Van Akkeren (Armour and Company) U.S. Pat. 2.571,375 (1957).
 St. U.S. Dept. of Commerce. Fats and Oils Situation, March (1966).
 Gooding, C. M. (Best Product Inc). U.S. Pat. 2,309,940 (1948).
 Barsky, G., and G. Zinzalian (E. F. Drew Company) U.S. Fat. 2,667,418 (1954).
 Hidd, U.S. Pat. 2,685,562 (1954).
 Bohrnan, W. M., and B. F. McGee (Glidden Company) U.S. Pat. 2,766,163 (1955).
 Steffen, A. H. (Swift and Company) U.S. Pat. 2,855,311 (1958).
 Cochran, W. M., M. L. Ott and C. W. Lantz (Glidden Company) J.S. Cochran, W. M., M. L. Ott and C. W. Lantz (Glidden Company) U.S. Pat. 2,852,311 (1958).
 Roylance, A. (Lever Brothers Company) U.S. Pat. 2,928,745 (1969).

30. Royance, A. (Levil 2000)
(1960).
40. Weiss, T. J. (Swift and Company) U.S. Pat. 2,936,238 (1960).
41. Lindsay, D. S. (Proctor and Gamble Company) U.S. Pat.

40. wors, 1, 5, (Proster and Gamole tompose), 2,996,388 (1961), 42. Babayan, V. K. (E. F. Drew Company) U.S. Pat. 3,006,771

42. Bahayan, V. K. (E. F. Drew Company, One. 1997) (1961).
43. Dutton, H. J., and C. R. Scholfeld (U.S. Dept. Agriculture)
U.S. Pat. 3,012,890 (1961).
44. Baur, F. J., AAOCS 37, 147-151 (1954).
45. Baur, F. J., and W. Lange (Protor and Gamble Company)
U.S. Pat. 2,614,927 (1952).
46. Jackson, F. (Proter and Gamble Company) U.S. Pat. 2,616,159 (1962).

- Baur, F. J. (Procter and Gamble Company) U.S. Pat. 2,615,160
- 47. (1952) Brokaw, G. Y. (Eastman Kodak Company) U.S. Pat. 2.808.421
- (1957)
- (1957).
 49. Thid., U.S. Pat. 2,879,281 (1959).
 50. Baur, F. J. (Protter and Gamble Company) U.S. Pat. 3,027,259 (1963).
 51. Feuge, R. O., E. J. Vicknair and K. S. Markley (U.S. Dept. of Agriculture) U.S. Pat. 2,745,749 (1956).
 52. Eckey, E. W. (Protter and Gamble Company) U.S. Pat. 2,378,005 (1945). 52. Rekey, E. W. (Proter and Gamble Company) U.S. Pst. 2,378,005 (1945).
 53. Mattil, K. W., and F. A. Norris (Swift and Company) U.S. Pst. 2,378,005 (1955).
 54. Dominick, W. E., and D. Nelson (Swift and Company) U.S. Pst. 2,625,485 (1953).
 55. Holman, G. W., T. B. Laycock, R. L. Wille (Proter and Gamble Company) U.S. Pst. 2,625,483 (1953).
 56. Mattil, K. W., and D. Nelson (Swift and Company) U.S. Pst. 2,625,483 (1953).
 57. Dominick, W. E., D. Nelson and K. F. Mattil (Swift and Company) U.S. Pst. 2,625,483 (1953).
 58. Yan Akkeron, L. A. (Swift and Company) U.S. 2,872,463 (1953).

- Company) U.S. Pat. 2,625,484 (1953).
 S.Y. Ma Akkeron, L. A. (Swift and Company) U.S. 2,872,463 (1955).
 S.Y. Ma Akkeron, L. A. (Swift and Company) U.S. 2,872,463 (1955).
 B. Hawley, H. K., and B. D. Dobson (Proeter and Gamble Company) U.S. Pat. 2,733,251 (1956).
 M. K. K., and K. F. Mattil (Swift and Company) U.S. Pats. 2,625,436-437 (1953).
 B. Eckey, E. W., U.S. Pat. 2,558,547 (1951).
 Betes, K. W., C. J. Davis Jr. and C. E. Morris (Armour and Company) U.S. Pat. 2,751,304 (1956).
 B. Bargers, J. C. W. Motl and P. Seiden (Proeter and Gamble Company) U.S. Pat. 2,856,578 (1959).
 Eckery, E. W. (Proeter and Gamble Company) U.S. Pats. 2,442,531-552 (1948).
 F. Stein, W., M. A. Mutsen and E. Sussner (Henkel and Cie. G.M.B.H.) U.S. Pat. 3,232,971 (1966).
 Ablott, A. D. (Proeter and Gamble Company) U.S. Pats. 2,452,676 (1959).
 Ablott, A. D. (Proeter and Gamble Company) U.S. Pat. 2,442,538 (1948).
 To. Eckey, E. W. (Proeter and Gamble Company) U.S. Pat. 3,250,660-607 (1956).

- 70. Eckey, E. W. (Procter and Gamble Company) U.S. Pat. 2.442,534 (1948).

New Gelman Instrument Courses

Gelman Instrument Company is sponsoring a new series of courses in October in Chicago, Los Angeles, and San Francisco.

The first, slated for October 13-14 in Chicago, provides one day of instruction in Basic Electrophoresis, and one day in Immunoelectrophoresis and Immunodiffusion. R. O. Briere, Johnston-Willis Hospital, Richmond, Va., teaches electrophoresis, and Curtis Williams, Rockefeller Foundation, New York, teaches immuno techniques. Tuition for the two-day session is \$65.

At a one-day session in Los Augeles on October 16, registrants will study under Dr. Williams, or practice TLC techniques under James Hamilton, Tulane University School of Medicine, New Orleans. Tuition for either class is \$35.

Dr. Williams and Dr. Hamilton will each instruct on October 18 in San Francisco. Tuition for the course on immuno techniques or for TLC is \$35.

Advance registration is mandatory and should be made through the Information Department, Gelman Instrument Company, P. O. Box 1448, Ann Arbor, Michigan 48106.