DIAMINES AND HIGHER AMINES, ALIPHATIC

1. Introduction

The aliphatic diamine and polyamine family encompasses a wide range of multi-functional, multireactive compounds. This family includes ethylenediamine (EDA) and its homologues, the polyethylene polyamines (commonly referred to as ethyleneamines), the diaminopropanes and several specific alkanediamines, and analogous polyamines. The molecular structures of these compounds may be linear, branched or cyclic, or combinations of these.
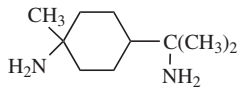
The ethyleneamines have found the broadest commercial application and are the primary focus of this article. The lower molecular weight ethylene-diamines, ie, EDA, diethylenetriamine (DETA), piperazine (PIP), and *N*-(2-amino-ethyl)-piperazine (AEP), are available commercially as industrially pure products. The tetramine (TETA), pentamine (TEPA), hexamine (PEHA), and higher polyamine products are commercially available as boiling point fractions consisting of natural mixtures of linear, branched, and cyclic compounds. Their compositions are largely determined by the chemical processes used in their production. The individual components in these higher ethyleneamines are generally not available in industrial quantities.

The predominant commercial diaminopropanes are 1,2-propylenediamine (1,2-PDA), 1,3-diaminopropane (1,3-PDA), iminobispropylamine (IBPA), and dimethylaminopropylamine (DMAPA). Other commercially important products include other higher alkylenediamines, such as hexamethylenediamine (HMDA); certain cyclic amines, such as triethylenediamine (TEDA); and various alkyl- and hydroxyalkyl-derivatives. These compounds have commercial significance in other specific areas (see also AMINES, AROMATIC AMINES-DIARYL AMINES; AMINES, CYCLOALIPHATIC AMINES; AMIDES, FATTY ACID; POLYAMIDES).

2. Physical Properties

Physical properties of some commercially available polyamines appear in Table 1. Generally, they are slightly to moderately viscous, water-soluble liquids with

Table 1. **Properties of Commercial Diamines and Higher Amines**

Commercial name	CAS Registry number	Structural formula	Molecular weight	Freezing point, °C	Bp[a], °C	ΔH_{vap}[a] kJ/mol	Refractive index, n_D^{20}	Viscosity at 20°C, mPa·s (=cP)
ethylenediamine	[107-15-3]	$H_2N(CH_2)_2NH_2$	60.1	10.8	117.0	40.7	1.4565	1.8
diethylenetriamine	[111-40-0]	$H_2N(CH_2)_2NH(CH_2)_2NH_2$	103.2	−39	206.9	54.0	1.4859	7.2
triethylenetetramine	[112-24-3]	$H_2N(CH_2CH_2NH)_2CH_2CH_2NH_2$[b]	146.2[b]	−35	277.4	56.4	1.4986	26
tetraethylenepentamine	[112-57-2]	$H_2N(CH_2CH_2NH)_3CH_2CH_2NH_2$[b]	189.3[b]	−40	315		1.5067	76
pentaethylenehexamine[c]	[4067-16-7]	$H_2N(CH_2CH_2NH)_4CH_2CH_2NH_2$[b]	232.4[b]	−30	180–280[d]			100–300
aminoethylpiperazine	[140-31-8]	$NH_2CH_2CH_2N(CH_2CH_2)_2NH$	129.2	−17	221	41.2	1.5003	15
piperazine	[110-85-0]	$HN(CH_2CH_2)_2NH$	86.1	109.6	144.1			
1,2-propylenediamine	[78-90-0]	$H_2NCH(CH_3)CH_2NH_2$	74.1	−27	120–123	38.2	1.4455	1.6
1,3-diaminopropane	[109-76-2]	$H_2NCH_2CH_2CH_2NH_2$	74.1	−12	137–140	46.4[e]	1.4555	2.0
iminobispropylamine	[56-18-8]	$H_2N(CH_2)_3NH(CH_2)_3NH_2$	131.2	−16	110–120	76.2[e]	1.4791	9.6
N-(2-aminoethyl)-1,3-propylenediamine	[13531-52-7]	$H_2N(CH_2)_2NH(CH_2)_3NH_2$	117.2		80			
N,N′-bis-(3-aminopropyl)-ethylenediamine	[10563-26-5]	$H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3$-$NH_2$	174.3		170			
dimethylaminopropyla-mine	[109-55-7]	$(CH_3)_2NCH_2CH_2CH_2NH_2$	102.2	−56	134.9	35.6	1.4350	1.1
menthanediamine	[80-52-4]		170.3	−45	107–126[f]		1.479	17.5[g]
triethylenediamine	[280-57-9]	$N(CH_2CH_2)_3N$	112.2	158	174	61.9[h]		
hexamethylenediamine[i]	[124-09-4]	$H_2N(CH_2)_6NH_2$	116.2	41	204.0	51.0		

Structural formula for menthanediamine:

[a] At 101.3 kPa = 1 atm unless otherwise noted.

[b] Linear component. Commercial product consists of a mixture of linear, branched, and cyclic structures with the same number of nitrogen atoms.

[c] Commercial higher polyamine products contain up to about 40% PEHA.

[d] At 0.67 kPa, 10–60% distills in this range.

[e] At 93.3°C.

[f] At 1.3 kPa.

[g] At 25°C.

[h] Heat of sublimation, below 78°C.

[i] For manufacture of HMDA in preparation of nylon-6,6, see POLYAMIDES.

mild to strong ammoniacal odors. Although completely soluble in water initially, hydrates may form with time, particularly with the heavy ethyleneamines (TETA, TEPA, PEHA, and higher polyamines), to the point that gels may form or the total solution may solidify under ambient conditions. The amines are also completely miscible with low mol wt alcohols, acetone, benzene, toluene and ethyl ether, but only slightly soluble in heptane. Piperazine, the lowest mol wt cyclic diamine, freezes above room temperature. As such, it is available commercially as either the anhydrous solid or an aqueous solution.

EDA forms the following binary azeotropes (at atmospheric pressure):

Secondary component	Bp, °C	Amine, %
water	119	81.6
isobutyl alcohol	120.5	50.0
n-butanol	124.7	35.7
toluene	103	30.8

3. Chemical Properties

The aliphatic alkyleneamines are strong bases exhibiting behavior typical of simple aliphatic amines. Additionally, dependent on the location of the primary or secondary amino groups in the alkyleneamines, ring formation with various reactants can occur. This same feature allows for metal ion complexation or chelation (1). The alkyleneamines are somewhat weaker bases than aliphatic amines and much stronger bases than ammonia as the pK_b values indicate (Table 2).
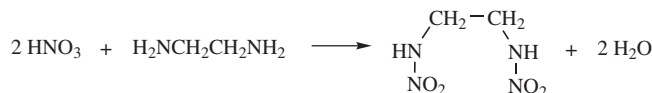
3.1. Inorganic Acids.   Alkyleneamines react vigorously with commonly available inorganic acids forming crystalline, water soluble salts. The free alkyleneamines can be regenerated by reaction of their salts with aqueous caustic.

Ethylenedinitramine [505-71-5], an explosive compound, is made by reaction of two moles of nitric acid [7697-37-2] per mole of EDA, splitting out two

Table 2. **Alkyleneamine pK Values**

Amine	pK_1	pK_2	Reference
EDA	3.83	6.56	2
1,2-PDA	4.03	6.90	2
1,3-PDA	3.70	5.71	3
DETA	3.89	4.60	4
TETA	3.84	4.47	4
NH_3	4.76		5
$CH_3CH_2NH_2$	3.25		5

moles of water from the salt at elevated temperatures (6).

$$2\,HNO_3\ +\ H_2NCH_2CH_2NH_2\ \longrightarrow\ \underset{\underset{NO_2}{|}}{HN}\overset{CH_2-CH_2}{\diagdown\underset{\underset{NO_2}{|}}{NH}}\ +\ 2\,H_2O$$

3.2. Alkylene Oxides and Aziridines. Alkyleneamines react readily with epoxides, such as ethylene oxide [75-21-8] (EO) or propylene oxide [75-56-9] (PO), to form mixtures of hydroxyalkyl derivatives. Product distribution is controlled by the amine to epoxide mole ratio. If EDA, which has four reactive amine hydrogens, reacts at an EDA to EO mole ratio which is greater than 1:4, a mixture of mono-, di-, tri,-, and tetrahydroxyethyl derivatives of EDA are formed. A 10:1 EDA:EO feed mole ratio gives predominantly 2-hydroxyethylethylenediamine [111-41-1]; the remainder is a mixture of bis-(2-hydroxyethyl) ethylenediamines (7). If the reactive NH to epoxide feed mole ratio is less than one and, additionally, a strong basic catalyst is used, then oxyalkyl derivatives, like those shown for EDA and excess PO result (8,9).

$$\underset{CH_3}{\triangleright}O\ +\ H_2NCH_2CH_2NH_2\ \longrightarrow$$

with products showing:
$$\begin{array}{c}\overset{CH_3}{\underset{|}{}}\\ H{+}OCHCH_2)_n\diagdown\\ \qquad\qquad NCH_2CH_2N\\ H{+}OCHCH_2)_n\diagup\\ \underset{CH_3}{\overset{|}{}}\end{array}\quad\begin{array}{c}\overset{CH_3}{\underset{|}{}}\\ (CH_2CHO)_{\overline{n}}H\\ \\ (CH_2CHO)_{\overline{n}}H\\ \underset{CH_3}{\overset{|}{}}\end{array}$$
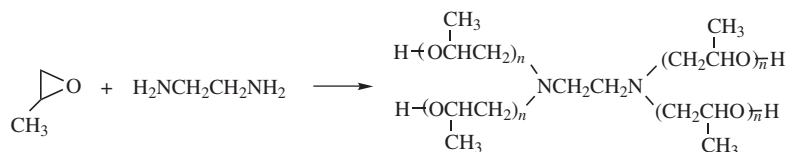
Aziridines react with alkyleneamines in an analogous fashion to epoxides (10,11). Product distribution is controlled by the alkyleneamine-to-aziridine mole ratio.

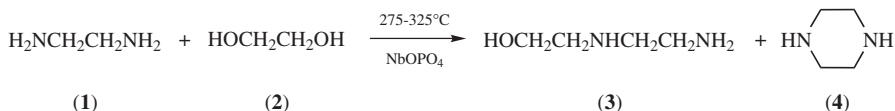$$\triangleright NH\ +\ H_2NCH_2CH_2NH_2\ \longrightarrow\ HN(CH_2CH_2NH_2)_2$$
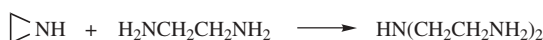
3.3. Aliphatic Alcohols and Alkylene Glycols. Simple aliphatic alcohols, such as methanol [67-56-1], can be used to alkylate alkyleneamines. For example, piperazine reacts with methanol over a reductive amination catalyst to yield a mixture of 1-methyl- [109-01-3] and 1,4-dimethylpiperazine [106-58-1] (12).

$$CH_3OH\ +\ HN\diagdown\diagup NH\ \xrightarrow{H_2/cat.}\ CH_3N\diagdown\diagup NH\ +\ CH_3N\diagdown\diagup NCH_3\ +\ H_2O$$
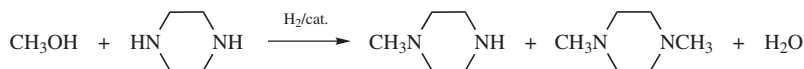
Either gas- or liquid-phase reactions of ethyleneamines with glycols in the presence of several different metal oxide catalysts leads to predominantly cyclic ethyleneamine products (13). At temperatures exceeding 400°C, in the vapor phase, pyrazine [290-37-9] formation is favored (14). Ethyleneamines bearing

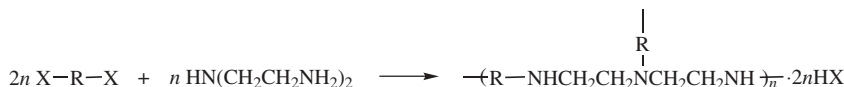2-hydroxyalkyl substituents can undergo a similar reaction (15).

$$H_2NCH_2CH_2NH_2 \ + \ HOCH_2CH_2OH \ \xrightarrow[\text{NbOPO}_4]{275\text{-}325°\text{C}} \ HOCH_2CH_2NHCH_2CH_2NH_2 \ + \ HN\overset{\frown}{}NH$$

(**1**)   (**2**)   (**3**)   (**4**)

Reaction of either (**1**) + (**2**) or (**3**) + (**4**) at 400°C over ZnO gives pyrazine (**5**).
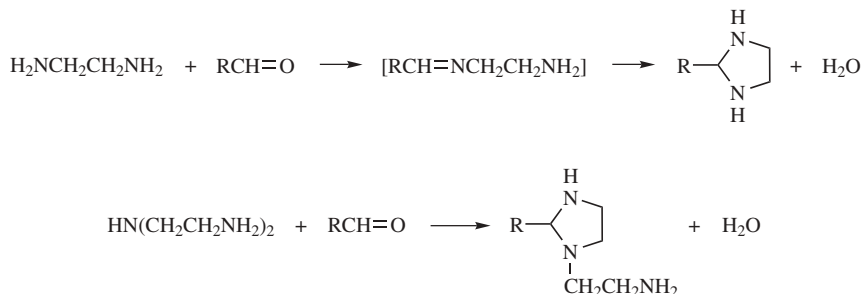
(**5**)
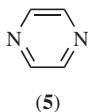
3.4. Organic Halides.   Alkyl halides and aryl halides, activated by elec-
tron withdrawing groups (such as NO_2) in the ortho or para positions, react with
alkyleneamines to form mono- or disubstituted derivatives. Product distribution
is controlled by reactant ratio, metal complexation or choice of solvent (16,17).
Mixing methylene chloride [75-09-2] and EDA reportedly causes a runaway
reaction (18).

$$RX \ + \ H_2NCH_2CH_2NH_2 \ \longrightarrow \ RNHCH_2CH_2NH_2 \ + \ HX$$

$$2\,RX \ + \ H_2NCH_2CH_2NH_2 \ \longrightarrow \ RNHCH_2CH_2NH_2 \ + \ 2\,HX$$

Aliphatic dihalides, like ethylene dichloride [107-06-2], react with alkylenea-
mines to form various polymeric, cross-linked, water soluble cationic products
(19) or higher alkyleneamine products depending on the reactant ratio.

$$2n\,X{-}R{-}X \ + \ n\,HN(CH_2CH_2NH_2)_2 \ \longrightarrow \ \overset{\overset{\displaystyle R}{|}}{{-}(R{-}NHCH_2CH_2NCH_2CH_2NH\,)_{\overline{n}}}\cdot 2nHX$$

3.5. Aldehydes.   Alkyleneamines react exothermically with aliphatic
aldehydes. The products depend on stoichiometry, reaction conditions, and struc-
ture of the alkyleneamine. Reactions of aldehydes with ethyleneamines like EDA
or DETA give mono- and disubstituted imidazolidines via cyclization of the inter-
mediate Schiff base (20).

$$H_2NCH_2CH_2NH_2 \ + \ RCH{=}O \ \longrightarrow \ [RCH{=}NCH_2CH_2NH_2] \ \longrightarrow \ R + H_2O$$

$$HN(CH_2CH_2NH_2)_2 \ + \ RCH{=}O \ \longrightarrow \ R + H_2O$$

Reaction of $H_2N(CH_2)_nNH_2$ with excess formaldehyde [50-00-0] is reversible and gives products of widely varying types which depend on the alkane chain length. For example, reaction of formaldehyde with EDA yields both 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane and 3-oxa-1,5-diazabicyclo[3.2.1]octane; the simple imidazolidine is not observed. However, 1,4-butanediamine [110-60-1] and diamines with longer chains give two-dimensional polymers (21).
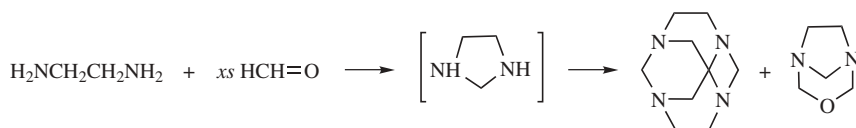
Substituted methyl- or dimethylamines are prepared by treating the appropriate primary or secondary amine with formaldehyde in the presence of hydrogenation catalysts (22,23).
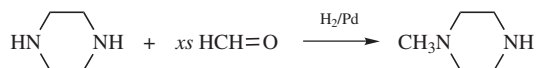
EDA reacts with formaldehyde and sodium cyanide under the appropriate alkaline conditions to yield the tetrasodium salt of ethylenediaminetetraacetic acid (24). By-product ammonia is removed at elevated temperatures under a partial vacuum. The free acid or its mono-, di-, or trisodium salts can be produced by the appropriate neutralization using a strong mineral acid. This same reaction with other amines is used to produce polyamino acetic acids and their salts. These products are used widely as chelating agents.

3.6. Organic Acids and Their Derivatives (Anhydrides, Nitriles, Ureas). Alkyleneamines react with acids, esters, acid anhydrides or acyl halides to form amidoamines and polyamides. Various diamides of EDA are prepared from the appropriate methyl ester or acid at moderate temperatures (25,26).

$$H_2NCH_2CH_2NH_2 \ + \ 2\,CH_2COOH \ \longrightarrow \ CH_3CONHCH_2CH_2NHCOCH_3 \ + \ 2\,H_2O$$

Diacids or carbonates are used with alkyleneamines to make amide polymers (27,28).

$$n\,H_2NCH_2CH_2NH_2 \ + \ n\,HOOC(R)COOH \ \longrightarrow \ HO{+}CO(R)CONHCH_2CH_2NH{+}_m H \ + \ n\,H_2O$$
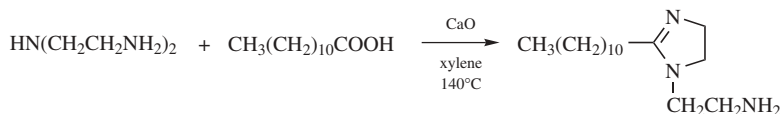
Under more forcing conditions with acid anhydrides, EDA can form tetraacyl derivatives (29). However, much milder conditions or less active acylating agents are needed to obtain the monoamide essentially free of the diamide (30−32).
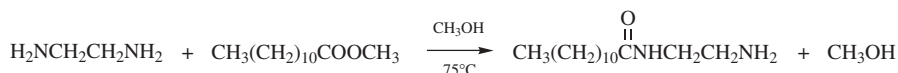

The monoamides can be cyclized to form imidazolines. This can be done without isolation of the monoamide by a variety of techniques including distilling
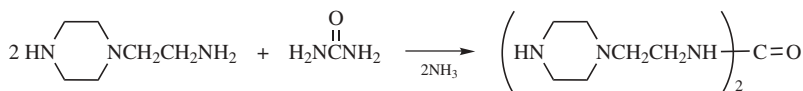
the alcohol and water away as formed (33), heating under vacuum (34), heating in a hydrocarbon solvent under vacuum (35), or heating in the presence of catalysts such as alumina treated with H_3PO_4 (36) or CaO (37).

$$HN(CH_2CH_2NH_2)_2 \quad + \quad CH_3(CH_2)_{10}COOH \quad \xrightarrow[\substack{xylene \\ 140°C}]{CaO} \quad CH_3(CH_2)_{10}—\overset{N}{\underset{\underset{CH_2CH_2NH_2}{N}}{\diagup}}$$

Hydrogen cyanide (HCN) and aliphatic nitriles (RCN) can be used to form imidazolines. For example, EDA and HCN form 2-imidazoline (38). In the presence of sulfur or polysulfides as catalysts, 2-alkyl-2-imidazolines can be prepared from aliphatic nitriles and EDA (39,40).

$$RCN \quad + \quad H_2NCH_2CH_2NH_2 \quad \longrightarrow \quad R—\overset{N}{\underset{N}{\diagup}}$$
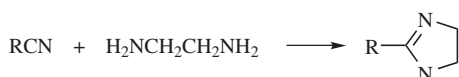
Alkyleneamines, like AEP, react with urea [57-13-6] to form substituted ureas and ammonia (41).

$$2\ HN\diagdown NCH_2CH_2NH_2 \quad + \quad H_2N\overset{O}{\overset{\|}{C}}NH_2 \quad \xrightarrow{2NH_3} \quad \left(HN\diagdown NCH_2CH_2NH\right)_2 C=O$$

DETA has been produced by reaction of monoethanolamine [141-43-5] (MEA) and EDA with urea (42). In this process, MEA reacts with urea to form 2-oxazolidinone which then reacts with EDA to form the cyclic urea of diethylene-triamine. Hydrolysis of the urea liberates the free amine.

Alkyl-substituted succinimides are prepared by reaction of alkyleneamines such as TETA or TEPA with the corresponding alkyl substituted succinic anhydride (43).

$$RNH_2 \quad + \quad \overset{O}{\underset{O}{R'\diagup\diagdown O}} \quad \longrightarrow \quad \overset{O}{\underset{O}{R'\diagup\diagdown NR}}$$
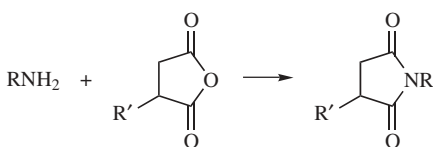
Amines and other bases catalyze the exothermic decomposition of molten maleic anhydride [108-31-6] at temperatures above 150°C, accompanied by the rapid evolution of gaseous products (44,45). The rate of reaction reportedly increases with the basicity of the amine and higher initial temperatures. The reaction mixture can become explosive.

The imidazolines can be dehydrogenated at high temperatures over metal oxide catalysts to give the corresponding imidazoles (46).

$$R—\overset{N}{\underset{\underset{H}{N}}{\diagup}} \quad \xrightarrow{ZnO/400°C} \quad R—\overset{N}{\underset{\underset{H}{N}}{\diagup}}$$
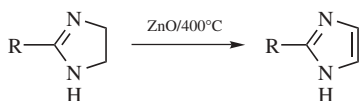
3.7. Sulfur Compounds. Ethylene thiourea [96-45-7], a suspected human carcinogen, is prepared by reaction of carbon disulfide [75-15-0] (CS_2) in aqueous EDA (47).
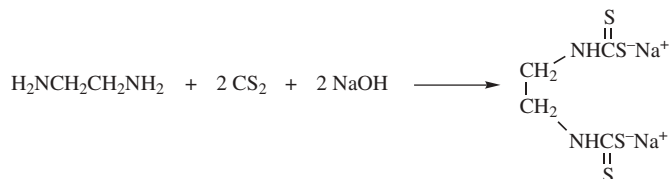
$$H_2NCH_2CH_2NH_2 \ + \ CH_2 \ \longrightarrow \ \underset{\underset{S}{\overset{\|}{}}}{HN \diagdown \diagup NH}$$
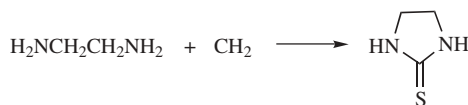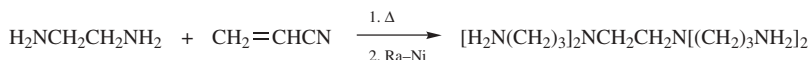
EDA reacts readily with two moles of CS_2 in aqueous sodium hydroxide to form the bis sodium dithiocarbamate. When aqueous ammonia and zinc oxide (or manganese oxide or its hydrate) is used with a basic catalyst, the zinc (or manganese) dithiocarbamate salt is isolated. Alternatively, the disodium salt can react with $ZnSO_4$ or $MnSO_4$ followed by dehydration in an organic solvent to yield the same salts (48–50).

$$H_2NCH_2CH_2NH_2 \ + \ 2\,CS_2 \ + \ 2\,NaOH \ \longrightarrow \ \begin{matrix} & & \overset{S}{\overset{\|}{NHCS^-Na^+}} \\ CH_2 \diagup & \\ CH_2 \diagdown & \\ & & \underset{\underset{S}{\overset{}{\|}}}{NHCS^-Na^+} \end{matrix}$$

3.8. Olefins. EDA reacts with isobutylene [115-11-7] over a borosilicate zeolite containing 3.2% Cr at 300°C to give the monoalkylation product (51).

$$(CH_3)_2CH{=}CH_2 \ + \ H_2NCH_2CH_2NH_2 \ \longrightarrow \ (CH_3)_3CNHCH_2CH_2NH_2$$

EDA and other alkyleneamines react readily with acrylonitrile or acrylate esters. EDA reacts with acrylonitrile to give tetrakis(2-cyanoethyl)-ethylenediamine which is reduced over Raney nickel to give tetrakis(3-aminopropyl)-ethylenediamine (52). With methyl acrylate and EDA under controlled conditions, a new class of starburst dendritic macromolecules forms (53,54).

$$H_2NCH_2CH_2NH_2 \ + \ CH_2{=}CHCN \ \xrightarrow[\text{2. Ra–Ni}]{\text{1.}\,\Delta} \ [H_2N(CH_2)_3]_2NCH_2CH_2N[(CH_2)_3NH_2]_2$$

Olefins can be aminomethylated with carbon monoxide [630-08-0] (CO) and amines in the presence of rhodium-based catalysts. For example, piperazine reacts with cyclohexene [110-83-8] to form N,N'-di-(1-cyclohexylmethyl)-piperazine [79952-94-6] (55).
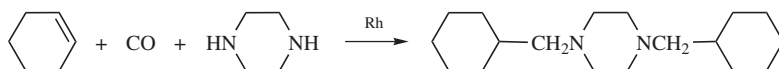
3.9. Environmentally Available Reactants. Under normal conditions ethyleneamines are considered to be thermally stable molecules. However, they are sufficiently reactive that upon exposure to adventitious water, carbon

dioxide, nitrogen oxides, and oxygen, trace levels of by-products can form and increased color usually results.

Carbon dioxide reacts readily with EDA in methanol to form crystalline *N*-(2-aminoethyl)carbamate [109-58-0] (56).

$$H_2NCH_2CH_2NH_2 \ + \ CO_2 \ \longrightarrow \ H_3\overset{+}{N}CH_2CH_2NHCOO^-$$

EDA, when heated with carbon dioxide under pressure (57), or treated with urea (58), or ethylene carbonate [96-49-1] (59), or CO and oxygen using a selenium catalyst (60), produces ethyleneurea.
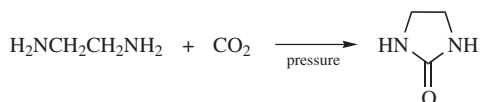
N-Alkylpiperazines and PIP can react with nitrosating agents such as nitrogen oxides, nitrites or nitrous acid to form nitrosamine derivatives (61,62). Piperazine dihydrochloride [142-64-3] reacts with aqueous sodium nitrite and HCl to give the dinitrosamine that melts at 156–158°C (61).
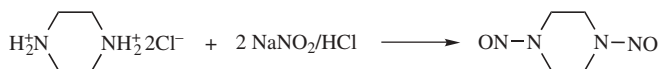
PIP, if ingested (as the acid salt) or inhaled, is nitrosated *in vivo*, and is excreted partially as the mono- and dinitrosamines (63,64).

Ethyleneamines are soluble in water. However, in concentrated aqueous solutions, amine hydrates may form; the reaction is mildly exothermic. The hydrates of linear TETA and PIP melt around 50°C (65,66).

4. Manufacture

4.1. Ethyleneamine Processes. Present industrial processes are based on ethylene and ammonia. The seventy year old ethylene dichloride (EDC) process is still the most widely practiced industrial route for producing ethyleneamines (67). In this process, aqueous ammonia reacts with EDC at high temperature and pressure to produce the total spectrum of ethyleneamine products as a mixture of amine hydrochloride salts. These salts are neutralized, usually with aqueous caustic, generating the free amines and forming inorganic salts, normally sodium chloride (68–70). Product distribution can be controlled by varying the NH$_3$:EDC mole ratio (71,72), product recycle (73–75), pH (72,76–78), and reactor geometry (70,71,77). A typical product distribution obtained at a 20:1 mole ratio of NH$_3$:EDC is EDA 55%, PIP 1.9%, DETA 23%, AEP 3.5%, TETA 9.9%, TEPA 3.9%, and higher polyamines 2.3% (72). Raising the NH$_3$:EDC mole ratio increases EDA, whereas lowering this ratio leads to the formation of higher mol wt polyethyleneamines. The higher mol wt ethyleneamines are made also by reaction of EDC with EDA, DETA, or mixtures of these

(75,79–81). The amine products can be separated from the aqueous salt solution by evaporative crystallization (82,83), dehydration (84,85), solvent extraction (86–90), or combinations of these. In one process, the amines can be extracted from a neutralized reaction mixture with a solvent system comprised of a reactive ketone and an alcohol, followed by back extraction with CO_2 and water, and thermally cracking the so-formed carbamates (91,92). After the amines are separated from their salts, they are purified by conventional fractional distillation.

Alternative processes for the manufacture of ethyleneamines have been actively sought since the late 1960s. The catalytic reductive amination of monoethanolamine (MEA), which was the first such process to appear, produces the lower mol wt ethyleneamines (EDA, DETA, PIP, and AEP) and coproduct aminoethylethanolamine [114-41-1] (AEEA), and hydroxyethylpiperazine [103-76-4] (HEP). Catalyst development has progressed from simple nickel catalysts to catalysts containing nickel with up to three additional metals such as Co, Cu, Cr, Fe, Re, Ru, and B or copper–cobalt catalysts associated with Re, W, and Zr (93–102). Aluminas, silicas, aluminosilicates, titania and zirconia are used as support materials. Most catalysts exhibit high selectivities to EDA, but produce more PIP than characteristically observed in the older EDC process. Product distribution can be controlled by temperature (103), NH_3:MEA mole ratio, hydrogen partial pressure (104), and conversion. A 9.3:1 NH_3:MEA mole ratio (96) gives the following selectivity to products at a 60% MEA conversion: EDA 71%, DETA 10.2%, AEEA 6.9%, PIP 9.2%, AEP 1.4%, and HEP 1.3%. An integrated two-step process produces MEA from a supercritical mixture of ethylene oxide and ammonia in the first stage and reductively aminates the ethanolamines in the second stage (105). The reductive amination of EDA or MEA without ammonia can be used to produce DETA or AEEA, respectively (106–108).

The condensation of MEA with EDA over heterogeneous catalysts to form primarily DETA represents the newest commercial technology for making ethyleneamines. Prior to 1977, commercial use of this type of condensation was primarily to make cyclic ethyleneamines (109), not the more linear alkyleneamines produced commercially for a few years in the early 1990's (110–112). Variations of this process operate at high temperatures (200–350°C) and in either the vapor phase (113–115) or liquid phase (116). Catalysts for this condensation include Group 4 (IVB), 5 (VB), and 6 (VIB) metal oxides (117,118); Group IVB and Group VB supported phosphates (119–123); and supported tungstates (124,125). Product distribution can be controlled by the EDA:MEA mole ratio (110,111,126,127), temperature (120), product recycle (116), and conversion. The TETA, TEPA, and higher polyamines produced by this technology have a higher linear content than similar products produced by the EDC-based technology. In a typical example (120), an EDA:MEA mole ratio of 2:1 yields the following product selectivities at 51% MEA conversion: DETA 77.2%, PIP 2.7%, AEEA 0.8%, AEP 2.0%, TETA 16.6%, TEPA 0.5%. The TETA fraction is comprised of over 99% acyclic ethyleneamines. This process is not being practiced commercially at this time.

A process for the production of ethylenimine [151-56-4], a suspect carcinogen, by the vapor phase dehydration of monoethanolamine has been developed (128–132). By using an alkyleneamine co-feed with the alkanolamine, higher

alkyleneamines are made *in situ* (133). The catalysts are tungsten-, niobium-, or phosphate-based.

At one time, alkyleneamines were made primarily from raw materials derived from methane or methanol. This technology is still being practiced selectively to form branched ethyleneamines, for example. The reaction of formaldehyde and hydrogen cyanide in the presence of water yields glycolnitrile [107-16-4] (134,135) or in the presence of ammonia yields aminoacetonitrile and its condensation products (136−138). Reduction of the glycolnitrile with hydrogen in the presence of ammonia or the reduction of the aminoacetonitrile with hydrogen yields alkyleneamines (139−141).

4.2. Diaminopropane Processes. 1,2-Propylenediamine can be produced by the reductive amination of propylene oxide (142), 1,2-propylene glycol [57-55-6] (143), or monoisopropanolamine [78-96-6] (144). 1,3-Propanediol [504-63-2] can be used to make 1,3-diaminopropane (143). Various propaneamines are produced by reducing the appropriate acrylonitrile−amine adducts (145−147). Polypropaneamines can be obtained by the oligomerization of 1,3-diaminopropane (148,149).

5. Economic Aspects

Ethyleneamine production capacities for 2001, broken down by geographical area and main producers in each area, are given in Table 3. Worldwide growth for most ethyleneamines is expected to parallel GDP. Some regional and certain applications demands will show somewhat higher growth rates.

Of the worldwide ethyleneamines capacity, well over 50% is EDC-based; the balance is monoethanolamine-derived. A complete breakdown of the

Table 3. **Ethyleneamine Production Capacities, 2001**

Company	Process technology[a]	Capacity, 10^3 t/yr
United States		
Dow	EDC, MEA	105
Huntsman	EDC	73
Total		*178*
Western Europe		
Dow	EDC	14
Huntsman		14
BASF	MEA	40
Delamine	EDC	35
Akzo Nobel	MEA, EDC	60
Total		*163*
Japan		
Tosoh	EDC	40
Others		
	EDC	4
Approximate world capacity		*385*

[a]EDC = ethylene dichloride−based, MEA = monoethanolamine−based.

Table 4. **Prices of Some Commercially Available Polyamines**

Product	Price, U.S. \$/kg[a]
ethylenediamine	3.06
diethylenetriamine	3.74
triethylenetetramine	3.33
tetraethylenepentamine	3.90
higher polyamines[b]	3.26
aminoethylpiperazine	2.98
piperazine (68% aqueous solution)[c]	2.98
1,2-propylenediamine	6.06
1,3-diaminopropane	7.28
iminobispropylamine	6.06[d]
dimethylaminopropylamine	2.20
hexamethylenediamine	3.57[d]

[a] List price for shipment of bulk quantities as of November, 1999.

[b] Product marketed under a variety of commercial names.

[c] Contained PIP basis.

[d] In drums.

ethyleneamines capacity by product is not feasible since most manufacturers can vary production mix to meet market demand. A rough estimate is that EDA represents about 40% of the total production of the family of ethyleneamines. In Europe, the product mix is skewed somewhat more toward EDA.

Prices of the principal commercial polyamines in 1999, in the United States, are given in Table 4.

6. Specifications and Test Methods

Typical specifications for the commercially available ethyleneamines are given in Table 5. For more detailed specifications on these products and for speci-

Table 5. **Typical Specifications of Some Aliphatic Polyamines**

Commercial name	Assay, min %	Amine value, mg KOH/g	Specific gravity, 20°C/20°C	Color, ALPHA, max
ethylenediamine	99.0		0.896–0.904	15
diethylenetriamine	98.5		0.948–0.954	30
triethylenetetramine	95.0	1410–1480	0.976–0.983	50
tetraethylenepentamine	90.0	1290–1375	0.987–1.001	2[a]
higher polyamines[b]		1100–1300	1.005–1.025	
1,2-propylenediamine	99.0		0.855–0.885	15
1,3-diaminopropane	99.0		0.886–0.890	20
iminobispropylamine	99.0		0.926–0.936	30
dimethylaminopropylamine	99.0		0.815–0.820	15
hexamethylenediamine	99.9[c]		0.889–0.900	10

[a] 1963 Gardner Scale.

[b] Commercial product contains 30–40% PEHA, remainder higher amines.

[c] Anhydrous basis, commercial material contains 9–16% water.

fications of other polyamines not listed, the individual manufacturers should be consulted.

The assay of ethyleneamines is usually done by gas chromatography. Compared to packed columns, in which severe tailing is often encountered due to the high polarity of the ethyleneamines, capillary columns provide better component separation and quantification. Typically, amines can be analyzed using fused silica capillary columns with dimethylsilicones, substituted dimethylsilicones or PEG Compound 20 M as the stationary phase (150).

Because the heavy ethyleneamines are very complex materials, assays by titration in aqueous and nonaqueous media are often performed (151). The result is usually expressed as an amine number or amine value, a measure of the total basic nitrogen content of the product. Titrimetric procedures are also available to define primary, secondary, and tertiary amine content (152).

Determination of ethyleneamines in air can be accomplished by absorbing the amines on NITC (1-naphthyl isothiocyanate) treated XAD-2 resin, then desorbing the derivative from the treated tubes and quantifying the amount using high performance liquid chromatography (hplc). Sensitivity is reported as 0.37 and 0.016 mg/m^3 for EDA and DETA, respectively, per sample (153,154).

7. Storage and Handling

By virtue of their unique combination of reactivity and basicity, the polyamines react with, or catalyze the reaction of, many chemicals, sometimes rapidly and usually exothermically. Some reactions may produce derivatives that are explosives (eg, ethylenedinitramine). The amines can catalyze a runaway reaction with other compounds (eg, maleic anhydride, ethylene oxide, acrolein, and acrylates), sometimes resulting in an explosion.

As commercially pure materials, the ethyleneamines exhibit good temperature stability, but at elevated temperatures noticeable product breakdown may result in the formation of ammonia and lower and higher mol wt species. This degradation becomes more pronounced at higher temperature and over longer time periods. Certain contaminants, such as mineral acids, can lower the onset temperature for rapid thermal decomposition. The manufacturer should be contacted and thermal stability testing conducted whenever ethyleneamines are mixed with other materials.

Like many other combustible liquids, self-heating of ethyleneamines may occur by slow oxidation in absorbent or high-surface-area media, eg, dumped filter cake, thermal insulation, spill absorbents, and metal wire mesh (such as that used in vapor mist eliminators). In some cases, this may lead to spontaneous combustion; either smoldering or a flame may be observed. These media should be washed with water to remove the ethyleneamines, or thoroughly wet prior to disposal in accordance with local and Federal regulations.

Since ethyleneamines react with many other chemicals, dedicated processing equipment is usually desirable. Proper selection of the materials of construction for ethyleneamine service is essential to ensure the integrity of the handling system and to maintain product quality. Amines slowly absorb water, carbon dioxide, nitrogen oxides, and oxygen from the atmosphere, which may result in

the formation of low concentrations of by-products and generally increased color. These same by-products can also contribute to increased color in certain derivatives, even though the color of the ethyleneamine itself is not significantly changed. Storage under an inert atmosphere minimizes this sort of degradation.

Galvanized steel, copper and copper-bearing alloys are unacceptable for all ethyleneamine service. Although corrosion of carbon steel is not extreme (<0.03 mm/yr) at typical storage temperatures, the lighter amines (particularly EDA and DETA) pick up iron and discolor badly. If this cannot be tolerated, then 300 series stainless steels or aluminum are recommended for the storage tanks. Carbon steel generally can be used for storage of the heavier ethyleneamines without noticeable impact on product quality if the storage temperature is modest (<60°C), nitrogen blankets are maintained to exclude air, and the material is anhydrous. A 300 series stainless steel is often specified for heating coils, transfer lines and small agitated tanks, because carbon steel can suffer enhanced corrosion due to the erosion of the passive film by the product velocity. Similar logic suggests cast 316 stainless steel for pumps and valves in ethyleneamine service.

Nonmetallic equipment normally is not used for ethyleneamine service. Ethyleneamines can permeate polyethylene and polypropylene, even at ambient temperature. However, certain grades of these materials may be acceptable in some storage applications. Baked phenolic-lined carbon steel is acceptable for storage of many pure ethyleneamines, except EDA.

Gaskets utilized in ethyleneamine service generally are made of Grafoil flexible graphite or polytetrafluoroethylene (TFE). There is no single elastomer that is acceptable for the entire product line, although TFE may be considered as an alternative to elastomers across the product line. However, because TFE is not a true elastomer, it may not always prove suitable as a replacement.

Most common thermal insulating materials are acceptable for ethyleneamine service. However, porous insulation may introduce the hazard of spontaneous combustion if saturated with ethyleneamines from a leak or external spill. Good housekeeping, maintenance of weather barriers, minimization of flanges and fittings, and training of personnel can reduce the potential for smoldering insulation fires. Closed cellular glass insulation is normally resistant to insulation fires because it is difficult for the ethyleneamines to saturate these materials.

Certain ethyleneamines require storage above ambient temperature to keep them above their freezing points (EDA and PIP) or to lower the viscosity (the heavy amines). As a result, the vapors "breathing" from the storage tank can contain significant concentrations of the product. Water scrubbers may be used to capture these vapors.

Solid ethyleneamine carbamates, formed by the reaction of the amines with carbon dioxide, can foul tank vents and pressure relief devices. Vent fouling can be minimized by using a nitrogen blanket that prevents atmospheric CO_2 from being drawn in, or by steam-tracing the vents (>160°C) to decompose the carbamates. Vents must be inspected regularly to ensure that the carbamate does not gradually accumulate and clog the lines.

Although the ethyleneamines are water soluble, solid amine hydrates may form at certain concentrations that may plug processing equipment, vent lines, and safety devices. Hydrate formation usually can be avoided by insulating and

heat tracing equipment to maintain a temperature of at least 50°C. Water cleanup of ethyleneamine equipment can result in hydrate formation even in areas where routine processing is nonaqueous. Use of warm water can reduce the extent of the problem.

8. Health and Safety Factors

Ethyleneamine vapors are painful and irritating to the eyes, nose, throat, and respiratory system. Extremely high vapor concentration may cause lung damage. Prolonged or repeated inhalation may lead to kidney, liver, and respiratory system injury. Contact with the liquids will severely damage the eyes and may cause serious burns to the skin. When swallowed, the concentrated liquid materials may produce considerable local injury. Repeated oral exposures may cause kidney and liver changes. Both vapors and liquid can cause sensitization in some individuals, resulting in contact dermatitis and/or the development of an asthmatic respiratory response. This may occur in certain susceptible individuals following exposure to extremely low concentrations of ethyleneamines, even below the irritation threshold.

The ACGIH has adopted TLVs of 10 ppm (25 mg/m^3) and 1 ppm (4.2 mg/m^3) for EDA and DETA, respectively; and the AIHA has adopted a Workplace Enviornmental Exposure Limit (WEEL) of 1 ppm (6 mg/m^3) for TETA. Thus, for a normal 8 hr work day, the time weighted average concentrations of EDA, DETA and TETA in the air of the workplace should not exceed these levels.

Strict precautions should be observed to prevent direct contact with all ethyleneamines, including eye, skin, and respiratory protection. If contact is made, medical treatment should be obtained immediately, in addition to flushing and washing with copious amounts of water. Vomiting is not to be induced following ingestion. Before handling any of these products it is important to contact the manufacturer to obtain complete toxicological information, safe-handling recommendations, and an MSDS.

9. Applications

Polyalkylene polyamines find use in a wide variety of applications by virtue of their unique combination of reactivity, basicity, and surface activity. With a few significant exceptions, they are used predominantly as intermediates in the production of functional products. End-use profiles for the various ethyleneamines are given in Table 6.

9.1. Fungicides. The ethylenebisdithiocarbamates (EBDCs) are a class of broad-spectrum, preventive, contact fungicides first used in the early 1940s. They have found application on many fruits, vegetables, potatoes, and grains for prevention of mildew, scab, rust, and blight. Following a 1989 proposed ban on use of EBDCs on most crops, the cancer risk potential of these products was reviewed by the United States Environmental Protection Agency (EPA), which ruled in early 1992 that these products were within guidelines for safe use on 45 specific crops (155). However, in July 1992, a California Federal Appeals

Table 6. **Approximate World End-Use Profiles for Ethyleneamines, 1997, 10^3 t yr**

Application	EDA	DETA	PIP	Higher homologues	Total
fungicide	29				29
oil and fuel additives	5	6		30	41
polyamides/epoxy curing	8	7	1	20	36
paper resins		30		3	33
chelating agents	29	12		2	43
fabric softeners/surfactants		7		1	8
petroleum production	2	3		3	8
bleach activator	20				20
anthelmintics/pharmaceuticals	2		7		9
ashalt chemicals				8	8
other	5	7	2	5	19
Total					*254*

court ruled that the use of the manganese/zinc salt [8018-01-7] (mancozeb) could not be allowed.

The EBDCs are prepared by reaction of EDA with carbon disulfide in the presence of sodium or ammonium hydroxide initially, then with zinc and/or manganese salts, as appropriate (156–160). A continuous process has recently been reported (161). The common names of these salts are nabam [142-59-6] (Na salt), amobam (ammonium salt), zineb [12122-67-7] (Zn salt), maneb [12427-38-2] (Mn salt), and mancozeb.

Other materials based on EDA have also been suggested as fungicides. The most important of the imidazoline type (162) is 2-heptadecyl-2-imidazoline (163), prepared from EDA and stearic acid [57-11-4]. It is used as the acetate salt for control of apple scab and cherry leaf spot. A 2:1 EDA–copper sulfate complex has been suggested for control of aquatic fungi (164).

9.2. Lubricant and Fuel Additives.   The preparation of ashless dispersants for motor oil and other lubricants, and of certain detergents for motor fuels, is one of the largest applications for polyamines. However, its growth has slowed in the past several years compared to some of the other applications. The most widely used derivatives are the mono- and bis-polyisobutenylsuccinimides. They are most commonly prepared by the condensation reaction of polyisobutenylsuccinic anhydrides with polyethylene polyamines (165–169). TETA, TEPA, and higher ethyleneamines are generally used; however, all of the ethyleneamines and many other polyamines, and substituted diamines and polyamines, have been employed for various products. Polyamines are also suggested for use in dispersant-varnish inhibitors for lubricating oils for two-stroke engines (170). Lubricating oil compositions for marine diesel engines containing TEPA in microemulsion form have also been reported (171). Reduced attack of fluoroelastomers is claimed for succinimides based on TEPA that have reacted with adipic acid [124-04-9] (172).

Although connection of polyalkylene or poly(alkylene oxide) groups to the polyamine is most commonly by the succinimide linkage, a different linking group is employed in another important class of ashless dispersants—the

Mannich bases. They are prepared on a commercial scale by reaction of an alkyl-phenol with formaldehyde and a polyamine (173–177). The alkyl and polyamine moieties are similar to those used in the succinimide products.

Additives for lubricating oils providing a combination of viscosity index improvement (VII) and dispersancy have also been reported. These additives are prepared from ethyleneamines by reaction with various VII-type polymers that have been chlorinated or modified in some other way to provide an ethyle-neamine reaction site. Antirust additives for lubricating oils have been prepared by reaction of polyamines with fatty acids followed by reaction with polyalkyle-nesuccinic anhydrides (178,179).

Over-based and other metal-containing oil additives providing detergency have also been prepared from polyamines (180,181). A number of antiwear/anti-scuff additives for lube oils and greases also use polyamines. The combination of 2,6-di-*t*-butylphenol [128-39-2] and AEP is said to be an effective antioxidant in lube oil formulations containing certain viscosity index improvers (182). The thermal oxidative stability of a lubricating composition containing zinc diisopro-pyl dithiophosphate is reportedly increased by addition of sulfur and ethylene-diamine (183). Polyamines are also used in preparation of fatty acid/amine soaps and poly(urea) thickeners for lubricating greases. A complex tolylene polyurea thickener made with EDA has been reported (184).

In the fuel additives area, EDA and DETA, as well as *N*-(2-hydroxyethyl) ethylenediamine, have found significant commercial application as dispersant detergent additives for gasoline after reacting with chlorinated polybutylenes (185,186). Improved antirust properties are reported when these compounds are neutralized with carboxylic acids (187). Numerous similar products made by alkylating or acylating EDA or DETA (188–196) have also been suggested as fuel detergent and deposit control additives. Cetane improvement in diesel fuels has been reported for a mixture containing EDA (197); and antiknock prop-erties of unleaded gasoline have been improved by addition of PIP or C-methyl substituted PIPs (198). The barium salt of a bis-nonylphenol (prepared by reac-tion of nonylphenol, DETA and formaldehyde) has been used as an antismoke additive in diesel fuels (199).

9.3. Epoxy Curing Agents. A variety of polyamines and their deriva-tives that contain primary and secondary amine functionality are used as epoxy resin hardeners in various functional coatings, adhesives, castings, lami-nates, grouts, etc (200). All of the commercial ethyleneamines have been used, DETA and TETA probably most commonly. There are numerous examples in the literature of adhesives using TETA (201) and DETA (202), coatings using EDA (203,204), tile adhesive and grout using EDA and DETA (205), casting or potting systems using DETA (206,207) and PIP (208,209). PIP (210) and AEP (211) also function as epoxy cure accelerators in certain applications (see EPOXY RESINS).

The ethyleneamines are commonly modified in various ways to achieve desired performance changes. Amidoamines and reactive polyamides, prepared by condensation of TETA or higher polyamines with fatty acids (212–214) and dimer acids (215,216), respectively, are widely used for longer pot life and better flexibility, adhesion, and solvent resistance (217). An amidoamine prepared from EDA and lysine methyl ester reportedly gives good low temperature cure (218);

and another prepared from TEPA and bis(salicylate)boric acid reportedly gives high reactivity, low toxicity, and unlimited solubility in epoxy resins (219). Most of the amidoamines and reactive polyamides contain significant imidazoline structure which provides improved compatibility with liquid epoxy resins (220–224).

Other modifications of the polyamines include limited addition of alkylene oxide to yield the corresponding hydroxyalkyl derivatives (225) and cyanoethylation of DETA or TETA, usually by reaction with acrylonitrile [107-13-1], to give derivatives providing longer pot life and better wetting of glass (226). Also included are ketimines, made by the reaction of EDA with acetone for example. These derivatives can also be hydrogenated, as in the case of the equimolar adducts of DETA and methyl isobutyl ketone [108-10-1] or methyl isoamyl ketone [110-12-3] (227), or used as is to provide moisture cure performance. Mannich bases prepared from a phenol, formaldehyde and a polyamine are also used, such as the hardener prepared from cresol, DETA, and formaldehyde (228). Other modifications of polyamines for use as epoxy hardeners include reaction with aldehydes (229), epoxidized fatty nitriles (230), aromatic monoisocyanates (231), or propylene sulfide [1072-43-1] (232).

9.4. Polyamide Resins.   Another class of polyamide resins, in addition to the liquid resins used as epoxy hardeners, are the thermoplastic type, prepared generally by the condensation reaction of polyamines with polybasic fatty acids. These resins find use in certain hot-melt adhesives, coatings, and inks. Diamines, typically EDA (233), are the principal amine reactant; however, tri- and tetramines are sometimes used at low levels to achieve specific performance.

In the adhesives area, thermoplastic, fatty polyamides are used in hot-melt and heat-seal adhesives for leather, paper, plastic and metal. Blends of EDA- and DETA-based polyamides are suggested for use in metal can seam sealants with improved toughness (234); pressure sensitive adhesives have been formulated with DETA-based polyamides (235); and anionic and cationic suspensoid adhesives are used as heat-seal coatings in paper converting (236). PIP and certain PIP derivatives are used with EDA in some applications (237).

Thermoplastic polyamides are used in coatings to modify alkyd resins (qv) in thixotropic systems (238) and to plasticize nitrocellulose lacquers (239). DETA-tall oil fatty acid-based polyamides are suggested for use as corrosion inhibitors in alkyd paints (240). Printing inks for flexo-gravure application on certain paper, film and foil webs rely on EDA- and PDA-based polyamides for their specific performance (241).

9.5. Paper Pulping, Resins and Additives.   Considerable interest has been generated in the sulfur-free delignification of wood chips with EDA–soda liquors since the late 1970s (242–244), with more recent interest in EDA–sulfide pulping (245,246). Improved rates of EDA recovery have been developed for the latter process (247).

Another significant end-use for polyamines is in preparation of paper wet-strength resins. These are polyamide, modified formaldehyde, and polyamine resins used to improve the physical strength of tissue, toweling, and packaging paper products. The cationic formaldehyde resins include both urea–formaldehyde and melamine–formaldehyde types (248,249). Cationic functionality is imparted by incorporation of DETA, TETA, and/or TEPA in the backbone of

the resins. This is accomplished either by reaction of the amine with the formaldehyde resin (250), by coreaction of the amine with the resin intermediates (251), or by prereaction of the amine with formaldehyde, followed by reaction with urea (252). The cationic functionality provides substantivity to the cellulose fibers in paper. Modifications of polyamine-modified formaldehyde resins with epichlorohydrin [106-89-8] (253) or ε-caprolactam [105-60-2] (254) have also been reported.

The most widely used paper wet-strength resins are the modified polyamide variety commonly prepared from DETA (sometimes TETA), adipic acid, and epichlorohydrin (255–259). In contrast with the polyamine-modified formaldehyde resins that require acidic conditions, these resins can be used under less corrosive neutral or alkaline conditions to make nonacidic papers. Stability of these resins reportedly can be improved by addition of formaldehyde (256) or alkoxylation prior to addition of epichlorohydrin (258). Polyamides made from polymeric fatty acids and ethyleneamines and neutralized with an organic base reportedly provide waterproofing as well as wet-strength (260). Polyamine wet-strength resins, that contain no amide functionality and that provide improved dry strength, are made by the reaction of ethyleneamines with epichlorohydrin (261).

Pigment retention and drainage additives made with polyamines include polyamines made from ethyleneamines, ethanolamines, and epichlorohydrin (262); ethyleneamines combined with phosphorus-modified polyamines made by reaction of ethyleneamines with $POCl_3$ [10025-87-3] (263); and a DETA–glutaric acid polyamide crosslinked with PEG-bis(3-chloro-2-hydroxypropyl) ether (264). Polyamines made from ethyleneamines and EDC are useful flocculating agents (265).

Waterproofing and sizing agents made with polyamines include amidoamines from ethyleneamines and fatty acids, used as is (266) or quaternized (267) or polyamides from polymeric fatty acids and ethyleneamines (268); ethyleneamine-based polyamides which have reacted with formaldehyde and sodium bisulfite and also provide antistatic properties (269); ethyleneamine-modified rosin gums (270), polyamides made from ethyleneamines and maleic anhydride which then further react with chlorinated paraffin (271); and ethyleneamine-treated sodium polyacrylate emulsions to give a waxy surface on Kraft paper (272). TEPA is incorporated in a heat-curable, polyamide–polyurea resin used in paper coating systems (273).

9.6. Chelates and Chelating Agents. Poly(aminoacetic acid)s and their salts derived from polyamines are used in a variety of systems where metal ions, commonly iron, need to be inactivated, buffered, concentrated, or transported. These chelating agents operate by forming stoichiometric complexes, called chelates, with most polyvalent metals. The most important industrial chelating agent is made by reaction of EDA with formaldehyde and hydrogen cyanide or an alkali metal cyanide in the presence of excess sodium hydroxide to form the tetrasodium salt of ethylenediamine tetraacetic acid (Na_4EDTA) (274–276). The intermediate ethylenediaminetetraacetonitrile may also be isolated and hydrolyzed to Na_4EDTA separately (277). The free tetraacid can then be formed by neutralization with HCl and precipitation from solution. The free ethyleneamines themselves are good chelating agents (qv) for many metals, such as copper and zinc. They are also used in specialized applications

such as electroplating and electroless metal coating with gold, silver, platinum, palladium, copper, zinc, nickel, and many alloys, where their metal complexing properties are required (278,279). This same property makes the ethyleneamines useful as ingredients in systems for etching, and for stripping nickel and nickel alloy coatings.

DETA is also used as the starting ethyleneamine in preparing analogous chelating agents. Diethylenetriaminepentaacetate [67-43-6] (DETPA) is used in chlorine-free paper pulp bleaching to prevent iron from decreasing the efficiency of the hydrogen peroxide (280).

Other developments in chelating resins include fibers made from poly(ethylene glycol) and poly(vinyl alcohol) to which EDA was attached with epichlorohydrin (281); and a styrene–divinylbenzene resin with pendant EDTA or DETPA groups (282).

9.7. Fabric Softeners, Surfactants and Bleach Activators. Mono- and bisamidoamines and their imidazoline counterparts are formed by the condensation reaction of one or two moles of a monobasic fatty acid (typically stearic or oleic) or their methyl esters with one mole of a polyamine. Imidazoline formation requires that the ethyleneamine have at least one segment in which a secondary amine group lies adjacent to a primary amine group. These amidoamines and imidazolines form the basis for a wide range of fabric softeners, surfactants, and emulsifiers. Commonly used amines are DETA, TETA, and DMAPA, although most of the polyethylene and polypropane polyamines can be used.

The most common alkyleneamine-based fabric softeners use bisamidoamines made from DETA, which are either cyclized by further dehydration to the corresponding imidazoline or lightly alkoxylated (283) to convert the central secondary amine group to a tertiary amine. The imidazoline or substituted bisamidoamine can then be quaternized with an alkylating agent, generally dimethyl sulfate, to yield softeners popular for household use (284–286). Bisimidazoline compounds are prepared by condensing TETA or TEPA with fatty acids (287) or triglycerides (288), followed by quaternization with dimethyl sulfate [77-78-1] to yield cationic fabric softeners. Another version uses sodium chloroacetate as the quaternizing agent to give amphoteric softeners (289). The products from the reaction of 1,3-PDA with alkyl isocyanates (290) or alkylene oxides (291) have also been suggested as softeners for use in detergent formulations (see DETERGENCY).

Many of the surfactants made from ethyleneamines contain the imidazoline structure or are prepared through an imidazoline intermediate. Various 2-alkylimidazolines and their salts prepared mainly from EDA or monoethoxylated EDA are reported to have good foaming properties (292–295). Ethyleneamine-based imidazolines are also important intermediates for surfactants used in shampoos by virtue of their mildness and good foaming characteristics. 2-Alkylimidazolines made from DETA or monoethoxylated EDA and fatty acids or their methyl esters are the principal commercial intermediates (296–298). They are converted into shampoo surfactants commonly by reaction with one or two moles of sodium chloroacetate to yield amphoteric surfactants (299–301). The ease with which the imidazoline intermediates are hydrolyzed leads to amidoamine-type structures when these derivatives are prepared under aqueous

alkaline conditions. However, reaction of the imidazoline under anhydrous conditions with acrylic acid [79-10-7] to make salt-free, amphoteric products, leaves the imidazoline structure essentially intact. Certain polyamine derivatives also function as water-in-oil or oil-in-water emulsifiers. These include the products of a reaction between DETA, TETA, or TEPA and fatty acids (302) or oxidized hydrocarbon wax (303). The amidoamine made from lauric acid [143-07-7] and DETA mono- and bis(2-ethylhexyl) phosphate is a very effective water-in-oil emulsifier (304).

Several cleaning formulations for specific uses contain unreacted polyamines. Examples include mixtures of ammonium alkylbenzenesulfonate, solvents, and PIP which give good cleaning and shine performance on mirrors and other hard surfaces without rinsing (305), and a hard-surface cleaner composed of a water-soluble vinyl acetate–vinyl alcohol copolymer, EDA, cyclohexanone [108-94-1], dimethyl sulfoxide [67-68-5], a surfactant, and water (306). TEPA, to which an average of 17 moles of ethylene oxide are added, improves the clay soil removal and soil antiredeposition properties of certain liquid laundry detergents (307).

Tetraacetylethylenediamine [10543-57-4] (TAED) has been widely adopted for use in home laundry products as an activator for peroxygen bleaches.

9.8. Petroleum Production and Refining. Specific polyamine derivatives are used in the petroleum production and refining industries as corrosion inhibitors, demulsifiers, neutralizers, and additives for certain operations.

The derivatives used in corrosion inhibitor formulations for down-hole use constitute a significant industrial application for polyamines. Again, mono- and bisamidoamines, imidazolines, and polyamides made from the higher polyamines are the popular choices. The products made from DETA and fatty acids have been widely used (308). A wide variety of other polyamine-based, corrosion inhibiting derivatives have been developed, generally incorporating some form of oil-soluble or oil-dispersible residue. Sulfur and its derivatives are also used in these polyamine-based corrosion inhibitors on occasion.

Other polyamine derivatives are used to break the oil/water emulsions produced at times by petroleum wells. Materials such as polyether polyols prepared by reaction of EDA with propylene and ethylene oxides (309); the products derived from various ethyleneamines reacting with isocyanate-capped polyols and quaternized with dimethyl sulfate (310); and mixtures of PEHA with oxyalkylated alkylphenol–formaldehyde resins (311) have been used.

In secondary operations, where chemicals are injected into hydrocarbon formations in conjunction with a chemical flooding process, polyamines are used to reduce the loss of injected chemicals to the formation by adsorption and precipitation (312). TEPA and other ethyleneamines are used with water-soluble polymeric thickeners in water–flood petroleum recovery operations to stabilize viscosity, mobility, and pH while imparting resistance to hydrolysis (313).

Ethyleneamines are used in certain petroleum refining operations as well. For example, an EDA solution of sodium 2-aminoethoxide is used to extract thiols from straight-run petroleum distillates (314); a combination of substituted phenol and AEP are used as an antioxidant to control fouling during processing of a hydrocarbon (315); AEP is used to separate alkenes from thermally cracked petroleum products (316); and TEPA is used to separate carbon disulfide from a

C$_5$ pyrolysis fraction from ethylene production (317). EDA and DETA are used in the preparation and reprocessing of certain cracking and hydrotreating catalysts (318–321).

9.9. Asphalt Additives and Emulsifiers.   Mono- and bisamidoamines, imidazolines and their mixtures are commonly used in formulating antistrip additives used to promote adhesion between the asphalt and mineral aggregate in bituminous mixtures for road paving, surfacing, and patching. They are commonly prepared from the higher molecular weight polyamines and tall oil fatty acids or other readily available organic acids and acylating agents (322–328). Similar polyamine derivatives are used, generally as their HCl or acetic acid salts, to make stable asphalt-in-water emulsions (329–337).

9.10. Other Applications.   Polyamines and their derivatives are used in a variety of other industries besides those already mentioned. In the fibers and textiles area, EDA, DETA, TETA, or TEPA are used to treat rayon (338), flax (339), hemp (340), jute (341,342), ramie (343), polyacrylonitrile (344,345), wool (346), polyester (347), acetate (348), and cotton (349) fibers and/or fabrics for modification of various properties (see Textile finishing). Durable press properties are developed in cotton fabrics using additives based on EDA or DETA (350); and compounds based on EDA are used as light stabilizers for spandex fibers (351), for shrink-proofing wool (352), as antistats for polypropylene carpet backing (353), and as moth-proofing agents (354). Industrial softening agents based on DETA and TEPA are also used (355,356), as are dyeing assists based on EDA, DETA, TETA, and TEPA for polyester (357), nylon (358), and other synthetic fabrics (359). Nylon-6 is a polyamide fiber based on DETA, ε-caprolactam and adipic acid (360) (see Caprolactam; Fibers, polyamides).

Iron and phosphate ore beneficiation processes, involving enrichment of the raw ores, use amidoamines and imidazolines made from polyamines and fatty acids as flotation agents that selectively adhere to silica particles and permit their removal by flotation procedures (361,362). A bis (fatty alkyl DETA) imidazoline is a flotation agent for beneficiation of niobium and tantalum ores (363). Ethyleneamines are used for extraction of copper, chromium, and nickel from their sulfide and oxide ores (364). EDA and DETA are used in lead ore processing and lead recovery processes (365–368). The principal use for PIP is as the active ingredient in anthelmintic preparations. These are inorganic or low mol wt organic acid salts of PIP that are used primarily in veterinary applications to combat intestinal worms, especially round worms (*Ascaris lumbricoides*) and pinworms [*Enterobium (Oxyuris) vermicularis*] (369) (see Antiparasitic agents, anthelmintics).

The polyamines also are used in several ways in the manufacture and processing of elastomers, polymers, and related materials. A significant volume of ethyleneamines is used in the coagulation of SBR and other synthetic rubber latexes (370–373) (see Elastomers, styrene–butadiene rubber; Latex technology). They also are used in vulcanization processes for various rubbers including thiodiethanol (374), vinyl acetate copolymer (375), ethylene copolymer (376), EPDM terpolymer (377–379), SBR (380), modified diene (381,382), chloroprene telomer (383), and urethane (384). Ethyleneamines and certain of their derivatives are also used in a variety of urethane systems as curing agents, catalysts, polyol precursors, stabilizers, and internal parting agents—even in the recycling of rigid

polyurethane waste. EDA also finds use as a curing catalyst for phenolic resins (qv), a stabilizer for urea resins, an antistatic treatment for polystyrene foam, and as a polymerization inhibitor for isoprene. EDA is a key component of the polymer in spandex fiber (see FIBERS, ELASTOMERS). TETA is a popular curing agent for furfural resin binders for molded graphite structures and foundry molds; and EDA finds use in systems for etching polyimide films. EDA reacts with haloalkylalkoxysilanes and phthalocyaninatosilanols to make agents that improve the adhesion between inorganic surfaces and polymers. Scrubber solvents containing TETA are used to remove acrylate and other monomer vapors from exhaust streams generated during handling and processing operations, such as latex paint vehicle manufacturing. The bisamide made by reaction of 1 mole of EDA with 2 moles of stearic acid, [ethylenebis(stearamide)], is used as an external lubricant for ABS resin and PVC, parting material, viscosity regulator, preservative, and surface gloss enhancer. It is also useful as a defoamer in paper mill operations and certain detergent formulations (see AMIDES, FATTY ACID).

The polyamines are also used in a number of other industries, including ceramics, coal−oil emulsification and coal extraction, polymer concrete, concrete additives, stone and concrete coatings and plaster systems, other industrial corrosion inhibitors (metal pickling, steel rolling, etc), coatings and adhesives systems other than epoxies, explosives, fire retardants, functional fluids (hydraulic, metal working, etc), gas treating, water treating, ion exchange resins, and membranes for gas separation, water treating, ion exchange, ultrafiltration, and electrolysis.

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