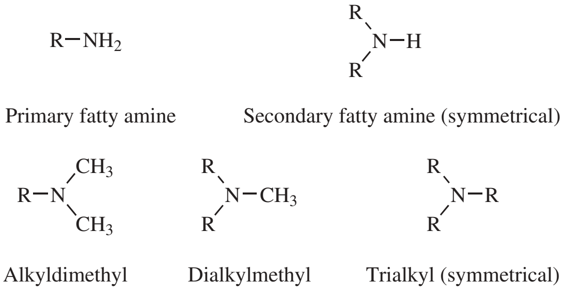
AMINES, FATTY

1. Introduction

Fatty amines are nitrogen derivatives of fatty acids, olefins, or alcohols prepared from natural sources, fats and oils, or petrochemical raw materials. Commercially available fatty amines consist of either a mixture of carbon chains or a specific chain length from C_8–C_{22}. The amines are classified as primary, secondary, or tertiary depending on the number of hydrogen atoms of an ammonia molecule replaced by fatty alkyl or methyl groups (Fig. 1). The amino nitrogen is most frequently found on a primary carbon atom, but secondary and tertiary carbon substitution derivatives have been made and are commercially available. Fatty



Primary fatty amine Secondary fatty amine (symmetrical)

Alkyldimethyl Dialkylmethyl Trialkyl (symmetrical)

Tertiary fatty amines

Fig. 1. Types of commercially available fatty amines. $R = C_8 - C_{22}$.

Table 1. **Typical Fatty Acid Composition**

	Fat		Fatty oils		
Fatty acid[a], %	Tallow	Coconut	Soya	Palm kernel	Palm
caproic (C6:0)		1.2		<0.5	
caprylic (C8:0)		3.4–15.0		2.4–6.2	
capric (C10:0)		3.2–15.0		2.6–6.2	
lauric (C12:0)		41–56		41–55	
myristic (C14:0)	3.0	13–23	0.9	14–20	1
palmitic (C16:0)	29.2	4.2–12.0	7–12	6.5–11.0	43.5
stearic (C18:0)	19.1	1.0–4.7	2.0–5.5	1.3–3.5	4.5
oleic (C18:1)	43.6	3.4–12.0	20–50	10–23	40
linoleic (C18:2)	2.1	0.9–3.7	35–60	0.7–5.4	
linolenic (C18:3)	0.5		2–13		
other	2.5				11

[a] The number of carbon atoms and number of double bonds are designated in parentheses.

amines are cationic surface-active compounds (see SURFACTANTS), which strongly adhere to surfaces by either physical or chemical bonding, thus modifying surface properties. Important commercial products are prepared using fatty amines as reactive intermediates.

Commercially available fatty amines are most frequently prepared from naturally occurring materials (see FATS AND FATTY OILS) by hydrogenation of a fatty nitrile intermediate using a variety of catalysts (1–3). Naturally occurring fats and oils (triglycerides) are continuously hydrolyzed at 200–280°C to yield saturated and unsaturated fatty acids and glycerol. Fatty nitriles are prepared from fatty acid mixtures by batch or continuous processes. The alkyl chain-length composition of the amines varies depending on the type of fat or oil. Other factors influencing alkyl chain composition include location of source, time of harvest, and, more recently, hybridization. Typical compositions for various fats and oils used to prepare commercially available fatty amines are given in Table 1 (4–8).

Fatty amines derived from fats and oils, containing several carbon-chain-length moieties, are designated as such by common names which describe these mixtures: tallowalkylamines [61790-33-8], cocoalkylamines [61788-46-3], and soyaalkylamines [61970-18-9], for example. High purity fatty amines are also commercially available. These amines are prepared by distillation of either the precursor fatty acid or amine product mixture. There are common names for single chain-length fatty amines in addition to IUPAC nomenclature, which uses the alkyl chain length in naming the amine. Secondary and tertiary amines have been named as primary amine derivatives, for example, *N*-hexadecyl-1-hexadecylamine instead of di-*n*-hexadecylamine (IUPAC). Examples include:

Common name	IUPAC name	Molecular formula	CAS Registry Number
laurylamine	1-dodecylamine	$C_{12}H_{27}N$	[124-22-1]
palmitylamine	1-hexadecylamine	$C_{16}H_{35}N$	[143-27-1]
stearylamine	1-octadecylamine	$C_{18}H_{39}N$	[124-30-1]
oleylamine	1-octadecen-9-ylamine	$C_{18}H_{37}N$ (unsaturated)	[112-90-3]

Trade names are commonly used for commercial products.

In the former USSR and Europe, synthetic fatty acids, prepared via hydrocarbon oxidation, have been used to prepare fatty amines (2,9).

Fatty alcohols, prepared from fatty acids or via petrochemical processes, aldol or hydroformylation reactions, or the Ziegler process, react with ammonia or a primary or secondary amine in the presence of a catalyst to form amines (10–12).

In addition to the nitrile and alcohol routes just described, many other methods of preparation of fatty amines are available. Some commercially available tertiary fatty amines are prepared via a petrochemical route (13). The amines have been prepared by reaction of an olefin with ammonia or a primary or secondary amine in the presence of a catalyst prepared from a Group 8–10 metal or an ammonium halide (14–16). Nitration of paraffins having from 6 to 30 carbon atoms with nitrogen dioxide at elevated temperatures followed by hydrogenation in the presence of a nickel or palladium catalyst produces secondary alkyl primary amines (17–20). Long-chain, unbranched, aliphatic tertiary amines can be prepared by reaction of an alkyl chloride with an alkyl secondary amine at 100–250°C (21,22). Other methods of producing amines include reaction of a carboxylic acid ester with a secondary amine in the presence of hydrogen at high pressure using a metal oxide catalyst, zinc oxide–chromium oxide or zinc oxide–aluminum oxide (23), or by catalytic hydroammonolysis of carboxylic acids at high pressure and temperature in the presence of a mixture of sulfides of metals of Groups 6 and 8–10 (24). The Hofmann rearrangement, preparation of an amine from an unsubstituted amide using solutions of chlorine in sodium hydroxide, has been useful in preparing long-chain primary amines (25). Amines prepared using the Hofmann rearrangement contain one less carbon atom than the amide. Thus, odd-chain-length fatty amines, not available from natural sources, can be prepared. The Ritter reaction of olefins with hydrogen cyanide in the presence of a strong acid, after hydrolysis, produces tertiary-alkyl primary amines. Rohm and Haas Primene amines are prepared using the Ritter reaction.

2. Physical Properties

Data on physical properties of fatty amines have been well documented and summarized in many reference works on fatty acids and nitrogen derivatives (3,8,13,26–29). Table 2 lists melting point data of some commercially available primary, secondary, and tertiary fatty amines, and it is evident that: (*1*) melting points within a homologous series of single-chain-length fatty amines increase with molecular weight, (*2*) symmetrical secondary amines have a higher melting point than the primary amine of the same alkyl group, but are lower melting than a primary amine with the same number of carbon atoms (hydrogen bonding), (*3*) symmetrical tertiary amines are lower melting than a symmetrical secondary amine of the same alkyl group, (*4*) symmetrical tertiary amines are lower melting than a primary or secondary amine containing the same number

Table 2. **Melting Points of Fatty Amines**

Amine	Molecular formula	CAS Registry Number	Mp, °C
Primary amines			
cocoalkylamines		[61788-46-3]	16.0
1-dodecylamine	$C_{12}H_{27}N$	[124-22-1]	28.0
1-hexadecylamine	$C_{16}H_{35}N$	[143-27-1]	46.2
1-octadecylamine	$C_{18}H_{39}N$	[124-30-1]	53.0
oleylamine	$C_{18}H_{37}N$	[112-90-3]	21.0
soyaalkylamines		[61970-18-9]	29.0
tallowalkylamines		[61790-33-8]	40.0
hydrogenated tallowalkylamines		[61788-45-2]	55.0
Secondary amines			
dicocoalkylamines		[61789-76-2]	43.0
di-*n*-dodecylamine	$C_{24}H_{51}N$	[3007-31-6]	47.0
di-*n*-hexadecylamine	$C_{32}H_{67}N$	[16724-63-3]	67.0
di-*n*-octadecylamine	$C_{36}H_{75}N$	[112-99-2]	72.3
ditallowalkylamines		[68783-24-4]	55.0
dihydrogenated tallowalkylamines		[61789-79-5]	62
Tertiary amines			
Alkyldimethyl			
cocoalkyldimethylamines		[61788-93-0]	−22
dimethyl-*n*-octylamine	$C_{10}H_{23}N$	[7378-99-6]	−57
dimethyl-*n*-decylamine	$C_{12}H_{27}N$	[1120-24-7]	−35
dimethyl-*n*-dodecylamine	$C_{14}H_{31}N$	[112-18-5]	−15
dimethyl-*n*-tetradecylamine	$C_{16}H_{35}N$	[112-75-4]	−6
dimethyl-*n*-hexadecylamine	$C_{18}H_{39}N$	[112-69-6]	8
dimethyl-*n*-octadecylamine	$C_{20}H_{43}N$	[124-28-7]	21
dimethyloleylamine	$C_{20}H_{41}N$	[28061-69-0]	−10
Dialkylmethyl			
di-*n*-decylmethylamine	$C_{21}H_{45}N$	[7396-58-9]	−6.3
dicocoalkylmethylamines		[61788-62-3]	−2
dihydrogenated tallowalkylmethylamines		[61788-63-4]	38
Trialkyl			
tri-*n*-octylamine	$C_{24}H_{51}N$	[1116-76-3]	−34.6
tri-*n*-dodecylamine	$C_{36}H_{75}N$	[102-87-4]	−9
tri-*n*-hexadecylamines		[67701-00-2]	3

of carbon atoms, and (*5*) unsaturation lowers the melting point of the fatty amine, eg, oleylamine versus 1-octadecylamine and ditallowalkylamines versus dihydrogenated tallowalkylamines.

Boiling points of fatty amines have been reported (13,27–29). A direct correlation between molecular weight and boiling point is observed. Mixtures of primary fatty amines prepared from fats and oils can be separated into component amines by fractional distillation; an approximately 10°C increment in boiling point per carbon in the chain length is maintained throughout the series. Symmetrical secondary and tertiary fatty amines have a tendency to decompose during distillation and boiling point data are not reliable. The presence of residual catalyst from the preparation of these amines can lead to decomposition products during distillation.

Fatty amines are insoluble in water, but soluble in organic solvents to varying degrees (26–29). Water, however, is soluble in the amines, and hydrates are formed. Solubility in organic solvents is dependent on solvent polarity and temperature. The solubilities of primary amine acetates and hydrochlorides have been documented (29). Fatty amine acetates, available commercially, are very soluble in 95% ethanol.

The unshared pair of electrons on the nitrogen atom provides the basic character to the fatty amines. Basicity of amines has been determined as (29):

$$\text{secondary amines} > \text{primary amines} > \text{tertiary amines} > \text{ammonia}$$

Water and carbon dioxide from the atmosphere can be absorbed by the amines to form hydrates and carbamates, from primary and secondary amines, respectively.

3. Chemical Properties

General amine chemistry is applicable to fatty amines. Many chemical reactions using fatty amines as reactive intermediates are run on an industrial scale to produce a wide range of important products. Important industrial reactions are as follows.

3.1. Salt Formation. Amines react with inorganic and organic acids.

$$RNH_2 + HCl \longrightarrow RNH_3^+Cl^-$$

$$RNH_2 + R'COOH \longrightarrow RNH_3^+R'COO^-$$

3.2. Methylation of Primary and Secondary Fatty Amines. This is done by the Leuckart reaction (1,30) or reductive methylation (1,29,31,32).

Leuckart reaction

$$RNH_2 + 2\ CH_2O + 2\ HCOOH \longrightarrow RN(CH_3)_2 + 2\ H_2O + 2\ CO_2$$

Reductive methylation

$$RNH_2 + 2\ CH_2O + 2\ H_2 \longrightarrow RN(CH_3)_2 + 2\ H_2O$$

The Leuckart reaction uses formic acid as reducing agent. Reductive alkylation using formaldehyde, hydrogen, and catalyst, usually nickel, is used commercially to prepare methylated amines. These tertiary amines are used to prepare quaternary ammonium salts.

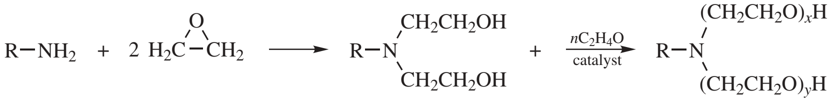
3.3. Quaternization. Quaternary ammonium compounds are formed by alkylation of alkyl, alkyldimethyl, dialkyl, and dialkylmethyl fatty amines with methyl chloride, dimethyl sulfate, or benzyl chloride (1,3,7,12,29).

$$RNH_2 + 3\ CH_3X + 2\ NaOH \longrightarrow RN(CH_3)_3^+X^- + 2\ NaX + 2\ H_2O$$

$$R_2NCH_3 + CH_3X \longrightarrow R_2N(CH_3)_2^+X^-$$

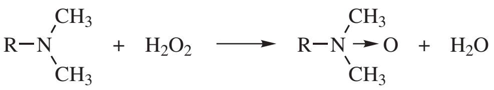
A wide variety of quaternaries can be prepared. Alkylation with benzyl chloride may produce quaternaries that are biologically active, namely, bactericides, germicides, or algaecides. Reaction of a tertiary amine with chloroacetic acid produces an amphoteric compound, a betaine.

3.4. Ethoxylation and Propoxylation. Ethylene oxide [75-21-8] or propylene oxide [75-56-9] add readily to primary fatty amines to form bis(2-hydroxyethyl) or bis(2-hydroxypropyl) tertiary amines; secondary amines also react with ethylene or propylene oxide to form 2-hydroxyalkyl tertiary amines (1,3,7,33–36). The initial addition is completed at approximately 170°C. Additional ethylene or propylene oxide can be added by using a basic catalyst, usually sodium or potassium hydroxide.



Ethylene oxide adds to the bis(2-hydroxyethyl) tertiary amine in a random fashion where $x + y = n + 2$. Ethoxylated amines, varying from strongly cationic to very weakly cationic in character, are available containing up to 50 mol of ethylene oxide/mol of amine. Ethyoxylated fatty amine quaternaries, cationic surfactants (both chloride from methyl chloride and acetate from acetic acid), are also available.

3.5. Oxidation by Hydrogen Peroxide. This reaction produces amine oxides (qv) (1,7,33,34,36).



Fatty amine oxides are most frequently prepared from alkyldimethylamines by reaction with hydrogen peroxide. Aqueous 2-propanol is used as solvent to prepare amine oxides at concentrations of 50–60%. With water only as a solvent, amine oxides can only be prepared at lower concentrations because aqueous solutions are very viscous. Fatty amine oxides are weak cationic surfactants.

3.6. Cyanoethylation. The reaction of primary fatty amines with acrylonitrile followed by hydrogenation produces diamines and triamines (4,7,31, 32,37,38).

Cyanoethylation (Michael addition)

$$RNH_2 + CH_2{=}CHC{\equiv}N \xrightarrow{70\ \text{to}\ 80^\circ C} RNHCH_2CH_2C{\equiv}N$$

$$RNHCH_2CH_2C{\equiv}N + CH_2{=}CHC{\equiv}N \xrightarrow{>150^\circ C} RN(CH_2CH_2C{\equiv}N)_2$$

Hydrogenation

$$RNHCH_2CH_2C{\equiv}N + 2\ H_2 \longrightarrow RNHCH_2CH_2CH_2NH_2$$

$$RN(CH_2CH_2C{\equiv}N)_2 + 4\ H_2 \longrightarrow RN(CH_2CH_2CH_2NH_2)_2$$

The addition of 1 mol of acrylonitrile (Michael addition) to the primary amine is an exothermic reaction, carried out at moderate temperature (70°C), either neat or using a polar solvent (water or low molecular weight alcohol). A fatty diamine, containing one primary and one secondary nitrogen, is formed when the nitrile adduct is catalytically hydrogenated. It is possible to add a second mole of acrylonitrile to the initial mononitrile adduct. However, the second addition does not occur as readily. Reduction of a dinitrile adduct forms a triamine, which contains one tertiary and two primary amino groups. Reduction of the nitrile can be problematic in that varying degrees of decyanoethylation occur depending on catalyst and temperature used during reduction.

Primary fatty amines also add (Michael addition) to esters of acrylic acid, $H_2C{=}CHCOOH$, methacrylic acid, $H_2C{=}C(CH_3)COOH$, or crotonic acid, $CH_3CH{=}CHCOOH$. Hydrolysis of the Michael ester forms an amphoteric surfactant. Crotonic acid can be used to form the amphoteric compound directly.

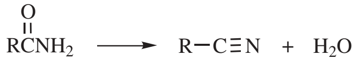
4. Manufacture

The principal industrial production route used to prepare fatty amines is the hydrogenation of nitriles, a route which has been used since the 1940s. Commercial preparation of fatty amines from fatty alcohols is a fairly new process, created around 1970, which utilizes petrochemical technology, Ziegler or Oxo processes, and feedstock.

In addition to the nitrile and alcohol routes for fatty amine preparation, processes have been described by Unocal and Pennwalt Corporation, using an olefin and secondary amine (14–16); by Texaco Inc., hydrogenation of nitroparaffins (17–20); by Onyx Corporation, reaction of an alkyl halide with secondary amines (21,22); by Henkel & Cie, GmbH, reduction of an ester in the presence of a secondary amine (23); by catalytic hydroammonolysis of carboxylic acids (24); and by the Hofmann rearrangement (25).

4.1. Nitrile Process. Fatty nitriles are readily prepared via batch, liquid-phase, or continuous gas-phase processes from fatty acids and ammonia. Nitrile formation is carried out at an elevated temperature (usually >250°C) with catalyst. An ammonia soap which initially forms, readily dehydrates at temperatures above 150°C to form an amide. In the presence of catalyst, zinc (ZnO) for batch and bauxite for continuous processes, and temperatures >250°C, dehydration of the amide occurs to produce nitrile. Removal of water drives the reaction to completion.

$$RCOOH + NH_3 \longrightarrow RCOO^-NH^+{}_4 \longrightarrow RCONH_2 + H_2O$$



$$R\overset{\overset{\displaystyle O}{\|}}{C}NH_2 \longrightarrow R{-}C{\equiv}N + H_2O$$

Hydrogenation of fatty nitrile to amine can be either a batch or continuous process (39–42). For preparing primary amines, ammonia is used to suppress secondary amine formation, at a minimum partial pressure of ~1 MPa (150 psig). Batch hydrogenation of a nitrile produces primary amine at 96% purity with low secondary (1.5%) and tertiary (<1%) amine levels (39). Reduction of the nitrile is carried out at elevated temperature (from 50 to 200°C), using hydrogen gas at high pressure, 3.5 MPa (500 psig) and higher total pressure of ammonia and hydrogen gases, in the presence of various catalysts. Catalysts useful for nitrile reduction include (*1*) aluminum–nickel Raney alloy (39), (*2*) Raney cobalt (40,43,44), (*3*) zinc–chromium or zinc–aluminum (41), (*4*) Raney nickel (42,45), (*5*) cobalt, copper, and chromium pellets (46), and (*6*) various nickel-supported catalysts (47–49).

A mixture of primary and secondary amines is formed when ammonia is not used during the nitrile reduction. It is possible to prepare high purity secondary amines by carrying the reduction out at low pressure and passing hydrogen through the reaction in a batch process (47,48), $2\ RNH_2 \longrightarrow R_2NH + NH_3$. A nickel–diatomaceous earth catalyst has been used at 220°C at low pressure and hydrogen purge to prepare secondary amines in high yield. Ammonia is removed continuously to drive the reaction to completion. The selectivity to secondary amine can be further enhanced by adding small amounts of an aliphatic carboxylic acid amide (48). Cobalt or copper chromite catalysts are also used to prepare secondary amines (1). Imines ($RCH{=}NH$ and $RCH{=}NCH_2R$) are suggested as intermediates in the process (3).

Symmetrical tertiary amines can be prepared in an analogous manner to secondary amines (1). Catalytic hydrogenation at elevated temperature and low pressure with a hydrogen purge produces a mixture of primary, secondary, and tertiary amines.

$$6\ R{-}C{\equiv}N + 12\ H_2 \longrightarrow RCH_2{-}NH_2 + (RCH_2)_2N{-}H + (RCH_2)_3N + 3\ NH_3$$

The rate of reaction slows down as the conversion to tertiary amine increases and primary amine concentrations drop below 1%. Conversion to 100% tertiary amine is difficult.

Alkyldimethyl and dialkylmethyl tertiary amines are commercially available. These amines are prepared by reductive methylation of primary and secondary amines using formaldehyde and nickel catalysts (1,3,47,48). The asymmetrical tertiary amines are used as reactive intermediates for preparing many commercial products.

Catalytic hydrogenation of raw materials prepared from natural fats and oils can be difficult because impurities are present which can affect the catalyst performance. Tallow fatty acid can contain the following catalyst poisons in differing amounts: sulfur, phosphorus, chlorine, and nitrogen (49). These catalyst poisons are removed to varying degrees during the refining process. Thus, catalyst loading levels can change from batch to batch.

Homogeneous and heterogenous catalysts which selectively or partially hydrogenate fatty amines have been developed (50). Selective hydrogenation of cis and trans isomers, and partial hydrogenation of polyunsaturated moieties, such as linoleic and linolenic to oleic, is possible.

4.2. Alcohol Process.

Fatty alcohols react with ammonia, or a low molecular weight primary or secondary amine, to form fatty amines. The fatty alcohols can be prepared from natural sources, fats and oils, or may be petroleum derived. Processes for manufacturing the fatty alcohol vary and depend on the raw material source, natural or petrochemical. Natural fatty acids, or preferably methyl esters of fatty acids, are catalytically reduced to alcohols by high pressure >20 MPa (3000 psig) and temperature (250–300°C) hydrogenation using copper chromite catalyst (11,51). Synthetic fatty alcohols are prepared using the Oxo (hydroformylation, reaction of carbon monoxide and hydrogen) or the Ziegler (ethylene and triethylaluminum) processes (10).

Primary amines can be prepared from alcohols and an excess of ammonia (52–55). Either a batch or continuous process can be used. The reaction is run at elevated temperature (50–340°C) and high pressure, 3.5 MPa (500 psig), with an ammonia-to-alcohol ratio of 5:1 to 30:1.

$$R\text{—}OH + NH_3 \longrightarrow R\text{—}NH_2 + H_2O$$

For example, a secondary alcohol of an average molecular weight of 202, containing 12–14 carbon atoms, is introduced into a reaction tube packed with a cobalt promoted zirconium catalyst on alumina at a rate of 60 mL/h along with liquid ammonia (90 mL/h) and hydrogen (5 L/h) to produce an amine mixture composed of 92.2% primary amine, 2.15% secondary and tertiary amines, and 5.7% unreacted alcohol (52). The reaction, at 180–190°C and 24 MPa (≈3500 psig), is run by withdrawing the liquid reaction product from the bottom of the reactor.

Secondary amines can be prepared from an alcohol and either ammonia (56) or primary amine (57).

$$6\,R\text{—}OH + 3\,NH_3 \longrightarrow R\text{—}NH_2 + R_2N\text{—}H + R_3N + 6\,H_2O$$

$$R\text{—}OH + R'\text{—}NH_2 \longrightarrow R\text{—}NH\text{—}R' + H_2O$$

When a mixture of long-chain alcohols, Neodol 25 (Shell Chemical Company) and Alfol 1618 [Conoco Inc. (E. I. du Pont de Nemours & Co.)], containing a nickel catalyst (Girdler G49B) is heated at 190°C for six hours with a hydrogen and ammonia sparge, a mixture of amines is formed: 3.7% primary, 76.7% secondary, and 16.9% tertiary (56). This is similar to what is observed when fatty nitriles are reduced at low pressure and high temperature. High purity secondary amines have been prepared by reaction of an alcohol with a primary amine at elevated temperature (to 250°C) and low pressure (atmospheric) using a selective catalyst; use of copper, nickel, and a noble metal catalyst such as platinum, palladium, or ruthenium is recommended (57). For example, dilaurylamine was prepared at 92% purity by reaction of lauryl alcohol with laurylamine in the presence of a ruthenium catalyst.

Batch or continuous processes can be used to prepare tertiary amines from alcohols and ammonia or a secondary amine, such as, dimethylamine.

$$3\,C_8H_{17}OH + NH_3 \longrightarrow (C_8H_{17})_3 + 3\,H_2O$$

Trioctylamine has been prepared, in a continuous process, using 5,200 kg of *n*-octanol, 100 kg of copper formate catalyst, 500 kg of *n*-octylamine, 10 kg of calcium hydroxide, and 240 kg of ammonia (58). Ammonia was added over a 10-h period while 10 m^3 of hydrogen/h was passed through the reactor at a reaction temperature of 180–200°C. The final product was composed of 94% trioctylamine, 2% dioctylamine, 1% octylamine, and 0.5% *n*-octanol. A tertiary amine was prepared from dodecanol and dimethylamine using a nickel promoted-catalyst.

$$C_{12}H_{25}OH + (CH_3)_2N{-}H \longrightarrow C_{12}H_{25}N(CH_3)_2 + H_2O$$

Thus, a 94% conversion to dimethyldodecylamine was obtained in five hours using nickel catalyst promoted with chromium and iron at 180°C and 1.1 MPa (160 psig) (59).

Catalysts used for preparing amines from alcohols include: cobalt promoted with zirconium, lanthanum, cerium, or uranium (52); the metals and oxides of nickel, cobalt, and/or copper (53,54,56,60,61); metal oxides of antimony, tin, and manganese on alumina support (55); copper, nickel, and a metal belonging to the platinum group 8–10 (57); copper formate (58); nickel promoted with chromium and/or iron on alumina support (53,59); and cobalt, copper, and either iron, zinc, or zirconium (62).

5. Shipment

Fatty amine products are normally shipped in 55-gal (208 L), lined and unlined, steel drums or in tank cars or tank trucks for bulk shipments. High melting amines can be flaked and shipped in cardboard cartons or paper bags. The amines are corrosive to skin and eyes. Protective splash goggles and gloves should be worn when handling these materials.

6. Economic Aspects

Demand for amines in the United States will grow to nearly \$2 × 10^9 in 2004. Advances will be led by the specialty amines. The fatty amines will show more modest gains since it is a mature market. Growth will exist in water treatment and plastics. The set markets, detergents, cleaning products, personal care products, and agricultural products will advance moderately. Fatty amines and derivatives are used in fabric softeners, dishwashing liquids, car wash detergents, and carpet cleaners (63).

Fatty amines and ethanolamines are the largest amine types used in the detergent and cleaner markets. The amine demand for 2004 is expected to be 70×10^6 kg up from 62×10^6 kg in 1999 (64).

The top U.S. producers of amines are Union Carbide, Air Products and Chemicals, Huntsman, and Dow Chemical.

The major source of raw materials for the preparation of fatty amines is fats and oils such as tallow, and coconut, soya, and palm oils. Commercially available high purity fatty amines are listed in Table 3. Cost of the amines can vary owing to supply of raw materials.

7. Specifications

Specifications of commercially available fatty amines are listed in product bulletins which are available from the manufacturers (31,65–72). For primary

Table 3. **Commercially Available Fatty Amines**

Fatty amine (common name)	Molecular formula	CAS Registry Number	Trade name	Manufacturer	Appearance
Primary amines					
2-ethylhexylamine	$C_8H_{19}N$	[104-75-6]	Armeen L8D	Akzo	liquid
cocoalkylamines		[61788-46-3]	Armeen CD	Akzo	liquid
			Alamine 21D	Henkel	
			Kemamine P-650	Humko	liquid
			Jet Amine PCD	Jetco	liquid
			Adogen 160-D	Sherex	liquid
dodecylamine	$C_{12}H_{27}N$	[124-22-1]	Armeen 12D	Akzo	semisolid
			Alamine 4D	Henkel	
			Adogen 163-D	Sherex	liquid
hexadecylamine	$C_{16}H_{35}N$	[143-27-1]	Armeen 16D	Akzo	solid
			Kemamine P-880D	Humko	solid
octadecylamine	$C_{18}H_{39}N$	[124-30-1]	Armeen 18D	Akzo	solid
			Alamine 7D	Henkel	
			Kemamine P-990D	Humko	solid
			Adogen 142-D	Sherex	solid
oleylamine	$C_{18}H_{37}N$	[112-90-3]	Armeen OD	Akzo	semisolid
			Alamine 11D	Henkel	
			Kemamine P-989D	Humko	liquid
			Jet Amine POD	Jetco	liquid
			Adogen 172-D	Sherex	liquid
soyaalkylamines		[61970-18-9]	Armeen SD	Akzo	paste
			Jet Amine PSD	Jetco	paste
			Adogen 115-D	Sherex	liquid
tallowalkylamines		[61790-33-8]	Armeen TD	Akzo	solid
			Alamine 26D	Henkel	
			Kemamine P-974D	Humko	paste
			Jet Amine PTD	Jetco	solid
			Adogen 170-D	Sherex	paste
			Tomah P-2B	Tomah	
hydrogenated tallowalkylamines		[61788-45-2]	Armeen HTD	Akzo	solid
			Alamine H26D	Henkel	
			Kemamine P-970D	Humko	solid
			Jet Amine PHTD	Jetco	solid
			Adogen 140-D	Sherex	solid

Table 3 (*Continued*)

Fatty amine (common name)	Molecular formula	CAS Registry Number	Trade name	Manufacturer	Appearance
eicosylamine/docosylamine	(C_{20}/C_{22})	[60800-66-0]	Kemamine P-190D and P-150D	Humko	solid
			Adogen 101	Sherex	solid
Secondary amines					
didecylamine	$C_{20}H_{43}N$	[1120-49-6]	Armeen 2-10	Akzo	liquid
dicocoalkylamines		[61789-76-2]	Armeen 2C	Akzo	solid
			Jet Amine 2C	Jetco	solid
diisotridecylamine	$C_{26}H_{55}N$	[57157-80-9]	Adogen 283	Sherex	liquid
dioctadecylamine	$C_{36}H_{75}N$	[112-99-2]	Armeen 2-18	Akzo	solid
ditallowalkylamines		[68783-24-4]	Armeen 2T	Akzo	solid
dihydrogenated tallowalkylamines		[61789-79-5]	Armeen 2HT	Akzo	solid
			Kemamine S-970	Humko	solid
			Jet Amine 2HT	Jetco	solid
			Adogen 240	Sherex	solid
dieicosylamine/didocosylamines		[53529-35-4]	Kemamine S-190	Humko	solid
Tertiary amines					
Alkyldimethylamines					
dimethyloctylamine	$C_{10}H_{23}N$	[7378-99-6]	ADMA-8	Ethyl	liquid
decyldimethylamine	$C_{12}H_{27}N$	[1120-24-7]	ADMA-10	Ethyl	liquid
dimethyldodecylamine	$C_{14}H_{31}N$	[112-18-5]	Armeen DM12D	Akzo	liquid
			ADMA-12	Ethyl	liquid
cocoalkyldimethylamines		[61788-93-0]	Armeen DMCD	Akzo	liquid
			Kemamine T-6502D	Humko	liquid
			Jet Amine DMCD	Jetco	liquid
dimethyltetradecylamine	$C_{16}H_{35}N$	[112-75-4]	ADMA-14	Ethyl	liquid
dimethylhexadecylamine	$C_{18}H_{39}N$	[112-69-6]	Armeen DM16D	Akzo	liquid
			ADMA-16	Ethyl	liquid
dimethyloctadecylamine	$C_{20}H_{43}N$	[124-28-7]	Armeen DM18D	Akzo	liquid
			ADMA-18	Ethyl	liquid
			Kemamine T-9902D	Humko	liquid
dimethyloleylamine	$C_{20}H_{41}N$	[28061-69-0]	Armeen DMOD	Akzo	liquid
			Jet Amine DMOD	Jetco	liquid
dimethylsoyaalkylamines		[61788-91-8]	Armeen DMSD	Akzo	liquid
			Kemamine T-9972D	Humko	liquid
			Jet Amine DMSD	Jetco	liquid

Table 3 (*Continued*)

Fatty amine (common name)	Molecular formula	CAS Registry Number	Trade name	Manufacturer	Appearance
dimethyltallowalkylamines		[68814-69-7]	Armeen DMTD	Akzo	liquid
			Kemamine T-9742D	Humko	liquid
			Jet Amine DMTD	Jetco	liquid
dimethylhydrogenated tallowalkylamines		[61788-95-2]	Armeen DMHTD	Akzo	liquid
			Kemamine T-9702D	Humko	liquid
			Jet Amine DMHTD	Jetco	liquid
dimethyleicosylamine/-dimethyldocosylamines		[93164-85-3]	Kemamine T-1902D	Humko	solid
Dialkylmethylamines					
di(C_8–C_{10})-methylamine	$C_{17}H_{37}N$	[4455-26-9]	DAMA-810	Ethyl	liquid
	$C_{19}H_{41}N$	[22020-14-0]			
	$C_{21}H_{45}N$	[7396-58-9]			
didecylmethylamine	$C_{21}H_{45}N$	[7396-58-9]	Armeen M2-10D	Akzo	liquid
			DAMA-1010	Ethyl	liquid
dicocoalkylmethylamines		[61788-62-3]	Armeen M2C	Akzo	liquid
			Kemamine T-6501	Humko	liquid
			Jet Amine M2C	Jetco	solid
			Adogen 369	Sherex	liquid
dioctadecylmethylamine	$C_{37}H_{77}N$	[4088-22-6]	Adogen 349	Sherex	solid
dihydrogenated tallowalkylmethylamines		[61788-63-4]	Armeen M2HT	Akzo	solid
			Kemamine T-9701	Humko	solid
			Jet Amine M2HT	Jetco	solid
			Adogen 343	Sherex	solid
Trialkylamines					
trioctylamine	$C_{24}H_{51}N$	[1116-76-3]	Alamine 336	Henkel	liquid
tri(isooctyl)amine	$C_{24}H_{51}N$	[25549-16-0]	Adogen 381	Sherex	liquid
tri(C_8–C_{10})-amines		[68814-95-9]	Adogen 364	Sherex	liquid
tri(isodecyl)amine	$C_{30}H_{63}N$	[35723-89-8]	Adogen 382	Sherex	liquid
trilaurylamine	$C_{36}H_{75}N$	[102-87-4]	Armeen 3-12	Akzo	liquid
			Alamine 304	Henkel	liquid
tri(isotridecyl)amine	$C_{39}H_{81}N$	[35723-83-2]	Adogen 383	Sherex	liquid

Table 3 (*Continued*)

Fatty amine (common name)	Molecular formula	CAS Registry Number	Trade name	Manufacturer	Appearance
trihexadecylamines		[67701-00-2]	Armeen 3-16	Akzo	solid
trioctadecylamine	$C_{54}H_{111}N$	[102-88-5]	Adogen 340	Sherex	solid
Diamines					
N-cocoalkyltrimethylenedi- amines		[61791-63-7]	Duomeen CD	Akzo	semisolid
			Diam 21D	Henkel	
			Kemamine D-650	Humko	liquid
			Jet Amine DC	Jetco	liquid
			Adogen 560	Sherex	liquid
N-tallowalkyltrimethylenediamines		[61791-55-7]	Duomeen T	Akzo	solid
			Diam 26	Henkel	
			Kemamine D-974	Humko	solid
			Jet Amine DT	Jetco	paste
			Adogen 570-S	Sherex	solid
			Tallow Diamine	Tomah	
N-hydrogenated tallowalkyltrimethylenediamines		[37231-11-1]	Kemamine D-970	Humko	solid
			Adogen 540	Sherex	flakes
N-oleyl-1,3-diaminopropane	$C_{21}H_{44}N_2$	[7173-62-8]	Duomeen O	Akzo	liquid
			Diam 11	Henkel	
			Kemamine D-989	Humko	liquid
			Jet Amine DO	Jetco	liquid
			Adogen 572	Sherex	liquid
N-eicosyl-1,3-diaminopropane/ *N*-docosyl-1,3-diaminopropanes		[89234-29-7]	Kemamine D-150	Humko	solid
N,N,N′-trimethyl-*N*′-tallowalkyltrimethylenediamines		[68783-25-5]	Duomeen TTM	Akzo	liquid
Triamines					
N-tallowalkyl dipropylenetriamines		[61791-57-9]	Triameen T	Akzo	paste
			Tallow triamine	Tomah	
Tetramines					
N-tallowalkyl tripropylenetetramine			Tallow tetramine	Tomah	

amines, specifications can include minimum and maximum values for the following: the percentage of primary and apparent secondary amines, color (Gardner), equivalent weight, amine number, moisture, and iodine value (IV). Secondary amine specifications, in addition to the above, have a minimum value for apparent secondary amine content, while tertiary amines would have specifications ona minimum percentage of tertiary and maximum percentage of primary and secondary amine content. Specifications for diamines can include a minimum percentage of diamine content. Some product bulletins in addition to listing specifications give typical analytical values.

8. Analytical Methods

To analyze fatty amines, both wet and instrumental methods of analysis are used. Wet methods routinely used are: total amine value (ASTM Method D2073); combining weight or neutralization equivalent; primary, secondary, and tertiary amine content (ASTM Method D2083); moisture, Karl-Fischer (ASTM Method D2072); and iodine value, measure of unsaturation (ASTM Method D2075). These provide important information on physical and chemical characteristics of the amine products used in various application areas (8,68,73). In addition to the ASTM methods available, the American Oil Chemists' Society has developed methods of analysis for fatty amines (74).

Instrumental methods of analysis provide information about the specific composition and purity of the amines. Qualitative information about the identity of the product (functional groups present) and quantitative analysis (amount of various components such as nitrile, amide, acid, and determination of unsaturation) can be obtained by infrared analysis. Gas chromatography (gc), with a liquid phase of either Apiezon grease or Carbowax, and high performance liquid chromatography (hplc), using silica columns and solvent systems such as isooctane, methyl *tert*-butyl ether, tetrahydrofuran, and methanol, are used for quantitative analysis of fatty amine mixtures. Nuclear magnetic resonance spectroscopy (nmr), both proton (^{1}H) and carbon-13 (^{13}C), which can be used for qualitative and quantitative analysis, is an important method used to analyze fatty amines (8,73).

9. Health and Safety Factors

9.1. Skin and Eye Irritation. Fatty alkylamines are generally considered to be irritating to both the skin and eyes (75). The severity or degree of irritation is usually dependent on the type of alkylamine, concentration of the chemical, time of exposure to the chemical, and sensitivity to the chemical. A small percentage of the population who come into contact with fatty amines may develop a skin hypersensitivity to certain amines and diamines.

Alkylamines and diamines are generally classified as corrosive to the skin based on results from laboratory animal (rabbit) studies performed in accordance with the Department of Transportation (DOT) test method (76); rabbits are considered to be especially sensitive to alkylamines which even at low concentrations can induce skin redness and swelling. Oleylamine has been shown to induce mild to moderate skin irritation in laboratory rats when applied at a concentration of 0.3% in mineral oil (Chemical Manufacturer's Association, 1985). Fatty amines which contain alkyl chains of 10–14 carbons are considered more irritating than related products which contain alkyl chains of 14–18 carbon atoms. Ethoxylation generally decreases the irritation potential of alkylamines.

9.2. Oral Toxicity. Depending on the chemical class, most fatty amines range from moderately toxic to practically nontoxic by acute oral ingestion. Laboratory animal testing has revealed that the amines and diamines can induce irritation and damage to the gastrointestinal tract. The acute oral LD_{50} of cocoalkyldiamine in rats is less than 200 mg/kg body weight (Armak Test Data, 1981), whereas the corresponding value for dihydrogenated tallowalkylmethylamine (Akzo Chemie Data, 1984) is greater than 5,000 mg/kg. Products which have LD_{50} values greater than 5000 mg/kg are considered practically nontoxic by accidental ingestion.

9.3. Dermal Toxicity. Fatty alkylamines are not considered especially toxic with regard to skin penetration and systemic absorption into the body; certain polyamines may be absorbed through the skin to a much greater degree. The acute dermal LD_{50} of decylamine in rabbits has been reported to be 350 mg/kg [RTECS, 1982 (77)]; dialkyl(C_{14}–C_{18})methylamine has been shown to have an acute dermal LD_{50} value of greater than 2000 mg/kg in rabbits (Dynamac Corporation, 1988). Products with acute dermal LD_{50} values greater than 2000 mg/kg are considered to exhibit a low degree of hazard by acute dermal exposure.

9.4. Inhalation. Long-chain amines are not considered an inhalation hazard at ambient conditions because of their relatively low volatility. Inhalation of aerosols or heated vapors may result in irritation of the nose, throat, and upper respiratory system. Lower molecular weight and branched-chain amines are more volatile and can cause irritation if inhaled. Volatile amines are easily recognized by their unpleasant, fishy odor.

10. Uses

Fatty amines and chemical products derived from the amines are used in many industries.

Amine salts, especially acetate salts prepared by neutralization of a fatty amine with acetic acid, are useful as flotation agents (collectors), corrosion inhibitors, and lubricants (3,8).

The single largest market use for quaternary fatty amines is in fabric softeners. Monoalkyl quaternaries (chloride) have been used in liquid detergent softener antistat formulations (LDSA), dialkyldimethyl quaternaries (chloride) in the rinse cycle, and dialkyldimethyl quaternaries (sulfate) as dryer softeners.

Another significant use for dialkyldimethyl quaternary ammonium salts and alkylbenzyldimethylammonium salts is in preparing organoclays for use as drilling muds, paint thickeners, and lubricants.

Betaines, or specialty quaternaries, are used in the personal care industry in shampoos, conditioners, foaming, and wetting agents.

A significant use of ethoxylated and propoxylated amines is as antistatic agents (qv) in the textile and plastics industry (78). Ethoxylates are also used in the agricultural area as adjuvants.

Examples of uses for amine oxides include: detergent and personal care areas as a foam booster and stabilizer, as a dispersant for glass fibers, and as a foaming component in gas recovery systems.

Important uses for the diamines include: corrosion inhibitors, gasoline and fuel oil additives, flotation agents, pigment wetting agents, epoxy curing agents, herbicides, and asphalt emulsifiers (3,75,77).

Fatty amines and derivatives are widely used in the oil field, as corrosion inhibitors, surfactants, emulsifying/deemulsifying and gelling agents (79). In the mining industry, amines and diamines are used in the recovery and purification of minerals, flotation, and benefication. A significant use of fatty diamines is as asphalt emulsifiers for preparing asphalt emulsions. Diamines have also been used as epoxy curing agents, corrosion inhibitors, gasoline and fuel oil additives, and pigment wetting agents. Oleylamine is a petroleum additive useful as a detergent in gasoline (8). In addition, derivatives of the amines, amphoterics, and long-chain alkylamines are used as anionic and cationic surfactants in the personal care industry (80).

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