



**BASF**



# Ethyleneamines Best Practices Manual

Ethyleneamines  
Product Stewardship  
Discussion Group  
EPSDG 2000



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# Introduction to Ethyleneamines Product Stewardship Discussion Group

The Ethyleneamines Product Stewardship Discussion Group (EPSDG) was formed in 1995 and is comprised of the following producers of Ethyleneamines: Akzo Nobel Functional Chemicals, LLC, BASF Corporation, Delamine, B.V., The Dow Chemical Company, Union Carbide Corporation and Tosoh Corporation. The purpose of the EPSDG is to provide a forum for producers of ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), aminoethylethanolamine (AEEA), aminoethylpiperazine (AEP), piperazine (PIP), hydroxyethylpiperazine (HEP), pentaethylenhexamine (PEHA) and heavy polyamines (HPA) to discuss and review product stewardship matters related to these products, in the hope of assisting in the safe use and handling of these chemicals by all who come into contact with them.

This product stewardship manual on the safe handling and storage of Ethyleneamines was prepared by the EPSDG as a service to the industries that utilize Ethyleneamines — industries to which EPSDG members have long supplied quality products and services, including Ethyleneamines.

Ethyleneamines are reactive with a variety of other chemicals, making them unique intermediates for a broad range of applications. As a group, they are slightly to moderately viscous, water-soluble liquids with a mild to strong ammoniacal odor. In their pure, as-delivered state, these materials are chemically stable and are not corrosive to the proper containers.

Ethyleneamines require substantial care in handling. Skin or eye contact can result in chemical burns. Breathing vapor can result in irritation to the nose or throat. Some individuals may experience sensitivity reactions to Ethyleneamines, resulting in skin rashes or asthma-like symptoms. Once sensitized, these individuals may experience these reactions on exposure to even very low concentrations.

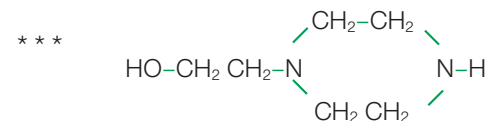
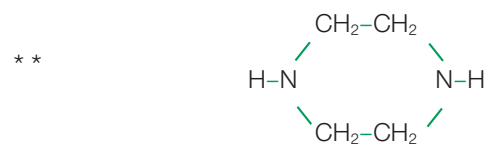
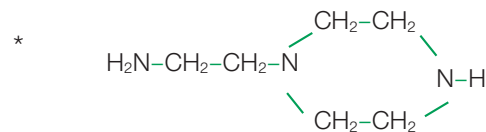
Handling Ethyleneamine products is complicated by their tendency to react with many other chemicals. They will react with carbon dioxide in the air to form solid carbamates that may clog vent units. Moreover, Ethyleneamines can be very corrosive to certain metals

and elastomers. Some Ethyleneamines form hydrates with water that are viscous liquids or solids, and some Ethyleneamines can freeze at ambient temperatures.

This manual is intended to provide you with information you may wish to consider in establishing safe storage and handling systems while maintaining product quality. You should refer to the product Material Safety Data Sheets for more specific health and safety information concerning the Ethyleneamine products of interest. Material Safety Data Sheets are updated as new information becomes available.

## Throughout this document, the following abbreviations will be used:

<b>EDA</b>	
Ethylenediamine	$H_2NCH_2CH_2NH_2$
<b>DETA</b>	
Diethylenetriamine	$H_2NCH_2CH_2NHCH_2CH_2NH_2$
<b>TETA</b>	
Triethylenetetramine	$H_2N(CH_2CH_2NH)_2CH_2CH_2NH_2$
<b>TEPA</b>	
Tetraethylenepentamine	$H_2N(CH_2CH_2NH)_3CH_2CH_2NH_2$
<b>AEEA</b>	
Aminoethylethanolamine	$HOCH_2CH_2NHCH_2CH_2NH_2$
<b>AEP*</b>	
Aminoethylpiperazine	$H_2NCH_2CH_2N(CH_2CH_2)_2NH$
<b>PIP**</b>	
Piperazine	$HN(CH_2CH_2)_2NH$
<b>HEP***</b>	
Hydroxyethylpiperazine	$HOCH_2CH_2N(CH_2CH_2)_2NH$
<b>PEHA</b>	
Pentaethylenhexamine	$H_2N(CH_2CH_2NH)_4CH_2CH_2NH_2$
<b>HPA</b>	
Heavy Polyamine	$H_2N(CH_2CH_2NH)_nCH_2CH_2NH_2$ (n = primarily 3 to 7)



The TETA, TEPA, PEHA, and HPA molecular formulas shown above are for the linear component. Commercial product is sold as a mixture of linear, branched and cyclic molecules. PIP may be an aqueous solution or an anhydrous solid. HEP is an aqueous mixture of PIP, HEP and dihydroxypiperazine. HPA is a mixture of higher molecular weight Ethyleneamines.

## Responsible Care®<sup>1</sup>

EPSDG members have a long-standing policy to ensure that their operations do not have an adverse impact on the community or the environment. To uphold this policy, EPSDG member companies are committed to Responsible Care®, a continuing effort by the chemical industry to improve the responsible management of chemicals.

Under Responsible Care, EPSDG members comply with the ten Guiding Principles and six Codes of Practice that cover all aspects of research, development, manufacture, distribution, transportation, use, and disposal of products. The Principles also extend to prompt reporting, customer counseling, community awareness, support of external research, participation with government and others, and promotion of Responsible Care worldwide.

EPSDG recognizes that no single entity can protect the quality of all of our air and water. However, by working together on a global basis, the public, industry, and government can make the future brighter and safer.

## Product Stewardship

The EPSDG has a fundamental concern for all who make, distribute, and use Ethyleneamines products, and for the environment in which we live. This concern is the basis for our Product Stewardship philosophy by which we assess the health and environmental information on our products and take appropriate steps to protect employee and public health and our environment. Our members' Product Stewardship programs rest with each and every individual involved with Ethyleneamines, from the initial concept and research to the manufacture, sale, distribution, use, and recycling or disposal of each product.

<sup>1</sup> Service Mark of the American Chemistry Council

## Customer Notice

EPSDG strongly encourages the users of Ethyleneamines to review both their manufacturing processes and their applications of Ethyleneamine products from the standpoint of human health and environmental quality. To help ensure that Ethyleneamines are not used in ways for which they are not intended or tested, EPSDG member company personnel are prepared to assist customers in dealing with ecological and product safety considerations.

EPSDG and its member companies believe the information and suggestions contained in this manual to be accurate and reliable as of January 1998. However, since any assistance furnished by EPSDG members with reference to the proper use and disposal of its products is provided without charge, and since use conditions and disposal are not within its control, EPSDG members assume no obligation or liability for such assistance and do not guarantee results from use of such products or other information herein; no warranty, express or implied, is given nor is freedom from any patent owned by EPSDG members or others to be inferred.

Information herein concerning laws and regulations is based on U.S. Federal laws and regulations except when specific reference is made to those of other jurisdictions. Since use conditions and governmental regulations may differ from one location to another and may change with time, it is the customer's responsibility to determine whether Ethyleneamines are appropriate for the customer's use, and to assure that the customer's workplace and disposal practices are in compliance with laws, regulations, ordinances, and other governmental enactment applicable in the jurisdiction(s) having authority over the customer's operations.

## Legal Notice

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The Manual is intended to provide helpful ideas for those involved in the distribution and sale of Ethyleneamines. The Manual is necessarily general in

nature and leaves dealing with product and site-specific circumstances to entities handling the product. The Manual is not designed or intended to define or create legal rights or obligations.

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## Physical Properties

Physical property information, including handling characteristics, for Ethyleneamines is available from your Ethyleneamine supplier.

## Reactivity

Because Ethyleneamines react with many other chemicals, sometimes rapidly and usually exothermically, it makes sense to establish dedicated processing equipment for all Ethyleneamine operations. Storage tanks could be segregated from other materials in separate dike enclosures. Consider avoiding opportunities for cross-contamination, such as multiple product hose switching stations. Contact with acids, organic halides, and oxidizing agents can result in particularly vigorous reactions. The Material Safety Data Sheet for each product includes information on specific reactivity hazards.

Ethyleneamines do not polymerize with themselves under normal processing conditions. However, exposure to air can result in the formation of solid amine carbamic acid salts and/or amine carbonates from the reaction with atmospheric carbon dioxide. These solids are commonly referred to as Ethyleneamine carbamates and are especially of concern when the solids plug vent lines or foul pressure relief devices. Also, product quality and performance in the customer's application may be affected. Ethyleneamine carbamates can also appear as a bluish-white "smoke" from venting points. Using nitrogen blankets on storage tanks may prevent the formation of Ethyleneamine carbonates.

Ethyleneamines are soluble in water. However, in the range of 20 to 80 weight-percent water the added water will result in increased heat of solution, which can be significant depending on the Ethyleneamine. Some Ethyleneamines will also form hydrates, which can cause plugging issues in various processes. When EDA hydrate is formed it may end up with a temperature above the flashpoint due to the exothermic reaction.

The reaction of water with the Ethyleneamine is exothermic, which will initially reduce the mixture viscosity; however, after cooling, the mixture thickens beyond the viscosity of the anhydrous Ethyleneamine. The solution continues to thicken on standing as the water and amine completely react to the amine hydrate, and, after standing for several hours, an extremely thick gel may result. With 10 to 35 weight-percent water, TETA and other Ethyleneamines can form solid hydrates that have melting points around 50°C.

Hydrates can be a significant nuisance in handling. In most cases, the increased viscosity of the hydrate makes pumping difficult or impossible. Hydrates can plug processing equipment, vent lines, and safety devices. If water and TETA are handled together, the hazards presented by the frozen hydrate must be evaluated and appropriate equip-

ment protection must be included in the process design. Hydrate problems are usually avoided by insulating and heat tracing equipment to maintain a temperature of at least 50°C. Water cleanup of Ethyleneamine equipment can result in hydrate problems, even in areas where routine anhydrous processing is hydrate-free. Warm water cleanup can reduce the extent of the problem.

Ethyleneamines in the liquid phase will slowly react with atmospheric oxygen at ambient temperatures. This reaction may introduce color to the product, and the rate is accelerated at the elevated temperatures typically found in amine storage to avoid freezing and reduce product viscosity. A nitrogen blanket on tanks generally prevents degradation of the product during storage.

As commercially pure materials, Ethyleneamines exhibit good temperature stability. Above 180°C, some product breakdown may be observed in the form of ammonia odors and the formation of lower and higher molecular weight species. This degradation increases in rate as the temperature is raised. Laboratory measurements in an accelerating rate calorimeter show the degradation becomes a self-sustaining exothermic reaction at temperatures as low as 275°C. Allowing the product to exceed the self-sustaining reaction temperature can cause rapidly accelerating thermal decomposition. Processes should be designed to operate well below this threshold, even during upset or abnormal conditions.

Contaminants can lower the onset of rapid exothermic thermal decomposition. For example, relatively low concentration (five weight-percent or less) of mineral acids can substantially reduce the decomposition temperature of Ethyleneamines. Caustic, alkali metals, or mineral acids will substantially reduce these temperatures for Ethyleneamines containing hydroxyl groups (AEEA and HEP). Since other contaminants may have similar effects on Ethyleneamines, testing for thermal stability is suggested whenever Ethyleneamines are mixed with other materials.

Like many other combustible liquids, self-heating of Ethyleneamines may occur by slow oxidation in absorbent or high surface area media, e.g., dumped filter cake, equipment thermal insulation, spill absorbents, and metal wire mesh (such as that used in vapor mist eliminators). In some cases, this may lead to spontaneous combustion, and either smoldering or a flame may be observed. To avoid this situation, any of these media contaminated with Ethyleneamine should be washed with water to remove the Ethyleneamine or be thoroughly wetted with water and then disposed of in closed, water-filled containers, consistent with user company requirements and government regulations.

Ethyleneamines undergo those reactions that are typical of compounds containing either primary or secondary amine functionality. For example, Ethyleneamines and adducts of Ethyleneamines may react violently with organic and inorganic acids, oxidizing agents (such as peroxides), and halogenated hydrocarbons (such as carbon tetrachloride, methylene chloride, and ethylene dichloride). Thus, contact with these substances must be avoided.

**Note: A serious reaction hazard exists between the two products commonly used in epoxy formulating: aliphatic amines and halogenated solvents. The reactivity increases with increasing halogen content. For example, TETA and TEPA Ethyleneamines react violently, after a short latent period, with methylene chloride.**

## Flammability/Combustibility

Although all Ethyleneamines (and the products made from them) are organic materials that will burn under the right conditions of heat and oxygen supply, they differ widely in their flammability characteristics, in their explosion potential, and in the methods and materials needed to extinguish fires. The definitions of flammable and combustible and the associated regulatory requirements vary by country. For example, UN/DOT classifies a material as flammable for transportation purposes if it has a flashpoint below 141°F while other regulatory agencies define a flammable material as having a flashpoint below 100°F. Consult your supplier for data.

In addition, certain components used with Ethyleneamines may contain solvents, which can pose additional hazards of fire and explosion. Also, in a fire situation, drums containing Ethyleneamines could rupture. The ignition of the contents of a ruptured drum could significantly increase the magnitude of the fire.

## Decomposition Products

Caution is needed in predicting the byproducts of thermal decomposition. The products generated, and their concentrations, depend on whether pyrolysis or combustion, or a combination of the two, occurs. Also important is the temperature of the decomposing materials and whether the surrounding atmosphere is oxygen-rich or oxygen-poor. The byproducts expected in the incomplete pyrolysis or combustion of Ethyleneamines include nitrogen oxides and carbon monoxide. Thus, the

thermal decomposition products of Ethyleneamines should be treated as potentially hazardous substances, and appropriate precautions should be taken, including the wearing of full protective clothing and respiratory protective equipment, when potential for personal exposure is present

## Static Electricity

Many operations in formulating plants generate static electricity. Static charges can cause fires and explosions in dusty areas and in areas where flammable solvents are used. The control of static electricity buildup is generally inexpensive and easy to accomplish with appropriate grounding.

To minimize the possibility of building up a static charge, tanks and lines should be well bonded and grounded. In addition, a nitrogen pad in storage tanks is generally used during storage of Ethyleneamines. This reduces hazards of combustibility as well as prevents oxidation of the product. Submerged filling is required for flammable liquids. To accomplish this, the inlet line should discharge at or near the bottom of the drum or tank and should make electrical contact with the drum or tank to prevent uncontrolled static buildup.

## Health Effects

Each EPSDG member publishes and regularly updates a Material Safety Data Sheet (MSDS) for each Ethyleneamine it produces. These documents are designed to help customers and others who handle these materials to meet both their own safe handling and disposal needs and those regulations promulgated by various governmental agencies, including the U.S. Occupational Safety and Health Administration (OSHA).

Current copies of these sheets should be carefully read before any of the various Ethyleneamines are handled, used, stored, shipped, or disposed of. MSDSs should also be consulted for information and instructions on containing and cleaning up spills and leaks, wearing personal protective equipment, and administering first aid.

**Note: Ethyleneamines vary considerably in the degree of health hazard they present. It is essential that the MSDS for each product that is handled be reviewed so that the user is familiar with that product's particular characteristics and can take proper protective measures.**

## General Precautions

Although certain Ethyleneamines are more hazardous than others, it is important for plant systems to be developed to protect personnel against the hazards to health and safety associated with any of the Ethyleneamines. In short, the goal should be to avoid direct contact with any of these materials. This may be accomplished by handling Ethyleneamines in an enclosed system. If this is not possible or feasible, the following precautions and recommendations, as pointed out in Ethyleneamine MSDSs, may help minimize the hazards and prevent potential health and safety problems:

- Avoid all contact with skin and eyes. (Remember, Ethyleneamines may cause severe burns, sensitization, and corneal injury, even blindness.)
- Do not take internally. (Do not smoke, eat, drink, or store food-stuffs where Ethyleneamines are handled, stored, or processed.)
- Avoid breathing vapors, mists or aerosols.
- Clothing and shoes should not contact Ethyleneamines. If clothing becomes contaminated, do not wear or reuse until it has been thoroughly cleaned. Destroy contaminated leather goods, such as shoes, belts, watchbands, etc.
- To avoid contaminating street clothes they should not be cleaned with work clothes.
- Practice strict personal cleanliness and careful housekeeping at all times.
- Wash hands, forearms, face, and neck thoroughly before taking a break, eating, drinking, or using toilet facilities. Note: There should be no smoking, eating or drinking in Ethyleneamines work or storage areas.
- Separate all Ethyleneamines work areas from other work areas to limit the exposure of employees who are unfamiliar with proper handling practices for Ethyleneamines and who may be exposed to contaminated tools and equipment.
- Educate all personnel who enter Ethyleneamines work areas on the potential consequences of exposure. Make certain personnel are familiar with recommended handling procedures and precautions and are trained in the administration of first aid.
- Make certain all personnel who enter Ethyleneamines work areas — including janitorial workers — are familiar with recommended disposal procedures and techniques.
- Clearly label containers that contain, or have contained, Ethyleneamines or contaminated waste, including rags, contaminated clothing, utensils, etc.
- Use volatile Ethyleneamines only in properly and adequately ventilated areas.

## Industrial Hygiene

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

Skin contact with one Ethyleneamine may result in cross-sensitization following exposure to other similarly structured amines.

Always be sure there is adequate ventilation in Ethyleneamine work areas. In the event of a gross exposure to Ethyleneamine vapor, remove the individual(s) to fresh air immediately 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 EDA and DETA. These figures represent the legal exposure limits for a workday. In Europe, the European Union has established an occupational exposure limit (OEL) – 8 hour time weighted average and OEL short term value for PIP. Similarly, the American Conference of Governmental Industrial Hygienists (ACGIH) has established threshold limit values/time-weighted averages (TLV- TWA) for EDA and DETA as guidelines for industrial use. The American Industrial Hygienist Association (AIHA) has established a workplace environmental exposure level (WEEL) for TETA. The time weighted averages noted in **Table 1** represent the average airborne concentrations to which most workers can be exposed, day after day, without serious adverse effects. The exposure limits set by the OSHA PEL and ACGIH TLV may not be adequate to protect hypersusceptible individuals from respiratory or dermal sensitization.

No such guidelines have been set for the higher molecular weight amines. However, these products are often handled at elevated temperatures to improve flow characteristics which may cause vapor contact and exposure similar to that of lighter Ethyleneamines. Furthermore, elevated temperatures may evolve trace concentrations of lighter Ethyleneamines contained in the heavier products.

**Table 1 – Exposure Limits**

	<b>OSHA PEL/TWA</b>	<b>ACGIH TLV-TWA</b>	<b>AIHA WEEL</b>	<b>EU OEL TWA</b>	<b>EU OEL Short Term</b>
EDA	10 ppm	10 ppm	—	—	—
DETA	1 ppm	1 ppm	—	—	—
TETA	—	—	1 ppm	—	—
PIP	—	—	—	0.1 mg/m <sup>3</sup>	0.3 mg/m <sup>3</sup>

Note: This data is current as of November 2000.

In 1997, the EPSDG sponsored an acute inhalation toxicity study of *aerosolized* DETA. Previous acute toxicity studies in rats resulted in lethality when the rats were exposed to DETA as an aerosol. These results were in contrast to toxicity studies of animals exposed to DETA as a vapor where no lethality had been observed. The purpose of this study was to determine a no-observed-effect-level (NOEL) for lethality for *aerosolized* DETA.

The results of this study indicated a NOEL for lethality to be 0.07 mg/L aerosolized total DETA species expressed as DETA. The treatment related effects are consistent with those observed in the earlier studies.

Industrial Hygiene monitoring methods are available. Contact your Ethyleneamines supplier.

## Respiratory Protection for Ethyleneamines

If an operation creates the potential for employee overexposure, accepted engineering or administrative controls, such as enclosure or confinement of the operation, general or local ventilation, or work practices that minimize exposures, should be the first choices for control. When effective engineering or administrative controls, are not feasible, or when they are being implemented or evaluated, appropriate respiratory protection can be used to control employee exposures.

This section is meant to provide reference resources on respiratory protection. Customers are encouraged to become familiar with these two references:

- Occupational Health and Safety Administration's (OSHA) Respiratory Protection Standard, 29 CFR 1910.134
- American National Standard Institute's (ANSI) Standard for Respiratory Protection, ANSI Z88.2-1992.



## Considerations in Determining the Need for Respiratory Protection

One way to determine the need for respiratory protection for employees working with Ethyleneamines is by conducting an assessment of the workplace, such as completing the following steps:

### Step 1. Conduct a Workplace Survey

The workplace may be surveyed to identify the job categories (facility areas, job tasks, and employees) that use or have the potential for exposure to Ethyleneamines.

### Step 2. Conduct Industrial Hygiene

#### Monitoring/Exposure Assessment

Industrial hygiene monitoring, or other acceptable exposure assessment methods, may be used to estimate the full-shift, time-weighted average (TWA) exposures and their ranges under normal operating conditions for Ethyleneamines. Any peak exposures should also be estimated.

Industrial Hygiene monitoring methods are available. Contact your supplier.

Should your facility not have the resources and/or expertise to conduct its own industrial hygiene monitoring, the American Industrial Hygiene Association, 2700 Prosperity Avenue, Suite 250, Fairfax, VA 22031-4307, (703) 849-8888 can be contacted for information on available industrial hygiene consultants.

### Step 3. Compare Exposure Assessment to Applicable Occupational Exposure Limits (OEL)

Once the potential exposures to Ethyleneamines have been estimated, they may be compared to the applicable occupational exposure limit (OEL) recommended for the particular Ethyleneamine in use. Reference sources for these OELs include:

- The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PEL) (29 CFR 1910.1000 and possibly others). Within the United States, the occupational exposure limit chosen must be at least as stringent as what is required by OSHA.
- American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV). (Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices for the current year.)
- Your Ethyleneamine Supplier (contained on the manufacturer's most recent material safety data sheet for each Ethyleneamine)
- European Union (EU) Occupational Exposure Limits (OEL)
- Individual countries outside of the United States and the European Union may also have established specific occupational exposure limits for certain Ethyleneamines.

### Step 4) Reduce Over-exposures Where Feasible

When the estimated exposures to Ethyleneamines have been determined to exceed the applicable occupational exposure limit (OEL) recommended for the particular Ethyleneamines in use, then acceptable control measures must be utilized. Examples of acceptable control measures include:

- Enclosure or confinement of the operation
- Increased general ventilation
- Local exhaust ventilation
- Work practices which minimize exposures.

As a point of reference, voluntary standard ANSI Z88.2-1992 4.2 suggests: "when effective engineering or administrative controls are not feasible, or while they are being implemented or evaluated, appropriate respiratory protection shall be used pursuant to" the requirements set out in ANSI Z88.2 section four.

## Ventilation

Good mechanical ventilation is the standard method for meeting the Ethyleneamine exposure limits noted in the Industrial Hygiene section. It is also used to control employee exposure to the airborne vapors of other materials and the Ethyleneamines not specifically addressed in the Industrial Hygiene section. Take care that the ventilation system design does not place workers between the source of vapors and the exhaust duct. A constant supply of fresh, uncontaminated air should always be available to all work areas. Ventilation must exhaust to an area that does not expose people. A vent scrubber may also be needed to further limit personnel exposure. An example of a scrubber design is found in Appendix B.

Ethyleneamine vapors may appear as bluish-white "smoke" or fumes from the venting point. The smoky fume is a finely divided solid, resulting from the reaction of the amine with atmospheric carbon dioxide to form an amine carbamate. EDA and PIP are particularly prone to exhibit this phenomenon in normal storage conditions, as are DETA and TETA to a lesser degree. Other higher molecular weight Ethyleneamines can act similarly if heated to high enough temperatures. This "smoke" may accentuate industrial hygiene concerns because the solids tend to settle rather than disperse away from normal working levels. For this reason Ethyleneamine vents should be routed to safe locations or water scrubbers.

# Personal Protection

## Protective Equipment

The principal goal of any system or plant operation design should be the elimination of the need for personal protective equipment. However, personal protective equipment may be necessary in certain operations or in areas where vapor or liquid exposure is possible. The selection and use requirements of this equipment require careful management consideration. For example, an overall appraisal of plant operations, exposure potential, the nature and duration of possible exposure, the level of training provided to workers on the use of personal protective equipment, etc., may be made. A qualified industrial hygienist in conjunction with engineering, maintenance, and the supervisory management staff could conduct this appraisal. Upon completion of the appraisal, a comprehensive program of personal protection could be prepared. As part of this program, specific approved equipment (including manufacturer, make, and model) could be identified. The plan could also cover equipment maintenance and repair, cleaning, and storage, as well as training on use, effectiveness, etc.

Among the specific issues or questions that can be considered in the management of the personal protection program and in the selection of personal equipment are:

- Are there practical ways to reduce or minimize exposure by changes in equipment and/or procedures?
- Is any anticipated exposure likely to be at levels above occupational exposure limits?
- What is the probable length or duration of the anticipated exposure — will it be short (after which decontamination can be immediately accomplished) or will it be lengthy?
- Is the exposure likely to occur infrequently (as when product is sometimes spilled during unloading or transfer operations), or is it expected to occur more frequently?
- Is “single-use” equipment desirable and/or available?
- What is the most effective and efficient respiratory protective equipment for a given exposure period and concentration?

**Note: Each material safety data sheet (MSDS) suggests that air-purifying respirators, supplied air devices, or self-contained breathing apparatus be used, depending on the nature and duration of the exposure.**

Areas in which Ethyleneamines are stored or used (including processing areas, work stations, laboratories, etc.) can be equipped with appropriate safety equipment, including the following:

- Eyewash fountain
- Safety shower
- Ventilation system capable of safely carrying away noxious fumes, dusts, and odors, and with the ability to provide an adequate supply of fresh air
- Fire extinguishing and personal protection equipment, including water fog, foam, alcohol foam, CO<sub>2</sub>, or dry chemical fire extinguishers, and self-contained positive-pressure breathing apparatus
- Disposable bench paper and utensils to minimize contact and reduce the possibility of contamination.

**Note: Take care that contaminated disposable items and materials do not become a fire or health hazard to other employees, including janitors and persons in charge of disposal.**

## Protective Clothing

Even well-engineered systems may require the use of personal protective clothing, especially in the event of spills, leaks, or other events and activities where there is a possibility of exposure.

When personnel will be unloading tanks or drums, sampling product, opening or cleaning Ethyleneamine-containing equipment, or doing other activities where there is potential for contact with Ethyleneamines, the proper protective clothing and equipment should include, at a minimum:

- Chemical-worker’s goggles (mono-goggles)
- Hard hat
- Impervious gloves (Appendix A) and boots.

Depending on the potential and severity of exposure, the following protective clothing and equipment may also be appropriate:

- Chemical-impervious suit (coat and trousers — trouser legs should be worn outside of the boots)
- Approved air purifying or positive-pressure supplied-air respirator depending on the potential airborne concentration
- Face shield when necessary.

When working with relatively small quantities of Ethyleneamines, as in a laboratory, suggested employee clothing could include, at a minimum, the following:

- Chemical worker’s goggles (mono-goggles)
- Impervious gloves and apron
- Closed-toe shoes.

When working with heated Ethyleneamines (i.e., above 60°C (140°F) in systems where there is potential for exposure, proper protective clothing and equipment should be worn to protect against thermal burns and fumes. These should include, at a minimum:

- Chemical-worker's goggles (mono-goggles)
- Hard hat
- Chemical-impervious slicker suit (coat and trousers – trouser legs should be worn outside of the boots)
- Impervious gloves that provide thermal burn protection
- Impervious boots
- Self-contained, positive-pressure breathing apparatus when necessary
- Face shield when necessary.

Employees should be taught the proper method of putting on and taking off protective clothing and equipment. For example, contaminated protective clothing can be a source of skin contact. Thus, care should be taken to remove gloves and other protective clothing without exposing clean skin to contact with Ethyleneamines .

***Note: Clothing type, make, and materials of construction should be evaluated using an “exposure control management” approach that evaluates each potential exposure situation. For example, protective clothing for splash protection (that is disposed of or immediately cleaned after exposure) may not need to be as durable as protective clothing for continuous exposure conditions. It is also important to recognize the hazards associated with each kind of material. For example, leather goods can be hazardous when they have been contaminated. That is, leather can absorb Ethyleneamines and maintain a continuous low level of exposure over a prolonged period of time. The result can be a severe chemical burn. In fact, such burns have been severe enough to require skin grafts. Thus, leather clothing and other items should not be specified as protective clothing for handling Ethyleneamines and should be destroyed promptly if they become contaminated.***

In short, when choosing impervious protective clothing, the intrinsic barrier property of the material is only one factor to consider. Other factors that affect performance include:

- Thickness of material
- Fabrication techniques, with particular reference to the sealing of the seams

- Whether or not the material is lined, laminated, or treated
- Physical strength of the material, including resistance to abrasion, tearing, etc.
- Resistance to damage or loss of effectiveness due to exposure to heat, cold, water, and/or chemicals.

It is suggested that customers obtain information from manufacturers and/or suppliers of protective clothing and equipment about the performance of their products under various work-related conditions.

It is also suggested that workers store a set of “street clothes” and a set of “work clothes” in separate locations on the job site. The street clothes should be stored away from the work area or other areas where the clothing might be contaminated.

## Training

Training for personnel and plant safety has value only to the extent that it is fully and properly implemented and practiced by all personnel involved. Thus, a comprehensive and ongoing training program in the handling, use, storage, and disposal of Ethyleneamines is of significant value to all personnel. Additional training – and periodic retraining – in emergency procedures should also be considered.

Finally, both employees and supervisors may want to be familiar with:

- Health hazards associated with Ethyleneamines
- First aid procedures
- Spill and leak containment and cleanup
- Disposal methods and regulations
- Fire and explosion hazards and preventive measures
- Personal protection and plant safety.

In addition, all workers must be trained – and periodically retrained – in the nature, use, and effectiveness of the various items of personal protective equipment. The use of respirators requires medical approval of the worker and a fit test to ensure effective protection. Training should also be documented and reviewed with the worker on a periodic basis. Finally, workers should also be instructed on how to wear, use, clean, and maintain all items of protective equipment.

# Bulk Transportation

## Product Unloading

The transportation equipment used to ship Ethyleneamines to the customer is not unique to these products but is identical to that used for many similar chemicals.

Upon receipt of any equipment, the customer should carefully check all paperwork and the seals and tags on the dome and outlet lines to verify the container contents prior to unloading. Ethyleneamines are very reactive with a wide variety of other chemicals and unloading an Ethyleneamine to the wrong tank or unloading another chemical to a tank containing an Ethyleneamine could result in a violent reaction in an uncontrollable environment. The vessel should also be secured to ensure that it is not moved while unloading is in progress.

The storage tank transfer pump may also be utilized to unload the container if the pump is located close to the unloading spot. (See Figure 4.) However, if the unloading spot is remote from the storage tank pump, a separate pump of similar specification may be employed. Often, separate pumps are used because the unloading pump typically has a high flow-rate capacity, while the pump used to transfer product to the customer's process is of a much lower flow-rate. Hose has a much higher pressure drop than the same nominal pipe size, and this fact should be considered when evaluating the net positive suction head (NPSH) requirements of the pump. Occasionally, a customer will utilize a single pump to unload several different Ethyleneamines. If this is done, then provision for cleanup between products (including proper disposal of wash water and personnel protection from exposure to amine liquid and vapor) is essential. Sometimes a customer may determine that minor contamination of one Ethyleneamine with another is acceptable and the pump service may be changed without cleanup. However, unloading equipment should not be shared outside the Ethyleneamine family of products because Ethyleneamines are so reactive with other chemicals.

An eyewash and safety shower should be provided at any spot where Ethyleneamines are unloaded.

Tank trucks may be requested to arrive at the customer's plant with an onboard truck pump for unloading. If an onboard truck pump will be utilized, the customer should inspect the pump for cleanliness prior to initiating unloading. However, a better scenario is for the customers to provide their own pumping station to reduce

the potential for leaks. (See "Transfer of Ethyleneamines – Pumps" section). If a truck-supplied pump is utilized, the pump should be of 300-Series stainless steel construction with no copper or copper alloys in contact with the product. The pump is driven by a hydraulic or mechanical connection to the truck tractor engine. TFE (tetrafluoroethylene)-type packing for these types of pumps should be requested where appropriate as certain other elastomers are not compatible (See "Materials of Construction – Elastomers" section pg. 18).

A low-pressure nitrogen pad is usually applied to the container during the unloading procedure. Alternatively, the dome may be cracked open, but this may not be desirable since there is the chance of exposure to amine vapors (especially serious for products that "smoke" or fume – See "Ventilation" and "Fuming Vents" sections), and the product quality may degrade because of contact with atmospheric carbon dioxide, oxygen, and water pickup.

Products that freeze at ambient temperature may arrive frozen, especially when shipped in tank cars. All products prone to freezing will be shipped in equipment that has heating coils. The product may be thawed by supplying low-pressure steam (15 psi) or hot water to the coils. A tank car may take 24 hours or more to thaw completely, and progress may be monitored by checking the product temperature. When it reaches 15 to 20°C above the freezing point, then the car is normally fully thawed, including the outlet connections. Do not rush thawing since Ethyleneamines are susceptible to scorching and discoloration. The lack of circulation and high coil skin temperature can cause quality problems if care is not taken. The container must be vented during heating to prevent pressure buildup. As EDA and PIP cars will fume while being thawed (See comments on "smoke" or fumes in "Ventilation" and "Fuming Vents" sections), vent scrubbers should be used for these cars. (See Appendix B for a diagram of a sample vent scrubber system.)

PIP and HEP tank cars will stratify when they freeze. Be sure the car is fully thawed and well-mixed before drawing a sample or transferring to the process or a tank.

Nitrogen pressure can be used on the container to unload product. If this approach is chosen, the customer must make sure the gas pressure does not exceed the safety valve set pressure stenciled on the container and must recognize that at the end of the unloading, gas will blow through to the tank and vent out the tank vent. This can cause odor complaints and increase the gas loading to the scrubbers employed for EDA and PIP service.

Tanks trucks and deck tanks should be unloaded on a paved pad with provisions for spill containment in case

a hose should rupture, and for control of drips and minor spills when disconnecting hoses. Tank cars require spill collection pads or pans between the rails and along the outside edges of the cars near the center of the unloading spot. Consult user company requirements and government regulatory agencies for mandatory spill containment measures that may apply. Drainage to a process sewer, provisions for flushing the unloading area with water, and proper disposal of rinse water will generally be necessary.

After unloading, consider blowing hoses clear with nitrogen and then breaking connections. Some product will remain in the hose and some minor spillage is likely. Proper personnel protective equipment is essential. Hoses not in service should be flushed with water or the ends capped to avoid continuing odor problems and the formation of amine carbamates in the hoses due to exposure to CO<sub>2</sub> in the air.

**Tank Cars** — Tank cars for transfer of Ethyleneamines are generally 20,000 to 28,000 U.S. gallon capacity and are constructed of either carbon steel or stainless steel, depending on the type of material transported. Many carbon steel cars contain a baked phenolic liner to protect product purity in transit. The tank cars are insulated and equipped with a safety valve typically set for 75 psi. Aluminum cars have been used for transit, but are not typical for normal shipping operations. The “Materials of Construction” section provides further details of these materials. Safety valves are typically set for 35 psi on the aluminum cars. Typically, these cars have a 4-in bottom outlet valve that is reduced to a 2-in. screwed outlet connection. Refer to “Materials of Construction” section. In general the dome area on top of the car contains:

- Purge gas connection: 1-in. screwed valve
- Safety valve
- Top manway: 18-in. diameter

Most cars also have one or two dip tubes from the top of the car to a small sump in the bottom of the car. These usually have 2-in. screwed valves in the dome area and may, if desired, be used to off-load product instead of using the bottom outlet. Steam coil connections are usually 1-in. screwed and are usually located near the bottom outlet.

**Tank Trucks** — Tank trucks for shipping Ethyleneamines vary in design, depending on the trailer manufacturer and specific government design specifications. Typical connections include:

- Bottom-unloading connection: 3-in. screwed outlet. The liquid outlet connection may be in the center, beneath the dome on the curb (right) side or at the rear of the trailer

- Top manway: 20-in. diameter
- Thermometer well: 1-in. thermometer well for measuring temperature of the material
- A few 3-in. screwed “cleanout” connections along the top that may be used for a nitrogen gas connection
- The truck will come with a pump, if specified by the customer.

**Portable Tanks/ISO Containers** — Portable tanks are available with different specifications to meet the shipping needs of the particular Ethyleneamine. Capacities range from 5000 to 5300 U.S. gallons. Each type of portable tank has fittings unique to its style and manufacturer. Usual connections include an approximately 50 to 100 mm (2- to 4-in.) bottom-screwed or flanged outlet, an approximately 500 mm (18-in.) diameter top manway, and an approximately 25 to 50 mm (1- to 2-in.) screwed or flanged nitrogen gas inlet. Most portable tanks use metric standard fittings. Adapters to ANSI flanges or US NPT threaded connections may be required.

## Dry-Break Hose Fittings

Breaking hose connections requires special considerations to reduce employee exposure to amines. Usually, the hose is blown with nitrogen prior to breaking; however, the hose often does not clear very well. Exposure can be minimized by utilizing dry-break connections that include a valve with the connection hub, so spill volume is small. (For names of manufacturers of dry-break connectors, contact your Ethyleneamines supplier.) Since hose connection ends are often subject to mechanical abuse, shut-off valves should still be installed where the hose connects to piping and these should be closed when a line is not in use. Do not rely on the dry-break valves alone for routine isolation. In any event, proper personnel protective equipment identical to that required for conventional hose handling is essential.

## General Unloading Procedures

The following procedure, while not exhaustive, provides good general guidelines that may be considered when developing an operating procedure for unloading Ethyleneamines from tank cars, tank trucks, and portable tanks. A specific operating procedure should be developed to deal with the particular unloading hardware and site conditions. All governmental transportation regulations must be followed for unloading.

1. Obtain necessary personal protective equipment, including (at least) mono-goggles, approved air-purifying or positive-pressure supplied-air respirator depending on the potential airborne concentration, and chemically-resistant gloves.

2. Confirm the correct vessel and vessel contents, checking the bill of lading and the tags on the dome and outlet connections. Ensure that seals on all vessel connections are still intact.

3. Ensure that the vehicle cannot be moved. Set the brakes and chock the wheels (both sides). Set a derail and provide a blue “men working” flag for tank cars.

4. Electrically ground the unloading piping to the vehicle frame. Do not use the jacket on insulated vessels, the rail trucks on tank cars, or truck bogey on tank trucks since these are not assured electrical grounds to the tank.

5. Some products will require heating to thaw or reduce viscosity. Open the caps on the heating coil connections carefully and make certain that no product has leaked into the coil. If unloading EDA, aqueous PIP or aqueous HEP, connect vent line to a scrubber, crack the dome lid or open the vent for other products, connect low pressure steam or hot water to the coils. EDA, aqueous PIP and aqueous HEP will fume while being thawed. (See comments on “smoke” or fumes in “Ventilation” section.) Apply heat slowly to avoid thermal shock to the coils, observe the first condensate or water that flushes through the coil, and stop heating if the flush appears to contain Ethyleneamines. Continue to heat slowly until the desired product temperature is reached. Aqueous product that has frozen may have separated into layers of varying composition. Circulation to obtain a homogeneous product may be necessary.

6. Make sure there is room in the receiving tank for the vessel’s contents. If appropriate, make sure the receiving tank vent is clear.

7. Connect the unloading hose to the vessel outlet connection. If unloading a multi-compartment truck, unload the front compartment first and proceed towards the rear. Make certain the vessel is vented so a vacuum is not pulled when unloading is started. Do not depend on the tank truck vacuum breaker. A nitrogen blanket can be provided on the vessel to retain product quality during unloading.

8. Start the pump and draw a sample. (See “Product Sampling,” pg. 16). If laboratory analysis is required prior to unloading, stop the pump until ready to proceed.

9. Unload the vessel contents to the tank.

10. When the vessel is empty, stop the pump. The hoses should be blown dry prior to disconnecting in order to reduce spillage. Close valves on the vessel and disconnect the hoses.

11. Prepare the empty vessel for return in accordance with the appropriate governmental transportation regulations.

12. Remove chocks, blue flag and derail as appropriate and release the vessel.

## Drum Handling

Although most Ethyleneamines customers receive product shipped in bulk via tank trucks and tank cars (rail cars), many customers receive these products in 55-gallon [200-liter] drums. Thus, at a minimum, drum-handling personnel should be fully trained on how to:

- Safely receive and store full drums
- Safely thaw drummed product
- Safely open drums and dispense the product
- Safely and legally dispose of empty drums.

## Drum Receiving

To help ensure that drum shipments are received and handled safely, written procedures can be prepared and distributed to all drum-handling personnel. These procedures may be designed to ensure such items as:

- The appropriate material safety data sheet (MSDS) has been carefully reviewed and is understood by those workers responsible for receiving, handling, or storing drums. (Note: MSDS should be stored or posted in the receiving area for quick reference.)
- All appropriate cleanup equipment and materials are readily available in the receiving area.

***(Note: Clay and cellulose-based absorbents will react with Ethyleneamines and should not be used. Instead, use sand or ground polyolefins, such as polypropylene.)***

- A careful check of the vehicle is conducted to locate any leaking or damaged drums before unloading.
- Appropriate personal protective clothing and equipment are specified and used, especially if any leaking or damaged drums are found.

***(Note: A hazardous concentration of Ethyleneamines can be created in the interior of a closed truck compartment if a leak occurs.)***

- Appropriate unloading equipment and procedures are used to ensure that the drums are unloaded and transferred to storage without damage.

## Drum Storage

Drum storage policies and procedures can be prepared and distributed to appropriate personnel. Such procedures may be designed to ensure that:

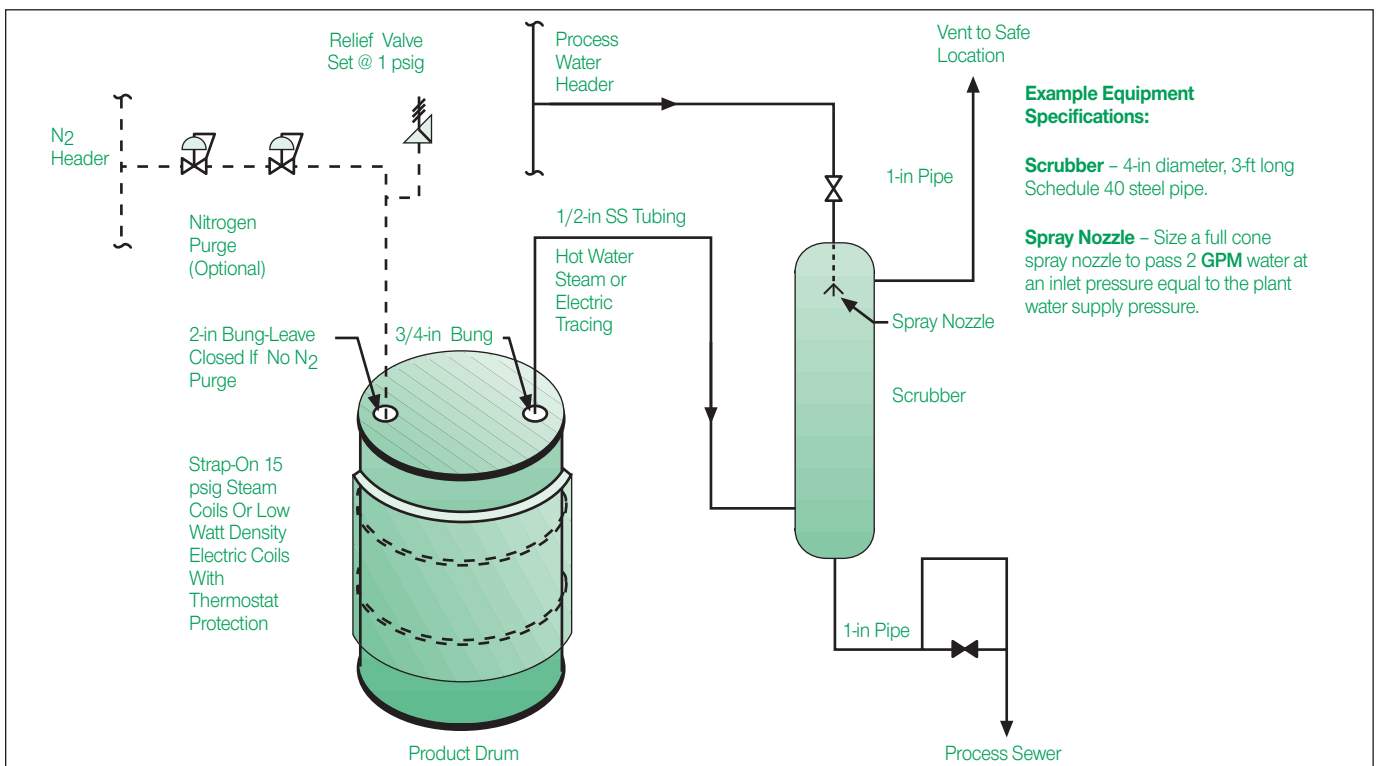
- Drums are covered and stored in a cool, dry, protected, and well-ventilated area.
- Storage and ventilation are independent of offices and other high traffic areas.
- Appropriate MSDSs are readily available in the storage area.
- Ethyleneamines are stored away from materials with which they may react.
- Drums are protected from damage or abuse that could cause leaks. (Note: Do not store or stack drums in such a way that they might fall, tip over, or roll.)
- Product from a leaking drum can be easily and effectively contained to prevent contamination of other areas.
- Appropriate instructions for cleaning up leaks and spills (55 gallons [200 liters] or larger) are prominently posted in the storage area.

Appropriate cleanup materials and equipment are readily available in the storage area.

## Drum Thawing

Customers who receive drum shipments of Ethyleneamines that are prone to freezing at ambient temperatures will occasionally need to thaw a drum. Storage in a “hot room” with a temperature 20 to 30°C above the freezing point is considered by many to be the most effective method of thawing drums. Alternatively, electric, low-pressure (15 psi) steam, or hot water strap-on drum heating coils may be employed. Electric coils should be suitable for the electrical classification of the surrounding area. Note especially that EDA may approach its tagged closed cup flashpoint (110°F, 43.3°C ASTM D-56) if heated somewhat above its freezing point (11°C). Drums must be vented to a safe location while heating to prevent pressure buildup. As EDA, DETA, PIP and AEEA can fume while being thawed (See comments on “smoke” or fumes in “Ventilation” and “Fuming Vents” sections,) routing to vent scrubbers may be necessary. (See Appendix B). **Figure 1** depicts a typical drum-thawing scheme. Note that frozen drums of aqueous products may separate into layers of different compositions. Make sure drums are completely thawed and well-mixed before transfer to a tank or process.

**Figure 1 - Drum Thawing**



## Product Dispensing

The activity where the potential for accidental exposure to Ethyleneamines is greatest is in the dispensing of the products. Thus, this activity must be very carefully managed to ensure that engineering controls, dispensing procedures, and personal protective clothing and equipment keep exposures below occupational exposure limits. Policies and procedures should be in place to ensure that these goals are met, including the following:

- All product-dispensing personnel are fully informed about the physical and chemical properties of the various Ethyleneamines and about the hazards to health and safety associated with each product.
- Written step-by-step instructions for safe product dispensing have been prepared and are being fully and carefully implemented by all product-dispensing personnel.
- A comprehensive program of industrial hygiene has been developed by a qualified industrial hygienist and that all elements of the program are faithfully practiced by all operating and maintenance personnel.
- Exposure data are collected on a routine basis to ensure that both personnel and equipment are performing as required.
- Safety showers and eyewash fountains are located in the immediate area where the product is being dispensed, that these devices are in good working order, and that they are readily accessible.
- All required personal protective equipment is in good working order and that it is being used correctly.
- Written, comprehensive (detailed) procedures for containing and cleaning up spills and leaks have been prepared and are posted wherever Ethyleneamines are handled, stored, or used.
- All necessary cleanup materials and equipment are readily available wherever Ethyleneamines are handled, stored, or used.
- All necessary ventilating equipment is in place and in good working order whenever bungs are loosened, drums are opened, or product is transferred. (Note: Workers should be aware that an aerosol spray could be released by a slightly pressurized drum.)
- Procedures are in place to ensure exposure-free transfer or use of Ethyleneamines .
- Procedures and equipment are in place to prevent or respond to cross-contamination or exposure to reactive materials.
- Procedures are in place to dispose of amine-soaked cleanup materials which could pose a fire hazard.
- The drum and all dispensing equipment have been properly grounded.

## Notes on Product Dispensing

Loosening and removing drum bungs present a potential hazard, as the drum may be slightly pressurized. This could cause the release of a fine spray of tiny droplets when the bung is loosened. Again, full protective clothing and equipment should be worn and adequate ventilation should be provided. One ventilating system used frequently is a local exhaust with flexible tubing to create a vapor and droplet capture zone in the immediate area of the bung being opened. The key to such an approach is to create a local airflow with a high enough velocity next to the bung so that capture is assured. The ventilation system must vent to a safe location where people are not exposed. A scrubber may be necessary. Be sure that the drum is fully grounded. Also, when removing bungs, it is best to start with the largest first. Unscrew it enough to allow any pressure to bleed off by shaking the bung in its threads. Be careful to avoid exposure.

Once any built-up pressure is gone, the bungs should be removed and immediately replaced with screwed fittings and closed valves. This will prevent any possible exposure and will prepare the drum for emptying, using the method described below.

***(Note: The vent fitting will need an elbow and an extension to prevent spillage.)***

There are several methods that may be used to empty drums. One method is to use a cradle to hold the drum on its side. The product is then pumped or vacuumed out of the drum. This method enables all but a few grams to be removed. It also minimizes the possibility of exposure. Avoid pulling excessive vacuum on the drum as this can result in a crumpled drum and potential for an Ethyleneamine leak. Another technique for unloading drums is to pull a vacuum on the receiving tank and pull the material from the standing drum via a lance and pipeline to the tank.

Drum pumps may also be used to transfer Ethyleneamines from drums. These may be either portable pumps mounted on a diptube or fixed pumps with a suction lance. It is important to avoid exposure to Ethyleneamine fumes while unloading a drum, and either a closed system with nitrogen makeup or proper breathing air protection (respirator or fresh air-supplied mask) will be necessary. Using a dip tube may leave more material in the drum than the option of mounting the drum in a drum cradle, and this must be considered when washing the drum prior to disposal. The pump



should be of stainless steel construction with no copper or copper alloy components in contact with the product. TFE is suggested for gaskets, seals, diaphragms, and other non-metallic components in the pump.

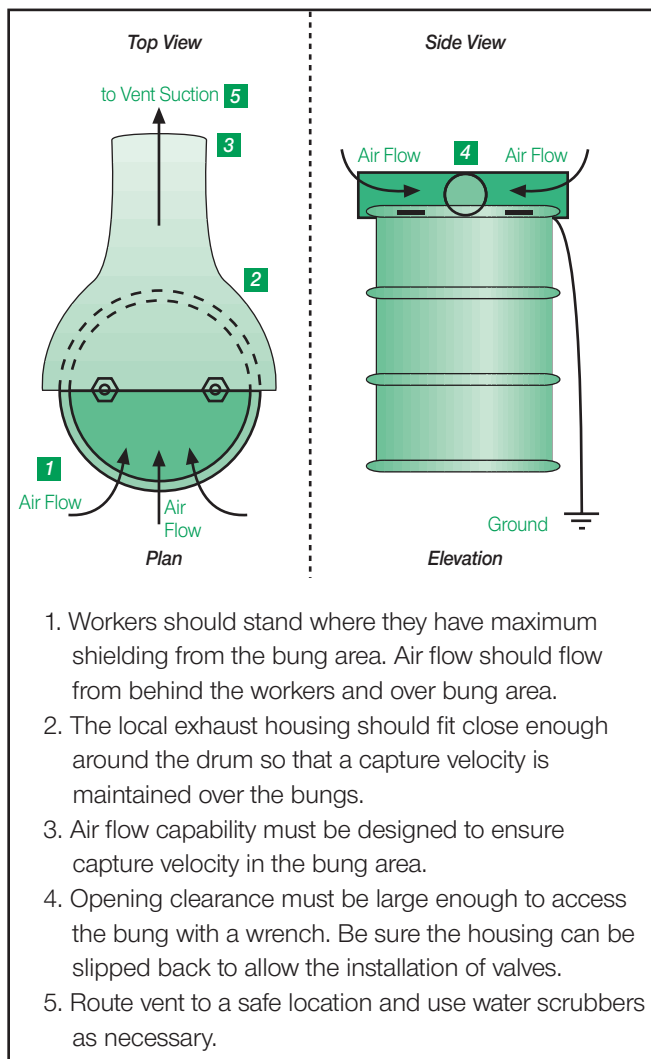
Finally, the use of pressure to empty drums is strongly discouraged, because 55-gallon (200-liter) drums are not designed for pressure and may rupture.

A valve on the drum vent is not critical, but great care should be taken to obtain a valve for the liquid outlet, which prevents any leakage when the unloading hose is disconnected. This is especially important when the entire drum is not emptied in one operation, and the hose is disconnected from a partially full drum. The best way to accomplish this is to use a dry-break fitting. It is possible to purchase a 2-inch (50-mm) male dry disconnect adapter fitting that can screw directly into the drum. This fitting provides a valve mechanism through an internal poppet. The product can then be removed using a flexible hose

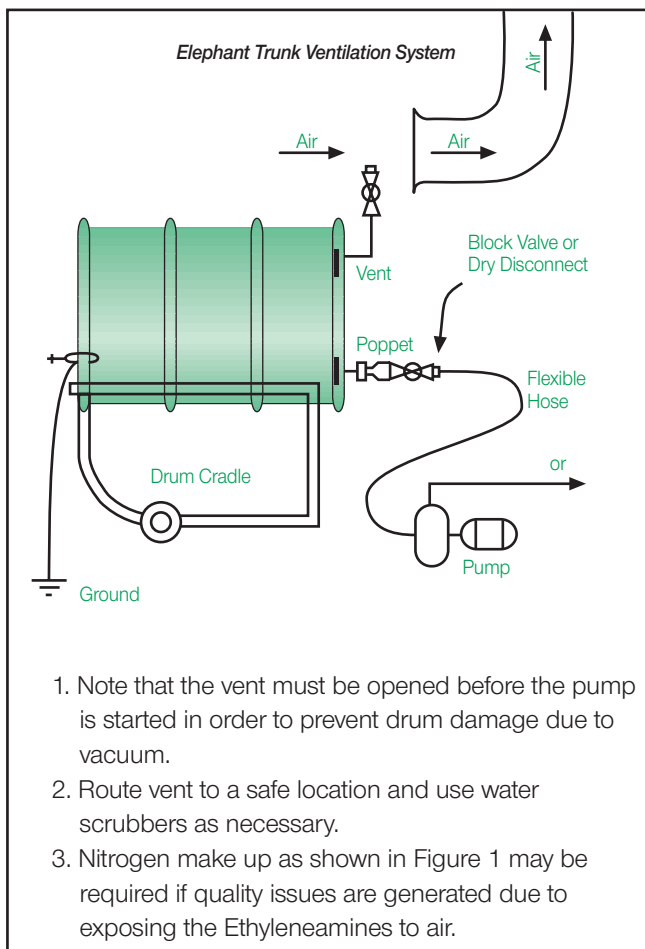
with a female coupler. When the female coupler mates with the male adapter and the valve is actuated, the poppet is pushed in and both halves of the valve are open and the product can flow. Because of the design, disconnection of the system results in the spillage of only a few drops of product. Such a system, with suitable seals, can be obtained from several manufacturers.

*(Note: The use of a flexible hose between the drum and the pump is important because it allows the drum to be tilted as the last of the material is removed. Flexible hoses made of cross-linked high-density polyethylene, cross-linked polypropylene, or flexible stainless steel are used frequently. Be sure, however, to check with your supplier to ensure suitability and recommended inspection and maintenance techniques. Also, electrical grounding cable should be provided and used to ground the drum.)*

**Figure 2 — Local Ventilation for Drum Opening**



**Figure 3 — Typical Dispensing Set-Up**



## Product Sampling

Product sampling is a potential source of personnel exposure to Ethyleneamines. While it is certainly possible to safely draw a product sample into an open glass bottle through the traditional valve with a small-diameter tubing nozzle, this type of procedure may not be desirable because of the high potential for personnel exposure. Closed sampling systems at Ethyleneamine sample points significantly reduce the potential for exposure. The U.S. Environmental Protection Agency has designated EDA as a Volatile Organic Chemical and requires closed sampling systems or other provisions to minimize releases when sampling.

Sampling transportation equipment is difficult to do without some risk of exposure. An effective procedure is to examine the product certificate of analysis; verify that the vessel identification marks, product tags, and bill of lading are correct; and ensure that the seals are in place on all vessel connections. Connect to the vessel and start the unloading pump to draw a sample through a closed system. Once the product is confirmed, unloading may commence.

## Materials of Construction

### Storage and Handling Systems Materials

Proper selection of materials of construction for Ethyleneamine service is essential to ensure the integrity of the handling system and to maintain product quality. Both aspects must be taken into account when selecting the most economical materials of construction.

Steel in general is a material that requires careful consideration for use in an Ethyleneamines handling system. Often it is the lowest cost material, and in many cases has fairly low corrosion rates. However, Ethyleneamines are excellent chelators of free iron, and this iron turns the products red or brown. Ethyleneamines exposed to even minor amounts of rust or mill scale in steel equipment are very prone to go off-color. The color formation is also time-dependent. A short term contact with steel (e.g., a few days) may result in only minor color development. Longer term contact, over several months, typical in a product storage system will result in much more significant color formation. Hence steel equipment is typically only used where it is in dedicated service and not exposed to any water or air that would promote rust formation and where some color growth is tolerable.

Chemical cleaning is usually required to remove free iron prior to putting the equipment into service. Even with these precautions, the initial product handled in the steel system is likely to have a high color. Because there are many difficult to control variables in the use of steel for Ethyleneamine service, producers can only provide qualitative guidance and are unable to estimate how significant the impact on the product will be.

Carbon steel transfer lines or agitated equipment will suffer enhanced corrosion because of the erosion of the passive film by the product velocity. The higher corrosion rates for carbon steel in EDA and AEEA service cause this material to be unacceptable for transfer lines. For other pure Ethyleneamines, carbon steel will not corrode at unacceptable rates from a mechanical strength/service life standpoint, but product quality will suffer from iron contamination. 300-Series stainless steel should be used for transfer lines. 316-Series stainless steel should be specified for tank heating coils.

**Table 2** summarizes materials that can be used for storage tank construction for pure Ethyleneamine service. Galvanized steel, copper and copper bearing alloys are unacceptable for all Ethyleneamine service. Special care should be taken when selecting such items as pumps and valves to ensure that no copper alloys (e.g., brass or bronze) are used in bearings or other internal components that may come in contact with the product. The materials for both storage tanks and pipelines are shown in the order of preference based on preservation of product purity and compatibility. Lower cost materials are listed last. If some reduction in product purity is acceptable, lower cost materials may be the economic choice for a particular installation. For example, if an increase in product color is acceptable, then a steel tank may be used for DETA instead of more expensive stainless steel.

316L stainless steel should be used for tank heating coils for all products. Do not use steel or aluminum coils as rapid corrosion will occur with all products due to elevated temperatures in contact with the coil; even low-grade stainless steel (like 304SS) will not give adequate service life.

**Table 2 – Suggested Storage Tank Construction Materials for Pure Ethyleneamines**

<b>Product</b>	<b>Storage Temp °C</b>		<b>Storage and Handling System Materials of Construction</b>
	<b>Min</b>	<b>Max</b>	
<b>EDA</b>	20	35	300-Series Stainless Steel Aluminum* (Acceptable)
<b>DETA</b>	Ambient	40	300-Series Stainless Steel Aluminum*(Acceptable)
<b>TETA</b>	Ambient	40	300-Series Stainless Steel Aluminum*(Acceptable)
<b>TEPA</b>	Ambient	40	300-Series Stainless Steel Aluminum*(Acceptable) Carbon Steel (will not corrode, but may discolor product)* *
<b>AEEA</b>	20	30	300-Series Stainless Steel
<b>AEP</b>	Ambient	40	300-Series Stainless Steel Aluminum*(Acceptable) (for storage tanks only) Carbon Steel (will not corrode, but may discolor product)**
<b>PIP (Aqueous)</b>	55	65	300-Series Stainless Steel
<b>HEP</b>	50	70	300-Series Stainless Steel
<b>PEHA &amp; HPA</b>	20	40	300-Series Stainless Steel Aluminum*(Acceptable) Carbon Steel (will not corrode, but may discolor product)**

\* Aqueous Ethyleneamines are particularly corrosive to aluminum systems. Aluminum is acceptable for storage tanks where noted, as long as the Ethyleneamines are non-aqueous; however, fabrication difficulties often make it economically unattractive compared to 300-Series stainless steel.

\*\* See comments on carbon steel in following discussion.

Carbon steel is not recommended for EDA, AEEA and PIP storage tanks. Corrosion is not extreme (less than 0.01 in/yr.), but the products will discolor very badly. DETA is less affected by carbon steel but will still experience some discoloration and iron pickup. 300-Series stainless steel is recommended for storage tanks for these four products. Aluminum exhibits modest (0.003 to 0.004 in/yr.) corrosion rates in DETA and AEEA service at typical storage conditions. This will not normally cause a noticeable product quality loss, but this corrosion rate is a little higher than is normally accepted for aluminum storage tanks.

The product quality of other Ethyleneamines can be degraded by the interaction of the storage tank material of construction and the storage conditions, especially at elevated storage temperatures and in the absence of a nitrogen blanket. Modest storage temperatures (less than 60°C) and nitrogen blankets may allow the use of carbon steel for nonaqueous TETA, TEPA, AEP, PEHA and HPA. However, if air is introduced into the tank vapor space or if water is added to the product, then some degree of iron contamination and discoloration is likely. Carbon steel should be considered only for dedicated product service

since system cleanup for product changes makes it likely that air and moisture will come into contact with the product and the cleanup process may destroy the protective film on the tank surface.

Do not use aluminum lines in EDA, DETA, AEEA, or AEP service since the passivation is rapidly eroded, causing potentially severe corrosion and product discoloration. Aqueous Ethyleneamines are also particularly corrosive to aluminum systems. Aluminum is acceptable for piping for the other non-aqueous Ethyleneamines; however, fabrication difficulties often make it economically unattractive compared to 300-Series stainless steel.

Where 300-Series stainless steel is selected for Ethyleneamine service, low-carbon grades (i.e., 304L or 316L) are more resistant to corrosion, and thus may be a better choice for welded equipment. Often in higher carbon stainless steels, the heat affected zone near the weld is not as resistant to subsequent corrosion as the base metal. This can lead to a rusty appearance and discoloration of the Ethyleneamine product due to iron pickup. In an extreme case, eventual failure, resulting from accelerated corrosion of the metal near the weld, may occur.

Nonmetallic equipment is not normally used for Ethyleneamine service. Glass-reinforced polyester may be attacked chemically. Ethyleneamines will permeate polyethylene and polypropylene, even at ambient temperatures. EDA and occasionally other Ethyleneamines are shipped in extra heavy polyethylene or polyethylene lined drums. Ethyleneamines are not known to attack chemically resistant glass lined vessels.

Common non-aqueous Ethyleneamine blends include mixtures of DETA, TETA, TEPA, PEHA, and HPA, mixed to provide the appropriate combination of amine number, volatility, reactivity, viscosity, and other physical properties. Materials of construction should be selected to be suitable for the worst-case component. For example, materials for use in DETA/HPA blend service would be governed by DETA since that component has the more stringent requirements.

Aqueous Ethyleneamines can be very corrosive. Ethyleneamines with up to 10 weight-percent water will corrode carbon steel, aluminum, and even 304 stainless steel at unacceptably high rates. The corrosion rate of 316 stainless steel increases at temperatures above ambient. Above 80 to 100°C, more resistant materials, such as titanium, may be necessary. Carbon dioxide (which may have been introduced into the Ethyleneamine because of storage in a non-nitrogen blanketed tank) can greatly accelerate aqueous corrosion rates. Generally, higher water concentrations result in somewhat decreased corrosion rates. Below about 20 weight-percent Ethyleneamines, the rates at ambient temperature are no higher than for water alone against the common materials of construction.

Corrosion testing, using specific conditions anticipated, is the only way of establishing proper material selection.

300-Series stainless steel has been found to have a corrosion rate within acceptable parameters for tanks for 30 to 60% EDA/water blends stored at ambient temperatures, 63 to 67% PIP/ water blend stored at 60°C and HEP stored at 80°C. 316 stainless steel should be used for transfer lines. Baked phenolic-lined steel was also found to be acceptable for 63 to 67% PIP/ water blend stored at 60°C and HEP stored at 80°C, but not the 30 to 60% EDA/water blend stored at ambient temperatures. Carbon steel, 3000, 5000 and 6000 series aluminum, low-temperature phenolic-lined steel and polyethylene, polypropylene have all been found to be unacceptable under these conditions.

## Elastomers

Elastomers for Ethyleneamine service are shown below. Notice that there is no single elastomer that is acceptable for all Ethyleneamines. These data are based on liquid immersion tests at 80°C for at least 90 days. Higher temperatures may substantially reduce elastomer resistance to the Ethyleneamine.

## Gaskets

Many commonly accepted gaskets may be used in Ethyleneamine service. Generally, TFE-type or flexible graphite spiralwound 316 stainless steel gaskets are used for this purpose. There are other non-asbestos materials that may fill the need as well. It is recommended that you contact your preferred gasket supplier or your Ethyleneamine supplier if you should need assistance.

TFE-type tape should be used on threaded connections.

**Table 3 – Elastomers for Ethyleneamine Service**

		<i>EPDM</i>	<i>EPR*</i>	<i>PDTF**</i>	<i>Buna S</i>	<i>Butyl Rubber</i>	<i>Neoprene</i>
Anhydrous	EDA	No	Yes	No	Yes	No	No
	DETA	Yes	Marginal	No	Yes	Marginal	No
	TETA	Marginal	Yes	Marginal	Yes	Yes	No
	TEPA	Marginal	Yes	Yes	Yes	Marginal	No
	AEP	Yes	Yes	Marginal	No	Marginal	No
	AEEA	Yes	Marginal	Marginal	Yes	Marginal	No
	PEHA	Marginal	Yes	Yes	Marginal	Marginal	No
	HPA	Marginal	Yes	Yes	Marginal	Yes	Yes
Aqueous Mixtures	EDA	No	Yes	No	Yes	No	No
	PIP	Yes	Yes	No	Yes	Marginal	Yes
	HEP	Yes	Yes	Yes	Yes	Marginal	No

\* “Parker” E-740 was the EPR material tested.

\*\* “Kalrez” 4079 was the PDTF material tested.

Ratings Key: Yes = Suitable for permanent service  
 Marginal = Marginal for long-term service (depending on the specific exposure conditions), but possibly okay for very short-term contact.  
 No = Unsuitable

The following have been found to be unsuitable for most Ethyleneamine service: “Viton” A, Buna N, Silicone Rubber and Gum Rubber.

TFE is an alternative to elastomers since it is resistant to Ethyleneamines. However, TFE is not a true elastomer and will not always prove suitable as a replacement material.

### Thermal Insulation Materials

Most common thermal insulating materials used in industry are acceptable for Ethyleneamines service. However, porous insulation may introduce the hazard of spontaneous combustion if the insulation is saturated with Ethyleneamines from a leak or external spill. Laboratory testing of Ethyleneamine-soaked 2-inch cubes of insulation has found that ignition can occur at temperatures as low as 50 to 60°C in porous insulation. Since many Ethyleneamines are handled at higher temperatures to prevent freezing or reduce product viscosity, the risk of a smoldering or flaming insulation fire may be present with these materials. Normally, this type of combustion by itself results in only minor equipment damage, but it can be an ignition source if a nearby leak of flammable material should occur. To reduce the chances of an insulation fire, the following procedures should be used, as well as any others that reduce this risk.

- Insist on good housekeeping. Do not spill product or allow thermal insulation to become contaminated with Ethyleneamines.
- Maintain the insulation weather barrier to reduce the chance that spills may soak into the insulation and also to reduce the air that may contact saturated insulation.
- Minimize insulated flanges and other fittings that may be leak points for Ethyleneamines to saturate insulation.
- Train personnel to be aware of this hazard and to deal with insulation fires. If a fire does occur, saturate the insulation with water. Be aware that removing Ethyleneamine-saturated, smoldering insulation will expose it to air, possibly causing a flare-up. Thoroughly soak the insulation with water prior to removal and dispose of product-soaked insulation in a container filled with water in accordance with applicable regulations.

Closed cellular glass insulation is normally resistant to insulation fires since it is difficult for the product to saturate these materials and also difficult for air to get at the product. Cellular glass insulation (ASTM Specification C-552) is recommended as the best choice for Ethyleneamines service. Aluminum, stainless steel, or mastic weather barriers are commonly used. Cellular glass is fairly resistant to external fires, especially when used with a stainless steel jacket.

Expanded perlite (ASTM Specification C-610) provides good thermal insulating properties and good fire resistance when applied with a mastic, aluminum, or stainless steel weather barrier. This material is also treated with a water repellent that seems to reduce the tendency of the insulation to soak up Ethyleneamines. Hence, the risk of an insulation fire is reduced but not eliminated, since the long-term resistance of the water repellent to Ethyleneamine contact is not known. Mastic, aluminum, or stainless steel weather barriers are common.

Rigid polyurethane foam is also used sometimes, especially on prefabricated insulated pipe. It must be limited to relatively low temperatures (120°C). Aluminum weather barriers are recommended. However, in the case of an external fire, this material is likely to be destroyed and thus provides no fire protection. The autoignition point of Ethyleneamines when saturated in polyurethane foam insulation is not known.

Calcium silicate (ASTM Specification C-533) and mineral wool (ASTM Specifications C-592, C-547, or C-612) insulation with mastic, aluminum, or stainless steel weather barriers are very commonly employed in industrial service and may be utilized in Ethyleneamine service. Although these materials are the most susceptible to the smoldering insulation fires previously described, both have excellent thermal insulation properties. Calcium silicate has excellent external fire exposure resistance. Mineral wool is quite good, especially high-density applications.

## Storage System Design

### Typical Arrangement

The typical arrangement of an Ethyleneamines storage tank and product handling system is shown in **Figure 4** “Bulk Storage and Transfer Schematic.”

### Storage Tanks

**Table 2** on page 17 provides guidance on tank materials of construction. As noted in the “Materials of Construction” discussion, stainless steel is generally the preferred or least corrosive material for storage tanks. Aluminum, lined steel and carbon steel may be alternate choices depending on the particular product handled and the necessary product color specification.

**Note: Because they are quickly corroded by amines, do not use copper, copper alloys, brass, or bronze in tanks or lines.**

To specify a tank, the owner must furnish the tank supplier with the required capacity, the required pressure and vacuum ratings, the physical properties of the product to be stored (including the flash point, viscosity, specific gravity, etc.), and other site information necessary to design the tank .

To ensure safe and orderly Ethyleneamine delivery, the capacity of the storage tank should be large enough to hold the maximum amount of product received in a single shipment, plus additional working inventory. Consider oversizing the tank sufficiently to create a space to accommodate bubbles that may be created by the gas flow used to clear the piping. Also, when calculating tank size, allow sufficient space for liquid expansion while heating. Where an inert gas blanket is used, it should be sized to provide inert gas makeup for worst case vacuum relief: typically, maximum pump-out rate in combination with sudden tank cooling (i.e., hailstorm). If the inert gas use rate is excessive, then provide capacity for pump-out only and install a pressure vacuum relief valve (PVRV) unit that will break the tank vacuum with air under sudden cooling conditions.

When determining the tank design pressure, keep in mind the potential need to vent the tank to a scrubber to reduce emissions of Ethyleneamines during unloading, normal breathing and product heating. To provide adequate working space for operation of the vacuum breaker, the inert gas blanket system, the vent to the

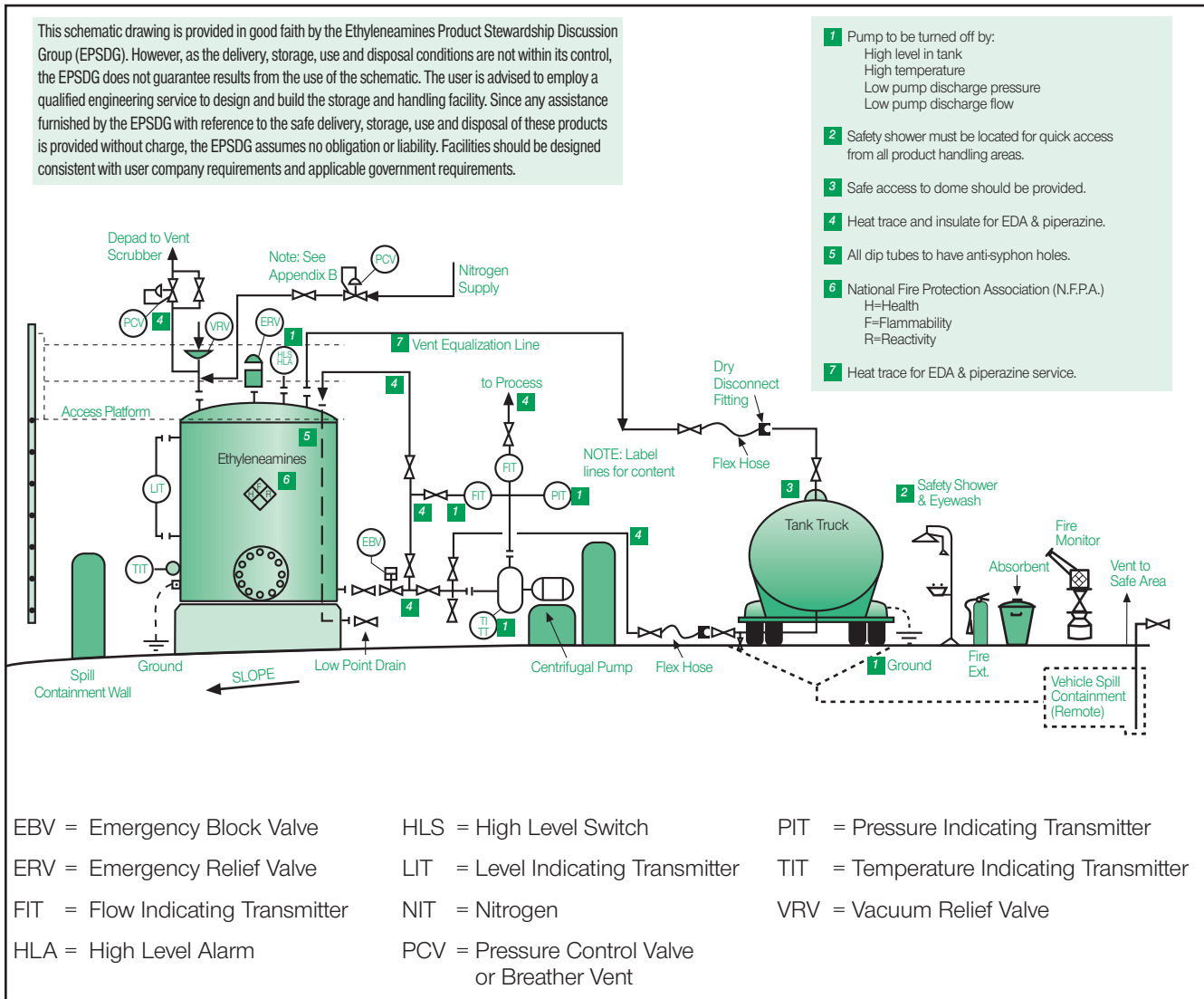
scrubber, and the vent to the atmosphere, a pressure rating of 0.5 to 1psig is typical.

A suitable foundation, grooved for leak detection, is required for all Ethyleneamine storage tanks. Storage systems should be designed to prevent drainage of spilled or waste product into sewers or other areas where environmental damage or accidental contact with persons could occur. Also, a tank should generally be dedicated for use for a single Ethyleneamine. Sharing equipment or lines between Ethyleneamines and other chemicals can degrade both product purity and performance. It can also be dangerous. For example, when organic base products (such as the Ethyleneamines ) are mixed with organic acid chemicals (such as acetic acid or

other carboxylic acids), an exothermic reaction can occur, which could lead to a pressure increase sufficient to rupture the tank.

Tanks located indoors must be vented outside to a safe area. Tank filling lines may connect at the top or bottom of the tank. For top connections, a dip tube to the tank bottom with an anti-siphon hole near the top is suggested. The dip tube eliminates any potential for a static spark generated in the vapor space from the falling liquid. The anti-siphon hole prevents inadvertent draining of the tank through the dip tube. Block valves should be provided on all tank nozzles that have piping connections. A bottom drain valve is desirable for draining the tank.

**Figure 4 – Bulk Storage and Transfer Schematic**



## Heating/Freeze Protection

To effectively handle and transfer Ethyleneamines, keep the product comfortably above the product freezing point; particularly note that EDA has a freeze point of 51°F (10.6°C) and Commercial PIP 63%-68% in water has a freeze point range of 95°F-113°F (35°C-45°C). In addition, it may be desirable to heat AEEA and the higher molecular weight products (TEPA, PEHA and HPA) to reduce the viscosity so that the product is easier to pump. For example, HPA does not have a definite freezing point, but at temperatures below 40°F (4.4°C), viscosity becomes sufficiently high that it cannot be satisfactorily pumped.

**Table 2** on page 17 shows typical storage temperature ranges for Ethyleneamines. The typical storage temperature for the product being handled should be compared to the ambient temperature if the product will be stored and handled outdoors, or to the indoor temperature if the product will be stored indoors in a controlled temperature environment. Provision for tank heating should be made when the product will not be able to be maintained above the freeze point, at the typical storage temperature.

If an aqueous or mixed Ethyleneamine product should freeze in a tank, then the material may not thaw uniformly and material pumped from the tank may not have a uniform composition. The tank should be circulated or otherwise mixed until it is completely thawed to assure that the product is uniform before transfer.

EDA has a flash point of 42 to 43°C (109° to 110°F). It is prudent to take care not to heat an EDA tank above 35°C to avoid a flammable vapor space in the tank.

## Tank Mixing

For good mixing within the tank, some provision should be made to avoid dead circulation areas by appropriate design. One method is to consider the use of tank eductors, particularly for mixing when starting with cold material. These devices enhance the circulation of a tank by drawing large amounts of material in the tank into the flowing stream of a much smaller flow circulated by a pump. Proper sizing of the pump and the eductor is necessary to ensure sufficient velocity through the eductor. The recycle flow may be varied to give sufficient volume to effectively mix the material in the tank. A simple jet on the return circulation line is another method of improving mixing. The jet may be angled upward to promote mixing, but the potential for static generation must be considered in such a design. Finally, if an agitator is required, a top-entering agitator should be used. Issues of flammability should be considered with the addition of an agitator.

## Grounding

Storage tanks and other processing equipment, including reactors and formulating vessels, must be grounded to prevent static electricity buildup. Loading lines may be introduced to the bottom of the tank or have an internal dip leg (with an anti-siphon hole at the top) that extends to near the bottom of the tank. Also, provisions must be made for positive attachment of all grounds to ensure dissipation of all static charges. Unsecured grounds must not be permitted.

## Venting/Gas Padding

Storage tanks must be vented to prevent excessive pressure or a vacuum from occurring in the tank during filling or emptying. The vent opening should be so constructed that neither rain nor dirt can enter the tank.

To avoid quality issues with liquid Ethyleneamines, an inert gas pad system for storage should be used. This system requires a source of dry inert gas in sufficient volume to allow for emptying the tank, for small leaks, and for temperature variations. The presence of the inert gas pad will minimize the possibility of oxidation by preventing air from entering the vapor space over the liquid.

**Note: When Ethyleneamines are exposed to air, especially in warm weather or in a heated tank, they tend to oxidize and discolor.**

Additionally, the gas pad can minimize moisture pickup from the air and will prevent the vent from plugging due to carbamate formation.

A breather vent can allow incoming dry gas to build to some preset pressure. A pressure vacuum relief valve (PVRV) can then be set to bleed off the gas if the pressure exceeds desired levels. The vacuum part of the PVRV should be specified not to exceed the vacuum rating of the storage vessel.

Vent scrubbers are essential for EDA and PIP storage systems. These products have sufficiently high vapor pressures (especially at storage conditions that are usually above ambient to avoid product freezing) to cause the vapors “breathing” from the tank to contain significant concentrations of product. The amines react with atmospheric carbon dioxide to produce amine carbamates, which will appear as a blue/white “smoke” or haze. Additionally, the odor is likely to be objectionable and the product may cause irritation to the upper respiratory tract. Repeated exposure to Ethyleneamines may cause an allergic reaction. See Appendix B for a typical scrubber design. Depending on the specific storage conditions, scrubbers may also be necessary on products other than EDA and PIP.



## Fuming Vents

Ethyleneamine vapor may appear as a bluish-white “smoke” from the venting point. The smoke is a finely-divided solid, resulting from the reaction of the amine with atmospheric carbon dioxide to form a carbamate. High ambient humidity may cause water to coalesce on the carbamate particles, increasing the volume of smoke and possibly shifting it to a bluish haze. EDA and PIP are particularly prone to this phenomenon at normal storage conditions, but other Ethyleneamines with lower vapor pressures can act similarly if heated to high enough temperatures. This smoke or haze may accentuate industrial hygiene concerns because the solids tend to settle rather than disperse away from normal working levels. All amine vents must be routed to safe locations and vents that exhibit “smoking” should be routed to water scrubbers

## Vent Fouling

Heat tracing of vent lines may be necessary to keep them clear for products with ambient temperature or higher freezing points. A vent line blocked by condensed and frozen product or a vent unit frozen shut by residual liquid left in the vent following a tank overfilling event could cause catastrophic failure of the tank.

Amine carbamates, formed as discussed above, may also clog and plug vent lines. In an extreme case, this solid buildup can result in vessel failure because of overpressure or excessive vacuum. Vent fouling can be reduced by using inert gas blankets on storage tanks to prevent drawing air into tanks and thereby excluding atmospheric carbon dioxide.

Vent units require periodic inspection to verify that fouling is not occurring and to ensure seals are functioning properly to exclude air from the tank.

## Transfer of Ethyleneamines

Ethyleneamines pose no major problems in transferring from storage to process areas. Care must be taken to use the proper materials of construction. Proper consideration to prevent freezing for products with freezing points above ambient conditions and proper design for the product viscosity are also necessary.

Particular care should be taken with EDA as its freeze point is 51°F (10.6°C). Outdoor lines used in processing or transfer of EDA must be heated in cold weather. This can be accomplished by insulating the lines and using heat tracers. Allowances for expansion of the piping during heating should also be considered when making these installations to prevent hydraulic overpressure, which could cause gasket failures and leaks. Similar precautions should be taken with Commercial PIP 63%-68% in water, as its freeze point range is 95°F-113°F (35°C-45°C). Contact your supplier for further information and recommendations.

## Piping

Piping systems used in handling Ethyleneamines may be constructed of steel or stainless steel. 300-Series stainless steel is a more corrosion-resistant choice for all product piping, except that the aqueous products (PIP and HEP) require the use of only 316 stainless steel. Low carbon grades (e.g., 304L and 316L) are suitable for welded piping. With some consideration, carbon steel may be used. Carbon steel piping is not acceptable for EDA, AEEA, and PIP due to excessive corrosion rates under flowing conditions. In addition, carbon steel piping can impart color to DETA as well as to other Ethyleneamines due to iron pickup. Steel may be often used successfully for TETA, TEPA, AEP, PEHA, and HPA products as long as it is in dedicated service and not subject to air or water exposure. This prevents rust from forming, which may discolor the product. Proper cleaning to remove mill scale and surface rust is essential to reduce color problems with the initial use of these steel systems. Aluminum pipe is acceptable for many of the non-aqueous Ethyleneamines (EDA, DETA, AEEA and AEP being exceptions) but difficulties in field welding usually make aluminum pipe more expensive than stainless steel.

Threaded connections tend to leak more frequently than flanged connections. Therefore, using flanged and welded connections will reduce the potential for leaks. If threaded connections on steel or stainless steel pipes are

used, an effective thread compound, such as TFE thread tape, should be used.

The design of a piping system should prevent excessive mechanical strain by including proper support for the pipe. Provisions must also be made for thermal contraction and expansion. If possible, install the lines with small drain valves at the low points to make it easy to drain the lines completely. Also, the piping system should be pressure checked before being placed in service, and the lines should be cleaned, dried and nitrogen purged before filling them with Ethyleneamines. As noted, steel pipe will require chemical cleaning prior to use for Ethyleneamines or the initial product will be badly discolored. (See **Figure 4.**)

The size of the lines depends on the quantity of material flowing, the length of the pipe line, the temperature of the material, and the available head.

Piping components, such as valves, in compatible materials of construction are widely available, and Ethyleneamines pose no unusual issues in selecting these components. **No copper alloys (e.g., brass or bronze) should come into contact with the Ethyleneamines;** these may be present as internal components of many purchased items that are not evident to external inspection. Proper gasket and elastomer selection during construction and good system maintenance will reduce fugitive leaks and the potential for employee exposure to Ethyleneamines.

## Piping System Heating

EDA, PIP, and HEP will freeze at temperate ambient temperatures. Usually lines outdoors, and lines indoors for PIP and HEP, must be heat-traced and insulated to prevent freezing in cold weather. Electric, steam or hot water are acceptable heat-tracing media. The piping must be insulated to avoid localized cold spots and frozen product. Any of the insulation materials discussed under “Thermal Insulation Materials” can be used for pipe insulation. Please note that since piping systems contain many components, there is a chance for leaks, and smoldering insulation fires occur most frequently in piping systems, so the proper choice of insulation material is important.

Ethyleneamines that do not freeze at ambient temperatures are often transferred at elevated temperatures to reduce the viscosity of the material. Lower viscosity allows more rapid transfer at less energy use; it may allow the use of significantly smaller pipe sizes. If the storage tank is heated and the line is continuously flowing

and not excessively long, then it may be that no heat tracing is required, and only insulation is necessary to accomplish the transfer goals. More often, tracing is also used on these systems to maintain the desired flowing temperature.

Thermal relief must always be provided for traced piping systems that can be blocked in. If a line is left full after a transfer, the product will warm up above the flowing temperature and may eventually reach the heating media temperature. This temperature rise will cause thermal expansion that must be accommodated or failure of a gasket or other piping component may occur.

Often a small safety valve is used for this thermal relief. Ideally, this relief valve discharges back to the storage tank, preventing loss of material to the environment. Sometimes, the discharge is to a compatible process sewer routed to a treatment facility when return to the tank is difficult.

Metal bellows thermal expansion compensators may also be used to absorb the expansion in an expandable chamber without releasing material to the environment. These devices can also absorb hydraulic hammer caused by the quick-closing valves in the lines but will fail if the nitrogen pad on the outside of the bellows is not maintained at the proper pressure.

Allowances for thermal expansion of the piping during heating should also be considered when making these installations.

## Loading and Unloading Hoses/Lines

Product transfer hoses/lines are usually made from stainless steel, highly crosslinked, high-density polyethylene or TFE inner liners with stainless steel braid reinforcement or a heavy, reinforced elastomer jacket. Be sure the operating temperature limits are not exceeded when using a hose with nonmetallic liners or jackets for handling product above ambient temperatures. Liner leaks can lead to rapid deterioration of non-Ethyleneamine resistant elastomers often used in jacketed hose, and this deterioration can lead to consequent failure under pressure.

## Pumps

Pumps used for Ethyleneamines may be centrifugal or positive displacement rotary, gear, or screw type. Give consideration to pumps constructed of stainless steel, especially if iron contamination is to be avoided. If, however, some iron contamination and discoloration are acceptable, ordinary carbon steel or ductile iron may be used.

Mechanical seals are preferred to avoid even minor drip leaks that are common with shaft packing. Carbon vs. silicon carbide sealing faces are effective in Ethyleneamine service and gaskets and elastomers for internal gaskets and O-rings should be selected from the discussion in the “Materials of Construction” section. Magnetically driven centrifugal pumps without seals can also be used to prevent personnel exposure from seal leaks. However, problems associated with running the pump dry, cold starts, and failure of the membrane between the fluid and the magnets must be addressed in the system design/operation.

For ease of starting, especially in cold weather, heatable jacketed or traced pumps are suggested.

**Note: Pumps not equipped with jacketing or tracing may be preheated by wrapping copper tubing around them and passing low-pressure steam through the tubing. Do not, however, apply steam directly on the pump.**

## Equipment Cleanup

Equipment used in Ethyleneamine service should be emptied of as much product as possible prior to cleanup. Since the product is water-soluble, the equipment can then be flushed with water prior to opening to the atmosphere. Introduce water at a low level, so that it overflows at high spots to ensure all equipment areas are well-flushed. To avoid the problems associated with hydrates, use warm water (50-60°C) in large quantities for the first flush and do not allow the first flush to stand stagnant. The system may then be drained and flushed a second time. After final draining, the equipment may be carefully opened. Some amines may still be trapped in pockets, so care in disassembly is prudent. Minor residual odors may be removed by steaming equipment (with necessary vacuum relief). All wastewater must be disposed of in a manner complying with government regulations.

## Spills and Leaks

Personnel must be thoroughly trained in safe procedures for handling spills and leaks and for the disposal of wastes. In disposing of wastes, be certain that all applicable government regulations are fully met.

## Spill Containment and Cleanup

Some concerns in any spill, large or small, include:

- To protect all personnel from eye and skin contact, from exposure to vapors, and from the possibility of fire and/or explosion
- To keep the spilled material from entering ground-water, water supplies, or waterways
- To keep the spilled Ethyleneamine from contact with organic acid (such as acetic acid or other carboxylic acids) and thus prevent the likelihood of a violent reaction
- To make certain that all persons engaged in spill containment and cleanup are familiar with the product’s MSDS and are adequately trained in the proper (i.e., safe) methods and techniques of containment, collection, cleanup, and disposal.

Methods of meeting these concerns might include:

- All personnel engaged in spill cleanup should wear appropriate protective clothing as described in “Protective Clothing,” pg. 8
- For small spills (less than 5 gallons [20 liters]), apply an absorbent or high-surface area material (e.g., sand or ground polyolefins, such as polypropylene), leave in place until all traces of liquid product are gone, and then shovel the mass into a suitable container for disposal. Add water to container holding the absorbent to prevent a fire hazard.

**(Note: Avoid cellulose-based absorbent materials, such as sawdust. These materials will react with Ethyleneamines and should not be used. Instead, use sand or ground polyolefins, such as polypropylene.)**

- In the event of a larger spill (55 gallons [200 liters] or more), evacuate and rope off the spill area; keep all employees upwind and away from the spill. Have properly trained and equipped personnel shut off all leaks and any potential sources of ignition. The spill should then be contained with a dike to prevent water pollution. Also, for more volatile amines, dilute vapors with water fog or spray. Then, with an air-driven pump, collect as much of the Ethyleneamine as possible and place in an appropriate container for final disposal.

- The use of solvents during cleanup is hazardous and should be avoided. Also, if the Ethyleneamine is EDA or in a solvent solution, be aware of the increased possibility of fire. Use cleanup tools that are non-sparking. Also, remove all possible sources of ignition from the spill area and have fire-fighting personnel — trained in fighting chemical fires — near at hand.
- For final cleanup, scrub the floor with soap and water, then rinse with very hot water.

***(Note: Wash/rinse water should be contained and collected for proper disposal. Also, prevent wash/rinse water from entering natural waterways or public water supplies. Advise appropriate authorities if spilled product or wash/rinse water enters public land, water supplies, or waterways.)***

## Firefighting

For large fires, alcohol-type or all-purpose-type foams should be applied according to the manufacturer's recommended techniques. Carbon dioxide or dry chemical media should be used for small fires. Do not direct a solid stream of water or foam into hot, burning pools because this may cause splattering and increase fire intensity. When fighting amine fires, use protective clothing, eye protection, and self-contained breathing apparatus. Consult the MSDS for additional firefighting information.

## Emergency Planning Overview

*The use of emergency planning materials prepared by the American Chemistry Council (formerly "CMA," Chemicals Manufacturers Association) is also recommended. (See "References" at the end of this section.)*

### Planning for Emergencies

Although the chemical industry has one of the highest safety records worldwide, an incident — such as an accidental spill or leak — affecting plant personnel and/or the local community can occur. It is important, therefore, to have a well-organized plan in place that will ensure a quick and effective response to any emergency situation. In short, effective emergency planning will anticipate and carefully consider every aspect of any potential emergency that might occur on or near a plant

site or other company facility. Special consideration should also be given to those emergencies that might also affect the community at large. Thus, plans for cooperating with — and fully informing — local safety officials and other appropriate authorities should be included. Again, be sure also to include plans for keeping the media fully and accurately informed.

### Crisis Management

The first step in emergency planning for an existing plant or other facility as outlined by the ACC is "crisis management," which begins with an identification and description of the crisis or emergency to be planned for (see "References" 1 and 2). The crisis management process then proceeds through 34 additional steps related to planning, preparation, mobilization, response, recovery, and post incident follow up. The recommended procedures are comprehensive and cover all aspects of the potential emergency, including warning alarms, evacuation, assembly areas, escape routes, personnel accountability, communications equipment and personnel, chain of command, notification of authorities, and media relations. Again, if your plant does not have a crisis management plan in place, one should be developed and put in place as soon as possible. It is also recommended that the plan be based on the recommendations and procedures as outlined by the ACC in "References" 1 and 2.

### Community Interaction

A fully comprehensive and effective emergency plan should be developed in cooperation with — and fully integrated into — the community-wide emergency response plan. If, however, your community does not have an emergency response plan that integrates civil and industrial emergencies — such as major chemical spills, fires, explosions, large numbers of exposed and injured workers, etc. — consult the Community Awareness and Emergency Response (CAER) guide from the ACC or CEFIC (the European Chemical Industry Federation).

***Note: CAER is a chemical industry initiative supported throughout the world. The CAER guide provides a step-by-step process for creating a fully integrated plan. Once the plan has been developed, however, it should be adequately tested to verify its effectiveness. Also, be sure it includes all appropriate community officials and agencies (including the local media) in both the planning and testing phases.***

## References

- Reference 1: “Crisis Management Planning for the Chemical Industry,” ACC, 1992. (Manual and videotape — Order no. 022012; ACC, 1300 Wilson Blvd., Arlington, VA 22209).
- Reference 2: “Site Emergency Response Planning Guidebook,” ACC, 1992. (Order no. 024041; ACC, 1300 Wilson Blvd., Arlington, VA 22209).
- Reference 3: “Process Safety Management (Control of Acute Hazards),” ACC, 1985. (Order no. 047023; ACC, 1300 Wilson Blvd., Arlington, VA 22209).
- Reference 4: “A Resource Guide for Implementing the Process Safety Code of Management Practices,” ACC, 1990. (Order no. 047024; ACC, 1300 Wilson Blvd., Arlington, VA 22209).

## Disposal Options

### Environmental Considerations

Ethyleneamines are water-soluble and may be initially resistant to biodegradation in a biological waste treatment plant. Biological waste treatment facilities may be able to handle significant wastewater loading once the biotreatment organisms are acclimated to the product. Consult with any biological waste treatment facility that may be utilized before forwarding wastewater to that facility. Cyclic Ethyleneamines, such as PIP and AEP, and heavy Ethyleneamines, such as HPA, are less readily degraded. Sudden loading to a non-acclimated waste treatment biomass should be avoided.

Ethyleneamines in wastewater are likely to react with acidic compounds in the sewer stream, resulting in a more neutral feed to the treatment plant. However, these reactions in the sewer may also produce undesirable odors or create potentially toxic byproducts, such as ammonia, which is a byproduct of Ethyleneamine digestion. Therefore, the customer must be careful, and segregation of sewers may be necessary.

Ethyleneamine spills should be dealt with promptly to avoid high vapor concentrations and possible personnel exposures. Flushing the spill to a process sewer with copious amounts of water can be an effective method of dealing with the spill. Alternatively, dry absorbents may be used to soak up most of the spill.

**Note: Avoid such cellulose-based absorbent materials as sawdust. These materials will react with Ethyleneamines and should not be used. Instead, use sand or ground polyolefins, such as polypropylene.**

The absorbent must be promptly cleaned up and disposed of in a manner consistent with environmental regulations. Disposal of Ethyleneamines-saturated absorbents may be controlled by provisions of the Resource Conservation and Recovery Act (RCRA) as well as other provisions of Federal, state and local laws and regulations. Prior to disposal check to ascertain what regulations may apply. Under certain conditions, when the used absorbent is exposed to air, thermal degradation of the product may begin, possibly resulting in spontaneous combustion. Consequently, the used absorbent should be put into a container (e.g., an open top drum) and thoroughly saturated with water before sealing.

### Drum Disposal

**Note: In general, waste disposal will require the services of a licensed hazardous waste-handling facility. Also, to dispose safely of drums that contained Ethyleneamines the following procedures, among others should be observed.**

- Drums must be completely empty and decontaminated prior to disposal. (Note: While the legal definition of an “empty” drum is one that contains less than one inch of liquid, it is suggested that “empty” drums should be completely drained of all product and then thoroughly rinsed with water three times to remove any residual material.)
- Rinse water (water is a suitable rinsing material) must be properly retained and disposed of in accordance with all applicable Federal, state, provincial, and local laws and regulations governing the disposal of hazardous wastes.
- Drums must not be reused for any unsuitable purpose. This can best be accomplished by having the drums cleaned and then turned into scrap metal by a licensed reclaimer.
- Drums that are to be disposed of in a permitted landfill should be completely empty, then thoroughly rinsed with water at least three times to remove any residual product. The drums should then be crushed and made physically unusable. (Note: Although the drums at this stage cannot be considered totally decontaminated, if cleaned appropriately, they should be clean enough to be handled further without special precautions.)

- Under no circumstances may the rinse water be allowed to enter sources of drinking water, public sewers, or natural waterways, including rivers, lakes, streams, etc. Furthermore, all rinse or wash water must be carefully contained and disposed of in strict accordance with all Federal, state, provincial, and local laws and regulations governing the disposal of hazardous wastes.
- Finally, an empty drum that has contained an Ethyleneamine should be handled with the same precautions and care as the original product. Also, and once again, final disposal of any residual product, all wash or rinse water, and the drum itself, must be in full compliance with all Federal, state, provincial, and local laws and regulations governing the disposal of hazardous wastes.

## Product Safety

When considering the use of any Ethyleneamine in a particular application, you should review the latest Material Safety Data Sheets and ensure that the use you intend can be accomplished safely. For Material Safety Data Sheets and other product safety information, contact your Ethyleneamine supplier. Before handling any other products mentioned in the text, you should obtain available product safety information and take necessary steps to ensure safety of use.

No chemical should be used as or in a food, drug, medical device, or cosmetic, or in a product or process in which it may contact a food, drug, medical device, or cosmetic until the user has determined the suitability and legality of the use. Since government regulations and use conditions are subject to change, it is the user's responsibility to determine that this information is appropriate and suitable under current, applicable laws and regulations.

The EPSDG requests that the customer read and understand the information contained in this publication as part of the educational process in the use and handling of Ethyleneamines.

Current Material Safety Data Sheet(s) will also provide specific information on Ethyleneamine products that may be used or handled. The customer may also wish to furnish the information in this publication to its employees, contractors, and customers, or any other users of the product(s), and request that their customers also become familiar with this information.

## Appendix A - Glove Selection

To assist customers in selecting appropriate gloves for their particular applications, available data was reviewed on the effectiveness of various glove materials for each of the Ethyleneamines listed in **Table A-1**.

When interpreting glove effectiveness, it is important to understand why gloves are recommended for use with Ethyleneamines. Some Ethyleneamines may be absorbed through the skin in harmful amounts and may cause skin burns and irritation. In some cases, there may also be allergic reactions in susceptible individuals. The following information will help in the selection of effective gloves. Please refer to the appropriate material safety data sheet for detailed health effects and safe handling information for the specific product being used.

### Permeation Testing

The relative effectiveness of glove materials as barriers to a given chemical may be established by "permeation testing." An American Society for Testing and Materials (ASTM) method has been established for permeation testing (ASTM-F739-91).

This test involves exposing one side of a glove material sample to the chemical of interest and noting the time at which the chemical can first be detected on the other side of the sample. This time is designated as the breakthrough time. Once the chemical has broken through the glove material, the rate at which the chemical passes through the material is determined. This number is called the permeation rate and is expressed in the mass of permeated chemical per area of glove material per unit of time (usually  $\mu\text{g}/\text{cm}^2/\text{minute}$ ).

Permeation tests are usually conducted for a maximum of eight hours. If no breakthrough is observed in that time period, it is reported as a breakthrough time greater than (>) 480 minutes, and no permeation rate is listed.

A summary of glove permeation resistance data is presented in **Table A-2**. This table summarizes the breakthrough times and permeation rates for five Ethyleneamines and five different glove materials. Generally, the glove with the longest breakthrough time is the most effective. However, while permeation resistance data provide a convenient comparison of the relative effectiveness of various materials as barriers to chemicals, this information must be evaluated in the context of a specific use situation.

## Other Factors Affecting Selection

In selecting a glove that is effective for a particular operation, the following factors should be considered.

### Glove Material

Gloves are made of different polymer materials, each of which will resist permeation by some chemicals better than others. The materials listed in Table A-2 represent a wide range of available glove materials.

### Chemical Mixtures

The permeation behavior of mixtures can be very different from that of the individual components. Since the test data were obtained with individual Ethyleneamines, this data may not apply to the various mixtures of Ethyleneamines and other solvents or water.

### Temperature

The test data were obtained at a room temperature of approximately 24°C (75°F). Gloves become less resistant to chemical permeation as the temperature increases. An increase in temperature of 10°C (18°F) causes approximately a two-fold decrease in the breakthrough time and a corresponding increase in permeation rate.

### Thickness

Permeation varies directly with thickness. The thicker the glove material, the longer the breakthrough time and the lower the permeation rate. This is important since the same glove material could have different thicknesses, even from the same manufacturer.

**Table — A-1**

<b>Ethyleneamines</b>	<b>Type of Ethyleneamine</b>
EDA	Ethylenediamine
DETA	Diethylenetriamine
AEP	N-Aminoethylpiperazine
TETA	Triethylenetetramine
TEPA	Tetraethylenepentamine
PEPA	Polyethylenepolyamines

<b>Glove Material Tested</b>	<b>Manufacturer and Model</b>
Viton North	F-091
Neoprene	Edmont 29-870
Butyl Rubber	North B-174
Polyvinyl Chloride (PVC)	Edmont 34-100
Nitrile	Edmont 37-155
Nitrile	Erista

### Manufacturer Information

Ansell Edmont Industrial, Inc 1300 Walnut Street Coshocton, OH 43812 U.S.A Tel: (614) 622-4311 Fax: (614) 623-3512	North Hand Protection 4090 Azalea Drive Charleston, SC 29405 U.S.A. Tel: (803) 554-0660 Fax: (800) 456-8317	Erista Rex Gummiwarenfabrik GmbH Ostendstrasse 5 64319 Pfungstadt, Germany Tel: (0) 6157-2057 Fax: (0) 6157-85810
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**Table A-2 — Ethyleneamines - Breakthrough Time in Minutes  
(Permeation Rate in  $\mu\text{g}/\text{cm}^2/\text{min}$ )**

<b>Material Construction</b>	<b>Thickness mm (Mil)</b>	<b>EDA</b>	<b>DETA</b>	<b>AEP</b>	<b>TETA</b>	<b>TEPA</b>	<b>PEPA</b>
Viton	0.23 ( 9)	Deg.	>480 (NL)	Not Tested	>480 (NL)	>480 (NL)	Use TEPA
Neoprene	0.46(18)	396 (14.7)	>480 (NL)	Not Tested	>480 (NL)	>480 (NL)	as Reference
Butyl Rubber	0.63 (25)	>480 (NL)	>480 (NL)	240 <sup>a</sup> NL	>480 (NL)	>480 (NL)	
Polyvinyl Chloride (PVC)	0.16 (6)	9 (50.8)	38 (1.7)	Not Tested	Deg.	Deg.	
Nitrile	0.38 (15)	Deg.	Deg.	Deg. <sup>b</sup>	>480 (NL)	Not Tested	

mm - millimeters

mil - 1/1000 of an inch

$\mu\text{g}/\text{cm}^2/\text{min}$  - micrograms per square centimeter per minute

NL - Not listed

Deg. - Material degraded

<sup>a</sup> Glove tested was North Butyl Model B-161

<sup>b</sup> Glove tested was Erista Nitrile Special, Tested at ambient laboratory temperature, 21-25°C (70-77°F)

> 480 indicates no breakthrough observed in an 8-hour time period.

## Glove Use

In addition to permeation resistance, there are a number of other factors that are also very important in selecting a glove that is effective for a specific use. For example, the physical characteristics of the glove — such as durability, dexterity, heat/cold resistance, and mode of use (reusable or disposable) — must also be considered in the selection process. Depending on the particular job, the amount of contact between the Ethyleneamine and the glove material will vary. The data presented in **Table B-2** represent a “worst-case” situation, where there is continuous liquid contact with the glove material. In some work situations, occasional splashes of small amounts of a chemical may be the only contact. In that type of use situation, even though a particular glove may have a relatively short breakthrough time in comparison to another glove material, it may still be an adequately protective and cost-effective choice.

Proper care and maintenance of protective equipment is important. For example, gloves should be inspected before and after each use. Also, proper decontamination and storage of gloves is important as continuous contact with chemicals during storage may cause decreased permeation resistance. Gloves that are damaged during use may have decreased permeation resistance; also, gloves that are torn or punctured may provide no protection at all. Gloves in these conditions should be properly disposed of and replaced with new ones.

***Note: Gloves that have been accidentally torn or punctured may expose the skin to harmful concentrations of Ethyleneamines. Thus, damaged gloves should be promptly removed and discarded. The hands should then be thoroughly and continuously washed for at least 15 minutes with copious amounts of soap and water.***

## Different Manufacturers

There are many different processes for making gloves. A given glove material from different glove manufacturers may have different breakthrough times and permeation rates when challenged with the same chemical. For this reason, we have listed the specific gloves that were tested. (See **Table A-1**.)



# Appendix B – Vent Scrubber System

## Typical Equipment Specifications

**Sizing Basis** – Up to 40 actual ft<sup>3</sup>/min of vapor containing up to 5 mole percent Ethyleneamines is fed at above atmospheric pressure. The scrubber height (13 ft of packing) and water flow (2200 lb/hr) are intended to reduce the outlet vapor to 1 ppm Ethyleneamine or less. Scrubber design vapor pressure drop is 0.5 oz/in<sup>2</sup> at this gas flow rate.

**Scrubber** – 8-in Schedule 40 steel pipe, 13-ft packed height, approximately 2-ft head and base sections.

**Packing** – 5/8-in stainless steel pall rings, approximately 4.5 ft<sup>3</sup>.

**Packing Support** – Norton Model 809 or equivalent, or fabricate from stainless steel screen mesh.

**Liquid Distributor** – Norton Model 845 or equivalent (sparger insert to feed at center of distributor).

**Strainer** – To remove suspended particles larger than nominal 1/16 in, sizing depends on water quality.

