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Fat Chemistry—Past, Present, Future

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FAT CHEMISTRY, the chemistry of triglyceride fats and oils and the fatty acids derived therefrom, had its beginning in antiquity with the preparation of soap from tallow and wood ashes. The Egyptians produced alkali soaps and used lime soaps to lubricate chariot wheels. Fat technology, as the term is used today, had its origin in the discovery by Chevreul in 1811 that fats were composed of fatty acids and glycerol. And probably the first major contribution of fat technology to better living arose through the substitution of solid fatty acids (produced by fractional crystallization) for tallow in the manufacture of candles, thus eliminating the acrid fumes which are produced when tallow candles are burned. The first synthetic surface-active agent (Turkey-red oil) was produced in the late 19th century by the sulfation of castor oil and was used in textile processing and as an emulsifying agent. It was the first hard-water-stable surfactant.

At the turn of the century, Twitchell discovered his process for the catalytic splitting of fats, thus simplifying the manufacture of fatty acids through elimination of the two-step saponification-acidulation process. Not long thereafter, Sabatier's procedure for catalytic hydrogenation was applied commercially for the hardening of liquid fats in the production of the so-called vegetable shortenings. This development had a tremendous adverse impact upon the animal-oil shortening industry. The relatively low stability of animal fats contributed to their loss of popularity.

The fatty chemical industry, as we know it today, probably began in the 1920's with the catalytic hydrogenation of fatty acids or esters to produce fatty alcohols. Introduction of salts of fatty alcohol sulfates in the early 1930's marked the beginning of the synthetic detergent industry.

Also in the early 1930's commercial fractional distillation of fatty acids provided a means for separating fatty acids according to chain length, and the consumer was then able to select the specific fatty acid best suited to his application. Heretofore, mixtures of solid and liquid fatty acids, such as are obtained by the old panning and pressing process, constituted the selections available. Solvent crystallization, first applied commercially in the 1940's, offers a substantial improvement over panning and pressing. Separation of solid and liquid acids is accomplished much more efficiently, thus making available fatty acids of relatively high purity.

A second important development occurred in the food-fat field in the middle 1930's with the introduction of a shortening containing fatty acid monoglycerides (actually predominantly a mixture of mono- and diglycerides). These shortenings made it possible to use a much higher ratio of sugar to fat in bakery goods.

The fifth decade of this century saw a number of significant developments in the field of fat and fatty-acid technology. Continuous, high-temp, high-pressure splitting of fats was introduced. This process adds both speed and economy to the splitting process. Also introduced commercially during the 1940's were the nitrogen-containing derivatives of the fatty acids based upon the reaction of the acids with ammonia to yield amides and nitriles. The latter were hydrogenated to amines which were converted to quaternary ammonium salts and other derivatives.

Two industrially important dibasic acids are produced from fats. Sebacic acid is manufactured by the alkaline fusion of ricinoleic acid from castor oil and azelaic acid by the oxidative cleavage of oleic acid with ozone. These products assumed commercial importance during the 1950's. Also during this period, epoxidation of unsaturated fats was applied on a commercial scale.

Having reviewed some of the highlights in the growth of the fatty chemical industry, it is appropriate to survey the areas in which fatty chemicals find application today. These areas are very extensive; in fact, it probably is safe to state that a fatty chemical has played an important role somewhere in the course of the manufacture of most of those items and goods which are essential to our way of life. Items with which we come in daily contact and which are based wholly or in part upon fat-derived materials include soaps and synthetic detergents, cosmetics, and pharmaceuticals. Even in our food products and especially bakery goods and prepared mixes, both chemically modified fats and emulsifiers produced from fatty acids are essential.

Although lime soaps have been used as lubricants for centuries, the use of metallic soaps in this application has expanded tremendously in recent years. Soaps not only of calcium, but also of barium, aluminum, and lithium find specialized applications. Also, an entirely different type of fatty chemical, a combination of a fatty quaternary ammonium compound with an acid clay such as bentonite, is being employed in certain grease formulations and other applications.

Fatty chemicals are widely used in petroleum technology. Cationic surface-active agents based upon fatty acids are employed in "down-the-hole" operations in secondary oil recovery. The function of the fatty chemical is three-fold. It assists in the penetration of water into the oil-bearing sandstone; it serves as an anti-microbial agent which inhibits the growth of sulfate reducers and other organisms which not only produce corrosive chemicals but also plug the pores of the rock; and it serves directly as a corrosion inhibitor for the steel casing. Fatty chemicals are also used as de-icers in finished gasoline.

The rapidly expanding industry based upon polymers, which includes plastics, rubber, and protective coatings, provides many important outlets for fatty chemicals. Traditionally, oil-based paints are composed of a naturally occurring drying oil plus a pigment. Synthetic coatings have, of course, been developed, and possibly most important of these are the alkyd resins consisting of the polymer obtained by the interaction of a dibasic acid with a polyfunctional alcohol. Properties of the resulting polymer are modified by the inclusion of a fatty acid in the formulation. Either saturated or unsaturated acids are used, depending upon the type of alkyd. Fatty acids have long been an important component of natural rubber formulations. With the advent of synthetic rubber, soaps of fatty acids are employed as the emulsifying agent for emulsion polymerization.

The plastics industry finds several uses for fatty chemicals. Fatty acid esters are widely employed as plasticizers. The epoxidized oils are finding increasing use as stabilizers and plasticizers for polyvinyl chloride polymers. Certain of the cationic fatty chemicals are providing antistatic properties for plastics.

Non-metallic froth flotation processes have long used both fatty acids and fatty amines. The separation of silica from phosphate rock was the first major application of fatty amines. This reagent is also used to separate sylvite (KCl) from halite ($NaCl$). Fatty chemicals have shown promise in the beneficiation of metal ores such as those of iron and copper.

Surface-active agents based upon fatty chemicals are used in various phases of metal processing and fabrication as lubricants, cutting and drawing compounds, and as corrosion inhibitors. In textile processing, fatty chemicals are important as lubricants, anti-static agents during spinning, and as dye assistants.

A recitation of the uses of fatty chemicals might continue indefinitely. We have tried to list some of the major uses of chemicals which are based upon the fatty acids derived from naturally occurring fats and oils. The list is not complete, but perhaps it will serve to demonstrate both the versatility of this class of compounds and their importance.

We cannot leave the discussion of applications of fats and fatty acids without mention of the current concern with the metabolism of fats, especially as it relates to certain circulatory disorders in man. Although there may be contrary opinions, final conclusions regarding the role of fats in heart disease are premature.

Reactions of fatty acids are classified under two major categories, those which involve the carboxyl group and those which involves the hydrocarbon chain. Combinations of the two are, of course, possible. Reactions of the carboxyl group have been most widely exploited, and most major applications of fatty chemicals involve compounds which fall into one of the following classes: soaps, including the "soluble" alkali and amine soaps and "insoluble" soaps of the alkaline earths and other metals; esters, including mono-, di-, and triglycerides; alcohols and salts of their sulfates; and the nitrogen-containing derivatives which will be discussed in detail in one of the following papers. Almost every conceivable reaction of aliphatic carboxylic acids has been applied to fatty acids. However, it is not safe to assume that all possible applications for all carboxyl derivatives have been explored; new uses for old compounds are frequently discovered, and those engaged in application research are well advised to review old preparations as new needs arise.

Although products obtained by reactions of the hydrocarbon chain of fatty acids may represent a smaller total volume than the carboxyl derivatives, they are by no means of minor significance. Today there is an increasing emphasis on fatty acid technology based upon reactions of the hydrocarbon chain. It is of interest to note that a majority of the papers to be presented at this Short Course are concerned with reactions of the hydrocarbon chain.

Most of the known reactions of the fatty acid hydrocarbon chain fall into one of five classes: replacement, addition, elimination, isomerization, and cleavage. Although it is possible to cite examples of the commercial application of all five classes, addition reactions are by far the most important today. Our program includes discussions of several addition reactions as well as replacement and cleavage reactions. Applications for products and processes based upon fatty acid hydrocarbon chain reactions probably have been less thoroughly explored than is the case with carboxyl derivatives. An expanded effort in this direction is justified.

It is not possible to predict with certainty that any compound or class of compounds will find useful applications; we still must depend largely upon trial and error methods in developing new products. The greater the variety of substances investigated the better will be the prospect of success. The technical literature contains descriptions of many fatty chemicals which have received little or no attention as potential products. In some instances, more process research is required to produce satisfactory yields. In other instances, the reagents involved are obviously costly and the product would demand a high price. However, we all are aware of uses in very substantial quantities of substances which are high in price and, although high-priced items may not provide outlets for large quantities of fats, they can offer a source of profits to a producer whose operations do not require large volume products.

A detailed discussion of chemical reactions will not be undertaken here. However, some products and some reactions which appear to be worth further investigation will be mentioned. Halogenated fatty acids may be of interest either as such or as intermediates for the introduction of other groups such as hydroxy, alkoxy, mercapto, amino, cyano, phosphono, etc. Some less thoroughly investigated addition products of unsaturated fatty acids include those obtained by means of nitrogen tetroxide, of esters of phosphorus acids, of silane derivatives, and of diborane. A number of reactions for the addition of carbon compounds to unsaturated fatty acids are known. These include the addition of nitriles, of aromatic compounds by the Friedel-Crafts reaction, of maleic anhydride, of carbon monoxide either by the Oxo process or by the acid-catalyzed carboxylation reaction, and of formaldehyde. Diene reactions of fatty acids have been studied extensively and some will be discussed later in the program. Also addition reactions of epoxidized fatty chemicals will be included in the paper on that subject. The possibilities based on known reactions seem endless, and surely there is still new chemistry to be discovered.

Current products derived by the chemical processing of fats and fatty acids represent a very substantial outlet for both edible and inedible fats. Many fats, however, are by-products of the production of other commodities and are, therefore, less susceptible to the control of supply based upon demand. As a result, there is a continuing search both in industrial and government laboratories for new products based on fats. There appears to be no indication that this effort will decrease. Actually, some fats, and especially animal fats, represent a very attractive raw material from the point of view of price.

As exploration in any field continues, the development of new knowledge and the discovery of new facts becomes increasingly more difficult. The easy and the obvious is always done first. A superficial survey of the knowledge in the field of fat and fatty acid chemistry might lead one to conclude that almost everything has already been done. However, a more careful scrutiny of this knowledge reveals many gaps and inconsistencies. New analytical techniques, especially chromatography and spectrophotometry, have been especially effective in dispelling the illusion that our knowledge of fat chemistry is even approaching completion.

Although it is usually not possible to predict wherein new fundamental knowledge will have practical significance, it is axiomatic that new facts will directly or indirectly lead to new useful applications. In industry, there seems to be a trend away from basic and long-range research which cannot clearly define objectives in terms of profits. Even the government Utilization Research laboratories are required to be quite explicit in terms of the end use for the results of their research. And in this country at least, the amount of academic research effort in the field of fat chemistry is grossly inadequate. There is a need for increased basic research on the organic chemistry of the fatty acid molecule. This research must be done by well-trained organic chemists with the skill and patience required to cope with the peculiar problems which arise as a result of the size and structure of the fatty acid molecule. Perhaps even a more pressing need lies in research on the relationship between structure and physical properties. Knowledge of this relationship is today almost completely empirical, yet most uses for fats and fatty chemicals are based upon their physical properties. Studies of structure and properties necessitates a source of compounds of known structure, which again emphasizes the need for adequate preparative skill.

The chemical processing of fats and fatty acids is part of the chemical industry and, like the chemical industry, its future lies in basic and long-range research. In concluding this review of the growth and present status of the fatty chemical industry, we wish to stress this need for basic research on the organic, physical, and biological properties of fatty chemicals. The three fields are inseparable, and each is dependent upon the others for satisfactory progress. Possibly the most difficult problem which confronts those of us who are still close to the technical aspects of fat chemistry lies in communicating our needs to those who set policy in the industrial government, and academic world.

Nitrogen Derivatives of Long-Chain Fatty Acids

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BY NECESSITY, a good deal of the material presented in this talk will be somewhat repetitious of the Nitrogen Fatty Acid paper given by H. J. Harwood in a similar symposium in 1954 (1). At that time, he reviewed the chemistry of these derivatives quite thoroughly. However, since that time, some of the products he mentioned have become even more important commercially and also there have been many additions to the nitrogen-containing derivatives of the fatty acid family. Also, there have become several other commercial factors in this area and we can now list four main producers of these chemicals along with several fringe producers. There is also production in several foreign countries. This increase in production can only mean that these compounds have a great many more uses or potential uses than was dreamed of when this research was started by Armour and Company in the early 1930's. It is also worthwhile noting at this time that the quality of these derivatives also have been steadily increasing.

During the course of this discussion, formulae will be written with frequent use of the term R for alkyl. In the fatty acid derivative business there can be considerable variation in the alkyl chains, depending on the starting fatty acid. It may be well to consider sources of composition at this time.

The main raw material is tallow which has the following average composition:

C-14	5%
C-16	30%
C-18 saturated	20%
C-18 unsaturated	45%

From this raw material is produced almost any combination of the above composition. Commercially, besides the total mixture, pure hexadecyl, pure octadecyl, commercial oleyl, and hydrogenated mixtures are available.

The second most important raw material is coconut oil which has the following average composition:

C-8	8%
C-10	7%
C-12	49%
C-14	18%
C-16	8%
C-18 saturated	5%
C-18 unsaturated	5%

Again, any single chain length and any combination of the above are available.

In addition to the above, there are many miscellaneous raw materials used. Among them are soybean oil, cottonseed oil, tall oil fractions, fish oil fractions, erucic acid, and various fat by-products.

The method of introduction of nitrogen into the fatty acid molecule still remains very much the same although other methods are beginning to be consid-