

1129

# TECHNOLOGY OF EDIBLE ANIMAL FATS

*W. C. Ault*

*Eastern Regional Research Laboratory, U.S. Department of  
Agriculture, Philadelphia*

## CONTENTS

I. INTRODUCTION . . . . .	264
A. Animal fat definitions . . . . .	264
B. Pre-rendering care . . . . .	265
II. RENDERING . . . . .	265
A. Dry rendering . . . . .	265
B. Wet rendering . . . . .	267
III. USE OF ANTIOXIDANTS . . . . .	269
A. Natural antioxidants . . . . .	269
B. Synthetic antioxidants . . . . .	271
C. Antioxidant synergists . . . . .	272
D. Governmental Regulations (U.S.A.) . . . . .	272
IV. DEODORIZATION . . . . .	273
A. General . . . . .	273
B. Laboratory studies . . . . .	275
C. Commercial development . . . . .	276
V. GLYCERIDE REARRANGEMENT . . . . .	277
A. Historical . . . . .	277
B. Present processes . . . . .	280
VI. SUMMARY AND CONCLUSIONS . . . . .	281
REFERENCES . . . . .	282

# TECHNOLOGY OF EDIBLE ANIMAL FATS

*W. C. Ault*

## I. INTRODUCTION

THE edible animal fats, aside from butter, are by-products of the meat packing industry. They may also be referred to as meat fats. Lard and 'rendered pork fat' are obtained from hog-slaughtering operations while edible tallow and certain derived products such as oleo oil are obtained from the carcasses of cattle and sheep.

Lard is by far the most important of these fats in an economic sense in the United States, production usually being in the range of  $2\frac{1}{2}$ -3 billion pounds per year. Production of each of the other edible animal fats seldom exceeds a few million pounds per year. Production of rendered pork fat has remained so small that for statistical purposes it is usually included with lard. From the legal standpoint, however, they have been separate entities since 1940. Since that time regulations of the U.S. Department of Agriculture have defined lard and rendered pork fat which is produced in federally inspected establishments.

### *A. Animal fat definitions*

*Lard.* The fat rendered from fresh, clean, sound fatty tissues from hogs in good health at the time of slaughter, with or without lard stearine or hardened lard. The tissues do not include bones, detached skin, head fat, ears, tails, organs, windpipes, large blood vessels, scrap fat, skimmings, settlings, pressings, and the like, and are reasonably free from muscle tissue and blood.

On 9 February 1945, a modifying and interpretive memorandum was issued providing that fresh, clean, sound fat obtained in the fleshing of fresh pork skins may be used in the rendering of lard. It was further provided that fresh ham skins, fresh pork shoulder picnic skins and the like may be used in the rendering of lard when, taken as a lot, they have at least 65 per cent trimmable fat.

*Rendered pork fat.* The fat other than lard, rendered from clean sound carcasses, parts of carcasses, or edible organs from hogs in good health at the time of slaughter, except that stomachs, tails, bones from the head and bones from cured or cooked pork are not included. The tissues rendered are usually fresh, but may be cured, cooked, or otherwise prepared and may contain some meat food products. Rendered pork fat may be hardened by the use of lard stearine and/or hardened lard and/or rendered pork fat stearine and/or hardened rendered pork fat.

## Rendering

The production of rendered pork fat usually does not comprise more than a few per cent of the total amount of hog fat rendered in federally inspected establishments. In fact, rendered pork fat seldom if ever appears as such on the retail market, being almost entirely used in the manufacture of shortenings or other trade-named items. It should be noted that rendered pork fat is not necessarily inferior to lard. Because the use of fats trimmed from cured cuts is permitted, it will frequently be a little darker in colour and higher in free fatty acids than lard; on the other hand its stability may frequently be higher than that of lard.

### *B. Pre-rendering care*

The production of animal fats having the highest possible quality begins even before the rendering process. Studies reported by VIBRANS (1949) of the American Meat Institute Foundation Laboratories have shown that enzymatic changes taking place in the tissues give rise to development of free acidity in the fat. This hydrolytic change is reduced at low temperatures and hence if tissues are to be kept for a prolonged period before rendering, refrigeration is desirable. Approximately 0.2 per cent free fatty acids developed in leaf fat held at 72-74°F in 24 h while only about 0.05 per cent developed over the same period when the fat was held at 40°F. Killing fats, particularly visceral fats, contain more hydrolytic enzyme than leaf fats and hence their refrigeration before rendering is even more important if free fatty acid development is to be minimized.

## II. RENDERING

The term rendering is most frequently applied to treatments designed to remove all or most of the fat from fatty animal tissues by processes which are basically thermal in character. The exact procedure to be followed will be indicated by the nature of the fatty stock, to some extent by the characteristics desired in the rendered fat, and, of course, primarily by the rendering equipment available.

Rendering processes may be classified in a number of different ways. For example, if water or steam is added in substantial amounts prior to or during the rendering, the process is referred to as being a wet process; otherwise, any process may be referred to as being of the dry type.

Rendering processes may be further differentiated upon the basis of the temperature attained during the operation. A further classification of rendering processes may be made upon the basis of the use of additional agents other than heat. Such agents include mechanical action and caustic or enzyme digestion of the proteinaceous tissue. Still another type of operation involves the use of an agent known to have adsorptive qualities in what otherwise would seem to be conventional rendering operations.

### *A. Dry rendering*

Open-kettle rendering was undoubtedly the first type of rendering to be used in packing houses. It represented merely a modification of the rendering methods used on the farm before the development of the meat packing industry.

Gradually the equipment was improved and at present steam-jacketed kettles equipped with stirring devices are commonly used. As customarily practised, open-kettle rendering is a dry-rendering process. Relatively high temperatures of the order of 230–240°F are usually attained. In plants having other types of rendering equipment available, open-kettle rendered fats may be produced from those tissues that are most easily rendered such as the leaf fats. In many small plants, including almost all locker plants doing custom butchering, however, all fresh fats are hashed and rendered in an open kettle. In general, however, the total commercial production of conventional open-kettle rendered fat is relatively small when compared with the total production of edible animal fats in the United States.

Dry rendering may be carried out in equipment other than the simple open kettle. In fact, the open-kettle method is so slow and inefficient that it is not often used for large-scale rendering. The large-scale dry rendering of fats is now usually conducted in closed tanks which during at least a portion of the rendering period may be maintained under reduced pressure. Vacuum-rendering equipment for vacuum dry rendering is frequently referred to as a dry melter. It usually consists of a horizontal steam-jacketed cooking tank equipped with charging door, vent line, vacuum line, discharging door, sampling device and a stirring arm. MERKEL (1936) has described a typical batch dry melting unit. Continuous dry melting systems have also been devised.

Efforts to improve the dry-rendering process continue. A recent United States patent describes a process (HORMEL, 1949) involving the fine hashing of a fat which is subsequently heated and discharged into a vacuum chamber where moisture is removed. Still another attempt to devise a process capable of yielding a high-quality lard is described by PAVIA (1950). This might aptly be described as a low-temperature kettle-rendering process.

SWIFT and HANKINS (1952) have described the results which they obtained during their investigation of the low-temperature open-kettle rendering of lard. In their experiments, leaf fat and skin-free cutting fats were used. A grinder capable of being adjusted to give a hashed fat of different degrees of fineness was used. The rendering was accomplished in a stainless kettle of 20 gal. capacity equipped with a steam jacket around the bottom and lower half of the vessel. Efficient mechanical agitation at 1,725 r.p.m. was provided.

Yields of rendered fat tended to be below desirable commercial levels in their experiments. Under optimum conditions, however, yields averaged 96.0–98.0 per cent, based on the fat content of the tissues, with cutting and leaf fats. They found that the degree of subdivision attained during grinding the fatty tissues markedly affected yield, the best yields resulting from the finest grinds. Highest yields were obtained when rendering tissues which had been cooled to 0°F and ground through a 0.125 in. plate. On the other hand these investigators did not find variations in the rate of heating during rendering nor the temperature of rendering, over the ranges studied, to be critical. The lard rendered at low temperatures had a good colour and a relatively mild odour and flavour. The stability of the resulting lard was acceptable but not

outstanding, averaging about 6 h as measured by the so-called Swift test (KING *et al.*, 1933). The moisture content of the lard rendered by these investigators tended to be high but they found that the production of lard having an acceptably low moisture content was possible provided a prolonged period of contact between the lard and the proteinaceous residue was maintained.

Reference to the patent literature indicates that a type of processing which involves the combined use of heat and a solvent has been investigated during the past few years. Thus LEADERS (1950) has described the rendering of fats by a process involving treatment of the tissue at a temperature of 160–190°F for about 5 h in the presence of a hydrocarbon such as propane. Sufficient pressure is maintained to keep the solvent in the liquid state. WORSHAM and LEVIN (1950) have described a process involving the use of a fat solvent such as a halogenated hydrocarbon for the simultaneous desiccation and defatting of wet organic tissue.

Other approaches to improvement of the rendered fats are based upon contacting the fat with an adsorptive material during the rendering process. LIBBY and HENDERSON (1948) have described a process in which the fatty tissue is rendered in conventional manner in the presence of silicic acid; any agent containing or capable of furnishing hydrated silica may also be used. The process seems to be directed chiefly towards use on inedible stock.

The so-called drip-rendering process combines the rendering operation with a carbon treatment into a single piece of equipment in a unique manner. The fat is charged into a rendering tank with a false bottom through which the lard drains away as soon as it separates from the tissues. In this way, time of contact between the hot fat and tissue is minimized. The melted fat may then be mixed with carbon in the lower part of the tank.

#### *B. Wet rendering*

Wet rendering is carried out by heating the fatty tissues in the presence of water. Low-temperature wet rendering has been used to produce a fat having a very mild flavour. Only the simplest apparatus is required usually consisting of an open tank equipped with a slow-speed agitator and suitable steam-heating provisions. Variable temperatures below 210°F are employed, and the blandest products are obtained by operating at the lowest possible temperature. Low-temperature wet rendering does not result in a satisfactory recovery of the fat, and the tissues are usually rendered again by a more effective process. This inefficiency combined with the shrinking outlet for animal fats in oleo-margarine has resulted in decreasing use of low-temperature wet rendering processes.

Most of the lard and tallow produced in the United States today, however, is steam rendered. Lard so produced is handled on the Board of Trade and is known as 'prime steam lard'. The relatively simple and inexpensive equipment required, its ease of operation and control, the almost complete recovery of fat obtained, and the adaptability to the widest possible variety of stocks combine to make steam rendering relatively attractive for operations of any

magnitude. On the other hand, the expense of evaporating large amounts of water to recover non-fatty residues, and hydrolysis of fats during steam rendering with consequent lowering of smoke point are important disadvantages of the process.

DEATHERAGE (1946, 1949) has described an interesting rendering process which involves the use of dilute caustic in producing lard and other animal fats. In this process the raw fat is ground through a  $\frac{1}{8}$  in. plate and mixed with up to half its weight of 1.75 per cent caustic soda solution. With high-quality fats somewhat less solution may be used, about 40 per cent being suggested for back fat and 25 per cent for leaf fat. The caustic solution may also contain 2-5 per cent of dissolved salt. After thorough mixing with caustic brine the whole is heated with atmospheric steam to 85-95°C for 45-60 min. The fat layer is then separated and washed first with brine and then water by centrifugation. A final acid wash as with 0.5 per cent phosphoric acid is stated to improve the flavour of the final product. Bones cannot be processed, but sweet pickle fat is reported to give a high-quality lard by the alkali process. The process also works quite well on beef tallow.

The lard from the caustic process was reported to have excellent characteristics including low free fatty acids (0.01 per cent); a smoke point of 450-480°F; good colour and mild odour. The product had satisfactory keeping quality, was stable to reversion and responded to the addition of antioxidants. It was also readily plasticized and easily deodorized. Deodorization of 400 lb of the resulting lard was accomplished by heating it to 400°F for 4 h during which it was blown with 14 lb of 420°F steam at 3-5 mm of mercury. The yields of lard from various tissues were generally satisfactory and comparable with those of other processes.

<i>Types of fat rendered</i>	<i>Range of yield per cent</i>
Ham	72-82
Back	79-90
Leaf	89-93

Several different procedures involving the use of proteolytic enzymes in the rendering of animal fats have been proposed during the past decade. Thus KEIL (1947) suggests the use of a proteolytic enzyme in fat which has had its pH adjusted to between 6.0 and 7.5. The resulting mixture is then heated to about 140°F. This inventor reports plant enzymes (papain or ficin) are superior to animal enzymes such as trypsin and pepsin.

HALMBACHER (1950) has claimed the use of an enzyme such as papain or ficin with a cysteine activator. This combination reportedly reduces digestion time and increases yield. A report (ANON. 1946) on the use of enzymes concluded that such use seems most promising for locker plant operators and other small meat-processing establishments using the open-kettle rendering process. In general, improved yields of fat were obtained in shorter rendering time, but definite overall economic advantages appeared to be lacking.

A continuous steam rendering process frequently referred to as the Titan Process has been developed in Denmark. A Canadian installation of the process has been described (ANON. 1949). In the Canadian plant, inspected fat is fed into a steam-jacketed grinder from which it passes into a pre-heater consisting of a horizontal cylinder with an internal rotating conveyor drum. At a temperature of about 176°F the fat then goes into an upright pressure boiler where it is subjected to live steam at a temperature in the range of 240–247°F. Under these conditions it rapidly changes into a mixture of water, cracklings, and melted fat. After a rapid release of the pressure, which causes further disintegration of the fat-bearing tissue, the mixture is discharged into a rotary screen. Here the solids are separated and moved into a mechanical screw press which extracts much of the residual fat. The fat-water mixture is further purified by contacting with fresh water and by centrifuging. The complete extraction process requires only 12–15 min from fat to finished lard, and the material is under heat process for only 3 min. The equipment may be used for rendering tallow as well as lard. High-quality fats are produced which are low in acid and moisture and almost neutral in flavour.

An attempt to eliminate entirely the undesirable effects of thermal action on fatty tissues has resulted in the CHAYEN or impulse method of rendering (CHAYEN and ASHWORTH, 1953). The process consists in the mechanical rupturing of the membranes of fat-containing cells by a series of high-speed impulses transmitted through the medium of liquid. The process seems to work quite well for the removal of fat from such material as bones which have a rather rigid structure. To date, however, attempts to adapt the process to the removal of fat from the softer fatty tissues do not seem to have met with commercial success in the United States.

### III. USE OF ANTIOXIDANTS

#### A. *Natural antioxidants*

Despite all efforts, improved rendering methods have not proved to be the panacea which would make the animal fats entirely competitive with the vegetable fats, on a quality basis. The properties which have remained open to improvement in animal fats are keeping quality or stability, odour, flavour, colour, smoke point and physical characteristics such as plastic range, consistency and creaming power. Although rendering conditions undoubtedly affect the quality factors noted above, except those that involve physical characteristics, the resulting products still have fallen far short of their competitive goals. For example, although careful rendering results in lard having good stability, i.e. 6–10 h A.O.M. value, even the best products do not adequately meet the need for shortenings which can be stored in the home at room temperature during use.

Stability is, in a sense, the key which opens the door to further improvements. Without good keeping quality, the application of other techniques have little value, because the best shortening is unfit for use if it is prone to rancidity.

Numerous investigators have contributed to the now well established opinion that animal fats contain little effective natural antioxidant. The literature on the subject has been reviewed by RIEMENSCHNEIDER (1955). HANSON *et al.* (1944) reported tocopherol to be the only antioxidant out of a considerable number included in test diets which was deposited in the adipose tissues of animals to any appreciable extent. Tocopherol seems to be the principal natural antioxidant in hog fats, being present to the extent of about 1-3 parts per 100,000 (CHIPAULT, LUNDBERG and BURR, 1945). In contrast the principal vegetable oils contain much higher percentages, reaching proportions of nearly 500 parts per 100,000 in wheat germ oil. The antioxygenic properties of pure tocopherols and tocopherol-rich concentrates have been extensively investigated (GOLUMBIC, 1943; BAILEY *et al.*, 1943; GRIEWAHN and DAUBERT, 1948; GYORGY and TOMARELLI, 1944; MITCHELL and BLACK, 1943; OLIVER, SINGLETON and BAILEY, 1944; RIEMENSCHNEIDER *et al.*, 1944a; SINGLETON and BAILEY, 1944; SWIFT, ROSE and JAMIESON, 1942).

Information regarding the occurrence of tocopherols and detailed knowledge of their protective antioxidant action in fats have contributed to the explanation of several observations formerly regarded as being anomalous. For example, it is now readily apparent that unless considerable care is exercised in rendering animal fats, the minute amount of tocopherol present may be destroyed, thereby reducing the stability of the fat to a very low order. In a similar manner the work has shown why addition of tocopherol or a phenolic antioxidant to animal fats is relatively much more effective in increasing stability than similar additions to vegetable fats.

Extensive efforts were directed towards the isolation and identification of antioxidants from natural edible sources on the logical assumption that the addition of such substances to foods prone to rancidity might be permitted. Patents claiming certain aspects of the use of tocopherols were issued (TAYLOR and JAKOBSEN, 1941; EASTMAN KODAK Co., 1939; BAXTER and JAKOBSEN, 1942; ANDREWS, 1941).

Since isolation or even concentration of tocopherols proved difficult and expensive, various proposals to utilize their antioxidant properties without such steps were made. Workers at the Eastern Regional Research Laboratory reported (RIEMENSCHNEIDER *et al.*, 1944) that addition of 1-10 per cent of certain tocopherol-containing vegetable oils or of corresponding vegetable oil shortenings to lard increased the stability from two-fold to five-fold. MAGOFFIN and BENTZ (1949) reported that potato chips fried in a mixture of equal parts of lard and vegetable shortening were nearly as stable as those fried in vegetable shortening alone. Other publications (LIPS and MCFARLANE, 1943; RIEMENSCHNEIDER and AULT, 1944; ANZALDI, 1948; THALER and SCHOTTMAYER, 1942), confirming these reports have appeared and patents have been issued describing mixed shortenings (ALDERKS, DISTEL and TAYLOR, 1935; GRETTE, 1936, 1940; GRETTE and NEWTON, 1934; MEHLENBACHER, 1938; NEWTON and RICHARDSON, 1932).

Vegetable lecithin, another component of vegetable oils, received early

consideration as an antioxidant. Its potential use was facilitated by a process for its isolation which was first proposed by BOLLMANN (1923). It is obtained chiefly as a by-product of the manufacture of soybean oil and corn oil as an extremely complex mixture containing lecithin, cephalin, phosphoinositides, sugars, sterols, glucosides, pigments and tocopherols. It is available in large quantities and at nominal cost.

Numerous investigations have been made of its antioxidant action in fats, even though the origins of this specific use seem vague. There appears to be some doubt, however, whether lecithin should be regarded as a primary antioxidant. Any slight primary antioxidant activity which it shows may be assigned to other antioxidants such as tocopherols present in small amounts.

Other fats and oils have been found to have components present which confer stability upon them. Probably the most notable example is the presence of sesamol in sesame oil. Naturally these oils as well as the antioxidant fractions contained in them have been investigated for use in the stabilization of lard.

Following early investigations which pointed to the chemical nature of natural antioxidants occurring in many vegetable oils, numerous attempts were made to find natural materials which would be rich in similar substances. In view of the work of MOUREU and DUFRAISSE (1922, 1923, 1926), particular attention was given to natural substances relatively rich in complex phenolic materials.

Work along these lines eventually proved fruitful; thus guaiac resin became the first substance of non-food origin permitted as a preservative for lard and rendered pork fats in the United States. This permission was granted on 26 December 1941. This resin, a secretion of a tropical evergreen tree, *Guaiacum officinales*, indigenous to the West Indies, was first proposed as an antioxidant for fats by NEWTON and GRETTE (1933). Gum guaiac contains complex phenolic constituents to which it presumably owes its antioxidant value.

Nordihydroguaiaretic acid (NDGA) is a phenolic compound which was isolated from a natural non-food source. It is obtained by extraction from the desert plant *Larrea divaricata*, one of a group of plants commonly known as creosote bush. It grows wild in desert areas of south-western United States. LUNDBERG *et al.* (1944) first described its antioxidant activity; its use as an antioxidant was patented by LAUER (1945) and the patent assigned to the Secretary of Agriculture.

Other naturally occurring materials which have been studied at various times include the tannins, gallic acid, conidendron and derivatives of the latter such as norconidendron and the  $\alpha$ - and  $\beta$ -conidendrols.

### *B. Synthetic antioxidants*

Knowledge of the chemical nature of the active constituents of these materials stimulated efforts toward the development of truly synthetic antioxidants. A large number of compounds were prepared and investigated particularly for use in lard. No complete review of this work is desirable here, but those which have found some acceptance are discussed briefly below.

Hydroquinone shows excellent antioxidant properties as evaluated in lard. Permission to use this compound in lard has been withdrawn, however, in the United States.

The use of propyl gallate as an antioxidant for fats was first proposed in 1941 by SABALITSCHKA and BOEHM. LEA (1944) showed that the methyl and ethyl gallates are also highly effective antioxidants. The higher alkyl gallates were first prepared by MORRIS and RIEMENSCHNEIDER (1946).

The first publication giving detailed information concerning the antioxygenic activity of butylated hydroxyanisole (BHA) in fats was that of KRAYBILL *et al.* (1949). The commercial product consists chiefly of two isomers, namely, 3-tertiary butyl-4-hydroxy anisole and 2-tertiary butyl-4-hydroxy anisole. Of these, the work of ROSENWALD and CHENICEK (1951) has shown that the 3-tertiary butyl isomer is the more effective as an antioxidant for lard.

Another compound of the 'hindered' phenolic type which has received considerable study is 2, 6-di-tertiary-butyl-4-methylphenol (2, 6-di-tertiary butyl paracresol). This compound is frequently referred to as butylated hydroxy toluene (BHT).

#### C. Antioxidant synergists

Early workers in the field of antioxidants for fats noted that some substances were quite effective for certain fats but much less effective with others. Gradually two distinct groups of 'antioxidants' came to be recognized, those which were quite effective in animal fats but much less so in vegetable fats and those which were relatively more effective in vegetable fats than in animal fats. It was soon noted that phenolic materials and other antioxidants of the type originally described by MOUREU and DUFRAISSE (1922) belonged to the former type. It was usually observed that other materials such as lecithin, phosphoric acid, citric acid and certain other acidic materials were found to function best in vegetable oils or in meat fats to which a phenolic antioxidant had been added.

Substantial evidence that these synergistic antioxidants functioned largely if not almost entirely by metal deactivation was presented by MORRIS *et al.* (1950).

#### D. Governmental Regulations (U.S.A.)

At present, regulations governing the Meat Inspection of the United States Department of Agriculture provide that, with appropriate declaration on the label, a number of preservatives may be added to rendered animal fat or a combination of such fat with vegetable fat. These preservatives which may be used in the amounts indicated are:

- (a) Resin guaiac not to exceed 0.1 per cent; or
- (b) Nordihydroguaiaretic acid (NDGA) not to exceed 0.01 per cent; or
- (c) Tocopherols not to exceed 0.03 per cent. (A 30 per cent concentration of tocopherols in vegetable oils shall be used when added as a preservative to products designated as 'lard' or as 'rendered pork fat'); or

- (d) Lecithin: Provided, that nothing in this paragraph shall prevent the use of this substance as an emulsifier in an approved manner; or
- (e) Butylated hydroxyanisole (a mixture of 2-tertiary butyl 4-hydroxyanisole and 3-tertiary butyl 4-hydroxyanisole) not to exceed 0.01 per cent; or
- (f) Butylated hydroxytoluene (2,6 ditertiary butylparacresol) (2,6 ditertiary butyl 4-methylphenol) not to exceed 0.01 per cent; or
- (g) Propyl gallate not to exceed 0.01 per cent; or
- (h) Combinations of two or more of the preservatives listed in sub-paragraphs (b), (e), (f), and (g) above not to exceed 0.02 per cent; or
- (i) Citric acid and/or phosphoric acid and/or monoisopropyl citrate not to exceed 0.01 per cent, either alone or in combination with the preservatives listed in subparagraphs (b), (e), (f), (g) or (h) above.
- (j) Recently dodecyl (lauryl) gallate was made permissive for addition to lard which is to be exported from the United States to the Netherlands.

#### IV. DEODORIZATION

##### A. General

As the commercial production of fats and oils increased during the nineteenth century methods for improving the yield from fat- and oil-bearing raw materials were developed. These newer production methods which invariably involved the use of heat generally resulted in products having strong flavours and odours. Frequently these flavours and odours were atypical of those which usually were associated with specific fats and oils and hence were quite undesirable. This led to the need for development of methods for removing the undesirable substances responsible for these unwanted characteristics. The desire for effective means of deodorizing fats was stimulated further by the advent of commercial hydrogenation, a process which imparts an undesirable and characteristic odour and flavour to fat.

The approach to the solution of the problem of undesirable odour and flavour of food fats required careful consideration of the physiology of taste and smell, which is actually quite well defined. The organ of taste is the mucous membrane of the tongue and in some persons, of the soft palate and fauces. In this organ are located the taste buds, each consisting of six or eight taste cells. In order for substances to be tasted they must be in solution. If the tongue is wiped dry and a crystal of sugar is placed on it, no taste will be noted until exuding moisture has dissolved some of the crystal. This fact is especially pertinent with regard to statements occasionally encountered concerning the flavour of fatty substances.

In contrast, the perception of odour depends upon stimulation of the olfactory nerve endings which are located in a small area high up in the nasal passage. The olfactory patches are located somewhat aside from the main channels through which the currents of air pass during breathing. The olfactory cells are stimulated therefore, only by such odorous substances as diffuse to them from the main air currents. By the conscious act of sniffing, however, the air current is directed more nearly upon the olfactory patches, thus effectively enhancing the keenness of smell.

Flavour sensitivity in man is not very great, the sense of smell being much more acute than the sense of taste. This means, of course, that many flavour problems are in reality odour problems, and that elimination of undesirable odours will eliminate in most cases the undesirable flavour, too. Since odours can only result from airborne materials it is logical that steps for removal of all substances having significant vapour pressures will result in practical deodorization.

Early methods for dealing with the problem of unwanted odours and flavours in fats included attempts at masking of odours by means of addition of aromatics, 'washing out' odours with water, and various chemical refining treatments particularly with acid or caustic. LEE and KING (1937), in their paper describing the development of edible-oil deodorizing equipment and methods, point out that the greatest commercial success attended the use of steam stripping. This became particularly true following the description (BATAILLE, 1924) of a steam ejector for the successful maintenance of vacua of 3-8 mm Hg. Names associated with the early development of steam deodorization processes are Rocca, Lurgi, Wecker and Wesson.

The availability of the vegetable oil shortenings completely devoid of any characteristic odour and flavour was followed by their increasing acceptance and favour, particularly by American housewives. Gradually the animal fats such as lard with their characteristic odour and flavour decreased in acceptability. Although the odour and flavour of lard may be desired by some people in certain products such as pie crust, very few wish to have it in a shortening which is to serve a variety of purposes.

In the meantime, considerable effort went into attempts to develop special methods for the manufacture of animal fats having little or no objectionable odour or flavour. In retrospect these efforts to produce a satisfactory bland product from animal fats without a specific deodorization step appear to have been foredoomed. It is hardly to be expected that treatment with adsorbents or mere modification of the rendering process will produce an animal fat so free from characteristic odour and flavour as to meet no objection on this count. Beginning recently, the lard, rendered pork fat or tallow being used in shortening manufacture may also be subjected to chemical processing, such as hydrogenation, which introduces an atypical odour or flavour that must be removed. Occasionally chemical processing such as treatment with sodium methylate may result in products (in this case methyl esters) that are most readily removed by a deodorization treatment. Finally, thorough steam deodorization is an effective way of removing free fatty acids from fats if the percentage present is relatively low. Since free fatty acids are an important factor contributing to low smoke point in shortenings, their simultaneous elimination from shortenings is very worth while. For these reasons steam-vacuum deodorization of animal fats has increased substantially during the past decade. This increase has resulted from a great variety of investigations on numerous aspects of the odour and flavour problem of fats. Numerous laboratory investigations have been reported.

### B. Laboratory studies

A simple, all-glass laboratory deodorizer has been described by BAILY and FEUGE (1943). In their apparatus a bulb heated by a so-called heat lamp serves as a source of scrubbing steam. After passage through the heated oil, the moisture is condensed along with entrained materials by two glass traps or condensers containing dry ice. Somewhat later LIPS (1950) also described a relatively simple all-glass laboratory set-up for deodorizing fats. He reported that with a treatment for 1 h at 240°C, he consistently obtained bland oils and shortenings containing less than 0.05 per cent free fatty acids calculated as oleic acid.

SANDERS (1944) in reporting his studies of attempts to predict the flavour stability of soybean oil gave a brief description of the metal deodorizer he used. His unit was constructed of stainless steel, was electrically heated and was capable of handling eight 1 lb samples simultaneously. An all glass laboratory deodorizer capable of being used for the simultaneous deodorization of four samples has been described by SCHWAB and DUTTON (1948). The authors report that they were able to obtain nearly identical conditions of time, temperature, pressure and rate of steam flow on four samples simultaneously by use of the apparatus.

Two different devices for the semi-continuous deodorization of oils in all-glass laboratory equipment have recently been described by Van der Wal and Van Akkeren (1951). One device which they used was constructed from a modified Oldershaw distillation column; the other column used operated on a bubble-cap principle. They found that either column would effectively deodorize an oil even when using steam at the low rate of 0.5 part based on the oil. The simultaneous removal of a substantial percentage of the free fatty acids present is also effected.

A number of investigators have turned their attention to study of the side-effects of steam deodorization. Riemenschneider and co-workers reported (1944a) that deodorization in all-glass equipment in the laboratory produced no appreciable increase in the stability of steam-rendered lard, but significantly increased the stability of kettle-rendered lard. They obtained variable results by deodorization of lard before and after addition of certain antioxidant mixtures. Working with tocopherol-containing fats, BAILEY and FEUGE (1944) found that addition of lecithin or phosphoric acid was usually equally effective whether added before or after deodorization. If such a fat, however, is nearly rancid, these phosphorus-containing materials are much more effective when added before deodorization.

Working with vegetable oils, BALDWIN found (1948) that the amount of volatile substances removed by a laboratory deodorization was usually of the order of 0.2–0.3 per cent. Volatile aldehydes, ketones and alcohols present are removed. Peroxides present are decomposed, and possibly for this reason the stability of deodorized vegetable oils is usually increased. Working with corn oil, soybean oil, and grain sorghum oil, this investigator found that the stability of the oils increases rapidly during the initial part of the deodorization and this increase in stability is caused apparently by the heat-destruction of

pro-oxidants rather than by any removal of volatile materials. These results are in contrast with the report of ROBINSON and BLACK (1945), that the stability of animal fats is usually reduced by deodorization.

In many cases the reduction of stability which occurs during deodorization is undoubtedly due to metal pick-up during the treatment. ZIELS and SCHMIDT (1945) by use of metal shavings placed in laboratory deodorizers showed aluminium and nickel to be the only metals examined which were free of any pro-oxidant effect. Lead, manganese, copper, cobalt and iron were the worst metals tested. Of a number of alloys tested their techniques indicated Inconel (International Nickel Co.) and Rezistal (Crucible Steel Co.) were the best. Workers at the NORTHERN REGIONAL RESEARCH LABORATORY showed (EVANS *et al.* 1952) that addition of metal scavengers to soybean oil was quite effective in overcoming the effects of increase in iron content during commercial deodorization.

### C. Commercial development

A brief but informative historical sketch of the development of commercial edible oil deodorizing equipment and methods was published by LEE and KING in 1937. After discussing the needs for deodorization, they outlined the principal steps in the development of deodorization equipment. Even at that early date they concluded that the trend was toward continuous processes with automatic control. In 1940 DEAN and CHAPIN described the commercial advantages which they had observed during the operation of a continuous deodorization plant over a 2 year period. They claimed marked savings in steam and condensing water by comparison with requirements for batch operation.

Several very excellent treatments of the theory and practice of deodorization have since appeared. BAILEY (1941) has discussed losses during deodorization, influence of temperature, absolute pressure, and vessel design, particularly with reference to the mathematical treatment of the theory of distillation by steam. In a paper presented before the Short Course of the American Oil Chemists' Society in 1949 BATES has given a more detailed treatment of the fundamental and theoretical considerations involved in deodorization. A companion paper by MORRIS (1949) has presented a comprehensive review of the operation from a practical point of view.

BARNEBEY (1949) in a paper on the high-temperature processing of fats has presented a flow sheet for a typical batch deodorization unit. He makes the very excellent point that, although the degree of removal of free fatty acids from a fat has been widely used as the measure of the extent of deodorization, the correlation is not necessarily a good one. Actually there is no completely satisfactory substitute for sensory odour and flavour tests. Since their description, the panel method for sensory testing outlined by MOSER *et al.* (1947) of the Northern Regional Research Laboratory seems to be the accepted standard in this respect.

WHITE (1951) has enumerated seven factors which influence the product obtainable from a commercial deodorizer. These are (a) condition of feed stock,

(b) condition of stripping steam, (c) condition of equipment, (d) materials of construction, (e) method of heating, (f) operating vacuum and (g) length of time involved. Two years later this same author (WHITE, 1953) has written a very good discussion of commercial deodorization. In this article he has presented a great deal of information about a number of the more generally used pieces of American equipment. Cuts are shown of a batch deodorizer with internal heating coils and one with external heating coils, both as designed by Foster-Wheeler; of a continuous deodorizer by the same company and another design by Wurster and Sanger, Inc. Some attention is also given to the semi-continuous deodorizer offered for sale by Girdler Corp. This last piece of equipment has been described in considerable detail by BAILEY (1949).

## V. GLYCERIDE REARRANGEMENT

### A. Historical

The animal fats have been treated in many ways in an effort to improve their physical properties. Lard, for example, has been blended with other fats and oils, it has been hydrogenated under a wide variety of conditions and it has been fractionally crystallized to achieve such improvement. Moreover, it has been subjected to a wide variety of purely physical treatments frequently referred to as homogenizing, plasticizing or texturizing. Yet none of these steps alone or in combination seem to have entirely eliminated such undesirable characteristics as the tendency to develop large crystals leading to a 'grainy' appearance. Fundamental alteration of the glyceride composition seems to be necessary to achieve this objective. The simplest way to achieve such alteration is by ester interchange.

An ester interchange reaction was first reported by FRIEDEL and CRAFTS (1865). These investigators noted that increased temperature tended to promote the reaction. They reported that upon heating a mixture of equal parts of ethyl benzoate and amyl acetate for 60 h in the temperature range of 200–240°C some amyl benzoate was formed but that the proportion was so small that its isolation was difficult. They further reported that on heating the same mixture for several hours at 300°C in a sealed tube a mixture resulted from which ethyl acetate and amyl benzoate were easily isolated by distillation. The idea that relatively high temperatures were essential to the progress of the reaction was to persist for some time.

NORMANN (1923) seems to have been the first to report the application of the inter-esterification reaction to triglycerides. He reported that by heating tributyrin with tristearin a stearo-butyric glyceride was formed. The following year VAN LOON (1924) described his experiments claiming tin, stannous hydroxide and sodium ethylate to be effective catalysts. Shortly thereafter, GRUN (1925) published further observations on this reaction.

NORMANN (1925) continuing his work described further experiments of interest in a patent which discloses that when mixtures of esters of fatty acids are heated at a high temperature for a prolonged period, with or without a catalyst,

mixed esters having lower melting points are formed. Suitable catalysts included aromatic and aromatic-aliphatic sulphonic acids, tin and its salts, and alkali alkoxides. In light of more recent information one experiment reported is particularly interesting; 20 parts of tristearin and 80 parts of coconut oil were mixed to form a product melting at 57.3°C. When a portion of this was heated for 2.5 h at 250°C with 1 per cent naphthalene sulphonic acid, a product was obtained which melted at 34.5°C. Another portion when heated in vacuo for 0.5 h at 140°C with 0.5 per cent sodium ethoxide gave a product melting at 31.4°C.

Apart from two patents issued to VAN LOON (1930, 1932) there seems to be no literature evidence of further activity in this field for more than a decade. It was undoubtedly recognized by these early investigators that the physical properties of a fat could be altered by a reshuffling or rearrangement of the fatty acids on the glyceride molecules. Nevertheless, the rearrangement as carried out at that time involved extremes of time and temperature and hence was undoubtedly accompanied by discoloration and even thermal breakdown of the fat. This discouraged attempts to put the reaction to practical use. Another problem of considerable magnitude and one which must have assumed almost forbidding proportions to the earlier investigators has been that of determination of the glyceride composition of fats. Available methods have been extremely tedious and time-consuming and frequently gave data of an inconclusive nature. Earlier efforts to apply the use of fractional crystallization from solvents to the study of glyceride structure were largely devoted to efforts to isolate pure glycerides.

For a number of years, however, HILDITCH and his associates employed the crystallization technique for a somewhat different purpose. A detailed review of the extensive work of HILDITCH and his associates in this field is beyond the scope of this paper. Most of his work is summarized in his treatise (HILDITCH, 1956) on the chemical constitution of fats. In the method used extensively by his associates the fat was separated by fractional crystallization from acetone at 0°C into several fractions less complex than the original. Each fraction was then examined for its fatty acid composition, fully saturated glyceride content, and content of tri-C<sub>18</sub> glycerides by determining the tristearin after partial or complete hydrogenation. With this analytical information available, it was possible within limitations, to deduce the approximate glyceride composition of the original fat on the basis of the assumption that the individual fatty acids are distributed as evenly as possible among the glycerol molecules. One of the limitations of this procedure is the inability to differentiate between the various types of mixed unsaturated glycerides, such as steardioleins and steardooleolinoleins, and steardilinoleins, which after complete hydrogenation are determined in the form of tristearin.

More recently, RIEMENSCHNEIDER *et al.* (1940) and HILDITCH and MADDISON (1940) independently found that crystallization at much lower temperatures, -40°C or lower, effects considerable fractionation of the liquid glycerides. From studies based on such low-temperature crystallization,

RIEMENSCHNEIDER *et al.* (1946) recognized that the glyceride distribution in lard which they found was significantly different from random, but thought these differences might well be due to metabolic changes occurring after the glycerides were formed and suggested that the formation by the animal probably followed a random pattern. At about the same time, however, NORRIS and MATTL (1946, 1947) concluded from their work that animal fats, unlike seed fats, have a random pattern of glyceride distribution.

Somewhat earlier than this, however, the groundwork was being laid for the practical application of glyceride rearrangement to animal fats. Thus BAILEY (1945) in his treatise discloses that he filed patent applications describing the use of a rearrangement process to change the crystal habit of lard. At about this same time GOODING (1943) described his work on the preparation of mixed esters of polyhydric alcohols by use of a rearrangement catalyst plus a material capable of furnishing excess alcoholic hydroxyl groups. As a catalyst he recommended up to 1 per cent of an alkali metal soap and up to 2 per cent of an hydroxyl-containing compound such as glycerol.

Some of the most interesting possibilities in the field of inter-esterification of glycerides have been pointed to by the directed inter-esterification work of ECKEY. His first reported work (ECKEY 1945) in this area describes carrying out the reaction under a fractionating column in such a manner as to remove the lowest boiling fatty component. This was accomplished by rearranging the fatty acid radicals in the presence of ester interchange catalysts, using volatile esters of the acids being introduced. Temperatures above 200°C were usually used for this work. The properties of the non-volatile glycerides were, of course, altered by this treatment.

Several years later (ECKEY, 1948a,b) this same investigator described his work on the development of a process of directed rearrangement carried out in the presence of a rearrangement catalyst at a temperature low enough to permit crystallization of solid triglycerides. Temperatures used were of the order of 0-50°C. Catalysts found useful for the low-temperature work include sodium and potassium methoxides. Sodium triphenyl methyl is also active. Compounds of sodium with material much more acidic than alcohol were not found useful. When the desired degree of reaction had been achieved, the catalyst was usually destroyed by washing with dilute phosphoric acid. If the product was to find edible use, methyl esters formed during the reaction were removed by steam deodorization techniques.

Numerous potential advantages can result from application of the directed process. When a fat is interesterified in a molten state or in solution a completely random distribution of the fatty acid radicals is always approached. When the reaction is carried out under conditions which result in removal of one of the components from the reaction site this same randomization reaction may lead to entirely different results, however. Thus, at low temperatures the reaction equilibrium is altered by removal of the more saturated components by fractional crystallization, thereby leading to products with novel properties.

Interest in rearrangement of fats, particularly lard, was stimulated

considerably by the work of VAN DER WAL and VAN AKKEREN (1951). These investigators reported that a relatively mild treatment of lard with an alkali metal alcoholate improved the product for use in cake baking by increasing the volume. Although lard has been considered to be excellent for use in pie baking, its use as a general purpose shortening was hampered by the fact that it did not produce cakes having a high volume. This deficiency also limited its use in most commercial mix formulations.

### *B. Present processes*

A paper describing the process for lard rearrangement as carried out by Armour and Co. has been published by SLATER (1953). A flow sheet and pictures of the process as carried out in the Kansas City plant of the company are presented. The lard is refined and dried prior to treatment with the sodium methylate catalyst at 175–180°F. Two 5,000 lb reactors are the heart of the process.

HOERR and WAUGH (1955) have discussed the results of their X-ray studies on rearranged lard. They find a generally more diffuse pattern with rearranged lard as compared with ordinary lard, indicating that it possesses a less well-ordered arrangement of its molecules. They also find that whereas rearrangement does not alter the short spacings, the long spacings are increased from 39 to 48 Å. In order to explain the fact that the large crystals characteristic of lard do not form after rearrangement, these authors have hypothesized that in lard close packing is possible, while in rearranged lard imperfect (or extended) packing is more likely. They conjecture that the imperfect packing of the rearranged lard crystals indicates that they possess a somewhat higher free surface energy and consequently they are unable to grow to the relatively large proportions of the ordinary lard crystals.

Quite recently an excellent description of the commercial use of directed esterification as a new processing tool for lard has appeared (HAWLEY and HOLMAN, 1956). Several advantages are claimed for the use of low-temperature directed interesterification. Among those are (a) the higher percentages of trisaturated glycerides formed by directed interesterification eliminate the need for addition of completely hydrogenated fat (hardstock) to lard in order to give it desirable heat resistance and (b) improved plastic range in the resulting product when compared with products made from similar stock by other available procedures.

The initial laboratory work and preliminary pilot-plant work were done batch-wise, but later pilot-plant work led to the development of a continuous process which is used in the commercial unit. The process is described essentially as follows: lard is pumped first through a vacuum drier and then cooled to a temperature just above its melting point by passage through a heat exchanger. A carefully metered stream of sodium-potassium alloy, the catalyst, is then pumped with the lard into a small continuous mixer where the catalyst is suspended throughout the lard in a finely divided form, 10–40  $\mu$  in diameter. The catalysed lard continues on through a scraped-wall heat exchanger in which the temperature is quickly dropped to the point desired for initiating

crystallization of trisaturated glycerides. Stock leaving the cooler goes to a vessel where the reaction proceeds under carefully controlled agitation. The resulting initial crystallization of trisaturated glycerides liberates considerable heat of fusion which leads to the necessity for a second cooling step. After the second cooling the lard passes to a second crystallizer where the precipitation of trisaturated glyceride continues to the desired level. The end point is determined by a cloud-point or solids-content measurement of the stock leaving the crystallizer. When the desired point is reached, the catalyst is 'killed' by adding water, and carbon dioxide is injected with the water to minimize saponification losses. The reaction mass is then warmed to melt the trisaturated glycerides, after which the soap phase is separated from the lard in a conventional centrifuging operation. The lard is then ready for final processing and packaging.

The use of an alloy of sodium and potassium as the catalyst is reported to offer several advantages largely associated with the fact that it can be used in a liquid form. This facilitates pumping and precise metering.

In conclusion it may be stated that glyceride rearrangement is now being practised commercially on lard in the United States to a significant extent. Adequate methods are available for control of the processes, although further developments along these lines may be anticipated. Principal advantages to be hoped for by the glyceride rearrangement operation as applied to lard include:

- (a) An improved plastic range in the product.
- (b) Greater uniformity in the finished product and a flexibility which permits a wider selection of raw materials; a percentage of cheaper fats such as edible tallow can frequently be used.
- (c) Improved appearance due to elimination of graininess.
- (d) An outstanding overall baking performance; and finally
- (e) Stability against change under market storage conditions.

## VI. SUMMARY AND CONCLUSIONS

The edible meat fats, lard and tallow are almost completely digestible. They are high-energy foods and contain substances necessary for good nutrition. They are also of great economic importance. Lard production alone in the United States usually exceeds 2.5 billion pounds a year. Edible tallow production, currently below 100 million pounds per year, could undoubtedly be expanded greatly if any economic advantage attended it.

For many years lard was considered to be the outstanding shortening. Because lard has reasonably satisfactory properties, producers have generally been anxious to consider it to be a finished product. Slowly but surely, however, research resulted in improvement of the characteristics of the hydrogenated vegetable oil products until they surpassed lard in a number of important respects. This had its effect in the market place and lard gradually fell into disfavour with many discriminating users. At first an attempt was made to meet this problem by price adjustments, but with the growing level of consumer income this approach did not give completely satisfactory results.

In the meantime research efforts were directed increasingly to the improvement of keeping quality or stability, physical characteristics, odour, flavour, and smoke point of lard and edible tallow. It was recognized early that stability was the key property without which the application of techniques for other improvement would have little value because the best shortening is unfit for use if it is rancid. This problem was vigorously attacked with salutary results. There are now available and approved for use antioxidant combinations which are inexpensive, easily used and quite effective; they have value not only in preserving the fat itself but also in delaying the onset of rancidity in foods which may be prepared from the animal fats. Moreover, these materials have all been found to be free of deleterious results in extensive feeding experiments.

Availability of suitable antioxidants makes feasible the further processing of lard. Subjecting it to modern deodorization techniques is now resulting in products which are essentially odourless and tasteless; moreover, elimination of the free fatty acids which takes place simultaneously effectively raises the smoke point.

In the meantime considerable progress has also been made in improving the physical properties of lard. Whether recently developed techniques such as rearrangement will be the ultimate solution to these problems cannot yet be answered, but the problem is being vigorously attacked and certainly progress has already been made along these lines. Increasingly, lard is coming to be viewed as a raw material which may be used to manufacture shortenings which are very acceptable to the consumer.

#### REFERENCES

- ALDERKS O. H., DISTEL W. R. and TAYLOR J. E. (1935) *U.S. Pat.* 1985969.  
ALLEN R. R., VAN AKKEREN L. A. and VAN DER WAL R. J. (1952) *J. Amer. Oil Chem. Soc.* **29**, 380.  
ANDREWS J. S. (1941) *U.S. Pat.* 2263550.  
ANONYMOUS (1946) *Nat. Provis.* **114**, (1), 15; (1949) *Ibid.* **121**, (4), 12.  
ANZALDI O. (1948) *Rev. Fac. Cienc. quim., La Plata* **23**, 163.  
BAILEY A. E. (1941) *Industr. Engng. Chem.* **33**, 404; (1949) *J. Amer. Oil Chem. Soc.* **26**, 166.  
BAILEY A. E. and FEUGE R. O. (1943) *Industr. Engng. Chem. (Anal.)* **15**, 280; (1944) *Oil and Soap* **21**, 286.  
BAILEY A. E., OLIVER G. D., SINGLETON W. S. and FISHER G. S. (1943) *Oil and Soap* **20**, 251.  
BAILEY A. E. (1945) *Industrial Oil and Fat Products*, 1st ed. p. 682. Interscience, New York.  
BALDWIN A. R. (1948) *J. Amer. Oil Chem. Soc.* **25**, 33.  
BARNEBEY H. L. (1949) *J. Amer. Oil Chem. Soc.* **26**, 493.  
BATAILLE E. (1924) *U.S. Pat.* 1489109.  
BATES R. W. (1949) *J. Amer. Oil Chem. Soc.* **26**, 601.  
BAXTER J. G. and JAKOBSEN J. L. (1942) *U.S. Pat.* 2269243.  
BOLLMANN H. (1923) *U.S. Pat.* 1464557.  
CHAYEN I. H. and ASHWORTH D. R. (1953) *J. Appl. Chem. (London)* **3**, 529.  
CHIPAULT J. R., LUNDBERG W. O. and BURE G. O. (1945) *Arch. Biochem.* **8**, 321.

## References

- DEAN D. K. and CHAPIN E. H. (1940) *Oil and Soap* **17**, 217.
- DEATHERAGE F. E. (1946) *Oil and Soap* **23**, 327; (1949) *Food Ind.* **21**, 1749.
- EASTMAN KODAK Co. (1939) *Brit. Pat.* 507471.
- ECKEY E. W. (1945) *U.S. Pat.* 2378005, 2378006, 2378007; (1948a) *U.S. Pat.* 2442531 (1948b) *Industr. Engng. Chem.* **40**, 1183.
- EVANS C. D., COONEY PATRICIA M., MOSER HELEN A., HAWLEY J. E. and MELVIN E. H. (1952) *J. Amer. Oil Chem. Soc.* **29**, 61.
- FRIEDEL C. and CRAFTS J. R. (1865) *Ann.* **133**, 207.
- GOLUBIC C. (1943) *Oil and Soap* **20**, 105.
- GOODING C. M. (1943) *U.S. Pat.* 2309949.
- GRETTIE D. P. (1936) *U.S. Pat.* 2052289; (1940) *U.S. Pat.* 2201692.
- GRETTIE D. P. and NEWTON R. C. (1934) *Brit. Pat.* 415205.
- GRIEWAHN J. and DAUBERT B. F. (1948) *J. Amer. Oil Chem. Soc.* **25**, 26.
- GRUN A. (1925) *Z. Angew. Chem.* **38**, 827.
- GYORGY P. and TOMARELLI R. M. (1944) *J. Biol. Chem.* **154**, 317.
- HALMBACHER P. (1950) *U.S. Pat.* 2527305.
- HANSON H. T., BARNES R. H., LUNDBERG W. O. and BURR G. O. (1944) *J. Biol. Chem.* **156**, 673.
- HAWLEY H. K. and HOLMAN G. W. (1956) *J. Amer. Oil Chem. Soc.* **33**, 29.
- HILDITCH T. P. (1956) "The Chemical Constitution of Natural Fats," 3rd ed. rev., John Wiley and Sons.
- HILDITCH T. P. and MADDISON L. (1940) *J. Soc. Chem. Ind.* **59**, 162.
- HOERR C. W. and WAUGH D. F. (1955) *J. Amer. Oil Chem. Soc.* **32**, 37.
- HORMEL J. C. (1949) *U.S. Pat.* 2467529.
- KEIL H. L. (1947) *U.S. Pat.* 2423102.
- KING A. E., ROSCHEN H. L. and IRWIN W. H. (1933) *Oil and Soap* **10**, 204.
- KRAYBILL H. R., DUGAN L. R., JR., BEADLE B. W., VIBRANS F. C., SWARTZ V. and REZABEK H. (1949) *J. Amer. Oil Chem. Soc.* **26**, 449.
- LAUER W. M. (1945) *U.S. Pat.* 2373192.
- LEA C. H. (1944) *J. Soc. Chem. Ind.* **63**, 107.
- LEADERS W. M. (1950) *U.S. Pat.* 2503205.
- LEE ALAM P. and KING W. G., JR. (1937) *Oil and Soap* **14**, 263.
- LIBBY L. H. and HENDERSON L. F. (1948) *U.S. Pat.* 2445374.
- LIPS H. J. (1950) *J. Amer. Oil Chem. Soc.* **27**, 422.
- LIPS A. and MCFARLANE W. D. (1943) *Oil and Soap* **20**, 193.
- LUNDBERG W. O., HALVORSON H. O. and BURR G. O. (1944) *Oil and Soap* **21**, 33.
- MAGOFFIN J. E. and BENTZ R. W. (1949) *J. Amer. Oil Chem. Soc.* **26**, 687.
- MEHLENBACHER V. C. (1938) *U.S. Pat.* 2108922.
- MERKEL A. H. (1936) *Food Ind.* **8**, 179.
- MITCHELL H. S. and BLACK H. C. (1943) *Industr. Engng. Chem.* **35**, 50.
- MORRIS C. E. (1949) *J. Amer. Oil Chem. Soc.* **26**, 607.
- MORRIS S. G., MYERS J. S., KIP M. L. and RIEMENSCHNEIDER R. W. (1950) *J. Amer. Oil Chem. Soc.* **27**, 105.
- MORRIS S. G. and RIEMENSCHNEIDER R. W. (1946) *J. Amer. Chem. Soc.* **68**, 500.
- MOSER H. A., JAEGER C. M., COWAN J. C. and DUTTON H. J. (1947) *J. Amer. Oil Chem. Soc.* **24**, 291.
- MOUREU C. and DUFRAISSE C. (1922) *C. R. Acad. Sci. Paris* **174**, 258; (1923) *Ibid.* **175**, 127; (1926) *Chem. Rev.* **3**, 113.
- NEWTON R. C. and GRETTIE D. P. (1933) *U.S. Pat.* 1903126.
- NEWTON R. C. and RICHARDSON W. D. (1932) *U.S. Pat.* 1890585.
- NORMANN W. (1923) *Chem. Umschau* **30**, 250 (1925); (Oelwerke Ger. G.m.b.H.) 1925 *Ger. Pat.* 417215.
- NORRIS F. A. and MATTL K. F. (1946) *Oil and Soap* **23**, 289; (1947) *J. Amer. Oil Chem. Soc.* **24**, 274.

- OLIVER G. D., SINGLETON W. S. and BAILEY A. E. (1944) *Oil and Soap* **21**, 188.
- PAVIA C. (1950) *U.S. Pat.* 2516071.
- RIEMENSCHNEIDER R. W. (1955) *Handbook of Food and Agriculture*, p. 254.
- RIEMENSCHNEIDER R. W., HERB S. F., HAMMAKER E. M. and LUDDY F. E. (1944a) *Oil and Soap* **21**, 307.
- RIEMENSCHNEIDER R. W., TURER J. and AULT W. C. (1944b) *Oil and Soap* **21**, 98.
- RIEMENSCHNEIDER R. W. and AULT W. C. (1944) *Food Ind.* **16**, 892.
- RIEMENSCHNEIDER R. W., SWIFT C. E. and SANDO C. E. (1940) *Oil and Soap* **17**, 145.
- RIEMENSCHNEIDER R. W., LUDDY F. E., SWAIN M. L. and AULT W. C. (1946) *Oil and Soap* **23**, 276.
- ROBINSON H. E. and BLACK H. C. (1945) *Industr. Engng. Chem.* **37**, 217.
- ROSENWALD R. H. and CHENICEK J. A. (1951) *J. Amer. Oil Chem. Soc.* **28**, 185.
- SABALITSCHKA T. and BOEHM E. (1941) *U.S. Pat.* 2255191.
- SANDERS J. H. (1944) *Oil and Soap* **21**, 357.
- SCHWAB A. W. and DUTTON H. J. (1948) *J. Amer. Oil Chem. Soc.* **25**, 57.
- SINGLETON W. S. and BAILEY A. E. (1944) *Oil and Soap* **21**, 224.
- SLATER L. E. (1953) *Food Eng.* **25**(9) 72.
- SWIFT C. E. and HANKINS O. G. (1952) *Food Tech.* **6**, 161.
- SWIFT C. E., ROSE W. G. and JAMESON G. S. (1942) *Oil and Soap* **19**, 176.
- TAYLOR A. E. and JAKOBSEN J. L. (1941) *U.S. Pat.* 2267224.
- THALER H. and SCHOTTMAYER A. (1942) *Fette u. Seifen* **49**, 646.
- VAN DER WAL R. J. and VAN AKKEREN L. A. (1951) *U.S. Pat.* 2571315; (reissue 23,499, 1952).
- VAN LOON C. (1924) *Brit. Pat.* 249916; (1930) *U.S. Pat.* 1744596; (1932) *U.S. Pat.* 1873513.
- VIBRANS F. C. (1949) *J. Amer. Oil Chem. Soc.* **26**, 575.
- WHITE F. B. (1951) *J. Amer. Oil Chem. Soc.* **28**, 438; (1953) *J. Amer. Oil Chem. Soc.* **30**, 515.
- WORSHAM E. M. and LEVIN E. (1950) *U.S. Pat.* 2503312.
- ZIELS N. W. and SCHMIDT W. H. (1945) *Oil and Soap* **22**, 327.