Nitrogen Derivatives (Secondary and Tertiary Amines, Quaternary Salts, Diamines, Imidazolines)

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ABSTRACT

A discussion of these five nitrogen derivatives of fatty acids is given in regards to the chemistry of their production and some of the reaction conditions. Also covered are some of the applications and properties of these derivatives.

The symmetrical secondary amines have been commercially available for some time and processes were being patented in the early 1940s (1). These products result from the catalytic hydrogenation of nitriles under controlled conditions. Generally speaking, the reaction is done at ca. 200 C and at above atmospheric pressure. The basic operation is a reaction of hydrogen with a nitrile to form a primary amine and then the subsequent reaction of two primary amines to form a secondary amine and liberate ammonia. There have been many theories postulated about the mechanism of this reaction, but most likely there is an intermediate imine formed (2) during the nitrile hydrogenation step.

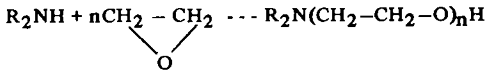
The reaction conditions required for secondary amines are high temperature, some hydrogen pressure, and the proper catalyst. High temperature is required to convert the primary amine to secondary amine, and the reaction is run at anywhere from ca 150 C up to ca. 230 C. The ammonia that is formed must be removed from the reaction in order that it not inhibit the secondary formation. This can be done in a variety of ways, but the two most frequently mentioned are continuous venting of the hydrogen or alternating pressuring with venting of the hydrogen (3). It is necessary to have hydrogen present at all times or degradation occurs leading to high levels of nonamine.

The catalyst used can be any one of a variety of active metal catalysts: nickel, cobalt, copper-chromium, the noble metals, etc. The choice of catalyst is determined by the product being made, the nitrile being used, economics, etc. Nickel catalysts are most widely used commercially, and generally speaking the copper-chromite catalyst is used to retain carbon to carbon unsaturation.

The secondary amines find most of their use as chemical intermediates. They have been the basic source of the difatty dimethyl quaternary ammonium chloride that is used in many areas that I will discuss later. The secondary amines have been used as ingredients of various textile aids and chemical intermediates for a variety of industrial compounds.

The secondary amines, as are all the fatty amines, are cationic and alkaline in nature leading to various possible chemical and physical reactions. Some of the reaction possibilities of secondary amines are:

With ethylene oxide:



$$R_2NH + nCH_2-CH_2 \; --- \; R_2N(CH_2-CH_2-O)_nH$$

With alkyl halides:

$$R_2NH + R'X \rightarrow R'R_2N + H_x$$

$$R_2NH + 2R'X \rightarrow [R'_2R_2N]^+X^- + HX$$

With acids:

$$R_2NH + HX \rightarrow R_2NH \cdot HX$$

$$R_2NH + HNO_2 \rightarrow R_2N - NO + H_2O$$

The reaction with nitrous acid is depicted here to show that secondary amines can afford nitrosamines under certain conditions.

There are many other reactions that have not been listed. The secondary amines can be as varied as the fatty acids used to make them.

Tertiary amines comprise a wider variety of products than the secondaries since there are more possibilities of what can be put on the nitrogen atom. There are commercially available symmetrical tertiary amines or trifatty amines and unsymmetrical tertiaries which consist of methyl difatty amines and dimethyl monofatty amines. As in the secondary amines, these various tertiaries can be made from any of the available fatty acids that can be converted to a nitrile since they too are made from the fatty nitriles.

The symmetrical tertiary amines are essentially a further catalytic hydrogenation product of nitriles. In simplified form, a nitrile is hydrogenated to a primary amine, two primaries react to give a secondary with liberation of ammonia, and then another primary reacts with the secondary and forms the tertiary with liberation of ammonia. The reaction is actually a series of reactions through intermediate imines during the reaction (3).

These trifatty amines are prepared much like the difatty secondaries in that they are made at high temperatures, low hydrogen pressures, and usually with a nickel catalyst.

An alternative method for making the trifatty tertiary amines is one in which the symmetrical secondary amine formed in the usual manner is reacted with a fatty alcohol with liberation of water (4). This reaction is carried out at the same high temperature of 180 C to 250 C and higher pressures in the range of 100 to 200 psig.

The basic products in commercial production are the trifatty tertiaries of short chain fatty acids in the C_8 and C_{10} range and the hydrogenated tallow fatty acids. They are primarily used in ore flotation.

The unsymmetrical tertiary amines are composed of methyl difatty tertiaries and dimethyl monofatty tertiary amines. These are both produced commercially by the reductive alkylation of either a primary or secondary amine using a nickel catalyst and formaldehyde or its polymers (5). The reactions as shown below show a primary amine reacting with two moles of formaldehyde and two moles of hydrogen to yield a dimethyl alkyl amine and water and a secondary amine reacting with one mole each of formaldehyde and hydrogen to give a methyl dialkyl amine and water:

$$RNH_2 + 2HCHO + 2H_2 \xrightarrow{cat.} RN(CH_3)_2 + 2H_2O$$

$$R_2NH + HCHO + H_2 \xrightarrow{cat.} R_2NCH_3 + H_2O$$

These reactions require moderate temperatures and pressures and usually require nickel catalyst.

Two additional methods that are used for making dimethyl alkyl amines commercially are:

$$RX + (CH_3)_2NH \rightarrow RN(CH_3)_2 + HX$$

$$RC{\equiv}N + (CH_3)_2NH + 2H_2 \xrightarrow{cat.} RCH_2N(CH_3)_2 + NH_3$$

The first is the reaction of a fatty halide with dimethyl amine giving the dimethyl alkyl tertiary and an acid (6). These are made from either the chloride or the bromide. The other method is the reaction of a fatty nitrile with dimethyl amine and hydrogen in the presence of a nickel catalyst to give dimethyl alkyl amine and ammonia (7).

The tertiary amines have many industrial uses such as corrosion inhibitors, fuel oil additives, bactericides, fungicides, pigment grinding, ore flotation, cosmetic ingredients and intermediates to many other chemical compounds, as well as catalysts for certain polymerization reactions. They are very versatile chemicals and undergo many chemical reactions such as with halides, peroxides, chloroacetic acid and ethylene oxide.

The next class of amines are the so-called diamines, the N-alkyl 1,3 propylene diamines. These are the hydrogenated reaction product of primary amines and acrylonitrile (8). This class of amines is prepared in a two-step operation:

$$RNH_2 + CH_2{=}CH{-}C{\equiv}N \rightarrow RNHCH_2CH_2C{\equiv}N$$

$$RNHCH_2CH_2C{\equiv}N + 2H_2 \xrightarrow{cat.} RNHCH_2CH_2CH_2NH_2$$

$$RNH_2 + 2CH_2{=}CH{-}C{\equiv}N \rightarrow RN(CH_2CH_2C{\equiv}N)_2$$

$$RN(CH_2CH_2C{\equiv}N) + 4H_2 \xrightarrow{cat.} RN(CH_2CH_2CH_2NH_2)_2$$

The first step is formation of the acrylonitrile adduct of the primary amine. The reaction can be done in almost any agitated system, but water and short chain alcohols act as catalysts for the reaction to help it proceed more smoothly and go to completion more readily. The cyanoethylated amine is then catalytically hydrogenated to convert the nitrile group to a primary amine. This hydrogenation is basically the same as described by Reck in the preceding paper when he covered primary amines. That is, the hydrogenation is made with a partial pressure of ammonia and possibly the use of water or alkali to retard the formation of secondary amines. The resultant product then has two amine functional groups, one primary amine at the end and one secondary amine within the chain. Thereby the name "diamine." This reaction of acrylonitrile with a primary amine can be carried further and afford two moles of acrylonitrile added to the primary amine and this adduct hydrogenated to give a product with two primary amine functional groups and one tertiary functional group (9).

These products are cationic in nature and have all the reaction potential of the primary amines as well as the secondary amines. They can react with acids, alkyl halides, ethylene oxide, and formaldehyde. As with other amines, there are a myriad of reaction possibilities.

The diamines have found very large markets in the mining industry as flotation agents because of their cationic nature and their specificity for certain ores. They have also found large usage in the paving industry as cationic emulsifiers for asphalts. They have been used as fuel oil additives, fabric softeners, carburetor deicers, germicidal products and as many other commercial products.

The next type amine, probably the largest volume class produced, is the quaternary amine. These amines are salts, but there are a variety of types depending on the amine and the quaternizing agent used. Some of the major quaternization reactions are:

Secondary amine plus methyl chloride:

$$R_2NH + 2CH_3Cl + NaOH \rightarrow [R_2N(CH_3)_2]^+ Cl^- + NaCl + H_2O$$

Tertiary amine plus methyl chloride:

$$R_2NCH_3 + CH_3Cl \rightarrow [R_2N(CH_3)_2]^+ Cl^-$$

Primary amine plus methyl chloride:

$$RNH_2 + 3CH_3Cl + 2NaOH \rightarrow [RN(CH_3)_3]^+Cl^- + 2NaCl + 2H_2O$$

Tertiary amine plus methyl chloride:

$$RN(CH_3)_2 + CH_3Cl \rightarrow [RN(CH_3)_3]^+Cl^-$$

Tertiary amine plus benzyl chloride:

$$RN(CH_3)_2 + C_6H_5CH_2Cl \rightarrow [RN(CH_3)_2CH_2C_6H_5]^+Cl^-$$

Tertiary amine plus dimethyl sulphate:

$$RN(CH_3)_2 + (CH_3)_2SO_4 \rightarrow [RN(CH_3)_3]^+ CH_3SO_4^-$$

Ethoxylated amine plus methyl chloride:

$$RNH(CH_2CH_2O)_nH + CH_3Cl \rightarrow [RNH(CH_2CH_2O)_nHCH_3]\ Cl^-$$

Diamine plus methyl chloride:

$$RNH(CH_2)_3NH_2 + 5CH_3Cl + 3NaOH \rightarrow$$
$$[RN^+(CH_3)_2(CH_2)_3N^+(CH_3)_3]\ 2Cl^- + 3NaCl + 3H_2O$$

A secondary amine can be reacted with methyl chloride in the presence of an alkali, which can be any one of many, but the predominant ones are sodium hydroxide and sodium bicarbonate. The product is a dimethyl dialkyl quaternary ammonium chloride plus one mole of salt. The required alkali can be added at the beginning of the reaction or can be metered in as the reaction progresses to neutralize the hydrochloric acid as it forms (10).

Another way to make the same product is to start with a dialkyl tertiary amine and react with methyl chloride and get the product without the formation of salt. Usually some alkali is used in this reaction because there will be some secondary amine present, and some of the methyl chloride will hydrolyze during the reaction giving some hydrochloric acid to be neutralized.

The same reaction occurs with a primary amine and methyl chloride to give a trimethyl alkyl quaternary ammonium chloride, but the large quantities of salt generated make it somewhat of a cumbersome reaction. This same product can be made by reacting a dimethyl alkyl amine with methyl chloride using a small amount of alkali.

Another large class of quaternary amines are the benzyl dimethyl alkyl quaternary ammonium chlorides. These are made by the reaction of dimethyl alkyl amines with benzyl chloride. As in the methyl chloride reaction, it is an addition reaction and requires only a small amount of alkali, if any, to control the pH.

All of these quaternary amine reactions are generally done in an alcohol-water solvent (usually isopropanol), and the products marketed as either a 75% or 50% active material.

Another major quaternary amine is produced by the direct reaction of dimethyl tertiary amine with dimethyl sulphate and is usually reacted without a solvent.

A somewhat different type quaternary amine can be made from the reaction of an ethoxylated amine with methyl chloride, as shown, or with any other quaternizing agent. These are of somewhat smaller volume than some of the ones mentioned above.

All of the products described above can be made from any fatty acid available, and there are a multitude of them made and sold in commercial quantities. The reaction conditions vary somewhat depending on the particular

TABLE I

Melting Point of Fatty Amines from Hydrogenated Tallow Acids

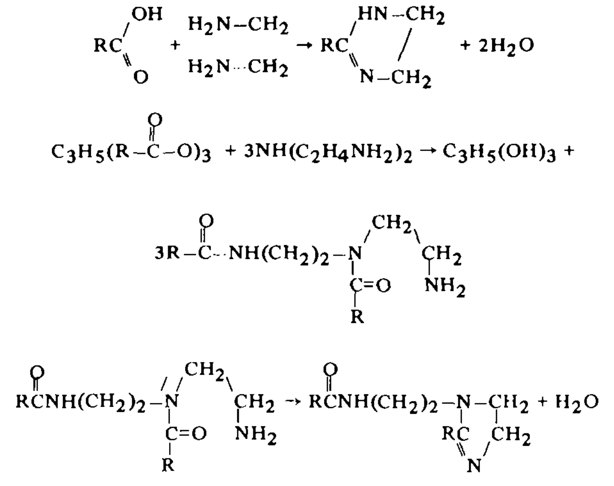
Amine	°C
Symmetrical secondary	68
Difatty monomethyl tertiary	42
Dimethyl monofatty tertiary	18
N Fatty 1,3 propylene diamine	49
Dimethyl difatty quaternary (75% active)	32
Benzyl dimethyl mono fatty quaternary (75% active)	15

product being made and the specific process being utilized. Generally, the temperature will be in the range of 80–110 C and the pressure will be whatever is generated by the solvent and the quaternizing agent. The amount of alkali used will essentially be dependent upon the starting amine and the quaternizing agent.

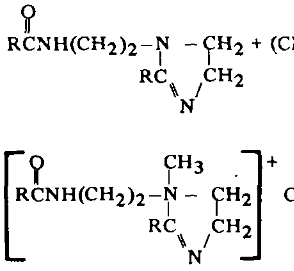
The quaternized diamines have been getting some attention. I have shown above the reaction of a diamine with methyl chloride, but consider the fact that the diamine can be ethoxylated or reacted with formaldehyde prior to quaternization and could be quaternized with reagents other than methyl chloride (11).

The quaternary amines are used in many different industries for many different uses: as fabric softeners, as corrosion inhibitors, as aids in sugar refining, in various hair care products, as reactants in specialty greases, and in down-well additives.

The next class of compounds are the imidazolines. These products, as differentiated from the previous ones covered, are not made from fatty nitriles, but by the reaction of fatty acids or glycerides with various diamines or substituted diamines (12). Several types of imidazolines are shown below:



The reaction of a fatty acid with ethylene diamine goes through an amide stage and then to a 2-imidazoline. The ring closure requires higher temperatures, in the range 200–300 C. Another reaction as shown here is with tallow glyceride and diethylene triamine. The reaction gives the diamide and glycerine, and with increased temperature, the diamide cyclizes to form the imidazolene. This same reaction can be carried out with fatty acids in place of the glyceride to yield the same product without the glycerine byproduct. The glycerine from the triglyceride reaction can be left in the reaction mix or can be stripped out. The final imidazolines can also be quaternized as other tertiary amines. The reaction of an imidazoline from diethylene triamine and a fatty acid being quaternized with dimethyl sulphate is:



These products, as tertiary amines, quaternize in much the same manner as do the various tertiary amines discussed earlier; i.e., the reaction is performed in isopropyl alcohol and water at a moderate temperature and usually with a small amount of alkali present. The imidazolines have found uses as fabric softeners, either alone or in conjunction with other quaternary amines, as corrosion inhibitors, as surfactants, as demulsifying agents, and as ampholytic detergents among other uses. The physical characteristics of these fatty amines vary considerably by type. Using one fatty acid base, hydrogenated tallow acids as an example, the melting points as shown in Table I have a wide spread of over 50 C. Of course, the quaternary products are low in melting point because they are in an alcohol-water solvent. The actual quaternary salts have melting points much higher than any of the amines, as would be expected.

Another area of difference is in the solubilities of these amines. Solubilities in isopropanol and in benzene are shown in Table II. At higher temperatures, generally above their melting points, all of the amines are very soluble.

The figures given are for only one product in each type of amine. The melting point and solubilities are affected by the different fatty acid base stock used. The longer chain fatty acids give higher melting points and somewhat lower solubilities, and the unsaturated fatty acids give lower melting points and increased solubilities.

The whole area of fatty amine chemistry is an open ended story. Over the last forty years, these products have been developed, improved, and characterized to the point

TABLE II

Solubility of Fatty Amine from Hydrogenated Tallow Acids in Isopropanol and Benzene (g/100 ml,

	In Isopropanol			In Benzene		
	10 C	30 C	60 C	10 C	30 C	60 C
Symmetrical secondary	1	10	<50	4	7	<100
Difatty monomethyl tertiary	<1	<10	>100	>75	>100	>100
Dimethyl monofatty tertiary	>100	>100	>100	>100	>100	>100
N Fatty 1,3 propylene diamine	<10	20	<100	2	50	<100
Dimethyl difatty quaternary (75% active)	<1	>100	>100	1	25	>100
Benzyl dimethyl monofatty quaternary (75% active)	<100	>100	>100	>100	>100	>100

where they are a solid part of a variety of commercial operations. They have found their way into many operations and are finding new and varied uses in industry daily. I feel the future for fatty amines is almost unlimited. They are such a wide variety of compounds because of the extreme number of possibilities available in the fatty acid sources, because of the many chemical reactions that can be made, and because of their particular cationic nature. Ask questions such as:

What chemistry do I need and can a fatty amine perform all or part of it?

What surface do I need modified and will a cationic chemical modify it?

What effect do I need to have in a particular cationic chemical and will a certain homolog distribution accomplish it?

What new chemical can I prepare with a fatty amine as a starting material?

How can I improve the quality or yield of any of the fatty amine products?

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Synthetic Fatty Acids

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ABSTRACT

Manufacture of fatty acids from petroleum and natural gas is a large industry worldwide and has important implications in the U.S. Eastern Europe produces an estimated 1.2 billion pounds by air oxidation of hydrocarbons compared to an estimated 956 million pounds of natural fatty acids from the U.S., in 1978 (exclusive of tall oil fatty acids). The enormous production of SFA's in Eastern European countries and in Russia is done by continuous air oxidation of fresh and recycled mixed aliphatic hydrocarbons. Since the products contain proportions of odd-numbered straight chain acids, they have not been used edibly, but have been applied to the manufacture of industrial products such as soap, lubricants, plasticizers and the like. Another European approach (Liquichimica, Italy) for SFA is the caustic fusion (and oxidation) of branched chain alcohols produced by carbonylation and reduction of olefins. American potential technology is diversified but has not yet been translated to production scale, presumably because of the plentiful supply of natural fats and oils that is available.

Synthetic fatty acids have indeed come of age. The USSR has a very large, thriving synthetic acid industry. France and Germany have important businesses. Italy has a large development. The U.S. does produce many synthetic acids and also does make many derivatives—synthetic alcohols and nitrogen derivatives, for example, that formerly required fatty acids.

In general, synthetics resemble (natural) acids in having at least two major factors in common: both classes are very dependent on byproducts of other industries and both are very energy dependent. Agrichemicals are unique in that their feedstocks are annually renewable. However, agriculture itself is very heavily dependent on petroleum and gas, using in excess of 17% of all the energy consumed in the U.S.

Farmers who raise cattle and hogs need animal feed, the growing of which depends on fertilizers from natural gas. They also need gasoline to run planting and harvesting equipment. The equipment used in agriculture requires large investments in energy: twenty percent of the cost of the steel alone is energy dependent. Food processors also depend on gasoline and fuel oil, all petroleum-derived. In contrast, the whole petrochemical industry uses only 6% of the petroleum and gas consumed in the U.S.—probably only about 5% of total U.S. energy if coal is included—and makes ca. 50 MM tons of primary petrochemicals.

Let's at this point review the current fatty acid industry to set the stage for evaluating synthetics. The agrichemical acids produced in 1978 are shown in Table I. Unsaturated acids (oleic plus tall oil acids) total ca. 58% of the production; coconut fatty acids ca. 9%. Since ca. 85% of natural acids are byproducts of other operations, this means that they will probably be produced and sold at any price, at least until other uses are found for tallow and tall oil. Much of the time, therefore, acids are sold as commodities.

Synthetics would use considerably lower percentages of their raw materials than naturals if produced in equal quantities. Total acids being ca. 600,000 tons requiring ca. 600,000 tons of ethylene, propylene, and paraffin waxes of which over 18,182,000 tons were produced in 1978. Thus, only 3.2% of these raw materials would be needed to replace all natural acids.

Now, what is the commercial status of synthetic fatty acids?

The commercially available petrochemical acids are shown in Table II. About 50,000 tons are commercial in the U.S. now and over 500,000 tons in the USSR and