

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:

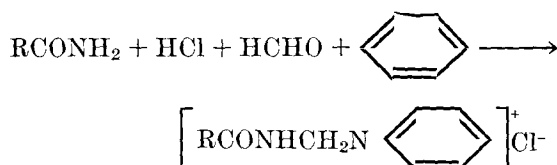
C-8.....	8%
C-10.....	7%
C-12.....	49%
C-14.....	18%
C-16.....	8%
C-18 saturated.....	5%
C-18 unsaturated.....	5%

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

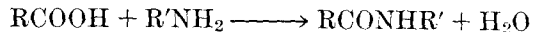
In addition to the above, there are many miscellaneous raw materials used. Among them are soybean oil, cottonseed oil, tall oil fractions, fish oil fractions, erucic acid, and various fat by-products.

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-

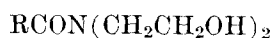
ered. The main procedure is the reaction of fatty acid with ammonia. The first reaction product, after soap preparation, is a simple unsubstituted amide (2). This process is done in one of two ways. Excess ammonia may be introduced continuously bleeding off ammonia and water of reaction, or the ammonia may be added batchwise with intermittent bleed off of ammonia and water. Both methods are used commercially today. In some instances the ammonia is recovered and recycled. In other instances, due to the lost cost of ammonia, it is not recovered. The reaction is conducted at about 200C and the yield of amide can be as high as 98%. This amide is sold in large quantities for a variety of uses. It is a hard waxy, high-melting material and can be an excellent lubricant. It is also an intermediate in the production of other derivatives, among them being the reaction of formaldehyde, pyridine, and hydrogen chloride to produce the water-proofing material, Zelan (3). Although there have been inroads on this water-proofing business, the product is still sold in large quantities.



The substituted amides that could be prepared by the reaction of fatty acids with amines are many in number. Fatty acids can be reacted with almost any primary or secondary amine to produce substituted amides.



Probably the most important of these reactions is the production of the surfactants by the reaction of fatty acids with diethanolamine (4,5) to give

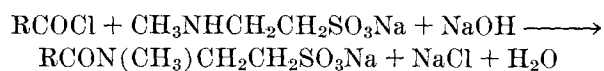


Another example of substituted amides that have become important in recent years is the polyamides formed by the reaction of dimer acids with diamines. These materials have found a great deal of use as modifiers and curing agents of epoxy resins.

Another class of amides that probably should be mentioned here is that produced by the reaction of simple primary amides with acid chlorides (6):



Of considerable commercial significance still, is the reaction product of fatty acid chlorides with n-methyltaurine. This reaction is conducted in a typical Schotten-Baumann method (7).



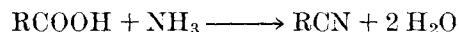
These products are, of course, the Igepons and have wide uses in the detergent field.

Another important class of substituted amides are those produced by the reaction of simple amides with ethylene oxide: $\text{RCONH}(\text{CH}_2\text{CH}_2\text{O})_x \text{H}$. Additional molecules of ethylene oxide render the amide surface-active and this leads to the usefulness of this class of material.

An interesting amido compound that is worth mentioning is the reaction product from 2 moles of primary fatty amide and 1 mole of formaldehyde to give $\text{RCONHCH}_2\text{NHOCR}$. These methylene bis-amides are very high melting, for fatty derivatives, (135-160C) and are used for binders in powder metallurgy and die lubricants.

Nitriles

The next important class of nitrogen-containing derivatives to be discussed are the nitriles. One can write the equation:



Empirically, it only takes one mole of ammonia to give one mole of nitrile. Practically, however, the reaction is carried out with a large excess of ammonia. Two methods are used today for the production of nitriles: (1) continuous vapor phase and (2) liquid batch method. In the vapor phase procedure, ammonia is blown through a pool of hot liquid fatty acid. In this part of the reaction, of course, some fatty acid is converted to amide and nitrile. As the ammonia is blown through the liquid pool, some of the fatty derivatives are vaporized and carried into the catalyst chamber containing aluminum oxide. Here the bulk of the reaction takes place and nitrile emerges as the main product.

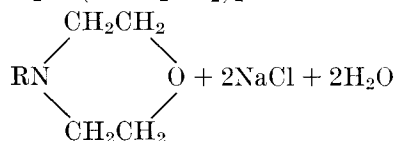
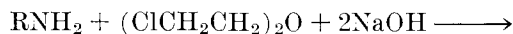
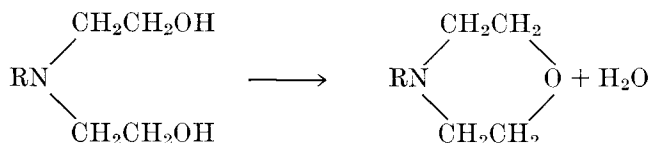
In the batch liquid phase method, the ammonia is blown through the liquid pool of fatty acid containing the catalyst, such as, manganese acetate. The reaction is continued until all of the derivatives are converted to nitrile. Both methods can produce an excellent yield of nitrile. Of course, at the temp of the reaction, some by-products can be produced. The elimination of these by-products, in many cases, gives a superior material. Nitriles themselves have found limited commercial use.

Amines

Primary Amines. While nitriles in themselves are not very important commercially, they do serve the important function in that they are intermediates in the production of fatty amines. There are two methods of producing fatty amines from nitriles: 1) catalytic reduction and, 2) chemical reduction. The latter does not enjoy any great commercial significance; however, it has the advantage of retaining all of the unsaturation of the fatty chain.

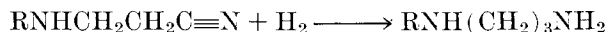
By far the most important method of producing amines from nitriles is catalytic reduction. Various catalysts can be used for this reaction. The most widely used in Raney nickel and the reaction can be conducted at pressures as low as 100 lb per square inch at 150C. There have been many modifications of this reduction and a great variety of catalysts and reduction conditions are being used. It would be presumptuous of me to judge which of them has the greatest merit. Many factors would enter into this decision. The use of relatively low temp, high pressure, alkaline conditions, and a solvent will give superior yields of primary amines (8,9).

At the present time, almost any combination of mixtures of commercially available fatty acids can be obtained in their amino derivative. There is commercially available fatty amino compounds with a purity of 99.5% in regards to primary amine content and chain length purity. In some instances, primary amines have been prepared by the reaction of alkyl



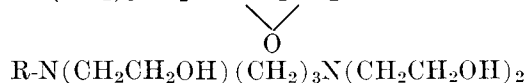
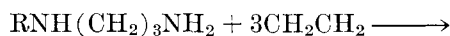
Diamines

One series of compounds that has enjoyed commercial success is the N-alkyl-1,3-propanediamines. These compounds are prepared by the addition of acrylonitrile to a fatty primary amine followed by the reductive amination of the resultant beta-cyanoethylalkylamine (12).

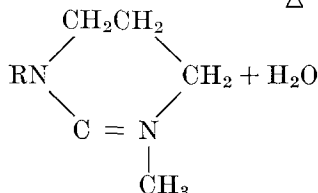
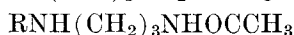
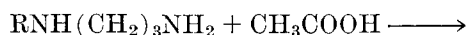


The R group in these compounds can embrace the typical fatty chains and can also include rosin acids (14).

These products have a primary and secondary amino function and both are available for any amine reactions. One series of compounds that have useful physical and chemical properties is the alkylene oxide reaction products (13). There are three reactive sites.



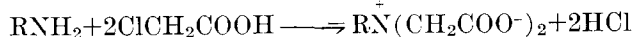
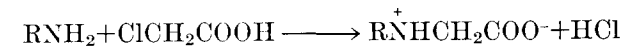
Of interest recently is a derivative of N-alkyl-1,3-propanediamine. These compounds are prepared by reaction of acids with diamines and have some interesting biological properties.



The reaction is carried on in two steps, the first is the preparation of an amide and the amide is dehydrated to form N-alkyl-3-methyl tetrahydropyrimidines.

Fatty amines are cationic in nature, form salts quite easily, and therein has the reason for other usefulness. They undergo reactions that are typical of aliphatic amines except that in this case the reaction products have the long aliphatic chain to alter physical properties.

A number of zwitterion derivatives of fatty amines are available. Primary amines may be reacted with one or two moles of chloroacetic acid to produce N-substituted glycines.



A zwitterion can also be prepared by the reaction of beta-propiolactone and primary amines (15):

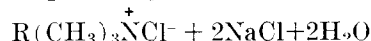
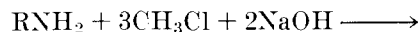


The same compounds can be prepared by the reaction of primary amines with acrylic acid. The use of crotonic acid produces a zwitterion with a methyl side-chain.

Quaternary Ammonium Compounds

The largest amount of fatty amines produced find their ultimate disposition in the preparation of "quaternary ammonium compounds." This term is applied to organic nitrogen compounds wherein the four alkyl groups are attached to the nitrogen atom through covalent bonds. Exceptions to this statement will be found in the heterocyclic nitrogen compounds wherein one of the alkyl groups may be replaced by a carbon-nitrogen double bond. A very large variety of quaternary ammonium compounds are available and their usefulness depends on the strongly positively charged nitrogen atoms.

Quaternary ammonium salts are prepared by the exhaustive alkylation of amines. Variations in amine or alkylating agents will give products of many different types. By far the most important of these types are produced by the reaction of amines with methyl chloride. This reaction is conducted in a closed vessel and gives very good yields.



The starting amine may be primary, secondary, or tertiary. Several alkylating agents are used commercially; among them are methyl sulfate, benzyl chloride, and alkyl halides. These compounds represent members of the so-called "Roccal" series.

Generally speaking, the quaternary ammonium compounds that contain one long-chain alkyl group are water soluble and highly biologically active (16). The compounds containing two long chains are not water-soluble, but are water dispersible. The largest single use for this class of materials is in the home laundry softening field. The cationic quaternaries are substantive to cotton and impart a soft "hand" to treated goods. Dimethyldihydrogenated tallow ammonium chloride (or methyl sulfate) is used almost exclusively.

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