

**HUNTSMAN**

Enriching lives through innovation

# ETHYLENEAMINES

A Global Profile of Products and Services





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### ETHYLENEAMINES – A GLOBAL PROFILE OF PRODUCTS AND SERVICES

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# Introduction



Huntsman offers a complete line of ethyleneamine products. These materials are useful in a wide range of applications. Capable of a broad range of reactions, ethyleneamines from Huntsman provide the highest levels of product quality, value and consistency to the customer.

Huntsman manufactures ethyleneamines by the ethylene dichloride/ammonia process. This process consists of the reaction of ethylene dichloride with ammonia, followed by neutralization with sodium hydroxide to produce a mixture of ethyleneamines and sodium chloride.

The salt is removed from the amine mixture, and the individual amines are separated by fractional distillation.

While most individual distillation fractions are sold as products, others are formulated to obtain desired physical or chemical properties or reacted further to obtain the final product.

Reliability, quality, and consistency are important in the production of ethyleneamines. A reliable supply of product is necessary for customer success.

With product available in Freeport, Texas and Temeuzen, The Netherlands, Huntsman can readily supply your global requirements. Both production sites are ISO 9002 certified. ISO certification assures that all functions related to manufacturing these products are strictly monitored and controlled according to global standards.

Ethyleneamines are useful compounds employed globally in a wide variety of applications. In this brochure, the properties and applications of these versatile products are described.

Analysis, storage, handling and use information is provided. For additional information, contact your local Huntsman sales or technical service representative. Contact information is given at the end of this brochure.

# Ethyleneamine Products

Huntsman offers a complete line of ethyleneamine products and other ethyleneamine co-products on an intermittent basis. These co-products include piperazine amine mix, higher molecular weight amines, and higher molecular weight alkoxyated amines.

The following standard products serve virtually all current commercial applications for ethyleneamines. Huntsman also stands ready to develop new derivations and custom blends of these products on demand.

Huntsman ethyleneamines comply with all applicable requirements of the U.S. TSCA inventory, the European EINECS, and the Canadian DSL. Product components are either listed on these chemical inventories or are not required to be listed.

Huntsman ethyleneamines are also listed on many other regulatory lists around the world. Contact your Huntsman representative if you need specific regulatory information.

**Table 2.1 — Product CAS Numbers**

| Products                      | CAS Numbers |
|-------------------------------|-------------|
| Ethylenediamine (EDA)         | 107-15-3    |
| Diethylenetriamine (DETA)     | 111-40-0    |
| Triethylenetetramine (TETA)   | 112-24-3    |
| Tetraethylenepentamine (TEPA) | 112-57-2    |
| Ethyleneamine E-100 (E-100)   | 68131-73-7  |
| Aminoethylpiperazine (AEP)    | 140-31-8    |
| Aminoethylethanolamine (AEEA) | 111-41-1    |

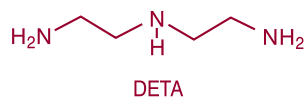
For additional information consult the appropriate safety data sheets or contact your Huntsman representative. Note: Some ethyleneamine products may have more than one CAS number assigned due to the composition of the product or for regulatory purposes.

## 2.1 Ethylenediamine (EDA)



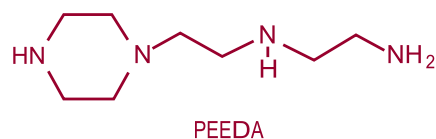
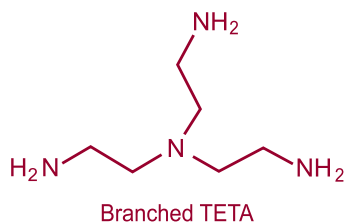
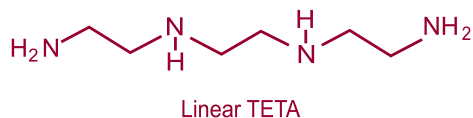
Ethylenediamine (CAS #000107-15-3, 1, 2-ethanediamine) is the lowest molecular weight ethyleneamine. It contains two primary nitrogens. EDA is a single-component product that is clear and colorless, with an ammonia-like odor.

## 2.2 Diethylenetriamine (DETA)



Diethylenetriamine (CAS #000111-40-0, N-(2-aminoethyl)-1, 2-ethanediamine) is the next higher molecular weight product containing two primary and one secondary nitrogen. DETA is a single-component product that is clear and colorless, with an ammonia-like odor.

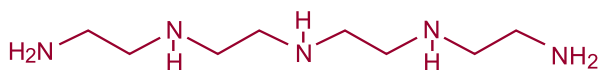
## 2.3 Triethylenetetramine (TETA)



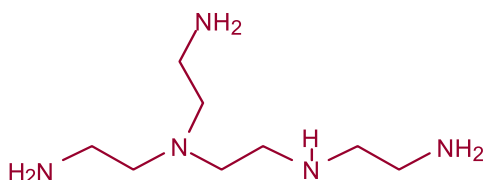
Triethylenetetramine is a mixture of four TETA ethyleneamines with close boiling points including linear, branched, and two cyclic molecules. These compounds are:

- TETA (CAS #000112-24-3, N, N'-bis-(2-aminoethyl)-1, 2-ethanediamine)
- Branched TETA (CAS #004097-89-6, tris-(2-aminoethyl)amine)
- Bis AEP (CAS #006531-38-0, N, N'-bis-(2-aminoethyl)piperazine)
- PEEDA (CAS #024028-46-4, N-[(2-aminoethyl) 2-aminoethyl]piperazine)

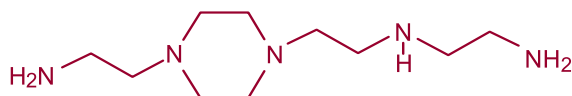
## 2.4 Tetraethylenepentamine (TEPA)



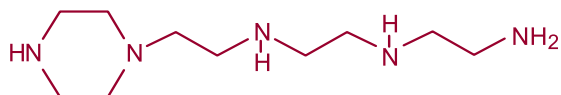
Linear TEPA



AETETA



AEPEEDA



PEDETA

Tetraethylenepentamine is principally a mixture of four TEPA ethyleneamines with close boiling points including linear, branched, two cyclic TEPA products, and higher molecular weight products. These compounds are:

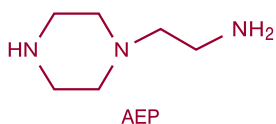
- TEPA (CAS #000112-57-2, N-(2-aminoethyl)-N'-{2-[(2-aminoethyl)amino]ethyl}-1,2-ethanediamine)
- AETETA (CAS #031295-46-2, 4-(2-aminoethyl)-N-(2-aminoethyl)-N'-{2-[(2-aminoethyl)amino]ethyl}-1,2-ethanediamine)
- AEPEEDA (CAS #031295-54-2, 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]-piperazine)
- PEDETA (CAS #031295-49-5, 1-[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]-piperazine)

## 2.5 Ethyleneamine E-100 (E-100)

Ethyleneamine E-100 (CAS #68131-73-7) is a mixture of polyethylenepolyamines consisting of TEPA, pentaethylenehexamine (PEHA), hexaethyleneheptamine (HEHA), and higher molecular weight products. E-100 is a complex mixture of various linear, cyclic, and branched products with a number-average molecular weight of 250-300 g/mole.

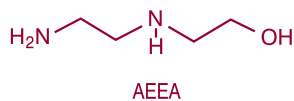
## 2.6 Aminoethylpiperazine (AEP)

Aminoethylpiperazine (CAS #000140-31-8, 1-piperazineethaneamine) is a cyclic ethyleneamine. It contains one primary, one secondary, and one tertiary amine. AEP is a single-component product that is clear and colorless and has an ammonia-like odor.



## 2.7 Aminoethylethanolamine (AEEA)

Aminoethylethanolamine (CAS #000111-41-1, 2-[(2-aminoethyl)amino]-ethanol) is a single-component product, with minimal ethylenediamine impurity. The product is water-soluble, clear, colorless, and slightly viscous. An ammonia-like odor is typical of the product.



## 2.8 Blends and Derivatives

Huntsman develops specifications for all of the ethyleneamines products in partnership with our customers. Custom blends and derivatives are available.

Your particular product needs are met via certificate of analysis assurance that each lot meets or exceeds your specifications.

# Applications

Ethyleneamine products are used in a wide range of applications, primarily as reactive intermediates used to produce other useful chemical products.

The applications listed below are described in published literature or in patents. The references noted can be found in the bibliography at the end of the brochure.

The user is encouraged to consider the environmental, health, and safety issues associated with the use of ethyleneamines and their applications before using these products, including issues associated with the derivative products and by-products.

In addition, the user should comply with all applicable regulatory requirements involved in the processing, end-use, and ultimate fate of their products.

**Table 3.1 — Ethyleneamine Applications**

| Applications                | EDA | DETA | TETA | TEPA | E-100 | AEP | AEAA | Blends & Der. |
|-----------------------------|-----|------|------|------|-------|-----|------|---------------|
| Asphalt Additives           |     | •    | •    | •    | •     | •   |      | •             |
| Bleach Activators           | •   |      |      |      |       |     |      |               |
| Chelating Agents            | •   | •    |      |      |       |     | •    |               |
| Corrosion Inhibitors        | •   | •    | •    | •    | •     | •   |      |               |
| Drainage Aids               |     | •    |      |      |       |     |      |               |
| Elastomeric Fibers          | •   |      |      |      |       |     |      |               |
| Epoxy Curing Agents         |     | •    | •    | •    | •     | •   |      | •             |
| Fabric Softeners            |     | •    |      |      |       |     | •    |               |
| Fungicides                  | •   |      |      |      |       |     |      |               |
| Hydrocarbon Purification    |     |      | •    | •    |       |     |      |               |
| Lube Oil & Fuel Additives   | •   | •    | •    | •    | •     |     | •    | •             |
| Mineral Processing Aids     | •   | •    | •    | •    | •     | •   |      |               |
| Pharmaceuticals             | •   |      |      |      |       |     |      |               |
| Plastic Lubricants          | •   |      |      |      |       |     |      |               |
| Polyamide Resins            | •   | •    | •    | •    |       | •   |      |               |
| Rubber Processing Additives | •   |      |      |      |       |     |      |               |
| Surfactants                 |     | •    | •    | •    |       |     | •    |               |
| Textile Additives           | •   | •    | •    | •    |       |     | •    |               |
| Urethane Chemicals          | •   | •    |      |      |       | •   | •    |               |
| Wet-Strength Resins         |     | •    | •    | •    |       |     |      | •             |

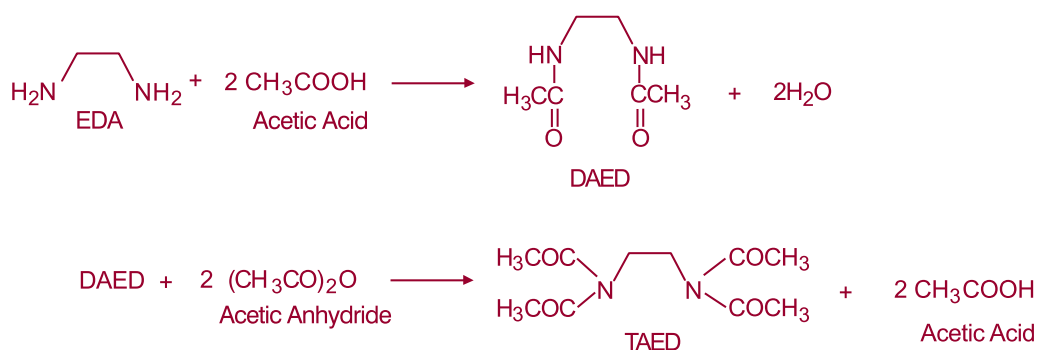
### 3.1 Asphalt Additives

Amidoamines, made by reacting ethyleneamines with fatty acids, are used in asphalt to improve performance in road surfacing. These amidoamines are complex mixtures of amides and imidazolines.<sup>1</sup>

Amidoamines are used as “anti-strip” additives which improve the adhesion of the rock used in asphalt concrete to the asphalt binder.<sup>2,3,4</sup> Loss of aggregate is the major cause for deterioration of asphalt roadway.

Products similar to anti-strip additives, with cationic modification, are used as surfactants to produce asphalt-in-water emulsions in top coatings on asphalt concrete roads.<sup>5,6</sup> The use of asphalt emulsions can improve skid-resistance and renew weathered asphalt roadways.

### 3.2 Bleach Activators



Since the 1980s, tetraacetythylenediamine (TAED) has been widely adopted in Europe for use in powdered detergent compositions as an activator for peroxygen bleaching agents. TAED has been successfully used in home laundry products as a low temperature bleach activator in combination with persalts such as sodium perborate or percarbonate.<sup>7,8,9,10,11</sup>

TAED delivers both bleaching and hygiene, since its formulations are able to effectively kill bacteria and other microorganisms under typical wash conditions for which thermal disinfection is not possible.<sup>12</sup> TAED is increasingly used in automatic dishwashing detergent (ADW) powders.<sup>13</sup> Activation of peroxide with TAED under acidic or near neutral pH conditions offers a safe and low capital alternative to using preformed peracids, such as peracetic acid or other strong oxidizing species.

Potential applications are hard surface cleaners, biocide formulations, industrial biocides/slimicide, clinical sterilants, agricultural disinfectants, textile bleaching and processing, pulp and paper bleaching, etc.<sup>14</sup>

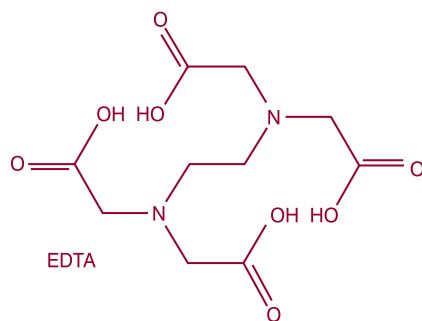
The ability of TAED to activate peroxide in a broad range of pH conditions lends itself to applications in pulp bleaching sequences. Potential benefits are improved yields, reduced corrosion, and improved pulp brightness.<sup>15,16,17,18</sup>

TAED is a colorless, odorless, solid which can be granulated. The product can be prepared by reacting ethylenediamine (EDA) with acetic acid to form the bisamide, which is then reacted with acetic anhydride to form the tetra-amide.<sup>9</sup> Under aqueous conditions, TAED reacts with perhydroxide anion to form DAED (diacetyleneethylenediamine) and peracetate anion, the species that delivers low temperature bleaching performance and, additionally, biocidal activity. Both TAED and DAED are non-toxic, non-sensitizing, and biodegradable to give carbon dioxide, water, nitrate, and ammonia as end products.<sup>13,16</sup>

### 3.3 Chelating Agents

Polyaminocarboxylic acids and their salts derived from ethyleneamines are used in a variety of applications where specific metal ions interfere with processing, require buffering, concentrating, separating, or transporting.

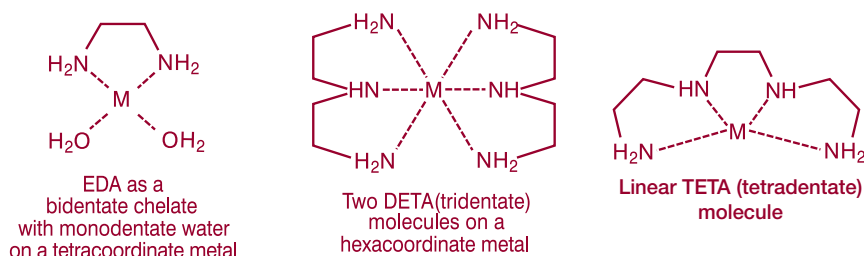
Chelants operate by forming stoichiometric complexes with most di- or polyvalent metals. A major industrial application of EDA is the manufacture of ethylenediaminetetraacetic acid (EDTA), a well-established chelating agent or chelant. All of the methods used industrially for manufacturing EDTA involve the addition of formaldehyde and hydrogen cyanide, or an alkali metal cyanide, to an aqueous solution of EDA.



The tetra-sodium salt of EDTA ( $\text{Na}_4$  EDTA) may be prepared directly by using excess sodium hydroxide in the reaction<sup>19,20,21,22,23</sup> or the intermediate ethylenediaminetetraacetonitrile may be isolated and hydrolyzed to  $\text{Na}_4$  EDTA in a separate step.<sup>24,25</sup>

DETA or AEEA can be substituted for EDA to prepare two other important industrial chelating agents: pentasodium diethylenetriaminepentaacetate and trisodium N-hydroxyethyl ethylenediaminetriacetate.

Unmodified ethyleneamines also form stable complexes with certain metal ions, such as zinc and copper. This property makes the ethyleneamines useful in specialized applications, such as electroplating and electroless metal coating, and as ingredients in systems for etching and for stripping nickel and nickel alloy coatings.



### 3.4 Corrosion Inhibitors

Amidoamines and substituted imidazolines, prepared by the reaction of DETA or TETA with fatty acids, find use as corrosion inhibitors in petroleum production operations.<sup>26</sup> Corrosion inhibition for various industrial processes is also achieved via reaction of ethoxylated amines and fatty acid anhydrides or in blends of these inhibitors with phosphate esters.<sup>27,28,29,30,31</sup>

Cyclic amidine polymers obtained by reacting EDA with vinyl nitriles or cyanohydrins in the presence of thiourea<sup>32</sup> and polymers prepared by the reaction of ethyleneamines with acrylate esters<sup>33</sup> are also used in this application. The substituted imidazolines may be further derivatized by reaction with benzyl halides, propane sultone, and thiourea<sup>34</sup> to give acid corrosion inhibitors for mild steel.

Nitrobenzoic acid salts of ethyleneamines function as metal corrosion inhibitors in coating formulations.<sup>35</sup> EDA acts as a corrosion inhibitor for aluminum alloys<sup>36</sup> in the presence of mineral acids and provides corrosion protection in distillation columns.<sup>37</sup> The entire range of ethyleneamines can be used to produce imides of hydrocarbyl succinic anhydride useful as filming inhibitors for crude oil distillation towers and providing added improvement in fractionation.<sup>38</sup>

For marine environments, polyamine cured epoxies provide effective coating and cladding to resist erosion, corrosion, and provide under sea-level protection.<sup>39</sup>

### 3.5 Drainage Aids

Flocculants and drainage aids are used to optimize the separation of a solid phase from the liquid phase in aqueous suspensions.<sup>40</sup> These suspensions usually consist of organic or inorganic particles, which are finely divided to colloidal consistency distributed in water as a dispersion medium.

Addition of ethyleneamine-based products drastically increases the rate of particle sedimentation so that a clear, supernatant liquid is obtained. The settled sludge can then be filtered rapidly or centrifuged, resulting in a more efficient separation.

Polyamines as cationic flocculants are used mainly in municipal and certain industrial wastewater treatment.<sup>41</sup> In papermaking, DETA improves the drainage rate and the flocculation or flotation for pulp recovery.<sup>42</sup>

### 3.6 Elastomeric Fibers

Polyurethane elastomeric fiber such as Spandex® and elastane are key components in high performance sports apparel. Elastomeric fiber is a long-chain synthetic polymer of segmented polyurethane.<sup>43,44,45</sup>

In Western Europe, the generic name elastane is used instead of Spandex®.

A segmented polyurethane is a block copolymer with alternating “soft” and “hard” blocks or segments.<sup>46</sup> The soft segments are nonrigid (fluid) and impart stretch to the polymer. The hard segments are rigid (solid) and impart tensile strength to the polymer and help limit plastic flow.

The soft segments are usually derived from polyether or polyester polyols. The hard segments are usually urethanes or urethane-ureas made by first reacting the polyols with a diisocyanate to form a prepolymer and then reacting this with chain extenders, diamines (e.g., EDA), to form segments that have high melting points.<sup>47,48</sup>

### 3.7 Epoxy Curing Agents

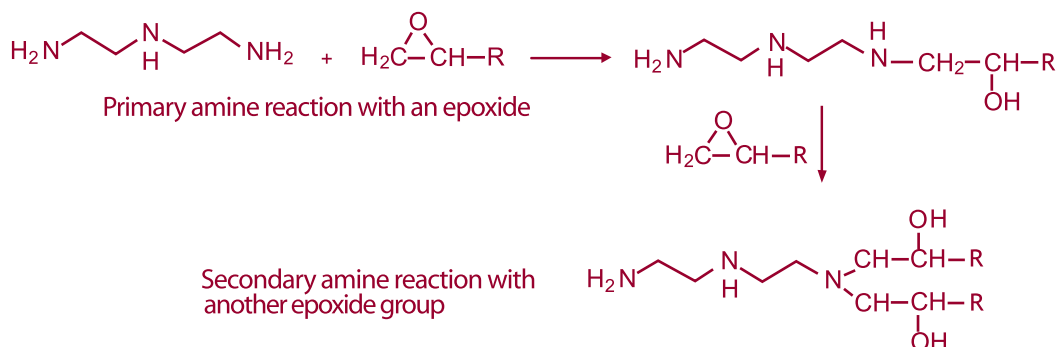
Ethyleneamines are widely used for curing (cross-linking) epoxy resins both as the pure amine or, more often, as a derivative that contains primary and secondary amines that can react with the epoxy resin functionality.<sup>49</sup>

Typically, ethyleneamines and their derivatives are used in epoxy products such as coatings, adhesives, and other applications that are cured under ambient conditions.<sup>50</sup> All of the ethyleneamine products have been used in epoxy curing, but the most widely used products are DETA, TETA and TEPA. Reactive polyamides made from dimer acids and TETA, or amidoamines made from tall oil fatty acids and TEPA, are the most widely used ethyleneamine derivatives in epoxy curing.<sup>51</sup>

These products will usually have various levels of imidazoline content to control viscosity and to improve compatibility with the epoxy resin. Polyamides and amidoamines are also used to increase pot life, improve film flexibility and increase adhesion to various substrates. Reactive polyamides can also be used as adhesion promoters in polyvinyl chloride coatings.<sup>52</sup>

Many other modifications of ethyleneamines for use as epoxy curing agents are known. Ethyleneamines are reacted with small amounts of epoxy resin to produce a prepolymer curing agent which has improved resin compatibility.

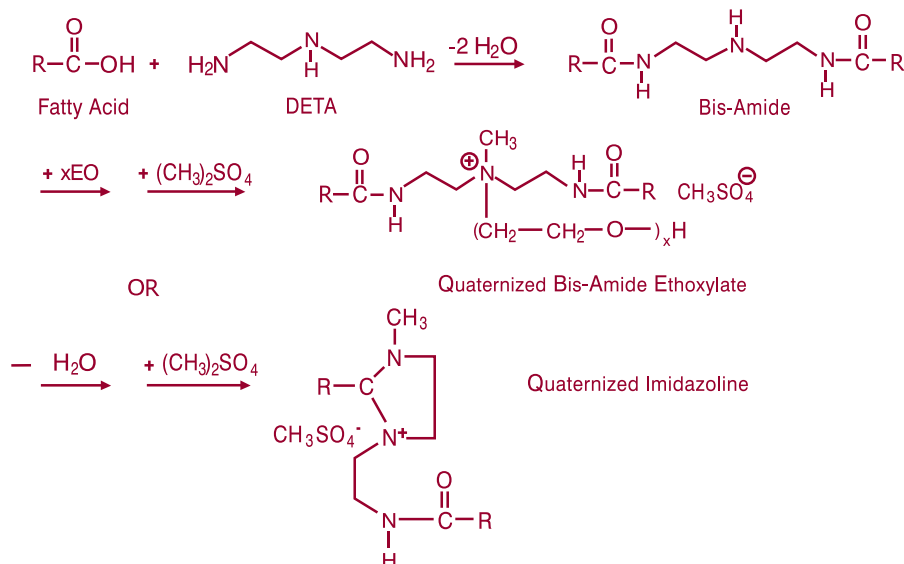
Modification of ethyleneamines with ketones (to produce ketimines) and acrylonitrile (to cyanoethylate the amine) are used for special applications. Ethyleneamines are reacted with propylene oxide and ethylene oxide to produce curing agents with reduced exposure concerns. Other modifications include Mannich bases which are prepared by reaction of a polyamine with phenol and formaldehyde.



### 3.8 Fabric Softeners

Fabric softeners are used to impart softness and antistatic properties to machine washed laundry.<sup>53,54</sup> These products can be introduced as part of the detergent package, added in the washing machine rinse cycle, or added in the clothes dryer.<sup>55,56</sup> Fabric softeners can be produced by reacting fatty acids with DETA to produce a bisamidoamine. The amidoamine can then be converted to the imidazoline or reacted with an alkylene oxide, such as ethylene oxide (EO), to produce a tertiary amine.

Both products are quaternized with dimethyl sulfate or methyl chloride to make the active softener.<sup>57</sup> Softeners similar to the DETA-based products have been made from AEEA to produce ester-amides.<sup>58</sup> These products are more readily hydrolyzed and have been shown to be more biodegradable than DETA-based products.



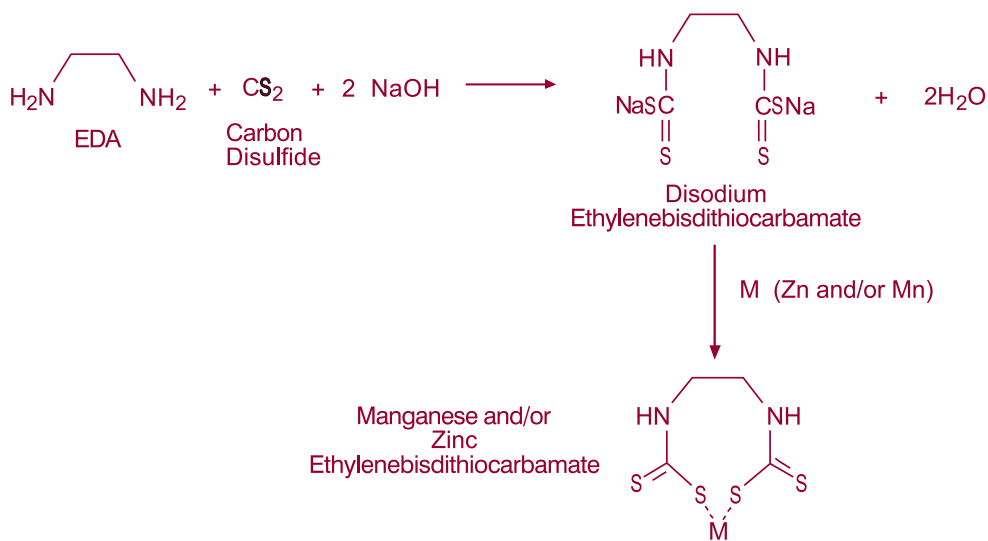
### 3.9 Fungicides

The ethylenebisdithiocarbamates (EBDCs), which were introduced in the early 1940s, represent the most important class of general purpose, broad spectrum fungicides currently used for the control of mildew, scabs, rusts and blights on fruits, vegetables, potatoes, cotton, and, to some extent, on grains.<sup>59</sup> They are used to prevent both crop damage in the field and harvested crops from deterioration in storage or transport.<sup>60</sup>

The EBDCs belong to the class of protectant fungicides, also known as residual or contact fungicides, which act on the surface of the plant, whereas systemic fungicides act internally.

They are organic sulfur compounds, derived from bisdithiocarbamic acid, more accurately called 1,2-bisdithiocarbamates, and available in a wide variety of mixtures and formulations.<sup>61,62</sup> The products are prepared in a two-step process. First, EDA and carbon disulfide are reacted in the presence of sodium or ammonium hydroxide to form the water-soluble disodium<sup>63</sup> or diammonium<sup>64</sup> salt of ethylenebisdithiocarbamate.

The water-soluble salt is then converted to the poorly soluble Zn and/or Mn salts by reaction with inorganic salts of these metals.<sup>65,66,67,68</sup>



These fungicides are commonly known as zineb (Zn salt), maneb (Mn salt) and mancozeb (Mn-Zn salt).

The first in this class was zineb, used to protect fruit and vegetable crops from a wide range of foliar and other diseases.<sup>69</sup> Zineb, first introduced in 1943 and 1944 to protect potatoes, but also used on grapes, apples, and many other crops, became the first successful synthetic organic fungicide.<sup>70</sup>

Other products followed, the most important of which were maneb (1950) and mancozeb (1961)<sup>61</sup>, which is a combination of maneb and zineb.<sup>71</sup> Maneb is used in the control of early

and late blights on potatoes and tomatoes and many other diseases of fruits, vegetables, and field crops and ornamentals.<sup>62,69</sup>

Mancozeb is used to protect many fruit, vegetable, nut, and field crops against a wide spectrum of diseases, including potato blight, leaf spot, scab (on apples and pears), and rust (on roses). It is also used for seed treatment of cotton, potatoes, corn, safflower, sorghum, peanuts, tomatoes, flax, and cereal grains.<sup>62,69,72,73</sup>

Mancozeb is the most widely used of the protectant fungicides for control of potato late blight and is commonly blended with systemic fungicides.<sup>61</sup>

### 3.10 Hydrocarbon Purification

TETA and TEPA are used to purify liquid hydrocarbons, particularly isoprene, by removing small concentrations of carbon disulfide (CS<sub>2</sub>).<sup>74,75,76,77</sup> In this application, the hydrocarbon is contacted with the ethyleneamine, which immediately reacts with the CS<sub>2</sub> to form thiocarbamates.

These thiocarbamates are water soluble and can be removed by contacting the hydrocarbon with water, and removing the water phase. The excess ethyleneamine used to react the CS<sub>2</sub> is also extracted in the water phase, leaving a clean hydrocarbon phase.

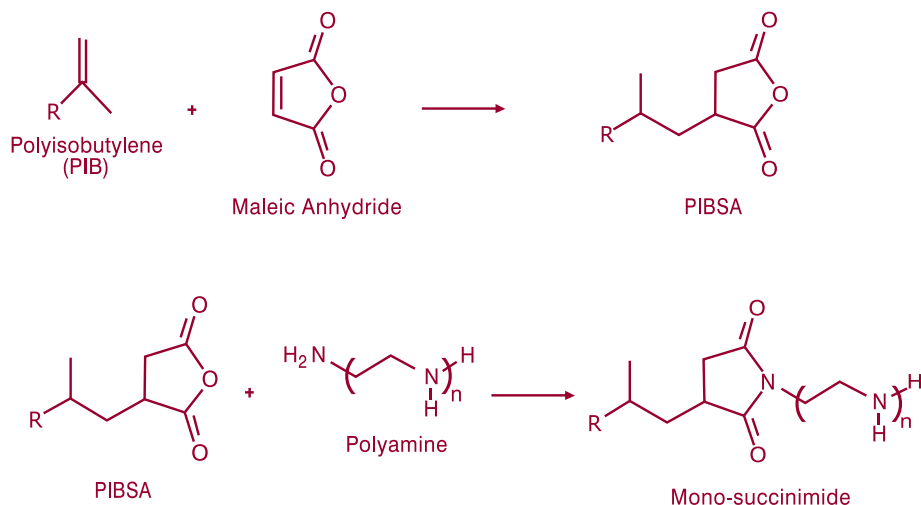
### 3.11 Lube Oil and Fuel Additives

A major use of ethyleneamines is in the manufacturing of lubricant and fuel additives.

Ashless dispersants are used in engine oils to reduce sludge and varnish deposits caused by the low-speed operation of motor vehicles.<sup>78</sup> These dispersants function by solubilizing polar species and neutralizing acids formed during the fuel combustion process.

One type of dispersant is the reaction product of polyisobutenylsuccinic anhydride (PIBSA) with ethyleneamines, typically the higher molecular weight polyamines.<sup>79</sup> The polyisobutene gives the dispersant oil solubility, while the polyamine supplies the polar end of the dispersant that interacts with combustion products in the lubricating oil.

Another type of ashless dispersant, the Mannich base, is produced by reaction of a polyisobutenylphenol with higher molecular weight ethyleneamines using formaldehyde as a coupling agent.

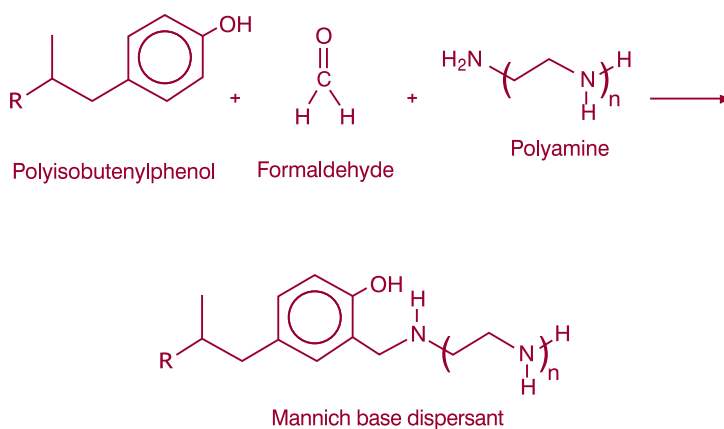


Recent patents have described Mannich bases that are made with alkylated phenols using ethylene/propylene copolymers rather than polyisobutene.<sup>80</sup>

Fuel additives that control deposits in the fuel system (fuel injectors, intake valves, combustion chamber) of motor vehicles are produced from ethyleneamines.

The chlorination of polyisobutene followed by reaction with EDA produces a polybuteneamine which is useful as a fuel additive.<sup>81</sup> Other deposit control additives, polyetheramines, have been produced from polyethers by reacting with phosgene and ethyleneamines.<sup>82</sup>

Fuel deposit control additives have also been made from PIBSA and ethyleneamines similar to lube oil dispersants.<sup>83</sup> Mannich base fuel additives made with DETA have been claimed to reduce intake valve deposits.<sup>84</sup>



### 3.12 Mineral Processing Aids

Amidoamines, made from fatty acids and ethyleneamines, have been used in the processing of minerals.<sup>85</sup> The reaction product of tall oil fatty acids and DETA can be used to separate silica from phosphate ore by flotation methods.<sup>86</sup>

The amidoamine, usually as an acid salt,<sup>87</sup> is attracted to the negatively charged silica, which float the silica to the surface when the flotation cell is aerated, while the purified ore sinks to the bottom.

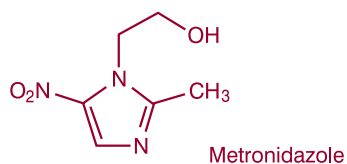
Amidoamines have also been used to prevent agglomeration of various granulated fertilizer products.<sup>88</sup> Higher ethyleneamines, such as TETA or TEPA, have been used to extract various metals from their sulfide or oxide ores.<sup>89</sup>

DETA is used in mining processes to aid in the separation of nickel ores from iron sulfide minerals, particularly pyrrhotite (FeS), an unstable form of pyrite (FeS<sub>2</sub>). In this process, an aqueous solution of DETA is added to the ores in the flotation step.

The amine depresses the pyrite which sinks during flotation and allows the separation of the nickel ores. This separation is used to reduce sulfur oxide emissions when the nickel ores are calcined.<sup>90</sup>

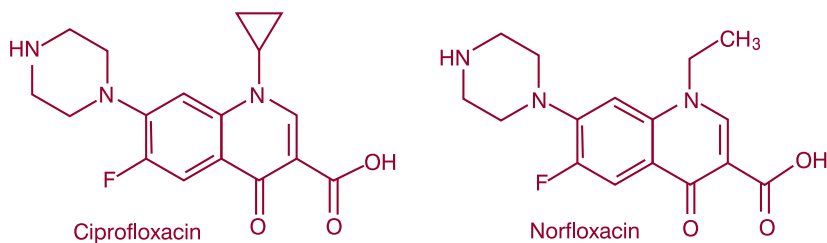
### 3.13 Pharmaceuticals

Ethyleneamines are used as raw materials for the production of several pharmaceutical products.

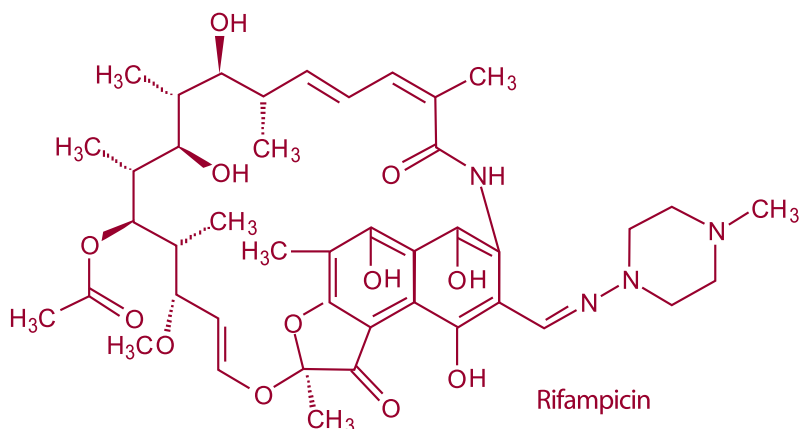


EDA is a raw material to manufacture metronidazole (1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole), which is an oral nitroimidazole medicine used for the treatment of amebiasis and trichomoniasis.

Piperazine is a reactant used to make ciprofloxacin and norfloxacin, which are drugs based on quinolones. The fluoroquinolones have a strong, wide spectrum antibacterial characteristic to common, sensitive, and drug-resistant bacteria. These products are semi-synthetic penicillins.

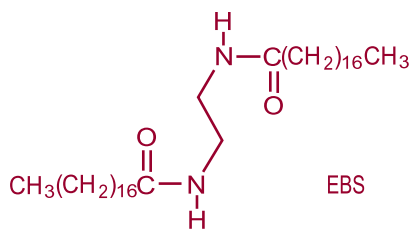


Piperazine is also used to make pipemidic acids, used as deworming agents for humans and animals. Other drugs based on piperazine are rifampicin ( $C_{43}H_{58}N_4O_{12}$ ) and piperazine antiscototic.



### 3.14 Plastic Lubricants

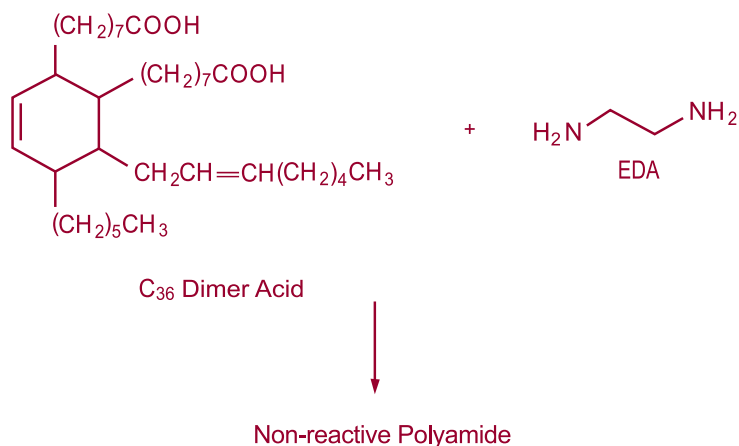
Ethylenebis(stearamide) (EBS) is a plastic lubricant made by the reaction of one mole of EDA with two moles of stearic acid. The EBS is used extensively as a demolding agent for plastic pieces made of acrylonitrile butadiene styrene (ABS) and polystyrene (PS).



### 3.15 Polyamide Resins

Thermoplastic polyamide resins made from dimer acid and ethylenediamine are used as hot-melt adhesives and as binders for flexographic or rotogravure printing inks.<sup>91</sup> Other difunctional amines like piperazine and 1,2-propylenediamine may be used to modify specific physical properties, such as melting point, of the polyamide.

Small amounts of other ethyleneamines such as DETA or TETA may also be used to modify the properties of the polyamides.



As a result of the amide functionality, these adhesives show outstanding adhesion to a wide variety of substrates including metal, leather, plastic, wood, and glass. The high fatty amide content of these resins, along with the highly polar nature of the amide moiety, gives these polyamides surfactant properties.

Polyamides can be formulated as water dispersed adhesives as well as in hot melt applications.<sup>92</sup> The use of thermoplastic polyamides in inks takes advantage of the good adhesion and flexibility properties of these resins.<sup>93</sup>

They are usually used in an alcohol solution, but can be formulated as aqueous based products.<sup>94</sup> The excellent mechanical properties of these resins also make them useful as overprint varnishes.

### 3.16 Rubber Processing Additives

EDA is reacted with carbon disulfide, sodium hydroxide, and a divalent metal such as manganese or zinc to produce dithiocarbamates. Dithiocarbamates are formulated to make various vulcanizing accelerators and promoters. EDA can also be reacted with carbon dioxide to make ethylenediamine carbamate. This carbamate is used in the initiation of vulcanization of fluorocarbon elastomers.

### 3.17 Surfactants

Amphoteric surfactants are mild surfactants used in shampoos that are active over a wide pH range. AEEA is used to make these surfactants by reaction with a fatty acid, cyclization to the imidazoline followed by reaction with chloroacetic acid and sodium hydroxide to produce the active surfactant.<sup>95</sup>

The details of the reaction chemistry in making these surfactants have been the subject of a number of studies.<sup>96,97,98</sup> Amphoteric surfactants have also been produced from TETA to give bis-imidazoline products.<sup>99</sup>

Surfactants have been produced from the reaction products of alkoxyated ethyleneamines and fatty acids.<sup>100</sup> A variety of additives useful in laundry detergents has been made from ethyleneamines such as a clay suspension additive made from TEPA and ethylene oxide which prevent the re-deposition of suspended soil on laundry.<sup>101</sup>

### 3.18 Textile Additives

Uses in man-made fiber manufacture and modification include EDA to improve dye sorption for acrylic fibers.<sup>102</sup> In fiber applications EDA improves adhesive properties of aramid fibers,<sup>103</sup> TEPA flameproofs polyester fibers,<sup>104</sup> EDA forms a cationic polyamidoamine to treat glass fibers,<sup>105</sup> and TEPA improves adhesion of carbon fibers.<sup>106</sup>

EDA improves wash fastness of dye in wool fibers.<sup>107</sup> DETA, TETA, and TEPA act as dye fixing agents with basic dyes on natural and regenerated cellulosic fibers.<sup>108</sup> Polyamines serve as binders for cellulose to acrylic fibers in superabsorbent polymers.<sup>109</sup> EDA improves resistance to abrasion<sup>110</sup> and increases the yield of cyanoethylation of jute fibers.<sup>111</sup>

Dimethylol ethylene urea is used in the treatment of cotton fabrics to impart durable press and crease resistance properties.<sup>112,113</sup> This compound is prepared by the reaction of EDA with urea, followed by the addition of formaldehyde to the resulting cyclic urea. Durable antistatic properties and improved hand may be imparted to synthetic fibers by treatment with polymers prepared by reacting DETA with stearic acid, urea, and formaldehyde.<sup>114</sup> EDA enhances the substantivity of cotton fabric for fiber-reactive dyes.<sup>115</sup>

### 3.19 Urethane Chemicals

Ethyleneamines are used in the manufacture of polyols and also in the production of catalysts to react polyols with isocyanates. EDA and AEEA are used as initiators in the production of polyols by the reaction with propylene oxide (PO).

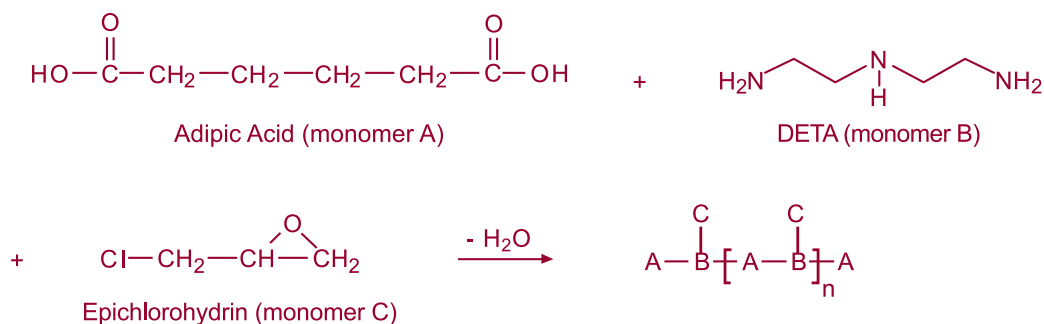
The main applications of these polyols are in urethane systems for appliances, spray foams, building panels, and elastomers. The reaction of the ethyleneamines with the PO takes place in uncatalyzed batch reactors. A variety of substituted ethyleneamines, particularly AEP, hydroxyethylpiperazine (HEP), and polyethoxylated EDA are used to manufacture triethylenediamine (TEDA) via a gas phase reaction of the amines over an acid catalyst.

The TEDA produced is a solid tertiary diamine used extensively as a catalyst in the formation of urethane foams from polyols and isocyanates. Another urethane catalyst based on ethyleneamines is pentamethyldiethylenetriamine, which is produced by the reaction of DETA with formaldehyde.

### 3.20 Wet-Strength Resins for Paper Applications

Applications for wet strength resins include paper towels, weather resistant packaging, and packaging for products such as milk cartons, frozen food packages, and vegetable boxes. Products requiring immersion in water such as photographic paper and filter paper, and even replacement of certain textiles in hospital bed sheets and gowns, are areas where wet strength are important.<sup>116</sup>

Various types of thermosetting resins are used to impart high wet strength to these types of paper products. Ethyleneamines are often used as components of these wet-strength additives. They are prepared by the reaction of an ethyleneamine (typically DETA or TETA) with a dicarboxylic acid, such as adipic acid, to form a low-molecular weight polyamide, which is further modified by reaction with epichlorohydrin.



The epichlorohydrin-modified polyamide resins are the major class of compounds widely used as wet-strength additives for paper.<sup>117,118,119,120</sup> These cationic thermosetting resins are highly

substantive to the paper. Additionally, they may be used under neutral to slightly alkaline conditions, which improves effectiveness and absorbency while reducing machine corrosion. Recent work also allows latest generations of these resins to be produced with reduced levels of organochlorinated byproducts<sup>121,122,123</sup> and for easier processing in recycle applications.<sup>124,125,126</sup>

The cationic urea-formaldehyde resins can be prepared by reacting an ethyleneamine with urea-formaldehyde condensation products, by co-reacting the ethyleneamine with formaldehyde and urea,<sup>127</sup> or by condensing the ethyleneamine with urea and then adding formaldehyde.<sup>128</sup>

These resins have greater substantivity to cellulose and, consequently, are more efficient wet-strength additives than unmodified urea-formaldehyde resins. Melamine-formaldehyde resins have also been modified with ethyleneamines for use as wet-strength additives.<sup>129,130</sup> Both of these types of resins require an amount of acidity to produce wet strength. Anionic polyamide resins, prepared by the condensation of ethyleneamines with polymeric fatty acids, followed by neutralization with an organic base, are readily dispersed in aqueous media and may be used to improve the wet strength of paper and impart waterproofing properties as well.<sup>131</sup>

# The Properties & Reactions of Ethyleneamines

These data do not represent a product specification, nor are they intended to change a product specification.

Table 4.1 – Typical Physical Properties of Ethyleneamines

|                                                       | EDA               | DETA              | TETA             | TEPA             | AEP      | AEAA             | E-100            |
|-------------------------------------------------------|-------------------|-------------------|------------------|------------------|----------|------------------|------------------|
| Molecular Weight (Linear Component)                   | 60.10             | 103.17            | 146.24           | 189.30           | 129.21   | 104.15           | NA               |
| (Typical Product)                                     | 60.1              | 103.1             | 151              | 200              | 128.8    | 104.2            | 271              |
| Boiling Point @ 760 mm, °C                            | 116.9             | 206.7             | 276.5            | 332              | 222.1    | 243.1            | decomp.          |
| Freezing Point, °C                                    | 11.1              | -39               | -35 <sup>a</sup> | -30 <sup>a</sup> | -17      | -38 <sup>a</sup> | -21 <sup>a</sup> |
| Density, g/ml @ 20°C <sup>b</sup>                     | 0.900             | 0.952             | 0.981            | 0.991            | 0.987    | 1.028            | 1.009            |
| Specific gravity 20°/20° <sup>b</sup>                 | 0.902             | 0.954             | 0.983            | 0.993            | 0.989    | 1.030            | 1.011            |
| Viscosity, cp @ 20°C                                  | 1.56              | 7.14              | 13.9             | 23.4             | 10.2     | 88.4             |                  |
| Kinematic viscosity, cst @25°C <sup>b</sup>           | 1.8               | 5.8               | 21.4             | 54.1             | 12.1     | 98               | 229              |
| Kinematic viscosity, cst @ 40°C <sup>b</sup>          | 1.5               | 3.7               | 10.3             | 24.6             | 6.5      | 48.5             | 84.1             |
| Vapor Pressure @ 20°C, mm Hg                          | 9.34              | 0.084             | <0.01            | <0.01            | 0.048    | <0.01            | <0.01            |
| Specific heat cal/g °C @ 20°C                         | 0.611             | 0.522             | 0.482            | 0.451            | 0.440    | 0.490            |                  |
| Thermal conductivity, cal/cm-sec-°C @ 20°C            | 0.000614          | 0.000523          | 0.000450         | 0.000435         | 0.000434 | 0.00059          |                  |
| Surface tension, dynes/cm @ 20°C                      | 42.0              | 41.8              | 22.2             | 39.3             | 44.9     | 44.8             |                  |
| Coefficient of expansion, 1/°C @ 20°C                 | 0.00106           | 0.00106           | 0.00075          | 0.000681         | 0.000842 | 0.000789         |                  |
| Refractive index @ 25°C <sup>b</sup>                  | 1.454             | 1.481             | 1.496            | 1.534            | 1.498    | 1.484            | 1.511            |
| Dielectric constant @ 25°C and 1 kHz <sup>b</sup>     | 13.5 <sup>c</sup> | 12.0 <sup>c</sup> | 11.4             | 12.0             | 6.4      | 22.0             | 9.6              |
| Electrical conductivity, μmhos/cm @ 20°C <sup>b</sup> | 5.2               | 0.32              | 0.038            | 0.0065           | 0.0054   | 0.47             | 0.24             |
| Heat of formation, kcal/mol                           | -14.9             | -17.3             | -17.6            | -19.7            | 8.07     | -64.8            |                  |
| Heat of vaporization, BTU/lb                          | 279.8             | 194.8             | 160.2            | 131.5            | 153.3    | 241.6            |                  |
| Heat of combustion, BTU/lb                            | 13371             | 14008             | 14297            | 14437            | 14887    | 12465            |                  |
| Ionization constants, K <sup>o</sup> 1                | 8.0E-5            | 7.1E-5            | 6.7E-5           | 6.5E-5           | 4.0E-5   | 3.0E-5           | 9.0E-5           |
| @ 25°C K <sup>o</sup> 2                               | 9.0E-8            | 5.2E-6            | 7.0E-6           | 6.5E-6           |          |                  |                  |
| pH of 1 wt % solution <sup>b</sup>                    | 11.7              | 11.6              | 11.5             | 11.5             | 11.4     | 11.4             | 11.4             |
| Nitrogen content, % <sup>b</sup>                      | 46.6              | 40.6              | 37.0             | 35.1             | 32.5     | 26.9             | 33.7             |
| Amine value, mg KOH/g <sup>b</sup>                    | 1855              | 1626              | 1443             | 1343             | 1293     | 1070             | 1257             |

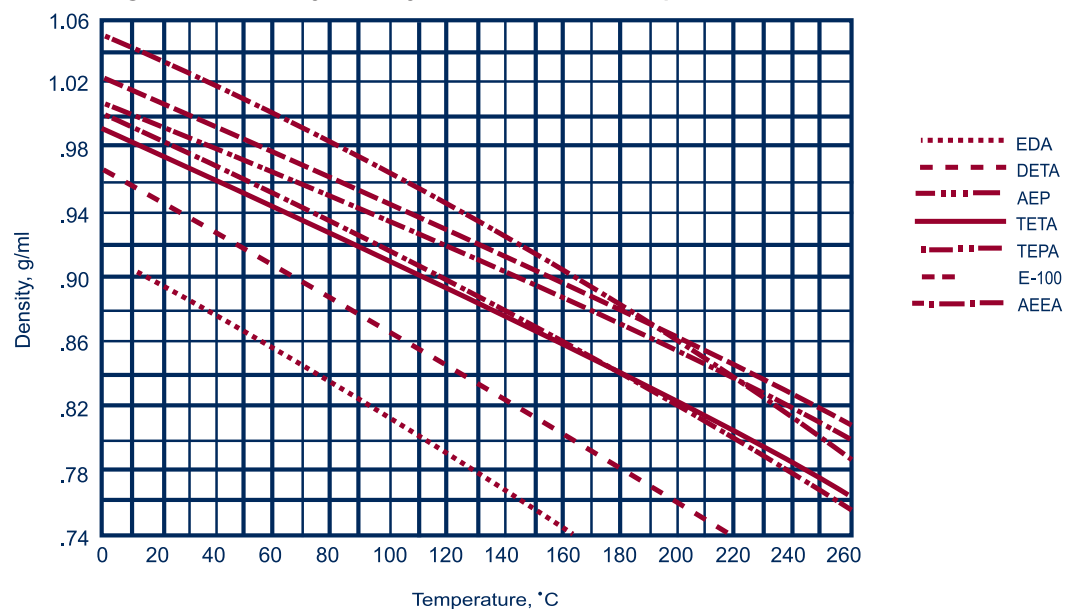
<sup>a</sup> Pour point

<sup>b</sup> Property of typical sales product

<sup>c</sup> Obtained at 100 kHz

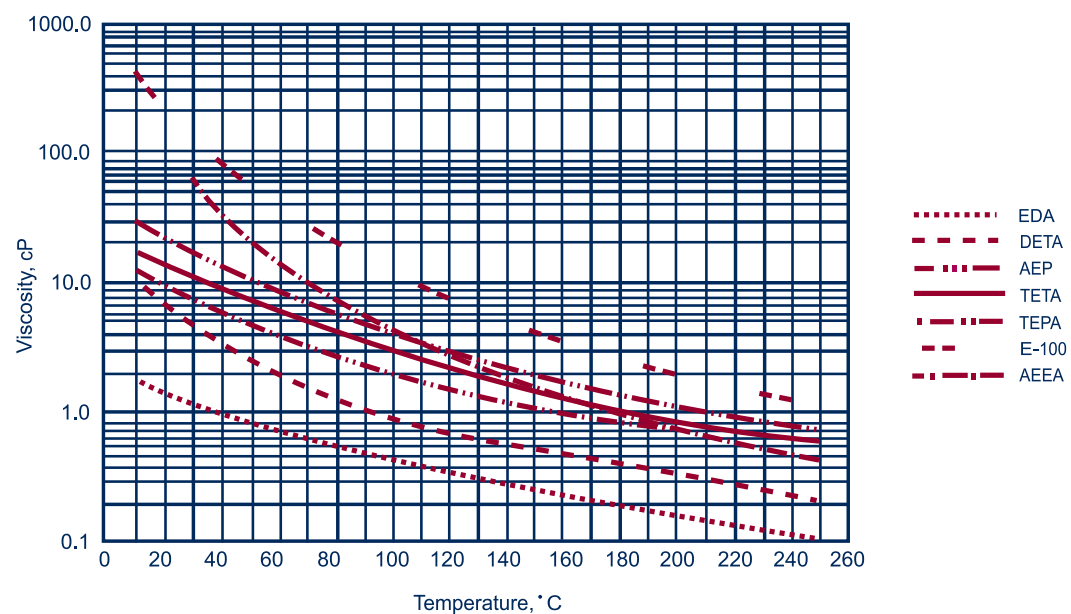
## 4.1 Density of Ethyleneamines vs. Temperature

Figure 4.1 Density of Ethyleneamines vs. Temperature



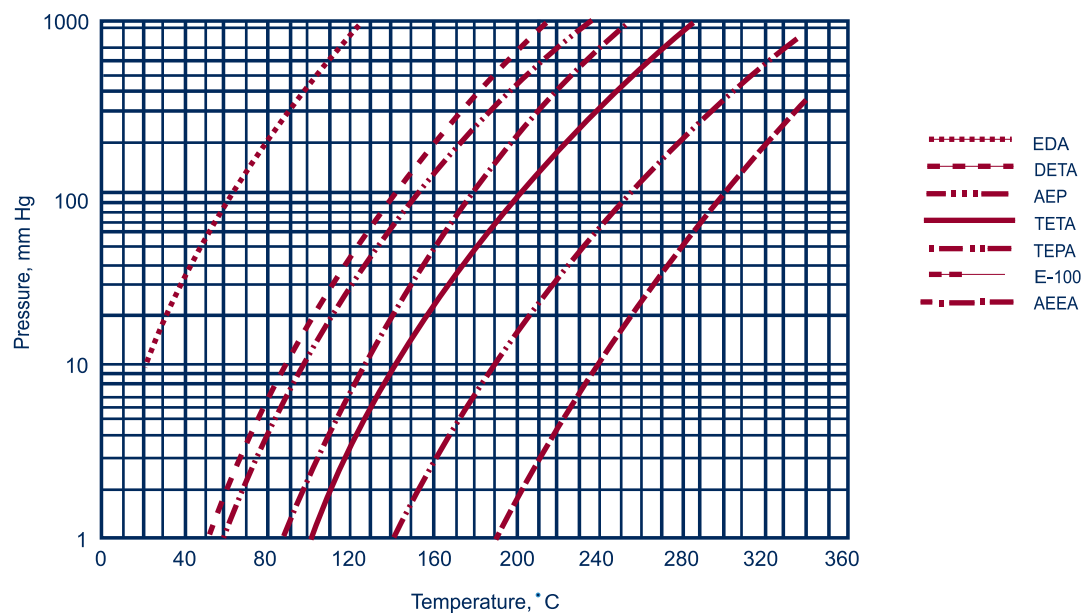
## 4.2 Viscosity of Ethyleneamines vs. Temperature

Figure 4.2 Viscosity of Ethyleneamines vs. Temperature



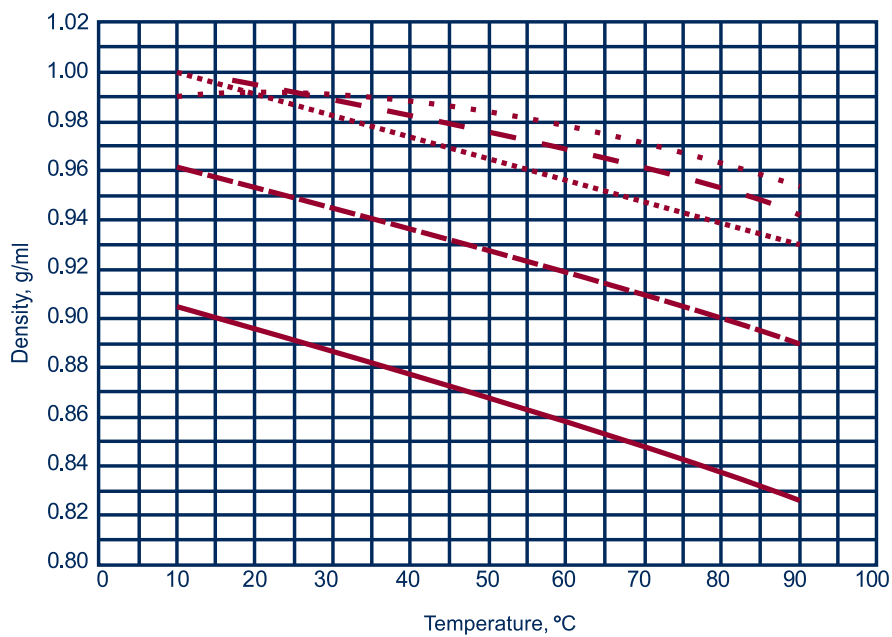
### 4.3 Vapor Pressure of Ethyleneamines vs. Temperature

Figure 4.3 Vapor Pressure of Ethyleneamines vs. Temperature

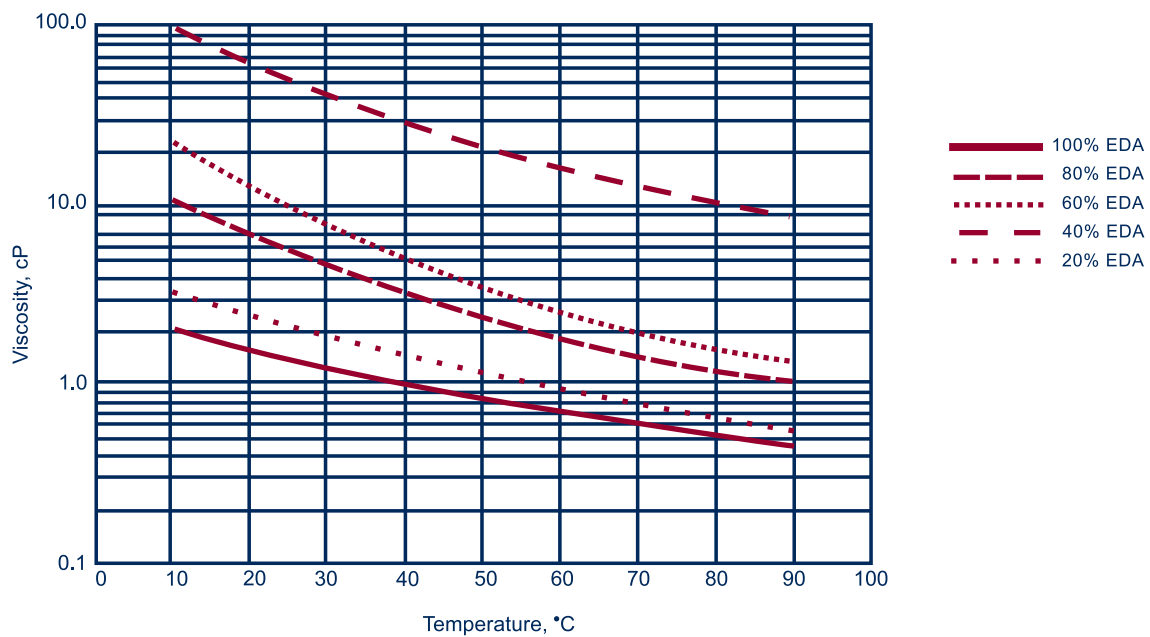


### 4.4 Properties of EDA Aqueous Solutions

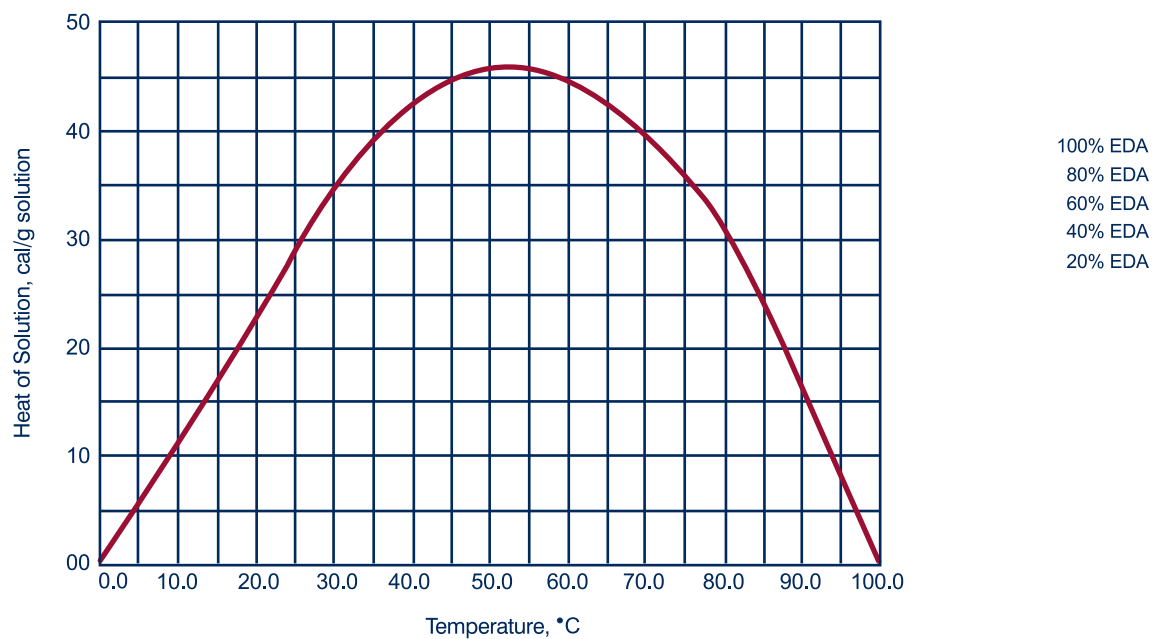
Figure 4.4 Density vs. Temperature



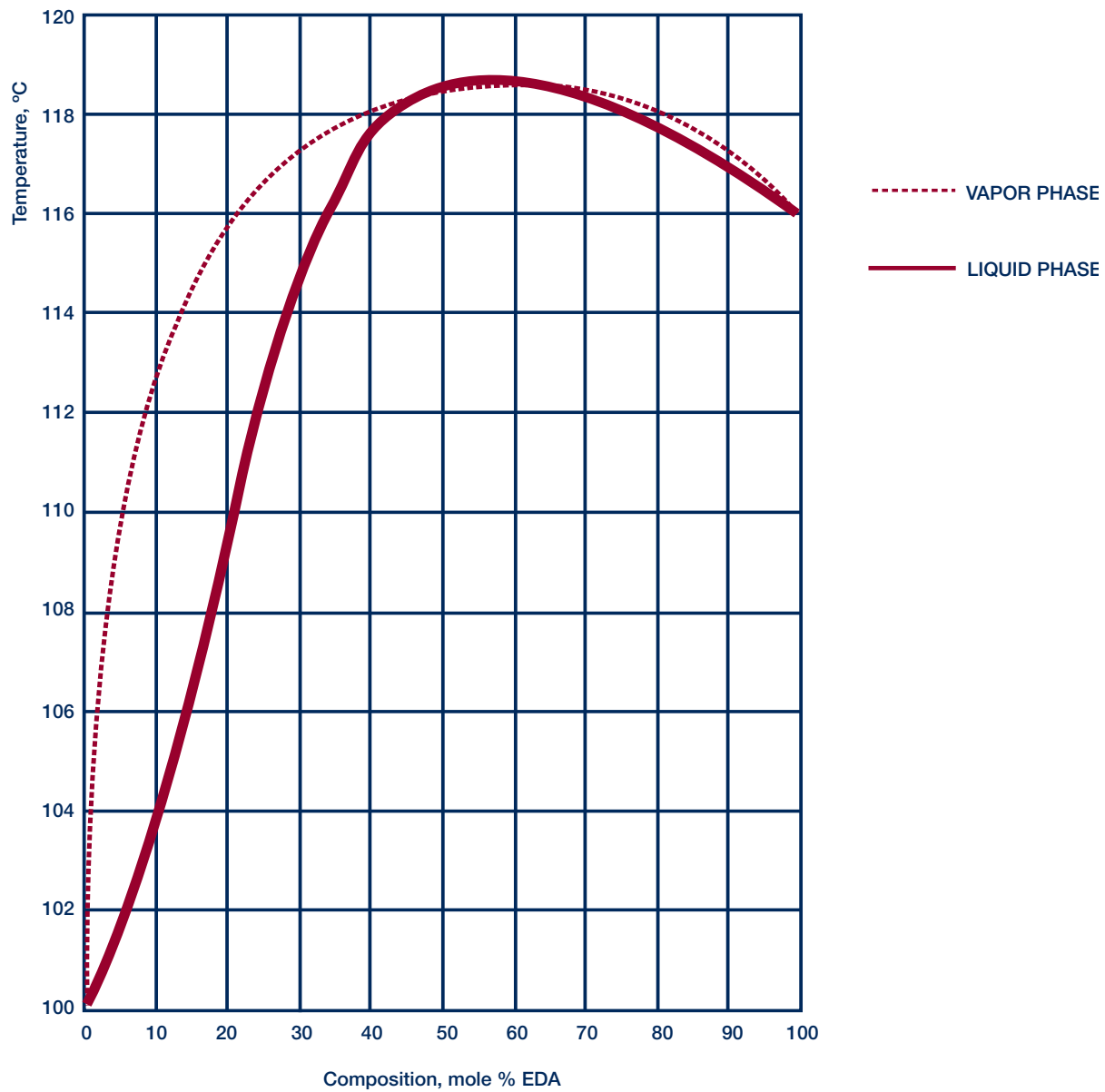
#### 4.5 Viscosity vs. Temperature



#### 4.6 Heat of Solution at 25°C



#### 4.7 Vapor-Liquid Equilibrium at 760 mm Hg



## 4.5 Chemical Reactions

Ethyleneamines undergo reactions that are typical of aliphatic amines. Since most members of the class contain at least two primary, and usually one or more secondary amine groups, they are also capable of forming cyclic derivatives.

This section summarizes some of the more important and interesting chemical reactions of these compounds, arranged according to the functional types of the coreactants.

### 4.5.1 Water, Carbon Dioxide, or Oxygen

Ethyleneamines react readily with water, carbon dioxide, and oxygen, which are found in the environment. These reactions are typically of most importance in connection with the storage of ethyleneamines.



Ethyleneamines are water-soluble. Amine hydrates, however, can form from the addition of moderate amounts of water to the higher molecular weight products TETA, TEPA, and E-100. Hydrate formation is mildly exothermic, and the resulting solid hydrates formed from the linear polyamines have melting points in the range of 25-50°C. Hydrate formation is facilitated by temperatures below 10°C, particularly for TEPA.



Carbon dioxide reacts readily with ethyleneamines, at ambient temperatures, to form salts. For example, EDA reacts with carbon dioxide to form N-(2-aminoethyl) carbamate.<sup>132</sup>

When reacted with carbon dioxide under pressure, EDA yields 2-imidazolidinone (ethylene urea).<sup>133</sup>

Reactions of EDA with urea,<sup>134,135,136</sup> ethylene carbonate,<sup>137</sup> phosgene, or carbon monoxide and oxygen (in the presence of a catalyst)<sup>138</sup> also yield ethylene urea.

Reaction of ethyleneamines with oxygen produces oxidized nitrogen species. Reaction of ethyleneamines with trace levels of oxygen (or other compounds capable of oxidizing amines) generally results in low levels of undesired by-products, which results in higher colored product.

#### 4.5.2 Inorganic Acids

Ethyleneamines are organic bases and react readily with common inorganic acids to form water-soluble salts. When EDA and hydrochloric acid, for example, are reacted at ambient temperatures, they form the dihydrochloride.



Other inorganic acids yield salts in a similar manner. The products are crystalline materials that react with strong bases to regenerate the original ethyleneamine.

At elevated temperatures, the reaction of EDA with 2 moles of nitric acid produces ethylene-dinitramine, an explosive compound.<sup>139,140</sup>

It is preferable, however, to prepare ethylenedinitramine by nitrating ethylene urea.



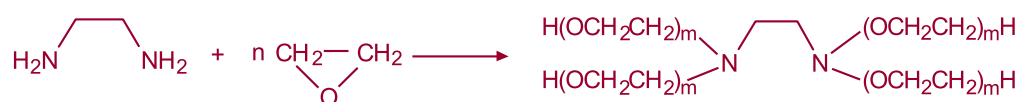
#### 4.5.3 Alkylene Oxides, Epichlorohydrin, and Aziridines

Ethyleneamines react readily with epoxides, such as ethylene oxide or propylene oxide, to form mixtures of hydroxyalkyl derivatives. The ratio of the reactants (epoxide to ethyleneamine) and the reaction conditions has an important bearing on the identity and proportion of the final products produced.

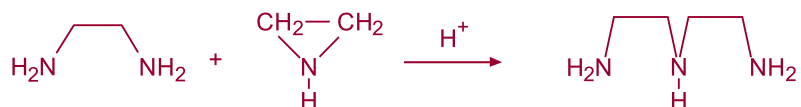
With low epoxide/ethyleneamine ratios and no additional catalyst, mono-, di-, tri-, and tetra-hydroxyalkylated products are obtained. In these, one oxide unit ( $\text{HOCH}_2\text{CH}_2-$ ) is substituted for each amine hydrogen in the starting ethyleneamine. For example, an epoxide/ethyleneamine ratio of 1 gives a 45% yield of monohydroxyalkylated products, plus smaller amounts of the higher homologs.<sup>141</sup> Product mixtures in which the molecular weights of the components are less than 200 are separable by distillation.

With a large excess of epoxide, and NaOH as a catalyst, all primary-amine hydrogen atoms are replaced and oxyethylene chains formed. The reaction of ethylene oxide with EDA is shown below (where m is variable and less than n).<sup>142,143</sup> Similar reactions with propylene oxide have also been reported.<sup>144</sup>

Water-insoluble, anion-active resinous materials are obtained when epichlorohydrin is substituted for the alkylene oxide. This reaction is carried out in aqueous solution.<sup>145</sup>

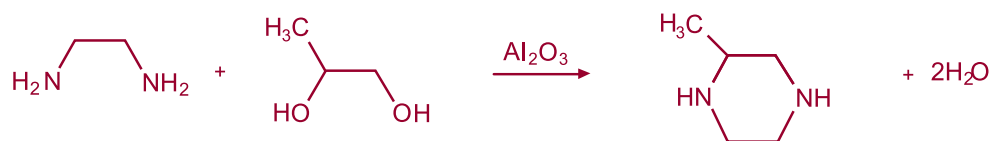


The reaction of ethyleneamines with aziridines is analogous to their reaction with epoxides. The reaction of ethyleneamines and aziridines generally requires acid catalysis. As is the case with the uncatalyzed epoxide/ethyleneamine reactions, the reaction ratio of the ethyleneamine and aziridine reactants controls product distribution.<sup>146,147</sup> DETA can be produced in this way from EDA.



#### 4.5.4 Alkylene Glycols and Alcohols

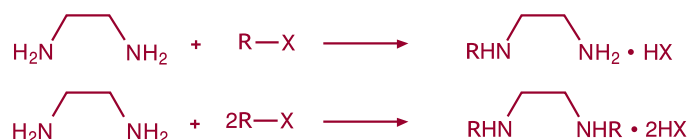
Reactions of ethyleneamines with glycols in the presence of one of several metal oxide catalysts produces cyclic ethyleneamines.<sup>148</sup> For example, the gas-phase reaction of ethylenediamine and propylene glycol over an alumina catalyst gives 2-methylpiperazine.<sup>149</sup>



#### 4.5.5 Organic and Inorganic Halides

Alkyl halides, and those aryl halides which are activated by electron withdrawing groups ( $\text{NO}_2$  or similar groups) in the ortho or para positions, can be reacted with

ethyleneamines to give mono- and di-substituted derivatives, depending upon the ratios and reaction conditions used.<sup>150,151,152,153</sup> Reaction of EDA with methylene chloride reportedly causes a runaway reaction.<sup>154</sup> The product of the reaction of EDA with a monosubstituted alkyl halide is dependent upon reaction stoichiometry.



With aliphatic dihalides, polymeric, cross-linked, water-soluble, cationic products are obtained with a high aliphatic dihalide/ethyleneamine reactant ratio.<sup>155</sup> With lower reactant ratios, higher molecular weight ethyleneamine products are obtained.

The following are some examples of the wide range of products that can be produced from the reaction of alkyl halides with ethyleneamines. Dimorpholinoethane can be prepared from ethylenediamine and 2,2'-dichloroethyl ether in the presence of  $\text{Na}_2\text{CO}_3$ .<sup>156</sup>



Trichlorotoluene reacts with ethylenediamine to give 2-phenyl-2-imidazoline.<sup>157</sup>



The reaction of EDA with chloroacetic acid gives ethylenediaminetetraacetic acid (EDTA). The tetrasodium salt of this acid is an important commercial chelant. The tetrasodium salt can also be obtained by reacting ethylenediamine with sodium cyanide and formaldehyde (see Aldehydes and Ketones section).



Reaction of ethylenediamine with ICl gives ethylenediamine tetraiodide.<sup>158</sup>

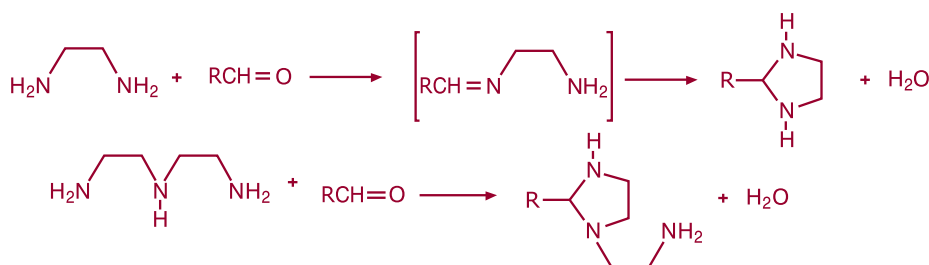


**NOTE:** Amine compounds can react vigorously with halogenated hydrocarbons. These reactions should be carried out with appropriate precautions.

#### 4.5.6 Aldehydes and Ketones

Ethylenamines react readily and exothermically with aliphatic aldehydes and ketones to form a variety of adducts.

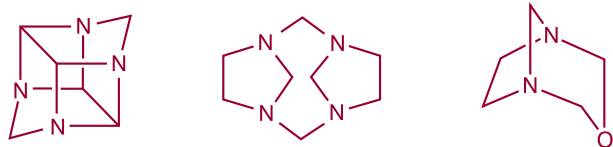
The products produced depend on the stoichiometry, the reaction conditions, and structure of the starting ethyleneamine. Reaction of an aldehyde with EDA or DETA yields imidazolidines via the Schiff base intermediate.<sup>159</sup>



Reactions with aldehydes and ethylenamines may be quite complex. A portion of the aldehyde may undergo aldol condensation to yield an unsaturated aldehyde. This, in turn, might condense with the ethyleneamine to give a second Schiff base.<sup>160</sup>

Upon further condensation of the reaction products with one another, complex cross-linked resins are obtained.<sup>161,162</sup> The extent to which each reaction occurs varies with the reactants.

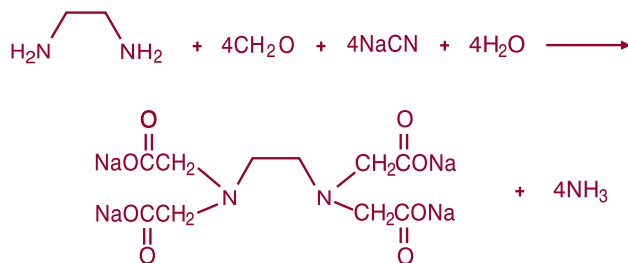
Ethylenamines and excess formaldehyde can react to give a variety of products, depending on reaction conditions and identity of the starting ethyleneamine. Some representative compounds that are the products of the reaction of EDA and formaldehyde are shown below.<sup>163,164</sup>



Linear resins are formed by reacting diethylenetriamine at 100°C with the condensation product of phenol and formaldehyde. When these resins are heated at 100-200°C with excess formaldehyde, they are converted to cross-linked insoluble polymers with excellent resistance to alkalis.<sup>165</sup> Condensation products of ethyleneamines with melamine and melamine-formaldehyde resins have also been prepared.<sup>166,167</sup>

When ethylenediamine is reacted with sodium cyanide and formaldehyde, under suitable alkaline conditions, the tetrasodium salt of ethylenediaminetetraacetic acid is obtained.<sup>168</sup>

The reaction is carried out at elevated temperatures and under a partial vacuum to remove ammonia, which is also formed. Another method of preparation involves the use of hydrogen cyanide in place of sodium cyanide.



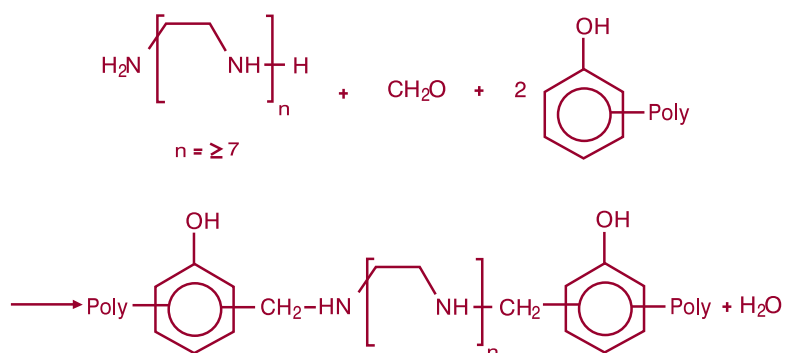
The tetrasodium salt is easily converted to the tri-, di-, and mono-sodium salts, or to the free acid, by treatment with sulfuric or hydrochloric acid. These products find wide use in a variety of industries as chelating agents. Diethylenetriamine reacts in an analogous fashion to yield the pentaacetic homolog which is also utilized commercially as a chelating agent.

In reactions similar to those with aldehydes, ethyleneamines react with aliphatic ketones to form imines. Reaction with one of the primary amines yields a ketimine and the evolution of one mole of water.



The addition of a second mole of the ketone to the monosubstituted ketimine would form the di-ketimine and result in the evolution of a second mole of water. The formation of a ketimine is a reversible reaction. With the addition of water, the ketimine readily hydrolyzes and regenerates the amine and ketone.

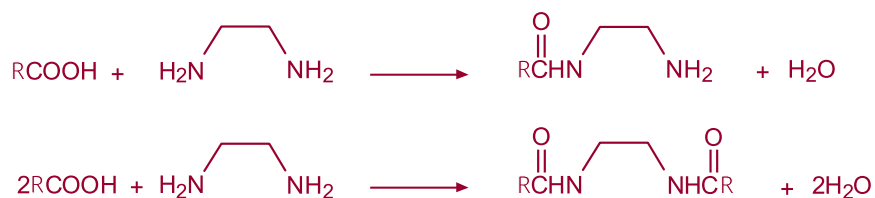
Another specialized reaction of ethyleneamines with aldehydes is called the Mannich reaction. Condensation of primary or secondary amines with formaldehyde and hydroxy aromatic compounds yield Mannich bases.<sup>169</sup>



#### 4.5.7 Organic Acid and Acid Derivatives

Ethyleneamines will react with organic acid derivatives (carboxylic acids, esters, acid anhydrides, acyl halides) to yield amides, amidoamines, and polyamides.

The type of final product obtained depends on the structure of the starting ethyleneamine, the acid derivative used, and the reaction conditions employed. For example, mono- or diamides can be obtained from EDA depending on the mole ratio of the acid/amine.<sup>170</sup>



Diacids and their derivatives can be reacted with ethyleneamines to prepare polyamides.<sup>171,172</sup>



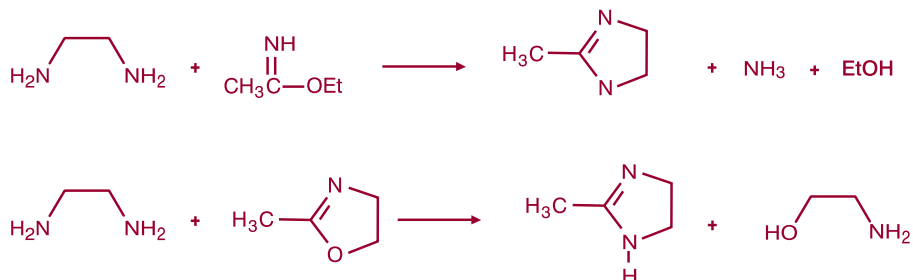
These dibasic acid derivatives, as well as dimerized and trimerized vegetable oils, polymerize with ethyleneamines, forming polyamide resins. These resins range from soft, viscous materials to hard, thermoplastic, heat-resistant, colored transparent products, depending upon the initial reactants.<sup>173</sup>

The extent of reaction between an ethyleneamine and an organic acid derivative depends highly on the type of acid derivative and the severity of reaction conditions. Under forcing conditions, acid anhydrides and EDA can form tetraacyl derivatives.<sup>174</sup> However, use of milder conditions or a less active acylating agent results in only the monoamide.<sup>175,176,177</sup>

The monoamides undergo further condensation to yield the cyclic imidazoline derivatives. This cyclization can be performed without isolation of the intermediate monoamide using a variety of techniques including catalysts.<sup>178,179,180,181</sup> Thus, when monoacetyl ethylenediamine is heated with calcium oxide, 2-methyl-2-imidazoline results.<sup>182</sup>



Imino ethers<sup>183</sup> and alkyl oxazolines<sup>184</sup> have also been used, along with ethylenediamine, as starting materials in the preparation of 2-substituted imidazolines.



Hydrogen cyanide and aliphatic nitriles can also be employed with ethyleneamines to produce imidazolines. EDA and hydrogen cyanide, for example, react in diethyl ether at 100°C to give 2-imidazoline.<sup>185</sup>



Diethylenetriamine reacts in a similar fashion to give the 1-aminoethyl derivative.

When ethylenediamine is reacted with aliphatic nitriles in the presence of sulfur<sup>186</sup> or polysulfides<sup>187</sup> as catalyst, 2-alkyl-2-imidazolines are formed.

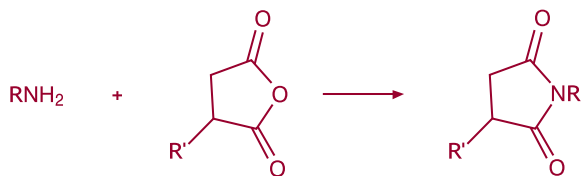


Ethyleneamines can be added readily to acrylonitrile in the presence of a catalyst, forming cyanoethyl derivatives.<sup>188,189</sup>



The reaction is exothermic, and requires cooling to prevent polymerization of the acrylonitrile.

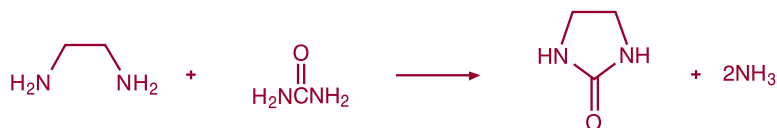
Alkyl succinimides can be prepared from the reaction of an ethyleneamine with the corresponding alkyl-substituted succinic anhydride.<sup>190</sup>



Ethyleneamine-organic amine derivative reaction products themselves may be further reacted with a wide variety of compounds to yield additional derivatives. Compounds which may be used in carrying out such condensations include formaldehyde, dibasic acids, dimethyl sulfate, and epoxy resins.<sup>191,192,193</sup>

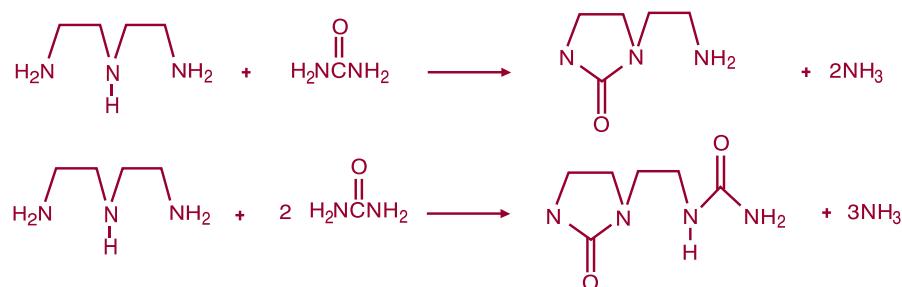
#### 4.5.8 Urea and Urea Derivatives

Ethyleneamines react with urea to form substituted ureas and ammonia. EDA reacts with urea to give 2-imidazolidinone (ethylene urea).<sup>194,195</sup>



With diethylenetriamine and the higher ethyleneamine homologs, a number of urea reaction products are possible.<sup>196</sup> Equimolar quantities of DETA and urea give, as the principal product, 1-(2-aminoethyl)-2-imidazolidinone.

When two moles of urea are heated with one mole of DETA, the principal product is 1-(2-ureidoethyl)-2-imidazolidinone.



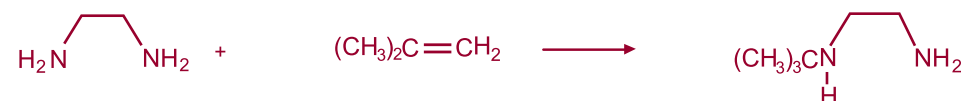
DETA has been prepared by the reaction of EDA, monoethanolamine and urea. In this process MEA reacts with urea to form 2-oxazolidinone which reacts further with EDA to form the cyclic urea of DETA. Hydrolysis of the urea liberates the free amine.<sup>197</sup> Similarly, linear TETA can be produced when two moles of 2-oxazolidinone and one of EDA are brought together. The amine nitrogen atoms replace the oxygen atoms of the heterocyclic ring and a bis-imidazolidinone compound is formed, which can be hydrolyzed to yield linear TETA.<sup>198</sup>



The acid salts of ethyleneamines also react with urea and formaldehyde, but the reaction follows a different course from that of the free amine, the end product being a cationic, water-soluble straight-chain resin.<sup>199,200,201</sup>

#### 4.5.9 Olefins

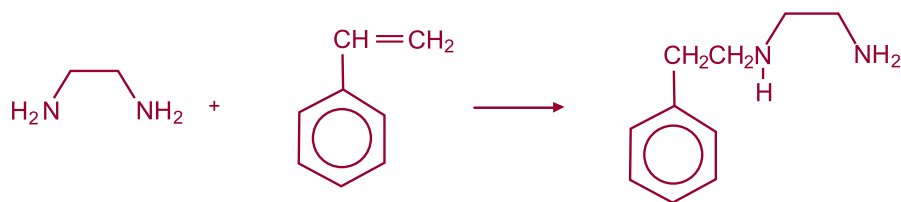
Ethyleneamines can react with olefins by addition to a double bond. EDA reacts with isobutylene in the presence of a zeolite catalyst at high temperature to give the monoalkylation product.<sup>202</sup>



Ethyleneamines can add as a nucleophile to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds, such as acrylate esters or acrylonitriles. The reaction, commonly referred to as the Michael's addition, results in the addition of the amine to the double bond of the  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound.

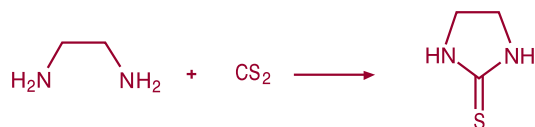


Starburst dendritic macromolecules can be formed from EDA and methyl acrylate under controlled conditions.<sup>203,204</sup> Similarly, ethyleneamines can add to other vinyl-containing compounds that do not have carbonyl groups. An example is the reaction of styrene with ethylenediamine.

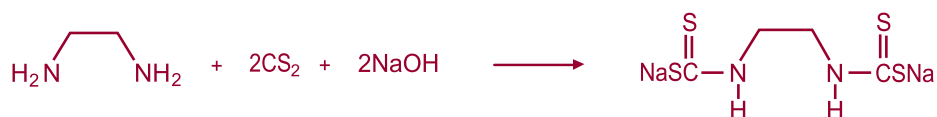


#### 4.5.10 Sulfur Compounds

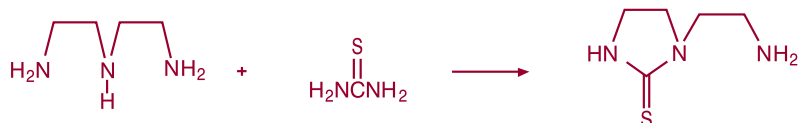
When one mole of carbon disulfide is reacted with one mole of EDA, cyclization occurs and ethylene thiourea is formed.<sup>205</sup>



In the presence of a base, such as caustic soda, ethylenediamine readily adds two moles of carbon disulfide to yield the di-sodium salt of ethylenebisdithiocarbamate.<sup>206</sup>



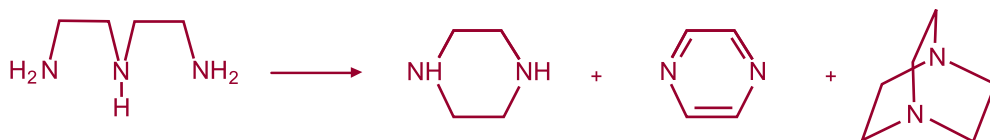
Sulfonamides can be prepared from ethyleneamines, by heating with a saturated aliphatic sulfonyl chloride,<sup>207</sup> or with mono-, di-, or tetra-substituted benzenesulfonyl chloride, or with p-toluenesulfonyl chloride.<sup>208</sup> The condensation of diethylenetriamine with thiourea gives 1-(2-aminoethyl)-2-midazolidonethione.<sup>209</sup>



#### 4.5.11 Cyclization

At elevated temperatures and pressures, in the presence of various catalysts, ethyleneamines are transformed into piperazines and pyrazines.

Over a kaolin-alumina catalyst at 280-400°C, for example, diethylenetriamine is converted into a mixture of piperazine, pyrazine, and triethylenediamine.<sup>210,211</sup>



Higher temperatures appear to favor pyrazine formation, while lower temperatures favor formation of piperazine and substituted piperazines.<sup>212</sup> Other catalysts that have been used in these cyclization reactions include mixed transition metal oxides<sup>213,214</sup> and Al-Ti-Ni alloys.<sup>215</sup>

# Analytical Methods

Table 5.1 — Summary of Methods

| Composition & Properties Analysis  | EDA                                                                                                     | DETA                                                                      | AEP | AEEA | TETA | TEPA                                                    | E-100 | Blends & Der. |
|------------------------------------|---------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-----|------|------|---------------------------------------------------------|-------|---------------|
| 1. Assay                           | Gas Chromatography (GC)                                                                                 |                                                                           |     |      |      |                                                         |       |               |
| 2. Color                           | APHA using a platinum-cobalt scale (ASTM D-1209)                                                        |                                                                           |     |      |      | Gardner method (ASTM D-1544), ASTM method (ASTM D-1500) |       |               |
| 3. Total Nitrogen                  | Calculated based on GC analysis                                                                         |                                                                           |     |      |      |                                                         |       |               |
| 4. Water (wt. %)                   | GC                                                                                                      | Karl Fischer method (ASTM E-203) using a salicylic acid/methanol solution |     |      |      |                                                         |       |               |
| 5. Specific Gravity                | Mettler-Paar digital density meter (ASTM D-5002)                                                        |                                                                           |     |      |      |                                                         |       |               |
| 6. Viscosity                       | Kinematic viscosity (ASTM D-445)                                                                        |                                                                           |     |      |      |                                                         |       |               |
| 7. Amine Value (total base number) | Non-aqueous titration using acetic acid as solvent & titrating with hydrochloric acid (mg KOH/g Sample) |                                                                           |     |      |      |                                                         |       |               |

## 5.1 Ethyleneamine Assay by Gas Chromatography

### 5.1.1 Assay of Lower Molecular Weight Ethyleneamines by Gas Chromatography

(Ethylenediamine, Diethylenetriamine, Aminoethylpiperazine, Aminoethylethanolamine)

A gas chromatograph equipped with a single-filament thermal conductivity detector, injection port with split injection capabilities, a wide-bore fused-silica capillary column, and an integrator or data handling computer station is required for this analysis.

- Column: 25m x 0.75 mm O. D. x 0.53 mm I. D. fused-silica CP-Sil 19CB (Chrompack)
- Stationary Phase: 2.2  $\mu$ m film of chemically bonded CP-Sil 19, 7% cyanopropyl, 7% phenyl, 86% dimethylpolysiloxane
- Carrier Gas: Helium
- Programmed Temperature Range: 100° - 290°C
- Recommended Flow Rates:
  - Column Flow - 5.2 ml/min.
  - Make-up Flow - 1.5 ml/min.
  - Reference Flow - 2.3 ml/min.
  - Split Flow - 200 ml/min.
  - Septum Purge Flow - 1.5 ml/min.

- Split Ratio: 39
- Injection Port Temperature: 300°C
- Detector Temperature: 300°C
- Detector Type: Thermal Conductivity
- Injection Size: 1 microliter

#### 5.1.2 Assay of Higher Molecular Weight Ethyleneamines by Chromatography

(Triethylenetetramine, Tetraethylenepentamine, Ethyleneamine E-100, Blends & Derivatives)

The equipment for analysis of the higher molecular weight ethyleneamines is the same as for the lighter ethyleneamines except a different column type is employed and a flame ionization detector is used.

- Column: 30m x 0.32 mm x 0.25  $\mu$ m DB-5 (Chrompack)
- Stationary Phase: 95% Dimethyl, 5% diphenyl polysiloxane thin film (0.25  $\mu$ m)
- Carrier Gas: Helium
- Programmed Temperature Range: 100 - 300°C
  - Column flow - 1.3 ml/min.
  - Make-up flow - 30 ml/min.
  - Split flow - 100 ml/min.
  - Septum purge flow - 1.5 ml/min.
- Split Ratio: 77
- Injection Port Temperature: 350°C
- Detector Temperature: 300°C
- Detector Type: Flame Ionization Detector (FID)
- Injector Size: 1 microliter

#### 5.1.3 Gas Chromatography Standardization and Calibration

(Applicable to all Ethyleneamines)

Gas chromatography (GC) standards must be prepared with detailed accuracy. An analytical balance and pure components are required for the calibration of the instrument prior to substrate analysis. One microliter of the standard is injected and analyzed according to the chromatographic conditions given until stable response factors are obtained.

An integrator or data handling computer station should be programmed according to instructional manual for area percent data or weight % composition using the response factors obtained.

Table 5.2 — Color Comparison Chart

| APHA | Gardner Standards | Gardner Holdt | NPA   | ASTM D-1500 | Saybolt | Rosin Standards | Parlin | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (g./100 ml. H <sub>2</sub> SO <sub>4</sub> ) |
|------|-------------------|---------------|-------|-------------|---------|-----------------|--------|--------------------------------------------------------------------------------------------|
| 3    |                   |               |       |             | +29     |                 |        |                                                                                            |
| 5    |                   |               |       |             | +27     |                 |        |                                                                                            |
| 8    |                   |               |       |             | +26     |                 |        |                                                                                            |
| 10   |                   |               |       |             | +24     |                 |        |                                                                                            |
| 15   |                   |               |       |             | +23     |                 |        |                                                                                            |
| 20   |                   |               |       |             | +22     |                 |        |                                                                                            |
| 23   |                   |               |       |             |         |                 |        |                                                                                            |
| 25   |                   |               |       |             | +21     |                 |        |                                                                                            |
| 30   |                   |               |       |             | +19     |                 |        |                                                                                            |
| 35   |                   |               |       |             | +17     |                 |        |                                                                                            |
| 40   |                   |               |       |             | +16     |                 |        |                                                                                            |
| 45   |                   |               |       |             | +15     |                 |        |                                                                                            |
| 50   |                   |               |       |             | +14     |                 |        |                                                                                            |
| 60   |                   |               |       |             | +12     |                 |        |                                                                                            |
| 65   |                   |               |       |             |         |                 |        |                                                                                            |
| 70   |                   |               |       |             | +11     |                 |        |                                                                                            |
| 80   |                   |               |       |             | +10     |                 |        |                                                                                            |
| 90   |                   |               |       |             | +9      |                 |        |                                                                                            |
| 100  |                   |               |       |             | +6      |                 |        |                                                                                            |
| 125  |                   |               |       |             | 0       |                 |        |                                                                                            |
| 130  |                   |               |       |             |         |                 |        |                                                                                            |
| 150  |                   |               |       |             | -9      |                 |        |                                                                                            |
| 170  |                   |               |       |             |         |                 |        |                                                                                            |
| 200  |                   |               | 0.5   | 0.5         | -13     |                 |        |                                                                                            |
| 250  | 1                 | 1             | 0.75  |             |         |                 | 4      | 0.0039                                                                                     |
| 300  |                   |               | 1.0   | 0.5         |         |                 |        |                                                                                            |
| 400  | 2                 |               | 1.25  |             |         |                 | 5      | 0.0048                                                                                     |
| 500  |                   |               | 1.25  |             |         |                 |        | 0.0071                                                                                     |
|      | 3                 |               |       |             |         |                 | 8      |                                                                                            |
|      |                   |               | 1.25+ |             |         |                 |        |                                                                                            |
|      | 4                 | 2             | 1.5   | 1.0*        |         |                 | 10     | 0.0112                                                                                     |
|      | 5                 |               | 1.75  | 1.5*        | +29     |                 | 20     |                                                                                            |
|      | 6                 |               | 2-    |             |         | X               | 30     | 0.0205                                                                                     |
|      |                   |               | 2.0   |             |         |                 | 35     | 0.0322                                                                                     |
|      | 7                 | 3             | 2+    | 2.0*        |         | WW              |        | 0.0384                                                                                     |
|      | 8                 |               | 2.25  |             |         | WG              | 45     | 0.0515                                                                                     |
|      | 9                 | 4             | 2.5   | 2.5*        |         | N               | 60     | 0.0780                                                                                     |
|      | 10                |               | 2.75  |             |         | M-K             | 80     | 0.1640                                                                                     |
|      | 10-11             |               | 3.0   | 3.0*        |         | K               |        | 0.2070                                                                                     |
|      | 11                |               | 3.25  |             |         | I               | 100    | 0.2500                                                                                     |
|      |                   | 53            | .5    | 3.5         |         |                 |        |                                                                                            |
|      | 12                |               | 3.75  | 4.0*        |         | H               |        | 0.3800                                                                                     |
|      |                   | 6             | 3.75  |             |         |                 |        |                                                                                            |
|      | 13                |               | 4.0   |             |         | G               |        | 0.5720                                                                                     |
|      | 14                | 7             | 4.25  | 4.5*        |         | F               |        | 0.7630                                                                                     |
|      |                   |               | 4.5   | 5.0*        |         |                 | 175    |                                                                                            |
|      |                   |               | 4.75  | 5.5*        |         |                 | 200    |                                                                                            |
|      | 15                |               | 5.0   | 6.0*        |         |                 | 250    | 1.0410                                                                                     |
|      |                   |               | 5.75  |             |         |                 |        |                                                                                            |
|      | 16                | 8             | 6.0   | 6.5         |         | E               | 300    | 1.2800                                                                                     |
|      |                   |               | 7.0   | 7.0*        |         |                 |        |                                                                                            |
|      | 17                |               | 7.5   | 7.5*        |         |                 | 350    | 2.2200                                                                                     |
|      |                   |               | 8-    |             |         |                 |        |                                                                                            |
|      |                   |               | 8.0   |             |         |                 |        |                                                                                            |
|      | 18                | 9             | 8+    | 8*          |         | D               | 500    | 3.0000                                                                                     |

\*Approximate

## 5.2 Color

The procedure used to test for color using the APHA scale is ASTM D-1209. This is a standard test method for determining the color of clear liquids (platinum-cobalt scale). A color comparator constructed to permit visual comparison of samples through tall-form Nessler tubes is required for accurate comparison. A series of platinum-cobalt reference standards or color disks, which duplicate the platinum-cobalt standards, are also required.

Use ASTM D-1544 (Gardner scale) for mid-range color ethyleneamines and ASTM D-1500 for ASTM color scale.

## 5.3 Total Nitrogen

The procedure for total nitrogen is identification of the individual components by gas chromatographic techniques followed by calculation of percent nitrogen from the known chemical structures of the components. As an alternate method, total nitrogen can be determined by using ASTM E-258, which is a modified Kjeldahl method for determining total nitrogen in organic materials.

## 5.4 Water

Water analysis for EDA can be performed with a gas chromatograph equipped with a thermal conductivity detector using the method given above for light amines (see section 5.1.1). Analysis of the remaining ethyleneamines can be determined with the Karl Fischer method as described below.

- a. Standardize the Karl Fischer reagent by adding to a titration flask 25 ml of anhydrous methanol and titrate until a constant microamp reading is obtained.
- b. Add 0.05 to 0.1 grams of water into the solution and titrate again with the reagent to the same microamp reading. The amount of reagent needed is used to determine the grams of water per milliliter of reagent which is the Fischer reagent factor F.
- c. Add 60 ml of a methanol/salicylic acid solution (150g salicylic acid in 1 liter of methanol) to a clean titration vessel and titrate to the end point with the Karl Fischer reagent. Disregard the volume and reset the buret to zero.
- d. Quickly add to the vessel enough sample to contain 0.01 to 0.4 grams of water and again titrate to the end point. Record the volume required, A, in milliliters.

e. Calculation of percent water is:

$$\% \text{ Water} = \frac{A \times F \times 100}{\text{grams sample}}$$

where: A = ml Karl Fischer reagent  
F = grams water per ml reagent

### 5.5 Specific Gravity

This can be determined by using the method described in ASTM D-5002 which determines specific gravity by a Mettler-Paar density meter.

### 5.6 Viscosity

Viscosity is determined by using the procedure described in ASTM D-445. This involves filling a viscosity tube with the sample to be tested past a mark on the tube.

The viscosity tube is then placed in a constant temperature bath. The set point temperature of the bath can vary depending on the viscosity of the sample. The sample is then forced above the mark by applying air pressure.

The pressure is then removed and a timer started as the meniscus touches the first mark. When the meniscus reaches the second mark, stop the timer. The time (seconds) is multiplied by the factor number of the viscosity tube. Make sure the factor number is correct for the temperature of the test. The result is reported in centistokes.

### 5.7 Amine Value

This procedure can be used to determine the amine value of ethylenamines. The amines are titrated with standard 1.0N HCl. The alkalinity is expressed as the equivalent in milligrams of potassium hydroxide per gram of sample. The procedure is as follows:

- a. To a 250 ml beaker add 150 ml of glacial acetic acid.
- b. Fill the 1 cc syringe approximately half full of sample and weigh to the nearest 0.1 mg. Add 60 to 100 mg of sample into the 250 ml beaker containing acetic acid. Reweigh the syringe.
- c. Allow sample to sit for 5 minutes.
- d. Titrate potentiometrically to an endpoint with 1.0N HCl.
- e. The amine value is calculated as: 
$$\frac{\text{ml titration} \times \text{normality} \times 56.1}{\text{grams of sample}} = \text{amine value}$$

# Product Stewardship

The Huntsman Corporation has a fundamental concern for all who make, distribute, and use our family of ethyleneamine products, and the environment we share. This concern is the basis for our Product Stewardship philosophy, by which we assess all available information on our products and then take appropriate steps to protect employee and public health and the environment.

In addition, Huntsman is committed to implementing the guiding principles and management practices of the

chemical industry's Responsible Care\* initiative, which includes Product Stewardship as one of the Management Practices. As part of our Product Stewardship effort, information such as Material Safety Data Sheets and this brochure are provided to assist our customers in handling our ethyleneamine products in a safe and responsible manner.

Additional information and services which are available for our ethyleneamine customers are described in Section 6.4.

**Table 6.1 — Storage and Handling Information for Huntsman Ethyleneamines**

|                                       | EDA      | DETA     | TETA             | TEPA             | AEP      | AEAA             | E-100            |
|---------------------------------------|----------|----------|------------------|------------------|----------|------------------|------------------|
| Weight (lb.)/Gallon                   | 7.46     | 7.89     | 8.12             | 8.23             | 8.18     | 8.55             | 8.35             |
| Boiling Point @760 mm, °C             | 116.9    | 206.7    | 276.4            | 332.0            | 222.1    | 243.1            | decomp.          |
| Freezing Point, °C                    | 11.1     | -39      | -35 <sup>a</sup> | -30 <sup>a</sup> | -17      | -38 <sup>a</sup> | -21 <sup>a</sup> |
| Flash Point (PMCC), °F(°C)            | 110(43)  | 215(102) | 245(118)         | >350(>177)       | 210(99)  | >300(>149)       | >360(>182)       |
| Upper Explosion Limit, vol %          | 14.2     | 11.6     | >6.4             |                  |          |                  |                  |
| Lower Explosion Limit, vol %          | 2.6      | 1.9      | 1.1              |                  |          |                  |                  |
| Thermal Conductivity, cal/cm-s-C 20°C | 0.000614 | 0.000523 | 0.000450         | 0.000435         | 0.000434 | 0.00059          |                  |
| Vapor Pressure mm Hg, 20 °C           | 9.34     | 0.084    | <0.01            | <0.01            | 0.048    | <0.01            | <0.01            |
| Solid Hydrate Formation               | No       | No       | Yes              | Yes              | No       | No               | Yes              |

| USA                     | EDA                | DETA                | TETA                  | TEPA                    | AEP                      | AEAA                                                        | E-100          |
|-------------------------|--------------------|---------------------|-----------------------|-------------------------|--------------------------|-------------------------------------------------------------|----------------|
| DOT Shipping Name       | Ethylene diamine   | Diethylene-triamine | Triethylene-tetramine | Tetraethylene-pentamine | N-Amino ethyl piperazine | Amines, Liquid, Corrosive, n.o.s. (Aminoethyl-ethanolamine) | Not Applicable |
| DOT Classification      | 8                  | 8                   | 8                     | 8                       | 8                        | 8                                                           | n/a            |
| Hazard Class            | Corrosive Material | Corrosive Material  | Corrosive Material    | Corrosive Material      | Corrosive Material       | Corrosive Material                                          | Not Applicable |
| Shipping Label          | Corrosive          | Corrosive           | Corrosive             | Corrosive               | Corrosive                | Corrosive                                                   | Not Applicable |
| UN Number               | 1604               | 2079                | 2259                  | 2320                    | 2815                     | 2735                                                        | n/a            |
| Package Group           | II                 | II                  | II                    | III                     | III                      | III                                                         | n/a            |
| NFPA H,F,R <sup>b</sup> | 3,2,0              | 3,1,0               | 3,1,0                 | 3,1,0                   | 3,1,0                    | 3,1,0                                                       | 3,1,0          |

| EUROPE                     | EDA              | DETA                | TETA                  | TEPA                    | AEP                      | AEEA                                                        | E-100                            |
|----------------------------|------------------|---------------------|-----------------------|-------------------------|--------------------------|-------------------------------------------------------------|----------------------------------|
| Shipping Name <sup>a</sup> | Ethylene diamine | Diethylene-triamine | Triethylene-tetramine | Tetraethylene-pentamine | N-Amino ethyl piperazine | Amines, Liquid, Corrosive, n.o.s. (Aminoethyl-ethanolamine) | Amines Liquid, Corrosive, n.o.s. |
| Hazard Class               | Corrosive        | Corrosive           | Corrosive             | Corrosive               | Corrosive                | Corrosive                                                   | Corrosive                        |
| UN Number                  | 1604             | 2079                | 2259                  | 2320                    | 2815                     | 2735                                                        | 2735                             |
| Package Group              | II               | II                  | II                    | III                     | III                      | III                                                         | III                              |

<sup>a</sup>Pour point

<sup>b</sup>H = Health, F=Fire, R= Reactivity<sup>c</sup> For road, rail and barge, shipping name preceded by UN number

<sup>c</sup>Service mark of The Chemical Manufacturers' Association

## 6.1 Health Effects

The following information is intended to provide a brief summary of health effects information and precautions. Consult the applicable Safety Data Sheet for the most up-to-date ethyleneamines information on health and safety of Huntsman ethyleneamine products.

### 6.1.1 Eye Contact

Because of the fragility of eye tissue, almost any eye contact with any ethyleneamine may cause irreparable damage, even blindness. Properly fitted chemical goggles should be considered as minimum eye protection, and a face shield which allows the use of chemical goggles should be worn when there is any likelihood of a splash.

If eye exposure occurs, immediate and continuous irrigation with flowing water for at least 30 minutes is imperative. Prompt medical consultation is essential.

### 6.1.2 Skin Contact

A single, short exposure to ethyleneamines may cause severe skin burns, while a single, prolonged exposure may result in the material being absorbed through the skin in harmful amounts. Exposures have caused allergic skin reactions in some individuals. Protective clothing, impervious to ethyleneamines, should be worn.

Specific items, such as gloves, boots, aprons, or full-body suits, are recommended depending upon the operation and the potential for skin contact. A face shield that allows the use of chemical goggles, or an appropriate full-face respirator, should be worn to protect the face and eyes when there is any potential for contact.

In the event of contact, immediately flush the skin with flowing water for at least 15 minutes, while removing contaminated clothing and shoes. If the irritation persists, seek medical assistance. Contaminated clothing can be washed and reused, but shoes, other leather items, or other articles that cannot be decontaminated should be destroyed.

### **6.1.3 Oral Toxicity**

Single dose oral toxicity of ethyleneamines is low. The oral LD 50 for rats is in the range of 1000 to 4500 mg/kg for the ethyleneamines. However, ingestion will cause burns to the membranes of the mouth, throat, and stomach, and may cause gastrointestinal irritation or ulceration.

If ingestion occurs, do not induce vomiting. Have the individual drink a large amount of water (or milk, if it is readily available) and transport them to a medical facility immediately.

### **6.1.4 Inhalation**

Overexposure to ethyleneamine vapors can cause painful irritations to the eyes, nose, throat, and lungs. It may also cause respiratory sensitization in susceptible individuals.

Always be sure there is adequate ventilation in ethyleneamine work areas. In the event of a gross exposure to ethyleneamine vapor, immediately remove the affected individual(s) to fresh air and seek attention.

In the United States, the Occupational Safety and Health Administration (OSHA) has established permissible exposure limit-time weighted averages (PEL-TWA) for ethylenediamine and diethylenetriamine. These figures represent the legal exposure limits for a workday.

Similarly, the American Conference of Governmental Industrial Hygienists (ACGIH) has established threshold limit values-time weighted averages (TLV-TWA) for ethylenediamine and diethylenetriamine as guidelines for industrial use. The American Industrial Hygienist Association has established a workplace environmental exposure limit (WEEL) for triethylenetetramine. This is based on an 8-hour TWA for a normal workday and 40-hour work-week.

These figures, shown in Table 6.2, represent the average airborne concentrations to which most workers can be exposed, day after day, without serious adverse effects.

**Table 6.2 — Representative Occupational Exposure Limits (OELs) for Ethyleneamine**

|      | OSHA PEL | ACGIH TLV    | AIHA WEEL | German MAK | Swiss MAK-Wert |
|------|----------|--------------|-----------|------------|----------------|
| EDA  | 10 ppm   | 10 ppm, skin | --        | 10 pppm    | 10 ppm         |
| DETA | 1 ppm    | 1 ppm, skin  | --        | --         | 1 ppm          |
| TETA | --       | --           | 1 ppm     | --         | --             |

OSHA PEL: U.S. Occupational Safety and Health Administrator Permissible Exposure Limit – expressed as an 8-hour time weighted average (TWA).

ACGIH TLV: American Conference of Governmental Industrial Hygienist Threshold Limit Value – expressed as an 8-hour time weighted average (TWA).

Skin notation for ACGIH TLV indicates the potential for dermal absorption of the material.

AIHA WEEL: American Industrial Hygiene Association Workplace Environmental Exposure Limit – expressed as an 8-hour time weighted average (TWA).

No such guidelines have been set for the higher molecular weight amines since they have substantially lower vapor pressures. However, in some circumstances, such as high temperatures, even these ethyleneamines can generate enough vapors to be hazardous.

### 6.1.5 Systemic Effects

For specific information on the possible systemic effects of a particular ethyleneamine, consult the Safety Data Sheet for that product.

## 6.2 Storage and Transfer

The ethyleneamine product family, as highly reactive intermediates, are potentially hazardous materials when released to the environment.

The following information is intended to provide a brief summary of storage and transfer information.

**Note: Copper or copper alloys should never be used with amines.**

## Рисунок 6.1 - Хранение и слив наливных этиленаминов Huntsman

Этот схематический чертёж добросовестно предоставлен Huntsman Corporation.

Однако, поскольку условия доставки, хранения, использования и утилизации не находятся под его контролем, Huntsman не гарантирует положительных результатов от использования схемы.

Заказчику рекомендуется нанять квалифицированную инженерную службу для проектирования и строительства своего хранилища и погрузочно-разгрузочного оборудования.

Поскольку любая помощь, предоставляемая Huntsman со ссылкой на безопасную доставку, хранение, использование и утилизацию наших продуктов предоставляется бесплатно, Huntsman не несет никаких обязательств или ответственности.

**a** Насос должен быть выключен:

Высокий уровень в баке

Высокая температура

Низкое давление нагнетания насоса

Низкий расход насоса

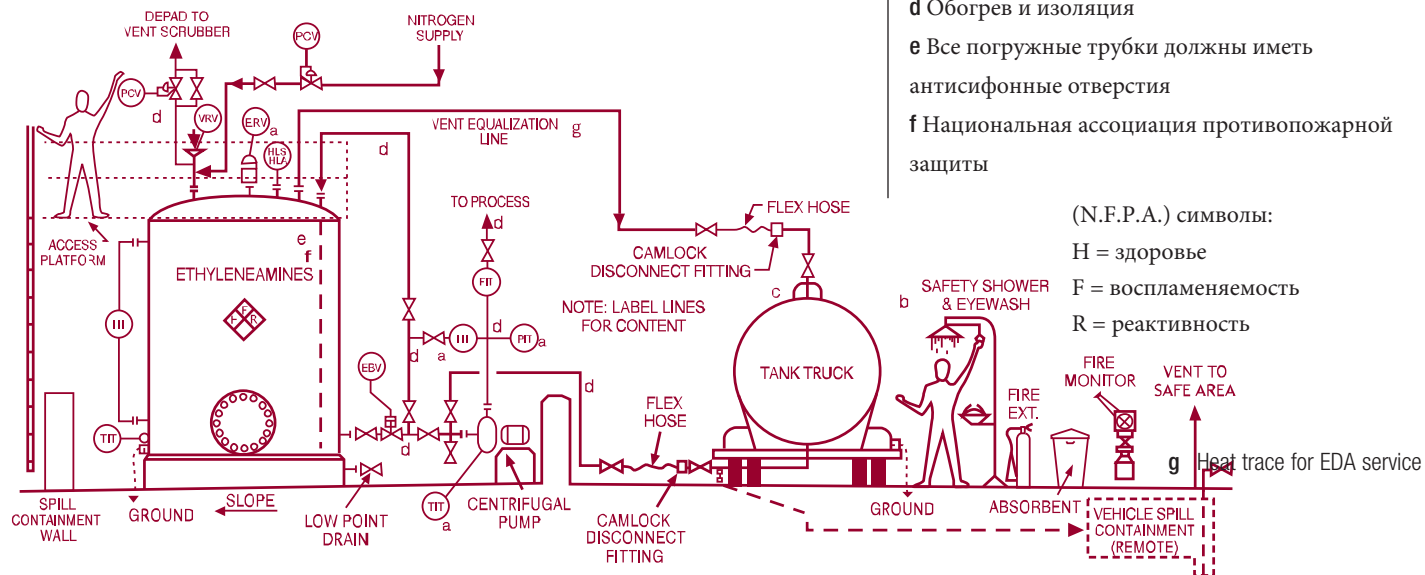
**b** Безопасный душ должен быть расположен так, чтобы к нему можно было быстро добраться из всех зон обработки продукта

**c** К куполу должен быть обеспечен безопасный доступ

**d** Обогрев и изоляция

**e** Все погружные трубки должны иметь антисифонные отверстия

**f** Национальная ассоциация противопожарной защиты



(N.F.P.A.) символы:

H = здоровье

F = воспламеняемость

R = реактивность

EBV Запасной клапан

ERV Аварийный предохранительный клапан

FIТ Индикатор потока

HLA Сигнализация высокого уровня

HLS Переключатель высокого уровня

LIТ Датчик уровня

NIТ Азот

PCV Клапан контроля давления

PIТ Индикатор давления

TIТ Датчик температуры

VRV Вакуумный предохранительный клапан

### 6.2.1 Танки и линии

Жидкие этиленамины не являются особенно сложными материалами для обработки или хранения; Однако при работе с этиленаминами важно знать следующую информацию.

На рисунке 6.1 представлена схема типичного оборудования для хранения и разгрузки этиленаминов, на которой показаны контрольно-измерительные приборы, которые следует учитывать при проектировании установки для разгрузки и хранения этиленамина. (Эта схема не является технической схемой.)

Хотя могут использоваться и горизонтальные резервуары, но рекомендуются вертикальные резервуары, поскольку они, как правило, более экономичны в установке, занимают меньше места и обеспечивают более точные измерения резервуаров. (Примечание. В соответствии с правилом 30.17 Национальной ассоциации противопожарной защиты, пункт 2-1.31 (b), для этиленаминов предлагается вертикальный резервуар, разработанный в соответствии со стандартом 650 Американского института нефти (API).)

Европейские эквиваленты включают конструкцию резервуара с плоским дном DIN 4119, части 1 и 2 и горизонтальный вертикальный DIN 6600-6625. Для более летучих этиленаминов, таких как EDA, использование стандарта API 620 обеспечит преимущество сокращения выбросов при операциях переноса.)

В таблице 6.1 приведены соответствующие физические свойства, связанные с обработкой этиленаминов Huntsman, а также ссылки на правила перевозки для США и Европы.

Если приемлема небольшая окраска этиленамина, резервуары могут быть изготовлены из углеродистой стали или черного чугуна, при условии, что они не содержат ржавчины и окалина. Однако, если амин хранится в таких резервуарах, цвет может появиться из-за загрязнения железом. Если загрязнение железом недопустимо, следует использовать резервуары, изготовленные из нержавеющей стали типов 304 или 316.

(Примечание: не используйте медь, медные сплавы, латунь или бронзу в резервуарах или трубопроводах, поскольку их быстро разъедают амины.)

В таблице 6.3 приведены рекомендуемые условия хранения этиленаминов.

**Таблица 6.3 - Рекомендованные материалы для изготовления резервуаров для хранения наливных этиленаминов**

| Продукт | Хранить в:                               |
|---------|------------------------------------------|
| EDA     | Нержавеющая сталь                        |
| DETA    | Нержавеющая сталь                        |
| TETA    | Нержавеющая сталь                        |
| TEPA    | Нержавеющая сталь или углеродистая сталь |
| AEP     | Нержавеющая сталь                        |
| AEAA    | Нержавеющая сталь                        |
| E-100   | Нержавеющая сталь или углеродистая сталь |

### **6.2.2 Защита От Нагрева / Замерзания**

Для простоты обращения с продуктом рекомендуемый диапазон температур перекачки этиленаминов составляет 10-32,2 ° C (50-90 ° F). Смотрите таблицу 6.1. Для достижения этих температур обычно требуется небольшое нагревание или его полное отсутствие, особенно если резервуар для хранения находится в теплом или умеренном климате, хорошо изолирован или хранится в помещении в отопляемом или изолированном здании. Однако продукт, хранящийся на открытом воздухе в неизолированном резервуаре, особенно в холодном климате, может потребовать некоторой степени нагревания.

Этиленамин Е-100 и аминоктилэтанолламин не имеют определенной точки замерзания, но при температуре ниже 40 ° F (4,4 ° C) вязкость становится настолько высокой, что его трудно перекачивать. В качестве меры предосторожности все линии передачи должны быть изолированы от тепла, а наружные резервуары должны быть оборудованы нагревательным устройством. В холодном климате или если материал должен храниться в тепле, резервуар должен быть изолирован.

#### **6.2.2.1 Слив этилендиамина**

Особую осторожность следует соблюдать с EDA, поскольку его точка замерзания составляет 52 ° F (11,1 ° C). Если резервуары не находятся в здании, где температура постоянно превышает 52 ° F, они должны быть оборудованы нагревательными змеевиками. Для включения пара в холодную погоду может быть установлено автоматическое устройство контроля температуры. Температура хранения не должна превышать 100 ° F. Наружные линии, используемые при обработке или передаче EDA, должны быть нагреты в холодную погоду. Это может быть достигнуто путем изоляции линий и использования либо пара низкого давления, либо электрической трассировки.

### **6.2.3 Насосы**

Насосы, работающие с этиленамином, также должны иметь конструкцию из нержавеющей стали, особенно во избежание загрязнения железом. Поскольку большинство обычных материалов легко разрушаются этиленаминами, насосы должны быть оснащены механическими уплотнениями. Также предлагаются центробежные насосы с магнитным приводом без уплотнений. Для простоты запуска, особенно в холодную погоду, предлагаются насосы с подогревом в рубашке или трассируемые.

### **6.2.4 Вентиляция / Газовая прокладка**

Резервуары для хранения должны вентилироваться для предотвращения возникновения избыточного давления или вакуума в баке во время наполнения или опорожнения. Вентиляционное отверстие должно быть сконструировано таким образом, чтобы ни дождь, ни грязь не могли попасть в бак. Для хранения жидких этиленаминов настоятельно рекомендуется использовать систему подушек инертного газа.

Эта система требует источника сухого инертного газа, такого как азот, в объеме, достаточном для опорожнения резервуара, небольших утечек и колебаний температуры. Наличие газовой подушки может минимизировать возможность окисления амина, поглощения влаги и CO<sub>2</sub>, а также пожароопасности, предотвращая попадание воздуха в паровое пространство над жидкостью. Когда этиленамины подвергаются воздействию воздуха, особенно в теплую погоду, они имеют тенденцию окисляться и обесцвечиваться.

#### **6.2.5 Затворы и соединения**

Обычно используемые материалы прокладок представляют из себя армированные металлом графитовые прокладки или спирально навитые прокладки с графитом или политетрафторэтиленом (ПТФЭ) для технологических линий и оборудования, а также полиэтиленовые фитинги для барабанов. PTFE лента рекомендуется для резьбовых соединений. Поскольку большинство трубных добавок вымываются этиленаминами, стыки следует по возможности фланцевать или сваривать.

#### **6.2.6 Реакционная способность**

Этиленамины являются реакционноспособными соединениями. Они легко реагируют с кислотами (как органическими, так и неорганическими), альдегидами, кетонами, акрилатами и галогенированными органическими соединениями. Реакции являются экзотермическими и немедленными, за исключением реакции с галогенированной органикой, которая является экзотермической, но не проявляет немедленной экзотермы. Эта задержка представляет собой скрытую опасность, против которой следует принимать меры предосторожности. Некоторые целлюлозные материалы, используемые для очистки от разливов, такие как древесная щепа или опилки, продемонстрировали реакционную способность с этиленаминами, и их следует избегать.

Специальные линии и насосы рекомендуются для предотвращения случайного перекрестного загрязнения во время операций перелива.

#### **6.2.7 Перевозки в бочках**

Хотя большинство потребителей этиленаминов получают продукцию наливом в автоцистернах и железнодорожных вагонах, многие клиенты получают эти продукты в 55-галлонных бочках. Таким образом, персонал по обработке бочек должен быть полностью обучен тому, как:

- Безопасно получать и хранить полные бочки
- Безопасно открывать бочки и извлекать продукт
- Безопасно и законно избавляться от пустых бочек

AEEA и EDA поставляются в бочках из полиэтилена высокой плотности (HDPE). Все остальные этиленамины поставляются в стальных бочках из полиэтилена высокой плотности или фенольной футеровки.

#### **6.2.8. Перевозки наливом**

Наливные этиленамины, перевозимые в автоцистернах и железнодорожных вагонах, загружаются при слегка повышенной температуре. При транспортировке в автоцистерне тепло также используется для поддержания подходящей температуры перекачки. Этиленамины, также отправляются железнодорожным транспортом. Эти цистерны представляют собой изолированные стальные агрегаты, оборудованные наружными нагревательными змеевиками.

Разгрузка этиленаминов из автоцистерн или железнодорожных вагонов требует, чтобы у клиента были соответствующее оборудование для разгрузки. Обратитесь к рисунку 6.1.

### **6.3 Процедура обращения и хранения продукта**

Надлежащая практика обращения и хранения сведет к минимуму вероятность несчастных случаев, но очень важно, чтобы были подходящие материалы для обработки разливов продукта.

#### **6.3.1 Разливы**

Небольшие разливы должны быть покрыты неорганическими абсорбентами и утилизированы надлежащим образом. Известно, что органические абсорбенты воспламеняются при загрязнении аминами в закрытых контейнерах. Некоторые целлюлозные материалы, используемые для очистки от разливов, такие как древесная щепа или опилки, продемонстрировали реакционную способность с этиленаминами, и их следует избегать.

Большие разливы должны быть локализованы и устранены. Можно использовать воду для очистки, но избегайте попадания материала в канализацию или природные водоемы. Утилизация должна осуществляться в соответствии со всеми федеральными, государственными и местными законами, правилами и постановлениями.

#### **6.3.2 Утечки**

Утечки этиленамина часто определяются по запаху (аммиачный) или по образованию белого твердого воскообразного вещества (карбаматы амина). Неорганические абсорбенты или вода могут быть использованы для очистки аминных отходов.

#### **6.3.3 Выбросы в воздух**

Низкомолекулярные амины, такие как EDA и DETA, являются летучими, и их пары будут реагировать с диоксидом углерода в воздухе. Эта реакция будет образовывать небольшие твердые частицы, которые плавают в воздухе и появляются в виде дыма. These particulates (amine carbamate) should be regarded as amine vapors, and exposures should be minimized with respiratory. Эти частицы (аминкарбамат) следует рассматривать как пары амина, а воздействие должно быть сведено к минимуму с помощью средств защиты органов дыхания и безопасности.

Значительные выбросы паров амина, которые могут произойти во время крупного разлива, требуют эвакуации из зоны до тех пор, пока пары не будут контролироваться. Такой дым может также наблюдаться с аминами с более высокой молекулярной массой, такими как ТЕТА, при нагревании. Следует также избегать воздействия аэрозолей, особенно для ДЕТА.

#### **6.3.4 Попадание в воду**

Этиленамины и их производные могут быть токсичными для водных организмов; Поэтому следует избегать загрязнения воды. Сточные воды, содержащие этиленамины, могут быть трудными для обработки, что может вызвать поломку очистного сооружения.

#### **6.4 Дополнительная информация**

Для получения дополнительной информации, касающейся обращения с этиленаминами, пожалуйста, запросите брошюру «Безопасное обращение с этиленаминами» (Технический бюллетень № 5001-701).

Информация, содержащаяся в этой брошюре, считается точной и надежной, но не может быть полной. Для обеспечения максимальной безопасности необходимо разработать специальные системы обработки и хранения для каждой производственной среды.

Информацию об этиленаминах и связанных с ними вопросах можно получить в корпорации Huntsman, чтобы помочь заказчику спроектировать соответствующие системы, отвечающие требованиям завода. Такая информация предоставляется добросовестно, но никакая гарантия, явная или подразумеваемая, не может быть предоставлена. Запросите текущие паспорта безопасности материалов, дополнительную информацию и / или техническую помощь у местного представителя Huntsman.

Обратитесь к соответствующему Паспорту безопасности материала для получения дополнительной информации о воздействии на здоровье, воздействии на окружающую среду, мерах первой помощи, реактивности, нормативах и утилизации.

A good general reference for ethyleneamines technology is: Kirk-Othmer, Encyclopedia of Chemical Technology, Fifth Edition, "Diamines and Higher Amines, Aliphatic," 2001 Wiley & Sons, New York.

## Asphalt Additives

- <sup>1</sup> Dobozy, O. K. *Egypt J. Chem.* 1973, 16 (5), 419-39.
- <sup>2</sup> Dobozy, O. K. *Tenside* 1970, 7 (2), 83-7.
- <sup>3</sup> Kalinowski, M. L.; Crews L. T. U.S. Patent 2,812,339, 1957.
- <sup>4</sup> Dickinson, W. J.; Jenkins, F. W. U.S. Patent 3,259,512, 1966.
- <sup>5</sup> Schilling, P. U.S. Patent 4,561,901, 1985.
- <sup>6</sup> Schilling, P. U.S. Patent 4,597,799, 1986.

## Bleach Activators

- <sup>7</sup> Heslam, R. S., DE 2616350, 1976.
- <sup>8</sup> Reinhardt, G.; Schuler, W.; and Wuack; J. M. *TAED – Manufacture, Effects and Environmental Properties*, 1989.
- <sup>9</sup> Grime, K.; and Clauss, A. *Laundry Bleaches and Activators, Chemistry & Industry*, October 1990, 657-653.
- <sup>10</sup> Reinhardt, G. *Organische Persäuren und Aktivatoreneinsatz in der Waschmittel-Industrie*, SÖFW-Journal, 118. Jahrgang, 8/1992, 473-480.
- <sup>11</sup> Jürges, P. *Activators and Peracids*, Proceedings of the 3rd World Conference on Detergents, Montreux, Ed. A. Cahn, 1993, AOCS Press, New York.
- <sup>12</sup> Croud, V.B.; and George, I.M. *The Biocidal Efficacy of TAED In Fabric Washing Formulas*, HAPPI — The Household and Personal Products Industry Journal (happi), January 1997, 82-92.
- <sup>13</sup> Warwick International Ltd., Mathews, A.J. *Use of TAED in Automatic Dishwashing (ADW) Powders*, 1997.
- <sup>14</sup> Croud, V.B.; and Tompsett, S.J. *The Generation of Strong Oxidation Solutions from Activators*, Presented at the Fourth World Surfactants Congress, Barcelona, June 1996.
- <sup>15</sup> Warwick International Ltd., *The Use of TAED in Pulp Bleaching*, 1996.
- <sup>16</sup> Warwick International Ltd., *T.A.E.D. – A New Activator For The Peroxide Bleaching of Pulp*, 1997.
- <sup>17</sup> Croud, V.; and Mathews, J. *TAED – A New Activator for the Peroxide Bleaching of Pulp*, Presented at the International Non-Chlorine Bleaching Conference (Pulp and Paper Magazine) Orlando, March 1996.

- <sup>18</sup> Leduc, C.; Montillet, C.; Daneault, C. *Activator for the Peroxide Bleaching of Mechanical Pulp*, 1996 TAPPI Pulping Conference, October 1996, Nashville, 361-368.

### **Chelating Agents**

- <sup>19</sup> Bersworth, F. C. U.S. Patent 2,387,735, 1945.
- <sup>20</sup> Bersworth, F. C. U.S. Patent 2,407,645, 1946.
- <sup>21</sup> Bersworth, F. C. U.S. Patent 2,461,549, 1949.
- <sup>22</sup> Kroll, H.; Dexter, M. U.S. Patent 2,845,457, 1958.
- <sup>23</sup> Kroll, H.; Butler, F. P. U.S. Patent 2,860,164, 1958.
- <sup>24</sup> Ulrich, H.; Ploetz, E. U.S. Patent 2,205,995, 1940.
- <sup>25</sup> Singer, J. J. U.S. Patent 2,855,428, 1958.

### **Corrosion Inhibitors**

- <sup>26</sup> Schilling, P.; Braddon, D. U.S. Patent 4,614,600, 1986.
- <sup>27</sup> Dougherty, J.; Outlaw, B.; Oude, A. U.S. Patent 5,582,792, 1996.
- <sup>28</sup> Olsen, J.; Brown, J.; Brock, G.; Mandlay, V. U.S. Patent 5,459,125, 1995.
- <sup>29</sup> Naraghi, A.; Grahmann, N. U.S. Patent 5,611,992, 1997.
- <sup>30</sup> Schilling, P. U.S. Patent 5,391,636, 1995.
- <sup>31</sup> Williams, D. U.S. 5,322,630, 1994.
- <sup>32</sup> Annand, R. R.; Redmore, D.; Rushton, B. M. U.S. Patent 3,514,251, 1970.
- <sup>33</sup> Rushton, B. M. U.S. Patent 3,514,250, 1970.
- <sup>34</sup> Higaki, Y.; Kataoka, T. JP Patent 7,551,046, 1975.
- <sup>35</sup> Voronchikhina, L. I.; Manucharyan, S. S.; Gorbokonev, V. P.; Basanov, A. N.; Krupatkin, I. L.; Loginova, Ta. A.; Boiko, A. N. *Chem. Abstr.* 1975, 2, 148-53, 86, 91859b.
- <sup>36</sup> Talati, J. D.; Pandya, J. M. *Chem. Abstr.* 1974, 21 (12), 7-10, 83, 17561v.
- <sup>37</sup> Go, T. S. U.S. Patent 3,819,328, 1974.
- <sup>38</sup> Babaian-Kibala, E.; Braden, V.; Poindexter, M.; Murphy, C. U.S. 5,556,575, 1996.
- <sup>39</sup> Crawford, D. U.S. 5,380,131, 1995.

### Drainage Aids

- <sup>40</sup> *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed.; 1988; Vol. A11, pp 251-261.
- <sup>41</sup> *Organic Polymer Coagulants and Flocculants*, Ed.; SRI International; 1990.
- <sup>42</sup> Scharf, E. U.S. Patent 4,144,123, 1979.

### Elastomeric Fibers

- <sup>43</sup> *Chemical Economics Handbook, Fibers, Specialty*, SRI International; 1995; 542.7002W.
- <sup>44</sup> Seo, S.; Kim, M. U.S. Patent 5,644,015, 1997.
- <sup>45</sup> Lehmann, W.; Rinke, H. DE Patent 2,761,852, 1956.
- <sup>46</sup> Wang, T.; Hsieh, T. *Polymer Journal* 1996, Vol. 28, 10.
- <sup>47</sup> Zimmerman, R.; Primeaux, D. U.S. Patent 5,189,075, 1993.
- <sup>48</sup> Caldwell, J. R. U.S. Patent 2,632,748, 1953.

### Epoxy Curing Agents

- <sup>49</sup> May, C. A. *Epoxy Resins*, 2nd Ed., Ed.; Marcel Decker, 1988.
- <sup>50</sup> Hare, C. H. J. *Protective Coatings & Linings*, 1994, 77-103.
- <sup>51</sup> Laudise, M. A. Henkel Corp., Minneapolis, MN, ACS Symp. Ser. 1985, 285 (*Appl. Polym. Sci.* [2nd Ed.]), 963-84.
- <sup>52</sup> Wozniak, D. S. U.S. Patent 5,021,482, 1990.

### Fabric Softeners

- <sup>53</sup> Laughlin, R. G. *Cationic Surfactants: Organic Chemistry*, Richmond, J. M., Ed.; *Surfactant Science Series*, 1990, Vol. 34, 449-467.
- <sup>54</sup> McCarthy, J. P.; Drozdowski, R. E. *Soap/Cosmetic/Chemical Specialties*, 1989.
- <sup>55</sup> McConnell, R. B. *INFORM*, 1994, 5 (1), 76-84.
- <sup>56</sup> Puchta, R. J. *Amer. Oil Chem. Soc.*, 1984, 61 (2), 367-376.
- <sup>57</sup> Ackerman, J. A. J. *Amer. Oil Chem. Soc.*, 1983, 60 (6), 1166-1169.
- <sup>58</sup> Lichtenwalter, G. D.; Rosario-Jansen, T.; Wahl, E. H. U.S. Patent 5,116,520, 1992.

## Fungicides

- <sup>59</sup> Kirk-Othmer, *Encyclopedia of Chemical Technology*, Fourth Edition; Wiley & Sons, New York 1993; Vol 8, p 88.
- <sup>60</sup> U.S. Environmental Protection Agency, 1988, *Guidance for the Registration of Pesticide Products Containing Maneb as the Active Ingredient*, Office of Pesticides and Toxic Substances, US EPA, Washington, DC.
- <sup>61</sup> Maxwell, D. P.; Maxwell, M. D. Ed., *Introduction to Plant Pathology*, S. M. Miller and B. W. Carlson, *Late Blight of Potato, Chemical Control, Protectant Fungicide* 1995 (Electronic Publication, University of Wisconsin-Madison).
- <sup>62</sup> Meister, R.T. *Farm Chemicals Handbook '92*, 1992, Ed.; Meister Publishing Company, Willoughby, OH.
- <sup>63</sup> Flenner, A. L. U.S. Patent 2,504,404, 1950.
- <sup>64</sup> Fike, E. A. U.S. Patent 2,844,623, 1968.
- <sup>65</sup> Hester, W. F. U.S. Patent 2,317,765, 1943.
- <sup>66</sup> Lyon, C. B.; Nemec, J. W.; Unger, V. H. Belg. Patent 617,407, 1962.
- <sup>67</sup> Nemec, J. M.; Unger, V. H.; Lyon, C. B. Belg. Patent 617,408, 1962.
- <sup>68</sup> Lyon, C. B.; Nemec, J. W.; Unger, V. H. U.S. Patent 3,379,610, 1968.
- <sup>69</sup> EXTONET, *Pesticide Information Profiles (PIPs)* 1993 (Electronic publication. EXTONET is a cooperative effort of University of California-Davis, Oregon State University, Michigan State University, and Cornell University).
- <sup>70</sup> Rohm and Haas Company, *About Rohm and Haas, Overview, History*, 1996 (Electronic Publication).
- <sup>71</sup> Morgan, D. P. *Recognition and Management of Pesticide Poisonings*, Fourth Edition. U.S. Environmental Protection Agency. U.S (1989). Government Printing Office, Washington, DC.
- <sup>72</sup> Berg, G. L. Ed., *Farm Chemicals Handbook '88*, 1988, Meister Publishing Co. Willoughby, OH.
- <sup>73</sup> Hayes, W.J.; Laws, E. R. Ed., *Handbook of Pesticide Toxicology, Vol. 3. Classes of Pesticides*, 1990, Academic Press, Inc., NY.

### Hydrocarbon Purification

- <sup>74</sup> Balogh, G. F. EP Patent 81,630,068, 1981.
- <sup>75</sup> Fakhriev, A. M. Otkrytiya, Izobret., Prom. Obraztsy, Tovaryne Znaki, 1980, (27), 97.
- <sup>76</sup> Japan Kokai Tokkyo Koho, JP Patent 58,188,824, 1983.
- <sup>77</sup> Japan Kokai Tokkyo Koho, JP Patent 58,189,123, 1983.

### Lube Oil and Fuel Additives

- <sup>78</sup> Mortier, R. M.; Orzulik, S. T. Eds.; *Chemistry & Technology of Lubricants*, Blackie & Sons, 1992, 62-80.
- <sup>79</sup> Harrison, J. J.; Ruhe, Jr., W. R. U.S. Patent 5,565,528, 1996.
- <sup>80</sup> Gutierrez, A. U.S. Patent 5,565,128, 1996.
- <sup>81</sup> Honen, L. R.; Anderson, R. G. U.S. Patent 3,565,804, 1971.
- <sup>82</sup> Honen, L. R.; Lewis, R. A. U.S. Patent 4,288,612, 1981.
- <sup>83</sup> Cherpeck, R. E. U.S. Patent 5,393,309, 1995.
- <sup>84</sup> Cherpeck, R. E. U.S. Patent 5,399,178, 1995.

### Mineral Processing Aids

- <sup>85</sup> Friedli, F. E. *Cationic Surfactants: Organic Chemistry*, Richmond, J. M., Ed.; *Surfactant Science Series*, 1990, Vol. 34, 51-99.
- <sup>86</sup> Hollingworth, C. A.; Schilling, K. F.; Wester, J. L. U.S. Patent 2,857,331, 1958.
- <sup>87</sup> Hathaway, F. S. U.S. Patent 3,485,592, 1969.
- <sup>88</sup> Jerzykiewicz, W.; Krasnodebski, Z.; Berkierz, G.; Simonides, J.; Szopa, Z.; Mlynarczyk, M.; Pandel, J. Pol. Patent 95,676, 1978.
- <sup>89</sup> Watson, J. D.; Mod, W. A.; Teumac, R. N. U.S. Patent 3,475,163, 1969.
- <sup>90</sup> Baure, D. J.; Lindstrom, R. E. *J. Metals*, 1971, 23 (5), 31.

### Polyamide Resins

- <sup>91</sup> Laudise, M. A. Henkel Corp., Minneapolis, MN, ACS Symp. Ser., 1985. 285 (*Appl. Polymer Sci.* [2nd Edition]), 963-984.
- <sup>92</sup> Hurd, P. W.; Heebner, G. W. *Adhesive Age*, 1992, 16-20, Jul.
- <sup>93</sup> Van Beek, D. A. U.S. Patent 5,138,027, 1992.
- <sup>94</sup> Peck, M. C. U.S. Patent 4,514,540, 1985.

## Surfactants

- <sup>95</sup> Earl, G. W. *Cationic Surfactants: Organic Chemistry*, Richmond, J. M., Ed., Surfactant Science Series, 1990, Vol. 34, 101-144.
- <sup>96</sup> Linfield, W. M. *J. Amer. Oil Chem. Soc.*, 1984, 61 (2), 437-441.
- <sup>97</sup> Watts, M. M. *J. Amer. Oil Chem. Soc.*, 1990, 67 (12), 993-995.
- <sup>98</sup> Wu, Y.; Herrington, P. R. *J. Amer. Oil Chem. Soc.*, 1997, 74 (1), 61-64.
- <sup>99</sup> Dahanayake, M.; Reiersen, R. L.; Tracy, D. J. EP Patent 0697,245, 1996.
- <sup>100</sup> Mercier, J. M.; Ricca, J. M. WO Patent 9,700,126, 1997.
- <sup>101</sup> Vander Meer, J. M.; Rubingh, D. N. EP Patent 112,593, 1984.

## Textile Additives

- <sup>102</sup> Simitzis, J. *Polym. Int.*, 1995, 36(3), pp 279-285.
- <sup>103</sup> Wu, S.; Sheu, G.; Shyu, S. *J. Appl. Polym. Sci.*, 1996, Vol. 62, pp 1347-1360.
- <sup>104</sup> Loss, R. U.S. Patent 3,956,243, 1976.
- <sup>105</sup> Klett, M. U.S. Patent 5,604,270, 1997.
- <sup>106</sup> Gardner, S. *Appl. Spect.*, 1997, Vol. 51, No. 5.
- <sup>107</sup> Lei, X.; Lewis, D.; Shen, X.; Wang, Y.; *Dyes and Pigm.*, 1996, 30 (4), pp 271-281.
- <sup>108</sup> Hofer, K. U.S. Patent 3,873,266, 1975.
- <sup>109</sup> Hansen, M. U.S. Patent 5,609,727, 1997.
- <sup>110</sup> Gupta, R.; Balakrishnaiah, B. *Colourage*, 1993, 40 (7), pp 33-36.
- <sup>111</sup> Saha, A.; Mitra, B. *J. Appl. Polym. Sci.*, 1996, 62 (5), pp 733-742.
- <sup>112</sup> Hoover, F. W.; Vasla, G. T. U.S. Patent 2,373,136, 1945.
- <sup>113</sup> Richardson, G. M. U.S. Patent 2,661,312, 1953.
- <sup>114</sup> Ibrahim, J.; Pusch, G.; Singer, H. DE Patent 2,402,258, 1975.
- <sup>115</sup> Lei, X.; Lewis, D. *J. Soc. Dyers Colour*, 1990.

## Wet-Strength Resins for Paper Applications

- <sup>116</sup> Suen, T.; Daniel, Jr., J. H. U.S. Patent 2,544,475, 1951.
- <sup>117</sup> Keim, G. I. U.S. Patent 3,227,671, 1966.
- <sup>118</sup> Dachs, N. W.; Wagner, G. M. U.S. Patent 3,565,754, 1971.
- <sup>119</sup> Keim, G. I.; Schmalz, A. C. U.S. Patent 3,058,873, 1962.

- <sup>120</sup> Espy, H. H. U.S. Patent 3,442,754, 1969.
- <sup>121</sup> Devore, D.; Fischer, S. U.S. Patent 5,189,142, 1993.
- <sup>122</sup> Dulany, M.; Ringold, C. U.S. Patent 5,256,727, 1993.
- <sup>123</sup> Espy, H. U.S. Patent H001,613, 1996.
- <sup>124</sup> Chan, L.; Lau, P. U.S. Patent 4,722,964, 1988.
- <sup>125</sup> Dulany, M.; Garvey, C. U.S. Patent 5,567,798, 1996.
- <sup>126</sup> Balos, B.; Clungeon, N. U.S. Patent 5,593,543, 1997.
- <sup>127</sup> Davidson, J. B.; Romatowski, E. J. U.S. Patent 2,683,134, 1954.
- <sup>128</sup> Yost, R. S.; Auten, R. W. U.S. Patent 2,742,450, 1956.
- <sup>129</sup> Suen, T.; Jen, Y. U.S. Patent 2,769,799, 1956.
- <sup>130</sup> Suen, T.; Jen, Y. U.S. Patent 2,769,800, 1956.
- <sup>131</sup> Wittcoff, H. U.S. 2,926,117, 1960.

#### **Water Carbon Dioxide, or Oxygen**

- <sup>132</sup> Gaines, Jr., G. L. *J. Org. Chem.*, 1985, 50, 410.
- <sup>133</sup> Larson, A. T.; Weber, A. G. U.S. Patent 2,497,309, 1950.
- <sup>134</sup> Arnold, H. W. U.S. Patent 2,145,242, 1939.
- <sup>135</sup> Schweitzer, C. E. *J. Org. Chem.*, 1950, 15, 471-4.
- <sup>136</sup> Crowther, M. U.S. Patent 3,597,443, 1971.
- <sup>137</sup> Levine, L. U.S. Patent 2,892,843, 1959.
- <sup>138</sup> Tsutsumi, S.; Sonoda, N. U.S. Patent 3,737,428, 1973.

#### **Inorganic Acids**

- <sup>139</sup> Hale, G. C. U.S. Patent 2,011,578, 1935.
- <sup>140</sup> Lee, K. Y. U.S. Patent 4,539,430, 1985.

#### **Alkylene Oxides, Epichlorohydrin and Aziridines**

- <sup>141</sup> Plucinski, J.; Prystasz, H.; Pawul, F. *Chemical Stosowana*, 1981, 25, 2, 195-202.
- <sup>142</sup> Hartmann, M. U.S. Patent 1,737,458, 1929.
- <sup>143</sup> Ryznar, J. W. U.S. Patent 2,701,239, 1955.
- <sup>144</sup> Schubart, R. DE Patent 2,716,946, 1978.

- <sup>145</sup> Dudley, J. R.; Lundberg, L. A. U.S. Patent 2,469,683, 1949.
- <sup>146</sup> Dalin, A. R. *Zh. Obshch. Khim.*, 1988, 58, 2098.
- <sup>147</sup> Deyrup, J. A.; Hassner, A. *Chemistry of Heterocyclic Compounds, of Small Ring Heterocycles*. Pt. 1: Aziridines, Eds.; New York: John Wiley & Sons, Inc., 1983, Vol. 42 pp 1-214.

### Alkylene Glycols and Alcohols

- <sup>148</sup> Hartwell, G. E.; Bowman, R. G.; Molzahn, D. C. U.S. Patent 4,983,735, 1991.
- <sup>149</sup> Okada, J.; Hayakawa, K. *Yakugaku Zasshi, Chem. Abstr.* 1976, 85, 160027x 96(6), 783-90.

### Organic and Inorganic Halides

- <sup>150</sup> Linsker, F.; Evans, R. L. *J. Am. Chem. Soc.*, 1945, 67, 1581-1582.
- <sup>151</sup> Linsker, F.; Evans, R. L. *J. Org. Chem.*, 1945, 10, 283-5.
- <sup>152</sup> Kruper, Jr. W. J. EP Patent 374,929, 1990.
- <sup>153</sup> Yaounanc, J. J. *J. Chem. Soc., Chem. Comm.*, 1991, 206.
- <sup>154</sup> Heskey, W. A. *Chem. Eng. News*, 1986, 64(21), 2.
- <sup>155</sup> Schiegg, D. L. U.S. Patent 3,523,892, 1970.
- <sup>156</sup> Krasulina, E. I.; Grigor'ev, F. P.; Aleksandrova, M. I. SU Patent 517,592, 1976.
- <sup>157</sup> T. Suzuki and K. Mitsunashi, Seikei Daigaku Kogakubu Kogaku Hokoku, *Chem. Abstr.* 1976, 86, 139916x, 22,1579-80.
- <sup>158</sup> Jander, J.; Knuth, K.; Trommsdorf, K. U. Z. *Anorg. Allg. Chem.*, 1972, 394 (3), 225-32.

### Aldehydes and Ketones

- <sup>159</sup> Hine, J.; Narducy, K. W. *J. Am. Chem. Soc.*, 1973, 95, 3362.
- <sup>160</sup> Poquin, A. M. *Chem. Ber.*, 1949, 82, 316-26.
- <sup>161</sup> Lichty, J. G. U.S. Patent 2,226,534, 1940.
- <sup>162</sup> Hughes, W. B. U.S. Patent 2,643,977, 1953.
- <sup>163</sup> Dale, J.; Sigvartsen, T. *Acta Chem. Scand.*, 1991, 45, 1064.
- <sup>164</sup> Krassig, H. *Makromol. Chem.*, 1955, 17, 77-130.
- <sup>165</sup> Walton, R. K. U.S. Patent 2,585,196, 1952.
- <sup>166</sup> Greenlee, S. O. U.S. Patent 2,760,944, 1956.

- <sup>167</sup> Kropa, E. L.; Wohnsiedler, H. P. U.S. Patent 2,582,594, 1952.
- <sup>168</sup> Anderson, E. V.; Gaunt, J. A. *Ind. and Eng. Chem.*, 1960, 52, 190.
- <sup>169</sup> Gutierrez, A. U.S. Patent 5,565,128, 1996.

### Organic Acid and Acid Derivatives

- <sup>170</sup> Weiner, N. U.S. Patent 2,387,201, 1945.
- <sup>171</sup> Kale, V. *J. Appl. Polym. Sci.*, 1988, 36, 1517.
- <sup>172</sup> Heitz, W.; Schwalm, R. DE Patent 3,542,230, 1987.
- <sup>173</sup> Keinle, R. H. U.S. Patent 2,371,104, 1945.
- <sup>174</sup> Coupland, K. GB Patent 2,096,133, 1982.
- <sup>175</sup> Jacobson, A. R.; Makris, A. N.; Sayre, L. M. *J. Org. Chem.*, 1987, 52, 2592.
- <sup>176</sup> Japan Kokai Tokkyo Koho JP Patent 6,023,3042, 1985.
- <sup>177</sup> Fukuda, S.; Kojima, S.; Kadoma, Y.; Kobashi, H. Japan Kokai Tokyo Koho JP, 1988, 63 208560.
- <sup>178</sup> Kita, M.; Yamada, Y. *Yukagaku, Chem. Abstr.* 84, 16712d, 1975, 24(2), 112-15.
- <sup>179</sup> Morril, H. L. U.S. Patent 2,508,415, 1950.
- <sup>180</sup> Piskov, V. B.; Kasperovich, V. P.; Yakovleva, L. M. *Khim. Geterotsikl. Soedin., Chem. Abstr.*, 86, 5372h, 1976, (8), 1112-18.
- <sup>181</sup> Piskov, V. B.; Kasperovich, V. P.; Yakovleva, L. M. SU Patent 480,708, 1975.
- <sup>182</sup> Kyrides, L. P. U.S. Patent 2,392,326, 1946.
- <sup>183</sup> Scholz, C. R. *Ind. Eng. Chem.*, 1945, 37, 120-122.
- <sup>184</sup> Magosch, K. H. DE Patent 2,154,948, 1973.
- <sup>185</sup> Jentzsch, W.; Seefelder, M. *Chem. Abstr.*, 62, 16239b, 1965, 98 (4), 1342-9.
- <sup>186</sup> Sawa, N. *Nippon Kagaku Zasshi, Chem. Abstr.*, 70, 19983q, 1968, 89(8), 780-4.
- <sup>187</sup> Frank, A.; Dockner, T. DE Patent 2,512,513, 1976.
- <sup>188</sup> Bruson, H. A. *Organic Reactions*, 1949, Vol. 5, Ed., New York: John Wiley & Sons, Inc., pp 79-87.
- <sup>189</sup> Graefje, H.; Hoffmann, H.; Hupfer, L.; Lebkuechet, R.; Merkel, K. DE Patent 2,446,489, 1976.
- <sup>190</sup> Malfer, D. J. EP Patent 417,990, 1991.
- <sup>191</sup> Wilson, M. W. U.S. Patent 2,570,895, 1951.
- <sup>192</sup> Gunderson, L. O. U.S. Patent 2,583,771, 1952.
- <sup>193</sup> Goldstein, H. B.; Charles, S. T. U.S. Patent 2,609,381, 1952.

## Urea and Urea Derivatives

- <sup>194</sup> Arnold, H. W. U.S. Patent 2,145,242, 1939.
- <sup>195</sup> Schweitzer, C. E. *J. Org. Chem.*, 1950, 15, 471-4.
- <sup>196</sup> Suen, T. J.; Daniel, Jr., J. H. U.S. Patent 2,554,475, 1951.
- <sup>197</sup> Harnden, R. M.; Calvin, D. W. U.S. Patent 4,387,249, 1983.
- <sup>198</sup> Graefje, H.; Stechl, H. H. DE Patent 2,230,735, 1974.
- <sup>199</sup> Hoover, F. W.; Vaala, G. T. U.S. Patent 2,373,136, 1945.
- <sup>200</sup> Daniel, J. H. *Chem. Abstr.* 1950, 467505.
- <sup>201</sup> Hurwitz, M. D.; Auten, R. W. U.S. Patent 2,613,212, 1952.

## Olefins

- <sup>202</sup> Hesse, M.; Hoelderich, W.; Schwarzmann, M. EP Patent 296,495, 1988.
- <sup>203</sup> Tomalia, D. A. *Polym. J.* Tokyo, 1985, 17, 117.
- <sup>204</sup> Smith, P. B. *Appl. Polym. Anal. Charact.*, Ed.; Munich: Hanser, 1987, 357.

## Sulfur Compounds

- <sup>205</sup> Cramm, D.; Barnikel, C. D. DE Patent 2,703,312, 1978.
- <sup>206</sup> Hester, W. F. U.S. Patent 2,326,443, 1943.
- <sup>207</sup> Fox, A. L. U.S. Patent 2,361,188, 1944.
- <sup>208</sup> Gunderson, L. O.; Denman, W. L. *Ind. Eng. Chem.*, 1948, 40, 1363-70.
- <sup>209</sup> Hurwitz, M. D.; Auten, R. W. U.S. 2,613,212, 1952.

## Cyclization

- <sup>210</sup> Andersons, S. Jurels, and M. V. *Chem. Abstr.*, 67, 100107s, 1967, (2), 346-59.
- <sup>211</sup> Herrick, E. C. U.S. Patent 2,937,176, 1960.
- <sup>212</sup> Andersons, A.; Jurels, S.; Shimanskaya, M. V. *Chem. Abstr.*, 75, 98037p, 1971, (1), 47-58.
- <sup>213</sup> Hillers, S.; Shimanskaya, M. V.; Gofman, B. E.; Lazdins, A. SU Patent 2,715,25, 1970.
- <sup>214</sup> S. A. Jurels, U. A. Pinka, and M. Shimanskaya, *Chem. Abstr.*, 82, 1551647, 1974, (6), 691-700.
- <sup>215</sup> Shimanskaya, M. V.; Hofmanis, B.; Lazdins, A.; Hillers, *Chem. Abstr.*, 76, 99615h, 1971, 185-94.

## Additional Literature

### Huntsman Ethyleneamine Literature

|          |                                                         |
|----------|---------------------------------------------------------|
| 5000-701 | Ethyleneamine — A Global Profile of Products & Services |
| 5001-701 | The Safe Handling of Ethyleneamines                     |
| 5002-701 | Selection of Gloves & Respirators                       |
| 5003-701 | Triethylenetetramine (TETA) Technical Bulletin          |
| 5004-701 | Ethylenediamine (EDA) Technical Bulletin                |
| 5005-701 | Aminoethylpiperazine (AEP) Technical Bulletin           |
| 5006-701 | Tetraethylenepentamine (TEPA) Technical Bulletin        |
| 5007-701 | Diethylenetriamine (DETA) Technical Bulletin            |
| 5008-701 | Aminoethylethanolamine (AEEA) Technical Bulletin        |
| 5009-701 | Ethyleneamine E-100 (E-100) Technical Bulletin          |





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