METHYLAMINES

1. Introduction

Methylamines are derivatives of ammonia with one, two, or all three of the hydrogen atoms replaced by methyl groups. Amines with alkyl groups of from 2 to 6 carbons are known as aliphatic amines, and amines with still larger alkyl groups are known as fatty amines. The names, chemical formulas, molecular weights, CAS Registry Numbers, and common names or abbreviations of the methylamines are given in Table 1. Methylamines are toxic, colorless gases or compressed liquids, highly flammable, and have very strong fishy or ammonia-like odors. They are water soluble and are sold as either aqueous solutions or in pure form.

Table 1. **Commercial Methylamines**

Alkylamine	CAS Registry number	Molecular Formula	Molecular Weight	Synonym or Common Abbreviation
methylamine	[74-89-5]	CH_5N	31.06	monomethylamine, aminomethane, MMA
dimethylamine	[124-40-3]	C_2H_7N	45.08	*N*-methyl-methanamine, DMA
trimethylamine	[75-50-3]	C_3H_9N	59.11	*N*,*N*-dimethyl-methanamine, TMA

Methylamines are basic, and consequently, they react with water and acids to form methylaminium compounds (1). The basicity of methylamines, although weak relative to hydroxide and alkoxide ions, is greater than that of ammonia due to the presence of the methyl groups. The alkyl groups act as electron donors to stabilize the positive charge generated upon reaction of the amine with an acid.

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

In the gas phase, the relative basicities of the methylamines show the order expected based on methyl group substitution:

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

However, in aqueous solution the order of basicity is as follows:

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

The lower basicity of trimethylamine observed in aqueous solution may be due to poorer solvation of the trimethylaminium ion, $(CH_3)_3NH^+$, which has only one hydrogen available for hydrogen bonding with water molecules.

Methylamines behave as nucleophiles due to the presence of an unshared pair of electrons on the nitrogen atom. Monomethylamine and dimethylamine readily react with a variety of substrates including carboxylic acids, acyl halides, anhydrides, esters, lactones, isocyanates, α,β-unsaturated nitriles and esters, epoxides, alkyl halides, carbon dioxide, and carbon disulfide. Trimethylamine reacts with organic and inorganic acids, alkyl halides, and epoxides to form quaternary ammonium salts and with hydrogen peroxide or peracids to form trimethylamine *N*-oxide. Products manufactured from methylamines are used as solvents, agricultural chemicals, pharmaceuticals, surfactants, rubber chemicals, and food/feed additives and in water treatment applications.

2. Properties

2.1. Physical Properties. Table 2 lists the physical properties of the methylamines. As mentioned, methylamines have a strong, fishy odor that

Table 2. **Physical Properties of Methylamines**[a]

Alkylamine	Mp, °C	Bp, °C	Vapor pressure at 20°C, kPa	Density, gm/mL at 20°C	Refractive index,[b] nD
methylamine	−93.0	−6.3	294	0.66	—
dimethylamine	−92.2	6.8	173	0.66	1.350 (17)
trimethylamine	−117.1	2.8	186	0.64	1.3631 (0)

[a] Refs. (3, 4).

[b] Temperature in °C noted in parentheses.

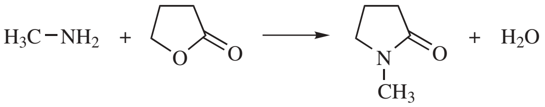
increases from mono- to di- to tri- methylamine. In high concentrations they all have the odor of ammonia. On cooling aqueous solutions of methylamines, the crystalline hydrates, $CH_3NH_2{\cdot}3H_2O$, $(CH_3)2NH{\cdot}7H_2O$, and $(CH_3)_3N{\cdot}10H_2O$ are formed (2). Methylamines are soluble in various organic solvents including methanol, ethanol, dimethylformamide, and ethylene glycol (2). Aqueous solutions of methylamines also are good solvents for many inorganic and organic compounds; however, the potential reactivity of the solute with the methylamine should be considered. At atmospheric pressure, trimethylamine forms minimum-boiling azeotropes with ammonia and other methylamines. With increasing pressure, the trimethylamine content of the azeotrope decreases, and none is formed above 2652 kPa (370 psig). At atmospheric pressure, trimethylamine boils lower than dimethylamine; this order is reversed at about 446 kPa (50 psig).

2.2. Chemical Properties.

Chemical properties of the methylamines are listed in Table 3.

Methylamines are used as intermediates for manufacture of solvents, agricultural chemicals, water treatment chemicals, pharmaceuticals, surfactants, rubber chemicals, and food/feed additives. The basicity and nucleophilic character of methylamines are responsible for their reactivity. Examples of some commercial processes that use methylamines as feedstocks are as follows:

1. Reaction of monomethylamine (MMA) with gamma-butyrolactone [96-48-0] to produce N-methylpyrrolidone [872-50-4] solvent (8).



2. Reaction of MMA with phosgene [75-44-5] to produce methyl isocyanate [624-83-9], an intermediate in the production of carbamate insecticides.

$$H_3C{-}NH_2 + Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \longrightarrow H_3C{-}N{=}C{=}O + 2HCl$$

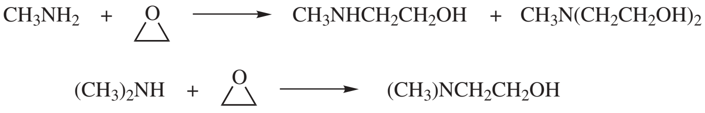
3. Reaction of MMA or dimethylamine (DMA) with ethylene oxide [75-21-8] to produce N-methylethanolamine [109-83-1] and N-methyldiethanolamine

Table 3. **Chemical Properties of Methylamines**[a]

Property	Monomethylamine	Dimethylamine	Trimethylamine
flash point, °C (closed cup)	0	−18	−6.7
lower explosion limit in air, vol%	4.95	2.8	2
upper explosion limit in air, vol%	20.75	14.4	11.6
autoignition temperature, °C	430	402	190
standard heat of formation, $\Delta_f H°$, kJ mol^{-1}, @ 25°C			
liquid	−47.3	−43.9	−45.7
gas	−22.5	−18.8	−23.6
standard entropy, $S°$, Jmol^{-1}K^{-1} @ 25°C			
liquid	150.2	182.3	208.5
gas	242.9	273.1	287.1
heat capacity, C_p, J mol^{-1}K^{-1}, @ 25°C			
liquid	102.1	137.7	137.9
gas	50.1	70.7	91.8
critical temperature, °C	156.9	164.5	160.1
critical pressure, kPa	7457	5310	4073
latent heat of vaporization, J/g @ 1 atm	839.3	595.3	393.6
pK_a @ 25°C	10.62	10.77	9.80

[a] Refs. (3–7).

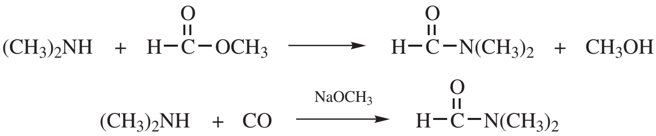
[105-59-9] or *N*,*N*-dimethylethanolamine [108-01-0] used in acid gas scrubbing, surfactant, and water treatment applications.



4. Reaction of DMA with fatty halides to produce alkyldimethylamines, which are precursors to amine oxide surfactants.

$$(CH_3)_2NH + CH_3(CH_2)nCH_2X \xrightarrow{NaOH} CH_3(CH_2)nCH_2N(CH_3)_2 + NaX + NaX$$

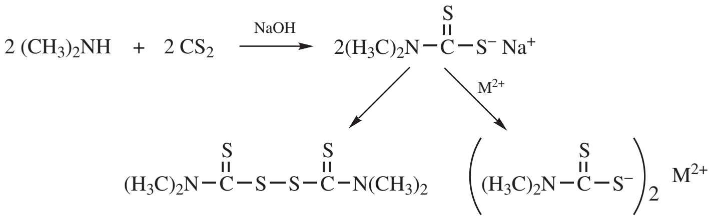
5. Reaction of DMA with methyl formate [107-31-3] or with carbon monoxide [630-08-0] in the presence of sodium methoxide to produce *N*,*N*-dimethylformamide [68-12-2] solvent (8).



$$(CH_3)_2NH + H{-}\overset{O}{\overset{\|}{C}}{-}OCH_3 \longrightarrow H{-}\overset{O}{\overset{\|}{C}}{-}N(CH_3)_2 + CH_3OH$$

$$(CH_3)_2NH + CO \xrightarrow{NaOCH_3} H{-}\overset{O}{\overset{\|}{C}}{-}N(CH_3)_2$$

6. Reaction of DMA with carbon disulfide [75-15-0] to produce dimethyldithiocarbamate salts and bis(dimethyldithiocarbamoyl) disulfide [1327-26-8] used as rubber accelerators.

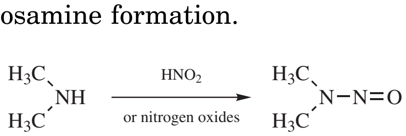


7. Reaction of DMA with allyl chloride [107-05-1] to produce diallyldimethylammonium chloride [7398-69-8] , a monomer that is polymerized and used as a flocculant in water treatment applications (9,10).

$$(CH_3)_2NH \;+\; 2\,H_2C{=}CHCH_2Cl \xrightarrow{NaOH} [(CH_3)_2N(CH_2CH{=}CH_2)_2]^+Cl^- \;+\; NaCl$$

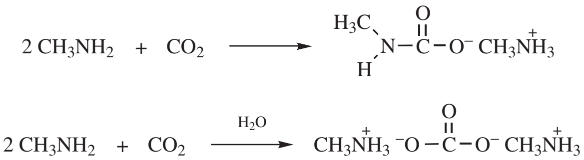
8. Reaction of trimethylamine (TMA) with hydrochloric acid and ethylene oxide [75-21-8] to produce choline chloride [67-48-1], a nutritional supplement in poultry feed (11).

Reaction of DMA with nitrous acid or with nitrogen oxides present in air or water produces dimethylnitrosamine [62-75-9], a probable carcinogen. Nitrosamine formation is a concern in several applications that use DMA as a raw material. Dimethylnitrosamine is not a by-product of DMA manufacture, and therefore, nitrosamine formation can be minimized by storage and use of anhydrous DMA under a nitrogen atmosphere. Aqueous solutions of DMA have been found to contain ppb levels of dimethylnitrosamine, which increase with time when the solutions are exposed to air. Storage of the solutions under nitrogen reduces the rate of nitrosamine formation.



Both MMA and DMA react with carbon dioxide to form amine carbamates under anhydrous conditions and amine carbonates in the presence of water. Trimethylamine cannot form the carbamate but will form the carbonate in aqueous solution. Carbamates are thermally unstable and decompose to the amine and carbon dioxide upon heating. Dimethylamine is marketed in the liquid carbamate form as Dimasol 63™ by UCB, and Akzo Nobel offers aqueous carbonate solutions of MMA and DMA (CARMA® M4031 and CARMA® D6046, respectively).

Advantages of these products are claimed to be ease of handling due to their higher boiling points and flash points, lower volatilities, and reduced odors.



$$2\,CH_3NH_2 + CO_2 \longrightarrow \underset{H}{\overset{H_3C}{N}}-\overset{O}{\overset{\|}{C}}-O^-\;CH_3\overset{+}{N}H_3$$

$$2\,CH_3NH_2 + CO_2 \xrightarrow{H_2O} CH_3\overset{+}{N}H_3\;{}^-O-\overset{O}{\overset{\|}{C}}-O^-\;CH_3\overset{+}{N}H_3$$

Methylamines are corrosive to aluminum, copper, copper alloys, galvanized metal, magnesium, zinc, and zinc alloys. Anhydrous methylamines and their aqueous solutions can be satisfactorily handled by using materials constructed of steel.

3. Manufacture

Although methylamines can be prepared by a variety of methods including alkylation of ammonia with methyl halides, alkylation of ammonium chloride with methanol (12), hydrogenation of hydrogen cyanide (13), and reductive amination of carbon monoxide (14) or carbon dioxide (15), commercial processes involve reaction of methanol with ammonia in the vapor phase to form the corresponding mono-, di-, and tri- methylamines. Technology to manufacture methylamines has been described by the Leonard Process Company (16) and involves use of a solid acid catalyst for the methanol amination reaction. An equilibrium distribution of MMA, DMA, and TMA is produced which favors TMA at low ammonia:methanol molar ratios. For example, at an ammonia: methanol molar ratio of 1, the equilibrium product composition is 17 mol% MMA, 21 mol% DMA, and 62 mol% TMA (17). Market requirements are such that DMA is in greatest demand, followed by MMA then TMA. In the United States, the demand was 33 mol% MMA, 56 mol% DMA, and 11 mol% TMA in 1995 (18). Recently, new catalyst technology has been utilized to change the relative product selectivities to more closely match market requirements. These two methods of methylamines manufacture are defined as follows:

Method 1. Methanol amination—acid catalyzed: high-temperature amination of methanol over a solid acid catalyst (Leonard Process). The acid catalysts used for this process are typically amorphous silica-aluminas (19,20) or non-shape-selective zeolites. Other solid acid catalysts have been evaluated but generally are not used commercially (21).

Method 2. Methanol amination—shape-selective acid catalyst: amination of methanol over a zeolitic catalyst with reduced formation of trimethylamine. Catalysts that exhibit good activity and desired product selectivities include naturally occurring or modified zeolites such as mordenite (22–24), chabazite (25,26), RHO (27,28), ZK-5 (28–30), and SAPO (31,32). Most commercial processes employ modified mordenites.

To manufacture methylamines by Method 1, ammonia and methanol are fed continuously to an adiabatic fixed bed reactor containing the solid acid catalyst. The reaction section consists of feed systems, vaporizers, heat recovery exchangers, and preheaters, which provide the feed mixture to the reactor at the desired feed ratio, temperature, and pressure. Operating conditions are maintained in the range 300–500°C and 790–3550 kPa (100–500 psig) at a gas hourly space velocity of 500–1500 vol reactants/vol catalyst per hour. Methanol conversion exceeds 95%, and yields typically approach stoichiometric.

Methanol amination is described by a network of two general types of reactions:

1. Sequential substitution reactions transforming methanol into a family of primary, secondary, and tertiary amines.

$$CH_3OH + NH_3 \longrightarrow CH_3NH_2 + H_2O \quad \text{primary amine}$$

$$CH_3OH + CH_3NH_2 \longrightarrow (CH_3)_2NH + H_2O \quad \text{secondary amine}$$

$$CH_3OH + (CH_3)_2NH \longrightarrow (CH_3)_3N + H_2O \quad \text{tertiary amine}$$

2. Disproportionation reactions which equilibrate the methylamines.

$$2\,CH_3NH_2 \rightleftharpoons (CH_3)_2NH + NH_3$$

$$CH_3NH_2 + (CH_3)_2NH \rightleftharpoons (CH_3)_3N + NH_3$$

$$2(CH_3)_2NH \rightleftharpoons CH_3NH_2 + (CH_3)_3N$$

As the reaction typically is run at high methanol conversion and the disproportionation reactions are fast relative to the amination reactions (33), the reaction product consists of an equilibrium mixture of MMA, DMA, and TMA. The ammonia to methanol molar ratio is varied from about 1:1 to about 6:1 to maximize production of the desired amine as shown in Figure 1. However, although MMA selectivity can be increased relative to TMA selectivity by increasing the ratio of ammonia to methanol, DMA selectivity is relatively

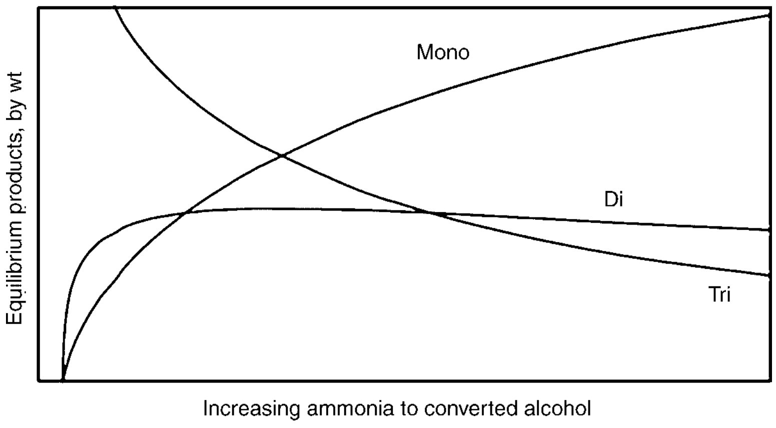


Fig. 1. Methylamine products vs increasing ammonia.

invariant (34,35). Kinetic studies of the methylamines reforming reactions have shown that maximum DMA selectivity can only be achieved under kinetic control at low conversions and not under equilibrium conditions (36). Because DMA has the highest demand, MMA and TMA often are produced in excess of market requirements. Therefore, to manage the production splits, MMA and TMA typically are recovered by distillation and recycled to the reactor. This practice is energy-intensive and provided the motivation for researchers to seek a catalyst that would afford the methylamines products in selectivities that more closely match market requirements.

Beginning in the late 1970s, extensive research was conducted to identify a catalyst capable of producing DMA in high selectivity and TMA in low selectivity. Given that TMA is larger in size than MMA and DMA (37), use of a shape-selective zeolite catalyst offered a potential solution to the selectivity problem, and a variety of zeolites have been studied as possible catalysts for methylamines synthesis (21). Zeolites that exhibit the desired activity and selectivity performance include modified mordenites, RHO, and chabazite. For example, use of an alkali metal-modified H^+-mordenite catalyst can reduce TMA selectivity from $>50\%$ by weight over an equilibrium catalyst at 2:1 ammonia:methanol (molar) and 320°C to $<20\%$ by weight (38). Mechanistic studies of mordenite and chabazite have shown that low TMA selectivity results from diffusion limitations of TMA to the bulk and also suppression of TMA formation within the zeolite pores (39–41). Silylation of the external surface of the mordenite with $SiCl_4$ further reduces TMA selectivity to <5 wt% by further narrowing the pore size (42).

In the early 1990s, Mitsubishi Rayon (formerly Nitto Chemical Industry Company) brought onstream the first commercial plant using Method 2 technology (43). The Mitsubishi Rayon methylamines process employs two reactors: One reactor contains a nonselective catalyst to disproportionate TMA to an equilibrium mixture of MMA, DMA, and TMA, and the second reactor contains a shape-selective zeolite catalyst (21,44). The disproportion reactor is required, as TMA does not react over the shape-selective catalyst due to the pore size limitations, which are responsible for the shapeselectivity. The effluent from the first reactor is fed to the second reactor along with additional methanol and ammonia to produce a nonequilibrium distribution of methylamines containing a relatively high level of DMA and a reduced level of TMA. Operating conditions are maintained in the range 280–340°C and 790–3550 kPa (100–500 psig) at a gas hourly space velocity between 1000 and 3000 vol/vol per hour. As the process according to Method 2 operates with a higher yield of the desired products and the zeolite catalysts are thermally unstable with respect to deactivation under high temperature conditions, additional measures are incorporated into the reaction system to remove the heat of reaction (45). These measures include using two or more catalyst beds and limiting the temperature rise across each bed to $<70°$C.1.

In 1997, a second shape-selective methylamines process was commercialized by Mitsui Chemical (formerly Mitsui Toatsu) (46). In this process, TMA is not recovered in a separate distillation column but is recycled as an azeotropic mixture with ammonia to a disproportionation reactor containing a nonselective H^+-mordenite catalyst (47,48). The effluent from the disproportionation reactor is combined with fresh methanol and fed to a reactor containing a shape-selective catalyst. Production of TMA during methanol amination is limited by use of a

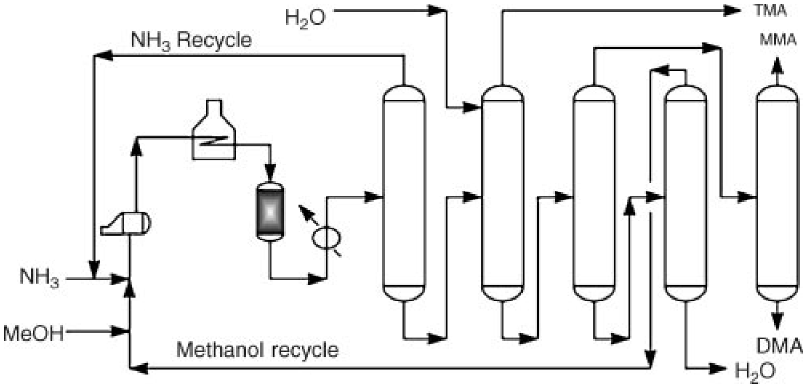


Fig. 2. Methylamine amination reactor and separation train.

silylated mordenite catalyst, which is prepared by liquid phase silylation of H^+-mordenite with tetraethoxysilane (49).

Both Methods 1 and 2 recover products in distillation trains as depicted for Method 1 in Figure 2. The separations involved are as follows:

1. Ammonia is recovered and recycled to the reaction section.
2. Product TMA is recovered using water to increase its volatility.
3. MMA and DMA are separated from reaction water and methanol.
4. Products MMA and DMA are recovered.
5. Unconverted methanol is separated from reaction water.

4. Shipment and Handling

Methylamines are flammable gases at normal temperature and pressure. The pure materials are shipped in pressurized cylinders, tank trucks, or railcars. Methylamines also are sold as aqueous solutions in various concentrations. The aqueous solutions are classified as flammable and corrosive liquids, and they are available in drums as well as tank trucks and railcars. Labeling and packaging of amines must conform with Department of Transportation (DOT) requirements. Methylamine shipments are regulated by the Coast Guard, the DOT, the International Air Transport Association (IATA), and the Drug Enforcement Administration (DEA).

In addition to federal regulations, state and local ordinances and insurance company requirements also apply to the storage and handling of methylamines (50). Recommendations of the National Electrical Code for Class 1 Hazardous Locations (NFPA No. 70) (51) should be followed. All equipment used around methylamines should be well grounded to reduce the chance of sparks caused by static electricity. Methylamines should be stored in steel containers, preferably aboveground and outdoors. Brass, copper, zinc, and aluminum must be avoided in methylamines service. Flexitallic Flexicarb or Graphoil are suitable gasket materials, and EPR, Teflon, or Kalrez 1050 are suitable elastomers in methylamines service. All storage and handling areas should be ventilated to keep them below the lower explosive limits. Vent gases can be directed to a water or acid scrubber or to a thermal oxidizer to prevent environmental pollution. Empty containers should be flushed with water to remove any residual explosive vapors. Manufacturers of methylamines can provide specific information regarding storage and handling.

5. Health, Safety, and Toxicology

Methylamines are toxic and have strong fishy odors. They are corrosive to the eyes, skin, and respiratory system. OSHA and ACGIH exposure limits and odor recognition data (52) are given in Table 4. Methylamine odors can be detected at extremely low levels. For example, MMA is detectable at levels of 0.9 ppb to 4.7 ppm, DMA at levels of 0.8 ppb to 1.6 ppm, and TMA at levels of 0.1 ppb to 0.9 ppm (53). Acute effects of exposure to methylamines include lacrimation, conjunctivitis, and corneal edema when absorbed into the tissue of the eye from the atmosphere. Contact of undiluted product with the eyes or skin quickly causes severe irritation and pain and may cause burns, necrosis, and permanent damage. Inhalation of vapors may damage contacted tissue and produce scarring. Possible longer-term effects may result in liver disorders or adverse respiratory, eye, or skin effects. When methylamines are contacted with the eyes or skin, the affected area should be flushed with water for at least 15 min. Upon inhalation of methylamines, the victim should be moved to fresh air.

A full face shield with goggles underneath, neoprene, nitrile, or butyl rubber gloves, and impervious clothing should be worn when working with methylamines. Respiratory protection is not required when working under normal conditions in a well-ventilated workplace.

6. Economic Aspects, Specifications, and Uses

Figures 3–5 show the U.S. percent consumption in various end uses for each of the three methylamines (54). As indicated by the data in these figures, the major derivatives of methylamines are solvents, alkylalkanolamines, water treatment chemicals, pesticides, and choline chloride. A list of specific products that are manufactured from methylamines for these applications is contained in Table 5. Table 6 lists worldwide manufacturers of methylamines, their plant

Table 4. **Exposure Limits and Odor Recognition of Methylamines**

Property	MMA	DMA	TMA
OSHA TWA, ppm	10	10	10
OSHA STEL, ppm	N/E[a]	N/E	15
ACGIH TWA, ppm	5	5	5
ACGIH STEL, ppm	15	15	15
100% odor recognition, ppm[b]	3	6	4

[a] Not established.

[b] Concentration at which 100% of the odor panel identified the odor as the chemical being studied.

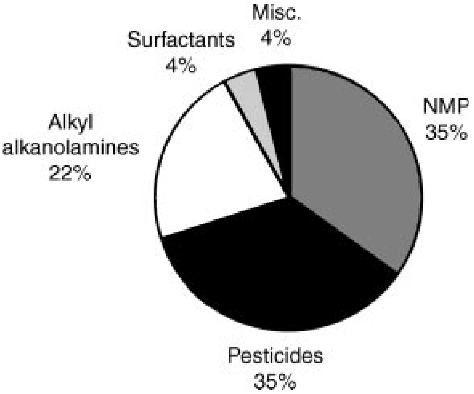


Fig. 3. MMA end uses.

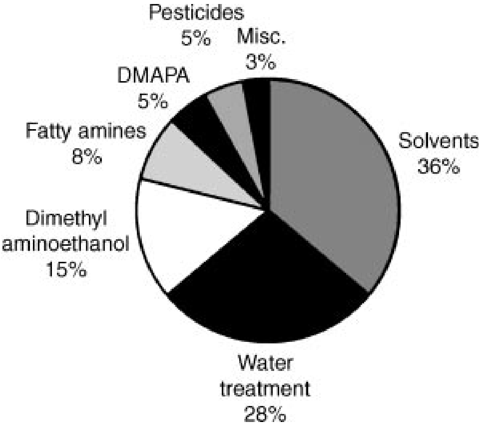


Fig. 4. DMA end uses.

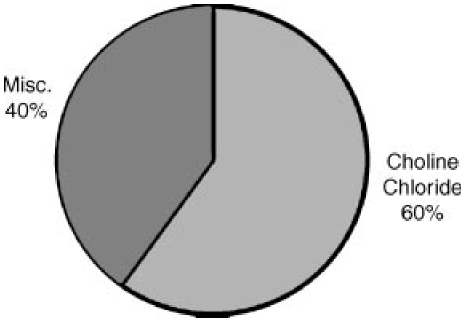


Fig. 5. TMA end uses.

Table 5. **Products Manufactured Using Methylamines**

Chemical Name	CAS Registry number	Trade/ Common Name	Use
From Monomethylamine			
N-methyl-2-pyrrolidone	[872-50-4]	NMP	solvent
N-methylethanolamine	[109-83-1]	Amietol® M11/ NMEA	acid gas scrubbing, electrostatic automotive coatings
N-methyldiethanolamine	[105-59-9]	Amietol® M12/ MDEA	acid gas scrubbing, surfactant intermediate
N,*N*'-dimethylurea	[96-31-1]	DMU	intermediate in caffeine manufacture
3,7-dihydro-1,3,7-trimethyl-1-*H*-purine-2,6-dione	[58-08-2]	Caffeine	stimulant, diuretic
sodium *N*-methyldithiocarbamate	[137-42-8]	Vapam®/ Metam-Sodium	soil fumigant, Pesticide
methylisocyanate	[624-83-9]	MIC	intermediate in carbamate insectide manufacture
1-naphthyl-*N*-methylcarbamate	[63-25-2]	Sevin®/ Carbaryl	insecticide
2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate	[1563-66-2]	Carbodan, Furadan®/ Carbofuran	insecticide
S-methyl *N*-[(methylcarbamoyl)-oxy]thioacetimidate	[16752-77-5]	Lannate®/ Methomyl	insecticide
monomethylammonium nitrate	[22113-87-7]	Tovex®	water gel explosive
2-deoxy-2-(methylamino)-*D*-glucose	[3329-30-4]	*N*-Methylglucosamine	surfactant
N-cyano-*N*'methyl'*N*"-[2-[[(5-methyl-1*H*-imidazol-4-yl) methyl]thio]ethyl]guanidine	[51481-61-9]	Tagamet®	antihistaminic, antacid
From Dimethylamine			
dimethyldithiocarbamate, zinc salt	[137-30-4]	Ziram	fungicide, rubber processing chemical
bis(dimethyldithiocarbamoyl) disulfide	[137-26-8]	Arasan®, Thiurad®/ Thiram	fungicide, rubber accelerator
dimethylformamide	[68-12-2]	DMF	solvent
dimethylacetamide	[127-19-5]	DMAC	solvent
alkyl(C_{10}–C_{18})dimethylamine oxides		Damox®/ Amine oxides	nonionic surfactants
3-dimethylaminopropylamine	[109-55-7]	DMAPA	surfactant intermediate
N,*N*-dimethylethanolamine	[108-01-0]	Amietol® M21/ DMEA, DMAE	intermediate in acrylate water treatment chemicals
copolymers of diallyldimethylammonium chloride and acrylates or acrylamides		DADMAC, DMDAC	water treatment
mannich polymers		Modified polyacrylamides	water treatment
poly[(3-dimethylamino)-2-hydroxypropyl chloride]		Polyamines, DMA/Epi polymers	water treatment
2,4-dichlorophenoxyacetic acid, dimethylamine salt	[2008-39-1]	2,4-D	postemergent herbicide

Table 5. (*Continued*)

Chemical Name	CAS Registry number	Trade/ Common Name	Use
From Trimethylamine			
choline chloride	[67-48-1]		animal feed supplement
tetramethylammonium hydroxide	[75-59-2]	TMAH	photoresist developer
benzyltrimethylammonium hydroxide	[100-85-6]	Triton B	phase-transfer catalyst
(3-chloro-2-hydroxypropyl)-trimethylammonium chloride	[3327-22-8]	Quat 188, Quab®	cationic starch
quaternary trimethylalkylammonium functionalized cross-linked polystyrene		Dowex®, Amberlyst®	ion-exchange resin

Table 6. **Manufacturing Data for Methylamines**

Company	Plant Location	Capacity, t/yr	Method
	United States Producers		
Air Products and Chemicals, Inc.	Pace, FLa	135,000	1
E. I. DuPont de Nemours & Co., Inc.	Belle, W.V.	91,000	1
		226,000	
	Other American Producers		
Chinook Chemicals	Sombra Ontario, Canada	85,000	1,2
Celanese Mexicana	La Cangrejera, Mexico	20,000	1
BASF	Brazil	10,000	1
		115,000	
	West European Producers		
BASF	Ludwigshafen, Germany	120,000	1
UCB	Leuna, Germany	60,000	1
	Ghent, Belgium	40,000	1
AKZO	Delfzil, Holland	27,000	1,2
	Marano-Ticino, Italy	18,000	1
Air Products and Chemicals, Inc.	Teesside, U. K.	38,000	1,2
Ertisa	Palos de la Frontera, Spain	10,000	1
		313,000	
	Far East		
Mitsubishi Gas Chemical	Niigata, Japan	35,000	1
Mitsubishi Rayon	Otake, Japan	35,000	1,2
Mitsui Toatsu	Hikoshima, Japan	8,000	1,2
Various	Korea, P.R.C., Taiwan	153,000	1
		231,000	
	Rest of World		
Akkim	Turkey	25,000	1
Rashtriya Chemicals and Fertilizer Ltd.	Thal, India	20,000	1
African Amines	South Africa	10,000	1
Alkyl Amines and Chemicals, Ltd.	Patalganga, India	10,000	1
Various	Eastern Europe	48,500	1
		113,500	
	Total	**998,500**	

Table 7. **Methylamines Specifications and List Prices**

Product	Assay, wt%	Other Amines, wt%	Water, wt%	2000 U.S. Price, $/kg
MMA, anhydrous	99.8	0.17	0.03	1.61
MMA, 40% solution	40–42	0.10	58–60	1.79
MMA, 50% solution	50–52	0.18	48–50	1.79
DMA, anhydrous	99.8	0.045	0.03	1.70
DMA, 40% solution	40–42	0.10	58–60	1.87
DMA, 60% solution	60–62	0.10	38–40	1.87
TMA, anhydrous	99.8	0.12	0.03	1.61
TMA, 25% solution	25–27	0.10	73–75	1.79
TMA, 40% solution	40–42	0.10	58–60	1.79

locations, and plant capacities. This information is based on market studies and capacity announcements published in the trade literature (55). Sales specifications and list prices of methylamines are shown in Table 7 (56,57). Detailed product specifications can be obtained from the manufacturers.

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