Symposium on Fifty Years of Progress in the Chemistry and Technology of Fats and Oils *

Fifty Years of Fatty Acid Applications

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WE FIND OURSELVES today living in a society which is highly dependent upon industrial science. Individually we require a great variety of devices, materials, and goods to maintain a way of life which the majority of us have come to regard as acceptable. For the most part these "essentials" are manufactured or processed in some way before they reach the consumer. If we examine the history of the production of such items, we shall find, in most cases, that somewhere during the course of manufacture a fatty chemical has played an important role.

Chemicals derived from fatty acids are used extensively today in the fields of metal technology, mineral production, and textile processing. They are used in the production of plastics and polymers, both natural and synthetic and including the very important material, rubber. Fatty acids enter into the formulation of many paints and protective coatings, of cosmetics and pharmaceuticals, and, of course, of detergents and lubricants. These are among the important areas of application of fatty chemicals. There are many others, some of which will be mentioned later.

Fifty years ago there were only three important products from fatty acids: soap, grease, and candles. Of these, two—soap and grease—date back almost as far as written history. Alkali soaps were produced by the Egyptians, and lime soaps were used to lubricate chariot wheels although "modern" manufacture of grease began about 1854. Candles were originally made from tallow. Then, after the discovery by Chevreul in 1811 that fats were composed of fatty acids and glycerol, followed by the development of processes for the separating of the acids into liquid and solid (stearine) fractions, stearine replaced tallow in candle manufacture, yielding a product which burned without producing acrid fumes. There were no other important changes in the fatty acid industry until about the turn of the century.

TURNING now to the fatty acid industry during the past 50 years, we can best gain an over-all view through the examination of statistics. The relationship of fatty acid production to total industrial production is illuminating. Based upon Department of Commerce figures for 1900 to 1956, industrial production tripled during this period whereas fatty acid production increased ten-fold. During the same period a population increase of about 55% occurred.

Until about 1900 fatty acid production was accomplished through three basic operations, depending upon the product desired. a) Fats were saponified, and the soaps were acidulated to yield the free fatty acids. b) Fatty acids, usually from tallow, were separated into liquid and solid fractions by the process known as panning and pressing, which is simply a crystallizing and filtering procedure. c) Refining of crude fatty acids was also accomplished by over-all vacuum distillation. At the turn of the century the splitting of fats was simplified by Twitchell's discovery of direct catalytic splitting, thus avoiding the saponification-acidulation step. This advance approximately marks the beginning of the period which we are discussing.

In the 1920's the hydrogenation of esters of fatty acids or the acids themselves to produce fatty alcohols was successfully accomplished. This represents the first industrial chemical modification of the fatty acid molecule that involved other than ionic bonds. The fatty alcohol sulfates were introduced in this country in the early 1930's as both industrial and consumer products. Thus began the synthetic detergent industry, growing out of the need in the textile industry for surface-active agents which are effective in hard water or at low pH. Prior to this time only Turkey-red oil (sulfated castor oil) met these requirements of the textile industry.

Also in the early 1930's fractional distillation of fatty acids was begun on a commercial scale, providing fatty acids better suited for specific uses. The consumer no longer found it necessary to "make do" with naturally-occurring mixtures or with solid and liquid fatty-acid mixtures obtained by the old panning and pressing method.

In the 1940's continuous, high-temperature, high-pressure, and direct splitting of fats was introduced, adding speed and economy to the production of fatty acids, and the first solvent-crystallization plant was put into operation, using methanol. This process separates liquid and solid fatty acids more cleanly and, by providing products of high purity, still further expanded the markets. Subsequently a second crystallization plant, which uses acetone as the solvent, was put into operation.

Also in the 1940's the nitrogen-containing derivatives of the fatty acids were introduced commercially. Beginning with simple amides, nitriles, and primary amines, this class of derivatives has expanded into a variety of amines, quaternary ammonium salts, and substituted amides.

The most recent period, the 1950's, is marked by the production of cleavage products of the fatty acids as well as by the introduction of chemicals produced by chemical modification of the hydrocarbon chain. We cannot yet say what will be considered the most important advance during this period.

STRUCTURALLY a fatty acid consists of a long, 12-to-18-or-more-carbon-atom, hydrocarbon chain terminating in a carboxyl group. The polar carboxyl group is highly reactive and is hydrophilic in nature. The nonpolar hydrocarbon portion of the molecule, on the

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*Condensed from the original versions, which were presented at the 50th anniversary meeting of the American Oil Chemists' Society, in New Orleans, La., April 20, 1959.

other hand, is relatively unreactive and is hydrophobic. It is this characteristic of mixed polarity which results in the surface activity of the molecule and is responsible for a great many of the applications of both fatty acids and derivatives thereof.

The natural fatty acids occur in a variety of even-carbon chain lengths. From the industrial point of view, those containing from 12 to 18 carbon atoms are most important. Eighteen carbon acids containing one or two centrally located double bonds are also very important. The length of the carbon chain and the degree of unsaturation exert a profound influence on the physical properties of the various fatty chemicals.

Utilization of fatty acids themselves, apart from their use as raw materials for conversion to derivatives, has expanded substantially during the first half of this century. Candles, although no longer a primary source of illumination, are still a large outlet for stearic acid. Possibly the largest single use of stearic acid is in the compounding of rubber; the acid serves as an activator and accelerator of curing and as a plasticizer. Many of the acids, as such, are used in protective coatings and especially as modifiers for alkyl resins. Nonmetallic mineral flotation, particularly in the phosphate industry, has also been a large outlet for unsaturated, liquid fatty acids.

Fatty acid soaps are produced by the interaction of the acid itself with a base. The base may be either inorganic (metal oxides, hydroxides, or carbonates, or ammonia) or organic (amines or ammonium compounds). The soaps may be water-soluble or water-insoluble. For the most part, the water-soluble soaps are used as detergents or emulsifying agents and are employed in cosmetics, textile processing, metal working, leather finishing, and synthetic rubber polymerization. The insoluble soaps are used as gelling agents in lubricants, as waterproofing agents, as flatting agents in paint, or in cosmetics and toiletries. Metallic soaps are used as dryers in paints.

Fatty acids may be converted to simple esters either through direct esterification or through interesterification of the triglyceride with the appropriate alcohol. Esters are used as plasticizers or as chemical intermediates. Two special types of esters are produced through interaction of fatty acids with acetylene or alkylene oxide. The first of these reactions leads to vinyl esters, which are used as copolymers and internal plasticizers. The alkylene oxide reaction products are nonionic surface-active agents and are used as detergents and emulsifying agents.

As mentioned previously, simple esters are reduced either by catalytic hydrogenation or through the use of metallic sodium to produce a fatty alcohol.

Sulfation of the fatty alcohol with sulfuric acid, followed by neutralization, leads to the alkali-sulfate type of synthetic detergent. This, the first commercially produced synthetic detergent, is still widely used as a component of household detergents, usually in combination with other synthetics and builders. Although somewhat higher priced than synthetic detergents based upon petroleum fractions, the alkali sulfates are still among the best of the detergents available today. Department of Commerce figures for production of fatty alcohols in 1956 exceed 165 million pounds.

Interaction of a fatty acid or a fatty-acid chloride with ammonia or an amine will lead to the formation of an amide. Simple amides are used as intermediates in the production of the Zelan-type of fabric water-repellent, as foam stabilizers for synthetic detergents, and as antiblocking agents for plastics. Substituted amides of the diethanolamide type are the active constituent of the Ninol-type detergent used in shampoos and other cosmetics. Production of these surface-active agents approached 70 million pounds in 1956 according to Department of Commerce figures. The acyltaurides, from fatty-acid chlorides and N-methyltaurine, are the Igepon-T synthetic detergents of industry, an important class of synthetic detergents widely used in household formulations as well as in textile processing.

THE Igepon-T types, the alkyl sulfates, and the soaps themselves belong to the class of surface-active agents known as anionics since the fatty portion of the molecule carries a negative charge. Representatives of the other classes of surface-active agents, the cationics, nonionics, and ampholytics, are also found among the fatty acid derivatives.

A second class of nitrogen-containing derivatives of the fatty acids also is formed through interaction with ammonia, with the elimination of two molecules of water to produce nitrile. Nitriles as such have few uses; they principally serve as intermediates in the production of amines through catalytic hydrogenation. Amines, in turn, are readily converted to the quaternary ammonium salts by such alkylating agents as methyl chloride. In addition to primary amines, secondary and tertiary amines are produced as well as molecules containing other groups. A variety of quaternary ammonium salts also is possible, including those containing two long hydrocarbon chains.

Many of the nitrogen-containing derivatives are basic in nature and are capable of forming salts. As opposed to the anionic surface-active agents, these nitrogen-containing derivatives carry a positive charge on the organic portion of the molecule and therefore are classified as cationic surface-active agents or, frequently, simply cationics. Because of their general similarity to soaps, but because of their positive charge, the cationic surface-active agents are also referred to as invert soaps. The nature of the charge is important to many of the applications of the nitrogen-containing derivatives.

Most surfaces carry a negative charge as a result of the presence of free electrons, and therefore most surfaces will adsorb the cationic surface-active agent with a resulting modification in the properties of the surface. It is this phenomenon which is usually considered responsible for the use of cationics as textile softeners and lubricants, corrosion-inhibitors, asphalt antistrip agents, flotation agents, antistatic agents, and even germicides, to mention a few. Amines and quaternary ammonium salts are also used as gelling agents in lubricants, as lubricant additives, and in emulsion-type paints. This is an extremely versatile class of chemicals; the limits of its usefulness are continually expanding. In 1956 over 12 million pounds of quaternary ammonium compounds were produced, according to Department of Commerce figures.

THE CLEAVAGE of certain naturally-occurring fatty acids has provided a series of higher aliphatic dibasic acids. Two important processes have reached commercial proportions: oxidative cleavage of oleic acid and pyrolytic cleavage of ricinoleic acid from castor oil.

Originally oleic acid was oxidized with chromic anhydride; more recently ozonolysis has been applied. The latter procedure is advantageous in that oxidative degradation of the cleavage products is less pronounced if it occurs at all. Along with the C_9 dibasic acid, azelaic, is produced the C_9 monobasic acid, pelargonic.

Cleavage of ricinoleic acid is accomplished through alkali fusion to yield the C_{10} dibasic acid, sebacic, together with "capryl alcohol." These dibasic acids are used in the production of polyesters and polyamides and, in the form of their esters, as plasticizers and high-temperature lubricants. Combined production of esters of azelaic and sebacic acids for 1956 was in excess of 21 million pounds, according to Department of Commerce figures.

Derivatives of fatty acids obtained by substitution or addition within the hydrocarbon chain are beginning to find commercial application. Two such products are the epoxide obtained from oleic acid or its ester and the sulfo acid produced by sulfonation of stearic acid. The epoxide, usually in the form of an ester or glyceride, is recommended as a halogen scavenger for polyvinyl resins. The sulfo acids have shown promise in detergent formulations and as flotation agents.

We have listed examples of the more important classes of fatty acid derivatives and have mentioned some of their applications. There are many other related compounds and types of compounds and many other important applications, each of which is probably deserving of extensive discussion. Here we have attempted to illustrate only in a very broad way the importance and usefulness of fatty chemicals.

In a discussion such as this, it is appropriate to speculate as to the future. As technology expands, we can expect our industry to expand. Opportunities for new uses for fatty chemicals will continue to arise, but it is the responsibility of the producers of these chemicals aggressively to seek these uses. As we have suggested earlier, a substantial proportion of the outlets for fatty acids is in applications of surface-active agents, and surface-active agents can be produced by other chemistry from other starting materials. The fatty acid industry has certain advantages through familiarity with this field. We must retain these advantages through continuing and expanding research, both basic and applied.

Supply of raw material is generally not a problem for fatty acid producers since much of the raw material is a by-product of other industries and is available in quantities which far exceed the demands of the fatty acid industry. As is true with any line of products, competition and obsolescence are constant threats to profitable operation. The only way to meet these threats is through new products which come only through research. Those who have been intimately concerned with the chemistry of fatty acids know that there are tremendous gaps in the existing knowledge of the field. It is to the best interest of the industry to increase the effort to fill these gaps since new facts are the basis for continued expansion.

Fifty Years of Progress in the Technology of Edible Fats and Oils

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A HALF CENTURY ago lard was the preferred shortening. It was solidified by dropping it on the exterior surface of a large chilled roll, then it was scraped off into a trough called a picker pan where it was beaten and conveyed to the filling station by a combination of blades and a screw conveyor.

By 1900 lard had a strong competitor in compound shortening. It is estimated that the domestic consumption of cottonseed oil was about 400 million pounds in 1900, and double that by 1905. Most of this oil went into compound shortenings, which at that time were largely blends of about 85 parts of cottonseed oil with 15 parts of oleostearine. The cottonseed oil was alkali-refined in open kettles, and the foots were separated by gravitation. The refined oils were decolorized by adsorption with fuller's earth in open tanks, filtered through presses, and deodorized with super-heated steam at oil temperatures from 275 to 340°F. at vacuums in the range of 28 to 29 in. Compound shortening was solidified on chill rolls, as was lard.

The fat ingredients of margarine were oleo oil, neutral lard, butter, and cottonseed oil. Only the cottonseed oil was refined and deodorized, and it was used only in the cheaper grades. The margarine ingredients were churned by hand or by steam power for about 30 min., run into ice water for about 10 min., thrown onto inclined tables with wooden shovels in a room at 70°F., and allowed to drain. Salt was put in the margarine while it was lying on the table. It was turned three to four times manually to facilitate draining, shoveled into a butter worker, and then packed by hand.

Can you imagine the cost of these processes and the acceptability of these products in today's market? We have indeed come a long way in 50 years. What have been the most important technological advances that have resulted in today's shortenings, margarines, and salad oils? The list is rather impressive.

It is perhaps fitting that hydrogenation should be mentioned first, inasmuch as the first hydrogenated shortening will soon celebrate its own 50th anniversary. Hydrogenation of food fats was introduced in this country in 1911 and grew at a rapid pace. The importance of hydrogenation to the growth of the shortening and margarine industries, also to the soybean industry, can scarcely be exaggerated. Just try