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## Nitrogen-Containing Derivatives of the Fatty Acids

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THE chemical literature describes the application of almost all reactions of organic acids to the higher fatty acids. Among these reactions are many by means of which the nitrogen atom is introduced into the molecule. Although the present discussion will emphasize those processes which are applied commercially, many other typical reactions will be mentioned.



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Within the past two decades an important industry has developed based upon derivatives of the higher fatty acids which contain nitrogen. To a very large extent the usefulness of these products results from the properties imparted by the nitrogen atom, in combination with the hydrocarbon chain. Generally these useful properties can be described in terms of the surface activity of the

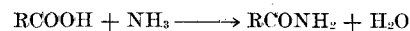
molecule. Frequent references to this property will be made throughout the following discussion.

Usually nitrogen is introduced into the fatty-acid molecule through the reaction of the carboxyl group with ammonia or amines. By this means are obtained amides and nitriles and, from these, amines and quaternary ammonium salts. Modifications and derivatives of these major classes make up the greater proportion of the material to be presented here. Methods of preparation and chemical reactions of various derivatives will be discussed. Properties and uses will be mentioned briefly.

Throughout the following discussion chemical reactions will be presented in general terms. The symbol R will be used to designate either saturated or unsaturated normal aliphatic chains.

### Amides

Simple amides are produced through the reaction of a molecule of fatty acid and a molecule of ammonia with the elimination of one molecule of water (1):



This process is employed for the commercial preparation of the higher aliphatic compounds. The fatty acids are heated in a closed vessel to a temperature of about 200° and are then subjected to a stream of ammonia gas under slight pressure; continuous venting removes excess ammonia and water as it is formed. The resulting product consists of approxi-

mately 90% amide together with small amounts of the fatty acid and fatty-acid nitrile.

In the laboratory, reaction of ammonia with esters or acid chlorides is frequently employed (2).

The simple saturated fatty-acid amides are relatively high melting crystalline solids. Their solubility in organic solvents is, in general, low (1); in water they are essentially insoluble. The high melting points and the low solubility of the amides are attributed to molecular association through hydrogen bonding.

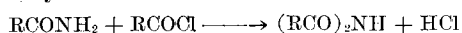
The higher saturated aliphatic amides undergo the reactions typical of this class of compounds; those derived from the more highly unsaturated fatty acids are subject to rapid deterioration when exposed to air (2). Pyrolysis of amides leads to disproportionation with formation of the corresponding fatty acid and fatty-acid nitrile (3).



Catalytic hydrogenation of amides proceeds with some difficulty to yield mixtures of primary and secondary amines (4). Lithium aluminum hydride has been employed in the reduction of amides to primary amines (5). Treatment of lauramide with aqueous alkaline hypobromite solutions leads to the formation of N-undecyl-N'-lauroylurea. However, treatment with sodium methoxide and bromine gives a high yield of methyl undecylcarbamate, which may be converted readily to undecylamine (6).

The higher aliphatic amides are used as anti-tack (to decrease adhesiveness) or anti-block (to prevent adhesion) agents, as foam stabilizers, as mutual solvents for blending of waxes with plastics, as ink additives for reducing slip and gloss, and as intermediates in the preparation of textile softeners and water repellents.

Secondary amides are prepared by the reaction of the primary amide with an acid chloride.

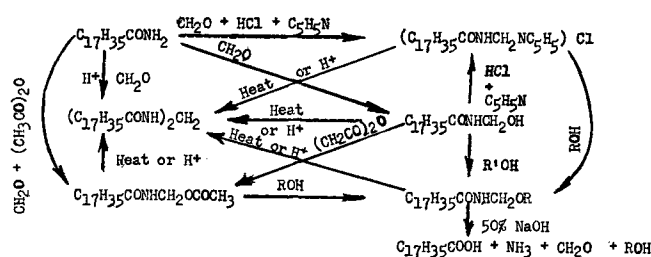


The use of distearamide as a textile water-proofing agent has been suggested.

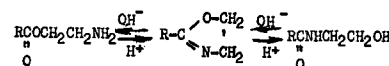
N-Substituted amides are prepared through the reaction of the fatty acid, its ester, or its chloride with amines (1, 7), or through the reaction of the simple primary amide with certain reagents. The properties of the substituted amide will depend upon the nature of the substituting group. Those derived from simple aliphatic or aromatic amines usually are waxy solids.

N-(Hydroxymethyl) (or methylol) amides are produced by the reaction of amides with formaldehyde; in the presence of acid catalysts, methylene diamides are formed. In the presence of pyridine and hydrochloric acid, amides and formaldehyde react to form the amidomethylpyridinium chloride. This class of substances is used in the application of water-repellent films to cotton fabrics. Formation of the amidomethyl ether of cellulose is postulated. Amidomethyl ethers are readily prepared by reaction of either an amidomethyl ester or the amidopyridinium chloride with an alcohol. The following scheme will illustrate these various reactions, as applied to stearamide (8).

N-(2-Hydroxyethyl) amides of the fatty acids ("ethanolamides") are produced by the reaction of fatty acids with 2-aminoethanol (ethanolamine) or 2,2'-iminodiethanol (diethanolamine). Under acid conditions the aminoethyl ester of the fatty acid is transformed to the hydroxy amide. The reaction is



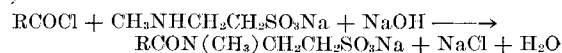
reversed under alkaline conditions. Transformation of the aminoethyl ester to the hydroxyethylamide proceeds through the oxazoline as intermediate (9).



The "ethanolamides" and "isopropanolamides" are extensively employed as foam stabilizers for synthetic detergents.

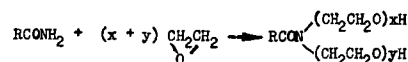
When reaction of the "ethanolamines" and fatty acids is carried out in the presence of excess amine, a mixture is produced which possesses remarkable detergent properties. The exact nature of the mixture is not known; a simple mixture of the amide and amine does not possess the desired properties, but if this mixture is heated, it becomes homogeneous and takes on these properties. This mixture forms the basis for the Ninol-type detergents (10).

A class of N-substituted fatty-acid amides which is produced commercially on a large scale, the acyl derivatives of N-methyltaurine, is marketed under the trade name Igepon. Reaction of a fatty-acid chloride with N-methyltaurine is carried out in the presence of excess aqueous caustic (Schotten-Baumann Reaction) (11).



The N-acyl-N-methyltaurines or Igepons are employed as detergents and surface-active agents. Characteristics of the product are influenced by the nature of the acyl group. The oleoyl derivative is most widely employed although recently an Igepon derived from tallow fatty acids has been offered.

Reaction of simple primary amides with ethylene oxide produces a class of nonionic surface-active agents sold under the trade name Ethomid.



Characteristics of these products can be altered by variation in the fatty-acid residues as well as in the length of the polyoxyethylene chains. Products containing 2 to 50 ethylene oxide units are produced.

### Nitriles

Fatty-acid nitriles may be produced through reaction of the acid and ammonia, with elimination of two molecules of water,



through reaction of an ester with ammonia, or through dehydration of a simple amide (3). Nitriles may also be prepared through reaction of an alkyl halide with sodium or potassium cyanide. This procedure is frequently employed in the preparation of odd-carbon homologs.

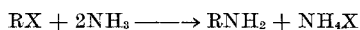
Commercially, production of nitriles is accomplished through a combined liquid vapor-phase process. Ammoniation of the fatty acid in the liquid phase results in the production of a mixture of fatty acid, amide, and nitrile. This mixture is vaporized through a catalytic bed, thereby accomplishing complete conversion to nitrile (12).

The saturated fatty-acid nitriles are liquids or low-melting solids which are very soluble in most organic solvents. Myristonitrile and lower homologs possess pungent and very distinctive odors. The compounds are reported to be non-toxic.

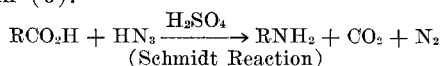
Nitriles are extremely reactive compounds. Of most importance commercially is their reduction to amines (see below). Nitriles may be hydrolyzed to produce either the corresponding amide or the fatty acid, depending upon conditions. Reaction with Grignard reagents offers a convenient method for the preparation of unsymmetrical ketones (13). Through reaction with stannous chloride and hydrogen chloride, nitriles may be converted to the corresponding aldehydes (14). In the presence of phenylethyllithiumamide, aliphatic nitriles condense to form iminonitriles (dinitriles). These may be hydrolyzed to the corresponding ketonitriles or reduced to the diamines (15).

### Amines

Amines or substituted ammonias are classified according to the number of substituent groups on the nitrogen: primary, secondary, and tertiary. Several methods are available for the preparation of higher aliphatic primary amines. These include nitrile or amide reduction, reaction of aliphatic halides with ammonia (16),

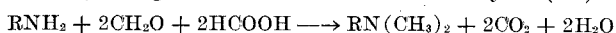


reductive amination of ketones (17), the Gabriel synthesis involving alkyl halides and phthalimide (17), and the Hofmann-Schmidt-Curtius procedures which result in the conversion of a fatty acid through its amide or azide to the amine containing one less carbon atom (6).



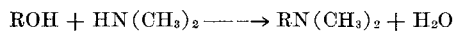
Methods which have been employed for the reduction of nitriles include catalytic hydrogenation (12) sodium reduction (18), and reduction with lithium aluminum hydride (19). In the laboratory the last two offer an advantage in that unsaturation in the hydrocarbon chain may be retained; commercially, catalytic hydrogenation is employed.

Secondary amines may be produced through the reaction of alkyl halides with ammonia (16) or primary amines, through the reduction of substituted amides with lithium aluminum hydride or directly from nitriles by catalytic hydrogenation under certain conditions. Tertiary amines containing three identical higher aliphatic groups are prepared most readily through reaction of the alkyl bromide or iodide with the secondary amine (20). A similar reaction may of course be employed for the preparation of mixed tertiary amines. *N,N*-dimethylalkylamines may be prepared from primary amines through the Leuckhart reaction, using formic acid and formaldehyde (21).

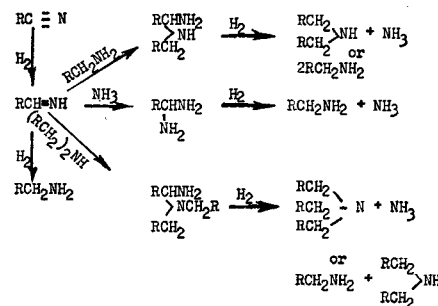


This reaction is not entirely satisfactory since yields seldom exceed 80% of the theoretical. Commercially,

dimethylalkylamines are also prepared from the higher aliphatic alcohols or chlorides and dimethylamine.



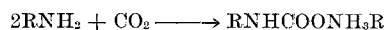
Under the conditions employed in the catalytic hydrogenation of nitriles, primary, secondary, and tertiary amines are produced; the proportions are influenced by several factors. The tendency toward higher alkylation increases with increasing temperature but decreases with increase in chain length. Above the 12-carbon chain length little if any tertiary amine is formed even at high temperatures. An atmosphere of ammonia will favor primary-amine formation as will an alkaline catalyst (22). The following reactions are among those which have been postulated as occurring during nitrile hydrogenation.



Raney nickel catalyst is employed in the commercial production of higher aliphatic primary and secondary amines. For primary amines the hydrogenation is carried out at about 150° and 200 p.s.i. Yields of about 85% primary amine are obtained. This product is purified by fractional distillation (12). For secondary amine production a temperature of 200-250° is employed.

The fatty amines are liquids or low-melting solids. The melting and solubility characteristics are intermediate between those of the fatty acid and the nitrile. The amines are weak bases; the secondary is slightly stronger than the primary or tertiary. Amines are capable of forming salts with organic and inorganic acids.

In addition to salt formation, amines undergo a wide variety of chemical reactions. Exhaustive alkylation leads to the formation of quaternary ammonium salts (see below). With carbon dioxide the amines form alkylammonium alkylcarbamates.

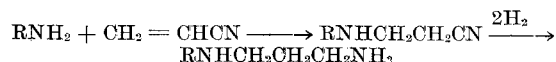


This reaction will occur on exposure to atmospheric carbon dioxide but can be reversed by heating the carbamate to a temperature of 90-100°. With carbon disulfide, primary amines are converted to alkylammonium alkyldithiocarbamates. Upon heating, these lose hydrogen sulfide to form dialkylthioureas (23). Treatment with phosgene converts primary amines to higher alkyl isocyanates (24).



With salts of heavy metals amines form coordination compounds and amine salts form double salts (25).

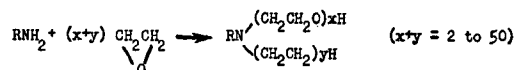
Addition of acrylonitrile to primary amines results in the formation of the *N*-(2-cyanoethyl)alkylamines. These may be reduced to the *N*-alkylpropanediamines.



These compounds are marketed under the trade name Duomeen. They exhibit unusual surface-active properties. The diamines or their salts are employed as corrosion inhibitors and asphalt anti-strip agents.

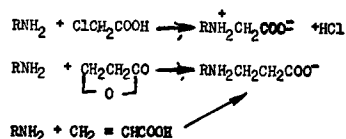
Certain mixed secondary amines may be prepared through alkylation of the N-(2-cyanoethyl)alkylamines. Pyrolysis of the resulting tertiary amine results in elimination of acrylonitrile with formation of the mixed secondary amine (26).

Like the simple amides, the primary amines react with ethylene oxide to produce polyoxyethylene derivatives.



Although containing a tertiary amino group, these substances may be regarded as nonionic surface-active agents. Here again, characteristics of the compound are determined by the lengths of the alkyl and polyoxyethylene chains. The lowest members of the series, bis-(2-hydroxyethyl)alkylamines, can be dehydrated to produce N-alkylmorpholines (27).

Primary amines may be reacted with chloroacetic acid, with *beta*-propiolactone (28), or with acrylic acid to produce alkyl amino acids. These have found some acceptance as detergents and surface-active agents.



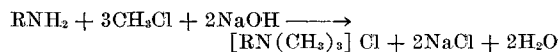
In addition to the uses as chemical intermediates which have been suggested, primary amines and their salts are finding wide application, primarily in connection with their surface-active properties. The amine salts, usually the acetates, are employed in non-metallic froth flotation. Among the separations which are accomplished using these reagents are silica from phosphate, potassium chloride (sylvite) from sodium chloride (halite), and silica from cement rock. Amines and their salts are also used as mold-releasing agents, flushing agents for pigments, anti-static agents, and germicides and fungicides.

### Quaternary Ammonium Salts

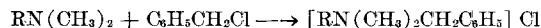
The term "quaternary ammonium compound" is applied to those organic nitrogen compounds in which four carbon atoms are directly linked to the nitrogen atom through co-valent bonds. Heterocyclic nitrogen compounds in which nitrogen is linked by two co-valent bonds and one carbon-nitrogen double bond are included. The resulting tetra-substituted ammonium ion carries a positive charge and is always associated with a negatively charged anion. This class of compounds permits an almost unlimited number of variations. Probably a wider variety of higher aliphatic quaternary ammonium salts have been reported than of any other fatty-acid derivative (see General References). Interest in these compounds centers around their surface activity whether they be applied to material surfaces or biological processes.

Quaternary ammonium salts are prepared by the exhaustive alkylation of amines or heterocyclic nitrogen compounds. The nature of the amine and the nature of the alkylating agent will determine the process employed and the characteristics of the product

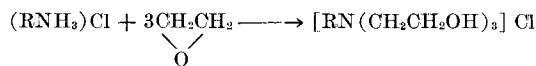
obtained. Higher aliphatic primary amines may be alkylated with simple alkylating agents, such as methyl chloride or dimethyl sulfate, thus leading to trimethylalkylammonium chlorides or methyl sulfates.



In a similar manner higher aliphatic secondary amines may be methylated to produce dimethyldi-alkylammonium salts. Tertiary amines, such as the higher aliphatic dimethylalkylamines, may be alkylated with alkyl halides in which the alkyl group differs from those present in the amine. Thus benzyl-dimethylalkylammonium chlorides are produced from dimethylalkylamine and benzyl chloride.



Heterocyclic quaternary ammonium salts are commonly prepared through the reaction of higher aliphatic alkyl halides with heterocyclic nitrogen bases. Quaternary ammonium salts containing 2-hydroxyethyl groups result from the interaction of ethylene or other alkylene oxides with amine salts.



The reaction of tertiary amines with alkyl halides has been studied extensively. This is a bi-molecular reaction whose rate is influenced by several factors including steric effects, the basicity of the amine, the activity of the halide, and the polarity of the solvent. Table I lists types of commercially available higher aliphatic quaternary ammonium salts.

TABLE I  
Commercially Available Higher Aliphatic Quaternary Ammonium Salts

General Formula	Fatty-Acid Source of Higher Aliphatic Radical
$(\text{RN}(\text{CH}_3)_3) \text{Cl}$	Lauric, Myristic, Palmitic, Stearic, Coconut, Soy, Tallow
$(\text{RN}(\text{CH}_3)_2\text{C}_2\text{H}_5) \text{Br}$	Coconut
$(\text{R}_2\text{N}(\text{CH}_3)_2) \text{Cl}$	Coconut, Tallow
$(\text{RN}(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5) \text{Cl}$	Coconut
$(\text{RN} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}) \text{Cl}$	Palmitic
$(\text{R-N} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}) \text{Br}$	Lauric

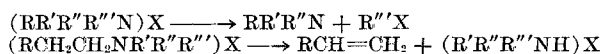
The higher aliphatic quaternary ammonium salts are usually white crystalline solids although those containing unsaturation in the higher aliphatic group are ordinarily obtained as viscous liquids. These salts are frequently deliquescent, and many form solvates with water and organic solvents. In general, they are very soluble in water and polar organic solvents and are very insoluble in non-polar solvents. The higher aliphatic derivatives containing more than one long chain are soluble in both polar and non-polar solvents.

Higher aliphatic quaternary ammonium salts are cationic surface-active agents sometimes referred to as invert soaps. The ion carrying the hydrocarbon group possesses a positive charge, and a great many of the uses of these compounds depend upon their tendency to be adsorbed on negatively charged surfaces.

Cationic surface-active agents, including both quaternary ammonium salts and amine salts, exhibit the property of aggregation or micelle formation in dilute aqueous solution. The concentration at which aggregation commences is dependent upon the length of the higher aliphatic chain as well as other factors; for simple alkyltrimethylammonium chlorides it lies between 0.000346*N* (*C*<sub>18</sub>) and 0.0228*N* (*C*<sub>12</sub>). At higher concentrations gels and liquid-crystalline phases are formed (29).

The quaternary ammonium ion is usually associated with the anions of common acids: halides, sulfates, etc. The hydroxide may be prepared by treating the halide with silver oxide or alcoholic potassium hydroxide, or through the use of ion-exchange resins. Although stable in solution, attempts to isolate the free base result in decomposition.

Quaternary ammonium salts are sensitive to heat. The halides dissociate into tertiary amines and alkyl halides or decompose into olefins and tertiary-amine salts.



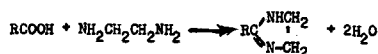
Both reactions may proceed simultaneously and accurate generalizations are not possible; the course of the decomposition is determined by the nature of the substituent groups. Where possible, ethylene or trimethylamine will be one of the products.

The higher aliphatic quaternary ammonium salts are among the most potent germicides and fungicides. A very large number have been synthesized and evaluated with respect to germicidal activity. Variation among test methods makes it difficult to generalize on the effect of structure on germicidal activity. In general, it can be said that this activity is maximum in those compounds containing the 16- or 18-carbon chain. The quaternary ammonium germicides are finding wide application in the food industry and medical fields although their use is not permitted where food contamination is possible.

These salts react with proteins, probably through ionic interaction with anionic sites on the protein. The quaternary ammonium ion will form a complex with the mineral bentonite. A complex of this type is employed as a thickening agent in the lubricant "Bentone" grease.

### Miscellaneous Nitrogen-Containing Derivatives

A number of other nitrogen-containing derivatives of fatty acids have received sufficient attention to justify mention. All are cationic surface-active agents. Alkylglyoxalidines (imidazolines) are prepared by the reaction of fatty acids with ethylenediamine or its derivatives.



Compounds of this type are now offered as plant fungicides. Similarly higher aliphatic 2-alkylbenzimidazoles are prepared by the reaction of fatty acids with *o*-phenylenediamine. Higher aliphatic amidines are prepared from nitriles via iminoethers (30). Higher aliphatic hydrazines are prepared from alkyl halides and anhydrous hydrazine. These may be alkylated with alkyl halides to form hydrazoneium salts (31). Like the quaternary ammonium salts, these compounds exhibit high germicidal activity.

Isothiouonium salts are produced through the reaction of higher aliphatic halides with thiourea (32).

Introduction of amino groups into the fatty acid hydrocarbon chain has been undertaken in connection with work on polyamide type polymers. Usually introduction of these groups has been accomplished through reaction of the halogen-substituted acid (usually substituted in the 2 position) with ammonia or amines (33).

Recently a preparation has been described involving the addition of nitriles to oleic acid. Hydrolysis of the resulting amido acids yields the corresponding 9- (or 10-) amino acid (34).

The foregoing brief review of the chemistry of the more important nitrogen-containing derivatives of the fatty acids will perhaps serve to indicate the versatility of this class of compounds. The industry which is based upon these chemicals is becoming an important factor in the effort to upgrade fats. Although one hesitates to predict what the future holds, from the point of view of the organic chemist the story is by no means complete.

Among all applications of fatty chemicals a need for greater selectivity and greater specificity has become evident. That these objectives can be attained has been demonstrated in more than one instance through empirical methods. The more scientific approach to the problem through studies of the relation of structure to specific properties offers a fascinating challenge. The wide variety of nitrogen-containing derivatives of the fatty acids which are potentially available makes this field especially attractive for scientific research at all levels. We can confidently expect such research to lead to continuing benefits to the fat and oil industry specifically and thus indirectly to industry as a whole.

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## Fatty Alcohols

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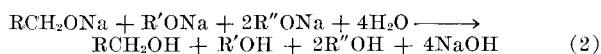
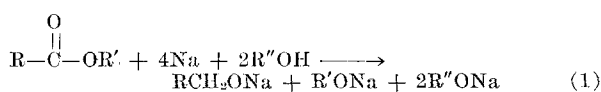
THROUGH an oversight, deliberate or accidental, Nature has left a rather wide gap in the oxidative chain from hydrocarbon to fatty acid. Compared with the almost unlimited quantities of hydrocarbons and fatty acids available, the fatty alcohols are found in rather limited quantities, occurring in the free or combined state only in certain animal, vegetable, and mineral waxes. Even in these, certain members of the homologous series of fatty alcohols are conspicuously absent, or present only in extremely small quantities.



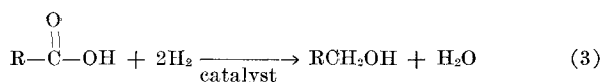
G. R. Wilson

As early as 1883 (1) researchers were attempting to fill these gaps in the homologous series of fatty alcohols by tedious and many-step syntheses, which were complicated by undesirable side reactions and very low yields. The first satisfactory laboratory

synthesis of fatty alcohols, starting with readily available raw materials, was discovered in 1903 by Bouveault and Blanc (2). Their procedure utilized the combined reductive action of sodium and ethanol toward an ester grouping, according to Equations 1 and 2.



Bouveault and Blanc's discovery remained a laboratory procedure for some 30 years. Near the end of this period, in the 1930's, a second and equally important reductive process for the preparation of fatty alcohols was discovered—hydrogenolysis (3). This method involves the high-temperature, high-pressure reduction of fatty acids, esters, or salts with hydrogen in the presence of a catalyst as in Equation 3.



Modified and improved, these two processes constitute the two major industrial methods for the current

production of fatty alcohols used in the preparation of synthetic detergents. A third method, not as important tonnage-wise, is the alkaline saponification of sperm oil, which yields a mixture of cetyl, stearyl, and oleyl alcohols. Present annual production of fatty alcohols (by sodium reduction and hydrogenolysis) is estimated at 130 million pounds, with the sodium-reduction route accounting for nearly 80% of this total.

### Hydrogenolysis versus Sodium Reduction

Since details for the preparation of fatty alcohols by hydrogenolysis or sodium reduction are found in the chemical and patent literature (4, 5), only the basic fundamentals of operation will be presented here, to point out differences, special problems that exist, and their solutions.

*The Sodium-Reduction Process.* The basic steps of the sodium-reduction process are diagrammed in Figure 1. All operations are conducted at atmospheric

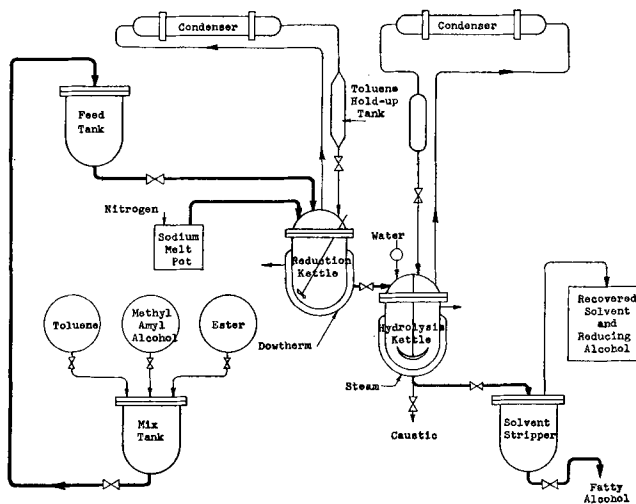


FIG. 1. Process flow sheet ester reduction unit.

pressure in conventional mild-steel reactors. A solution of ester, reducing alcohol, and solvent (in the correct proportions) is fed into a reactor containing metallic sodium suspended in a solvent (inert to sodium). An exothermic reaction occurs, yielding a solution of sodium alcoholates. This solution of alcoholates is then fed into a reactor containing water, resulting in hydrolysis of the alcoholates and the formation of a two-phase system—an organic layer (consisting of solvent, reducing alcohol, and fatty alcohol)