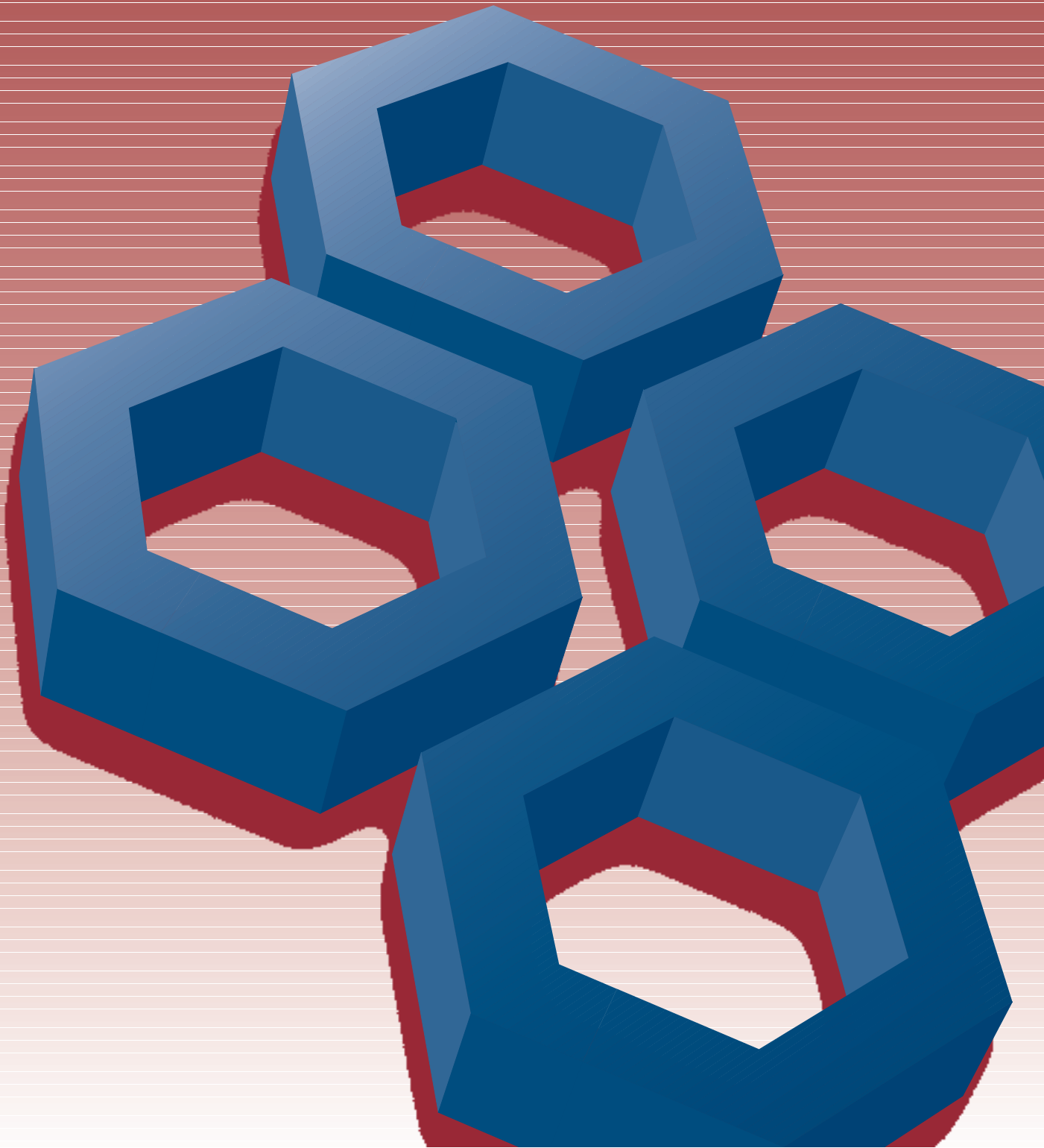


Dow

# Ethyleneamines

## Storage & Handling



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## Ethyleneamines ... Storage & Handling

The Dow Chemical Company manufactures ethyleneamines for a wide variety of end uses. Proper storage and handling will help maintain the high quality of these products as they are delivered to you. This will enhance your ability to use these products safely in your processes and maximize performance in your finished products.

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.

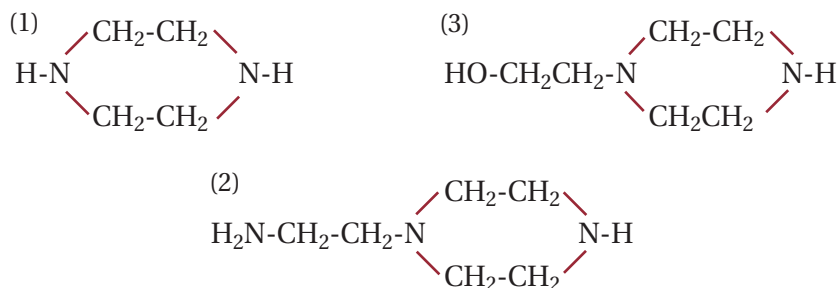
Ethyleneamines require substantial care in handling. Skin or eye contact can result in chemical burns. Breathing a vapor can result in irritation to the nose or throat. Some individuals may experience sensitivity reactions to ethyleneamines, resulting in skin rashes or asthma-like symptoms. Once sensitized, 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 booklet is intended to provide you with the data needed to establish safe storage and handling systems while maintaining product quality. You should refer to our 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:

EDA	Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
PIP <sup>1</sup>	Piperazine	$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$
DETA	Diethylenetriamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
AEP <sup>2</sup>	Aminoethylpiperazine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}$
HEP <sup>3</sup>	Hydroxyethylpiperazine	$\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}$
AEEA	Aminoethylethanolamine	$\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
TETA	Triethylenetetramine	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_2\text{CH}_2\text{CH}_2\text{NH}_2$
TEPA	Tetraethylenepentamine	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3\text{CH}_2\text{CH}_2\text{NH}_2$
PEHA	Pentaethylenehexamine	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_4\text{CH}_2\text{CH}_2\text{NH}_2$
HPA	Heavy Polyamine	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2$ (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. HPA is a mixture of higher molecular weight ethyleneamines. PIP is sold as an aqueous solution and as an anhydrous flaked product. HEP is sold as an aqueous mixture of PIP, HEP, and dihydroxyethylpiperazine.

Physical property data, a summary of common chemical reactions, and typical applications are available from your Dow representative.

## Product Characteristics

This section highlights some general concerns in the typical industrial handling of the ethyleneamine product family. Specific detailed safety information is contained in the Material Safety Data Sheet provided for each product.

### Occupational Health

Exposure to ethyleneamine vapor or liquid can cause sensitization in some individuals. This may be manifested as a skin rash or asthma-like breathing problems by individuals who are unusually sensitive. Our experience has been that symptoms cease when affected individuals are removed from exposure to ethyleneamines. Since it is unclear how low the exposure level must be to ensure that no individual is adversely affected, facilities must be designed to minimize personnel exposure to these products. Spills must be prevented and cleaned up promptly should they occur. Equipment located indoors should be vented to a safe location. Workplace ventilation must be very good.

Heavy ethyleneamines have low vapor pressures at ambient temperatures, which reduce the risk of employee contact with amine vapors. However, these products are often handled at elevated temperatures to improve flow characteristics and ease flow operations, and, hence, vapor contact may result in exposure similar to that of lighter ethyleneamines. Furthermore, elevated temperatures may evolve trace concentrations of lighter ethyleneamines contained in the heavier products.

Respiratory protection, such as a fresh-air-supplied, full-face mask, should be used if exposure to ethyleneamine vapor may occur. The use of non-porous gloves is essential to reduce incidental skin contact to ethyleneamines. Contaminated gloves and other clothing must not be carried into office buildings or eating areas and must be disposed of properly. Contaminated work clothes must not be taken home. If they are reusable, they should be laundered separately and stored separately from street clothing.

### Reactivity

Ethyleneamines react with many other chemicals, sometimes rapidly and usually exothermically. We recommend dedicated processing equipment for all ethyleneamine operations. Storage tanks should be segregated from other materials in separate dike enclosures. Opportunities for cross contamination, such as multiple product hose switching stations, should be avoided. 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.

### Carbamate Formation

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. Using nitrogen blankets on storage tanks is the best prevention.

### Hydrate Formation

Ethyleneamines are soluble in water. However, in the range of 20 to 80 weight percent water, hydrates may form. 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 equipment 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.

### Oxidation

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 will prevent degradation of the product during storage. The following section emphasizes that very thin, high-surface-area ethyleneamine liquid films exposed to air can oxidize very rapidly.

### Liquid Thermal Stability

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 local and Federal regulations.

## Materials of Construction

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.

### Pure Ethyleneamines

Table 1 summarizes our recommendations for pure ethyleneamine service. As shown in the table, 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.

Carbon steel is not recommended for EDA and AEEA 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 pick-up. Three hundred (300) series stainless steel is recommended for storage tanks for these three products. Aluminum exhibits modest (0.003 to 0.004 in/yr) corrosion rates in AEEA and DETA 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 will allow the use of carbon steel for nonaqueous AEP, TETA, TEPA, PEHA, and HPA without noticeable impact on product quality. 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, as noted in Table 1. 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. Stainless steel is usually used for non-dedicated storage.

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 stand-



point, but product quality will suffer from iron contamination. Three hundred (300) series stainless steel should be used for transfer lines. Three hundred sixteen (316) stainless steel should be specified for tank heating coils.

**Do not use aluminum lines in EDA, AEP, AEEA, or DETA service since the passive film is rapidly eroded, causing potentially severe corrosion and product discoloration.** 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 preferable 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.

Common non-aqueous ethyleneamine blends include mixtures of DETA, TETA, TEPA, PEHA, and HPA 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.

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.

Carbon steel with phenolic lining is acceptable for storage of many pure ethyleneamines. Two general types of linings are shown in Table 1 (pg. 9). Baked phenolic linings refer to products that are applied to 5-mil (0.005-in) thicknesses and then cured with heat at about 230°C. Low-temperature phenolic linings are applied 10-15 mils (0.010-0.015 in) thick and contain catalysts that cure the coating at ambient or near-ambient temperatures. Baked phenolics are the superior coatings, but are limited to shop-fabricated tanks because of the required curing temperature. Low-temperature phenolics are often used in large field tanks. Specific coating systems are shown in Table 2 (pg. 11).

Anhydrous piperazine is shipped in standard weatherpac fiber drums with two interior polyethylene bags. Three hundred (300) series stainless steel is recommended when handling this product as a solid.

➤ **Table 1 ••• Materials of Construction for Pure Ethyleneamines**

		Storage Temp., °C	Carbon Steel	300 Series Stainless Steel
Ethylenediamine	EDA	35	(1)	OK
Diethylenetriamine	DETA	Ambient	(3)	OK
Triethylenetetramine	TETA	Ambient	(6)	OK
Tetraethylenepentamine	TEPA	40	(6)	OK
Pentaethylenehexamine	PEHA	60	(6)	OK
Heavy Polyamine	HPA	60	(6)	OK
Aminoethylpiperazine	AEP	Ambient	(6)	OK
Aminoethylethanolamine	AEEA	30	(3)	OK

BASIS: Long-term product storage at the temperature specified.

NOTE: Galvanized steel, copper, and copper alloys are not suitable for any ethyleneamine services.

- (1) Carbon steel storage tanks will not suffer excessive corrosion (less than 0.01 in/yr), but will discolor the product and cause a high iron content. Three hundred (300) series stainless steels are recommended for tanks. Use 316 stainless steel for tank heating coils. Aluminum or 300 series stainless steel are suitable for unheated transfer lines; use 300 series stainless steel for heated lines and other equipment in this service.
- (2) OK for storage tanks. Use 316 stainless steel for tank heating coils. Use 300 series stainless steel for transfer lines and other equipment in this service.
- (3) Carbon steel equipment will not suffer excessive corrosion (less than 0.01 in/yr), but will discolor the product and cause a high iron content, even if a nitrogen blanket is used. The use of 316 stainless steel for tank heating coils is preferred. Use 300 series stainless steel for transfer lines and other equipment.
- (4) Since aluminum corrodes at 0.003 to 0.004 in/yr, it is marginally suitable for large, unagitated storage tanks. Use 316 stainless steel for tank heating coils. Use 300 series stainless steel for smaller agitated tanks, transfer lines, and other equipment.
- (5) OK for storage tanks. Use 316 stainless steel for tank heating coils. Use 300 series stainless steel for transfer lines and other equipment.
- (6) Carbon steel equipment will not suffer excessive corrosion (less than 0.01 in/yr), but will discolor the product and cause a high iron content. Carbon steel can give acceptable service for storage tanks (with minimal product contamination) if the tank is in dedicated service, if water is excluded from the product, and if a tight nitrogen blanket is provided. Use 316 stainless steel for tank heating coils and aluminum or 300 series stainless steel for heated or unheated transfer lines and other equipment in this service.
- (7) OK for storage tanks. Use 316 stainless steel for tank heating coils; aluminum or 300 series stainless steel for heated or unheated transfer lines and other equipment in this service.
- (8) See text on page 8.

## Materials of Construction

3000, 5000, 6000 Series Aluminum	Baked Phenolic- Lined Steel	Low-Temp., Phenolic- Lined Steel	Polyethylene, Polypropylene	Gasket Materials	
				TFE	Grafoil
(2)	No	No	(8)	OK	OK
(4)	(5)	No	(8)	OK	OK
OK	(7)	No	(8)	OK	OK
OK	(7)	(7)	(8)	OK	OK
OK	(7)	(7)	(8)	OK	OK
OK	(7)	(7)	(8)	OK	OK
(5)	(5)	No	(8)	OK	OK
(4)	(5)	No	(8)	OK	OK

➤ **Table 2 ... Phenolic and Phenolic-Modified Linings for Steel Tanks**

#### Baked Phenolic Linings

*Apply in accordance with manufacturer's recommendations; typically, 5-mil thickness and cured at 230°C.*

Plastite 3070	Plasite 614 Elizabeth St. P.O. Box 8147 Green Bay, WI 54308-8147 920-437-6561
Heresite P-403/L-66	Heresite Protective Coatings Manitowoc, WI 54220 800-558-7747

#### Low-Temperature, Catalytic-Cured Epoxy/Phenolic Linings

*Apply in accordance with manufacturer's recommendations; typically, 10-15 mils thickness and forced-heat curing.*

Phenoline 378	Carboline Co. 328 Hanley Industrial Court St. Louis, MO 63144 314-644-1000
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### Aqueous Ethyleneamines

PIP and HEP are frequently sold as aqueous solutions. We also market some EDA/water mixtures. Table 3 (pg. 13) summarizes our recommendations for aqueous ethyleneamine service materials of construction. Three hundred (300) series stainless steel should be specified for transfer lines.

If ethyleneamine/water mixtures are required as a step in processing, recognize that they can be very corrosive. Ethyleneamines with up to 10 weight percent water will corrode carbon steel, aluminum, and even 304 stainless steel at unacceptable 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.

## Gaskets and Elastomers

Recommended gaskets for ethyleneamine service are:

- Grafoil Flexible Graphite GHR
- Spiralwound 316 Stainless Steel/Grafoil Flexible Graphite GTB
- Spiralwound 316 Stainless Steel/TFE
- Gylon Style 3500 (Fawn-Colored)
- TFE molded around perforated 316 Stainless Steel disc (e.g., Task Line from Duriron or Sir from Chemplast)
- 316 Stainless Steel corrugated metal gasket (Lamons Style 340 or 360; or Parker Seal Style 900 or 929) with Grafoil Flexible Graphite GTH tape

Compressed asbestos was often used in the past on pipe and equipment flanges. However, because of current health concerns, compressed asbestos should not be used. Laboratory evaluations indicate that Garlock 3700 non-asbestos compressed fiber gaskets have chemical resistance and sealing properties similar to compressed asbestos at near-ambient temperatures. However, this material and most other non-asbestos compressed fiber gasket materials suffer severe loss in properties above 150°C. Consequently, use of this material for conditions outside typical storage and handling systems is limited.

TFE tape should be used on threaded connections.

Recommended elastomers for ethyleneamine service are shown in Table 4 (pg. 15). Notice that there is no single elastomer that is acceptable for the full product line. As noted, 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. 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.

## Transfer Hose

Product transfer hoses are usually made from stainless steel 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.

➤ **Table 3** ... **Materials of Construction for Aqueous Ethyleneamines**

	Storage Temp., °C	Carbon Steel	300 Series Stainless Steel
EDA/Water Blends <sup>(1)</sup>	Ambient	No	OK (4)
Piperazine <sup>(2)</sup>	60	No	OK (4)
HEP <sup>(3)</sup>	80	No	OK (4)

(1) Typically, 30 to 60 wt% EDA, balance Water.

(2) Typically, 67 to 69 wt% PIP, balance Water.

(3) Typically, 40-45 wt% HEP, 13-19 wt% PIP, 18-23 wt% Dihydroxyethylpiperazine, balance Water.

(4) 300 series stainless steel OK for tanks; 316 stainless steel should be used for transfer lines.

### Preparation for Service

Stainless steel, aluminum, and lined-steel equipment may normally be put into ethyleneamine service with only washout and drying.

Plant water often contains suspended rust particles that may be left in equipment, and the initial ethyleneamine product can thus be contaminated. Where plain carbon steel equipment is used, it should be brushed to remove all loose scale and rust, thoroughly washed, and then immediately dried and inerted with nitrogen. Alternatively, chemical cleaning, using a dilute ammoniated citric acid, may be used to remove rust and scale. Thorough washing, immediate drying, and inerting must also follow. Even with care, some product discoloration is likely to the initial product charges. Eventually, a passive film will be formed on the surface and subsequent product will remain pure. Each time carbon steel equipment is washed or exposed to air, the same product quality concerns are likely.

### Materials of Construction

3000, 5000, 6000 Series Aluminum	Baked Phenolic- Lined Steel	Low-Temp., Phenolic- Lined Steel	Polyethylene, Polypropylene	Gasket Materials	
				TFE	Grafoil
No	No	No	No	OK	OK
No	(5)	No	(6)	OK	OK
No	(5)	No	(6)	OK	OK

(5) OK for storage tanks. Use 316 stainless steel for tank heating coils. Aluminum is suitable for unheated transfer lines; use 316 stainless steel for heated transfer lines and other equipment in this service.

(6) Polyethylene and polypropylene are not suitable in this applications because of the storage temperature.

PHENOLIC LININGS: See Table 2 (pg. 11).

### 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. We have run laboratory tests on ethyleneamine-soaked 2-in cubes of insulation and 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, we recommend that you:

- 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.

➤ **Table 4 ••• Elastomers for Ethyleneamine Service**

		EPDM	Parker E-740	Viton A
<b>Anhydrous</b>	EDA	No	Yes	No
	DETA	Yes	Marginal	No
	TETA	Marginal	Yes	No
	TEPA	Marginal	Yes	No
	PEHA	Marginal	Yes	No
	HPA	Marginal	Yes	No
	AEP	Yes	Yes	Yes
	AEEA	Yes	Marginal	No
<b>Aqueous Mixtures</b>	EDA/Water Blends <sup>(1)</sup>	No	Yes	No
	PIP <sup>(2)</sup>	Yes	Yes	No
	HEP <sup>(3)</sup>	Yes	Yes	No

NOTE: Evaluations are based on 90-day tests at 80°C.

(1) Typically, 30 to 60 wt% EDA, balance Water.

(2) Typically, 67 to 69 wt% PIP, balance Water.

(3) Typically, 40-45 wt% HEP, 13-19 wt% PIP, 18-23 wt% Dihydroxyethylpiperazine, balance Water.

- 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 (Foamglas from Pittsburgh-Corning Corporation, ASTM Specification C552) 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 (Goodtemp 1500 from Howred Corporation, 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



Kalrez 4079	Buna S	Butyl Rubber	Buna N	Silicone Rubber	Gum Rubber	Neoprene
No	Yes	No	No	No	No	No
No	Yes	Marginal	No	No	No	No
Marginal	Yes	Yes	No	No	No	No
Yes	Yes	Marginal	No	No	No	No
Yes	Marginal	Marginal	No	No	No	No
Yes	Marginal	Yes	Marginal	No	No	Yes
Marginal	No	Marginal	No	No	No	No
Marginal	Yes	Marginal	No	No	No	No
No	Yes	No	No	No	No	No
No	Yes	Marginal	Marginal	No	No	Yes
Yes	Yes	Marginal	Yes	No	No	No

RATINGS KEY: Yes = Suitable for permanent service  
 Marginal = Marginal for long-term service (depending on the specific exposure conditions), but possibly OK for very short-term contact  
 No = Unsuitable

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. Dow has not tested the autoignition point of ethyleneamines when saturated in polyurethane foam insulation.

Calcium silicate (several manufacturers, ASTM Specification C-533) and mineral wool (several manufacturers, 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.

## Typical Storage and Piping System

Figure 1 (pg. 18), depicts a typical ethyleneamine storage system. The selection of various components obviously depends on the needs of the user, but typical specifications are noted for the various components. Table 5 (pg. 20) shows typical storage conditions and considerations for various ethyleneamines.

### Vent Scrubbers

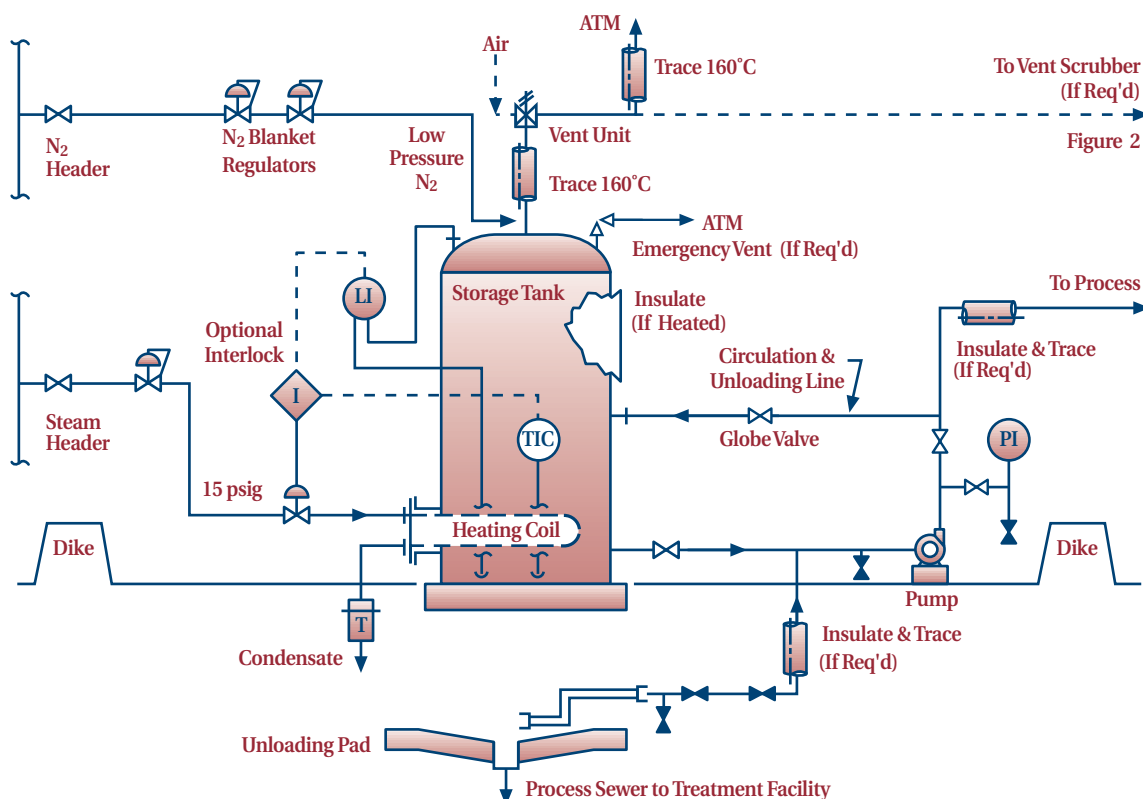
As shown in Table 5 (pg. 20), we specify vent scrubbers for EDA and PIP storage systems. These products have sufficiently high vapor pressures (especially at storage conditions that are usually above ambient to avoid product freezing) to cause the vapors “breathing” from the tank to contain significant 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 health problems because of the sensitization potential of ethyleneamines. Figure 2 (pg. 19) shows the typical scrubber design we have used on many of our tanks. Depending on the specific storage conditions, scrubbers may also be necessary on products other than EDA and PIP.

### Tank and Line Heating

Table 5 (pg. 20) also gives recommended storage temperatures. We typically maintain products well above their freezing points. In addition, heavier ethyleneamines are kept above ambient temperature to ease in-plant handling. The Materials of Construction in Table 1 (pg. 8) used at the temperatures shown in Table 5 (pg. 20) will result in no significant deterioration of product quality for 90 days or more of storage. The selection of equipment suggested in Figure 1 assumes these storage temperatures. Other conditions chosen by the user may require some adjustment. For example, if TEPA is stored at ambient temperatures in the northern United States, then winter viscosities of 150 to 400 cP would probably preclude the use of centrifugal pumps. Continuous circulation of heated ethyleneamine tanks is highly desirable to provide more even heating of the contents and to combat scorching and discoloration of the product on the heating coil surface.

Tanks are most commonly heated using internal coils supplied with hot water or low-pressure (15 psig) steam. Type 316 stainless steel coils are generally preferred for the best maintenance of product quality. Carbon steel or aluminum coils must not be used for EDA, PIP, HEP, or AEEA service because corrosion is unacceptable. Sometimes an external heat exchanger with pumped circulation is utilized for heating in amines service, but this type of installation is usually more costly.  
*(cont'd pg. 20)*

➤ **Figure 1** ..... Typical Storage Tank System



### Typical Equipment Specifications

**Tank** – API 650 Field-Erected Tank or API 12F Shop-Fabricated, Low-Pressure Tank with at least 3 oz/in<sup>2</sup> pressure rating, 0.5 oz/in<sup>2</sup> vacuum rating. Non-heated tanks are normally not insulated, and there is no reason to insulate the tank roof. Insulated tanks typically have 2 to 2-1/2 in of insulation.

**Pumps** – Centrifugal pump, reinforced TFE or Grafoil gaskets and packing, single mechanical seal with carbon vs. silicon carbide faces. Electrical motor in accordance with customer's area electrical classification. Flow rate capacity and head determined by customer. 50 GPM or more capacity is typical if used to unload tank cars or trucks. EDA is a Volatile Organic Chemical and will require dual mechanical seals, canned or magnetic drive pumps, or additional monitoring.

**Vent Unit** – Breather vent typically sized for worst case of: (a) vapor displacement at maximum tank filling rate, (b) fire exposure relieving rate from tank, or (c) nitrogen blowthrough where unloading cars or trucks or in cleaning lines. Trace and insulate vent unit, inlet

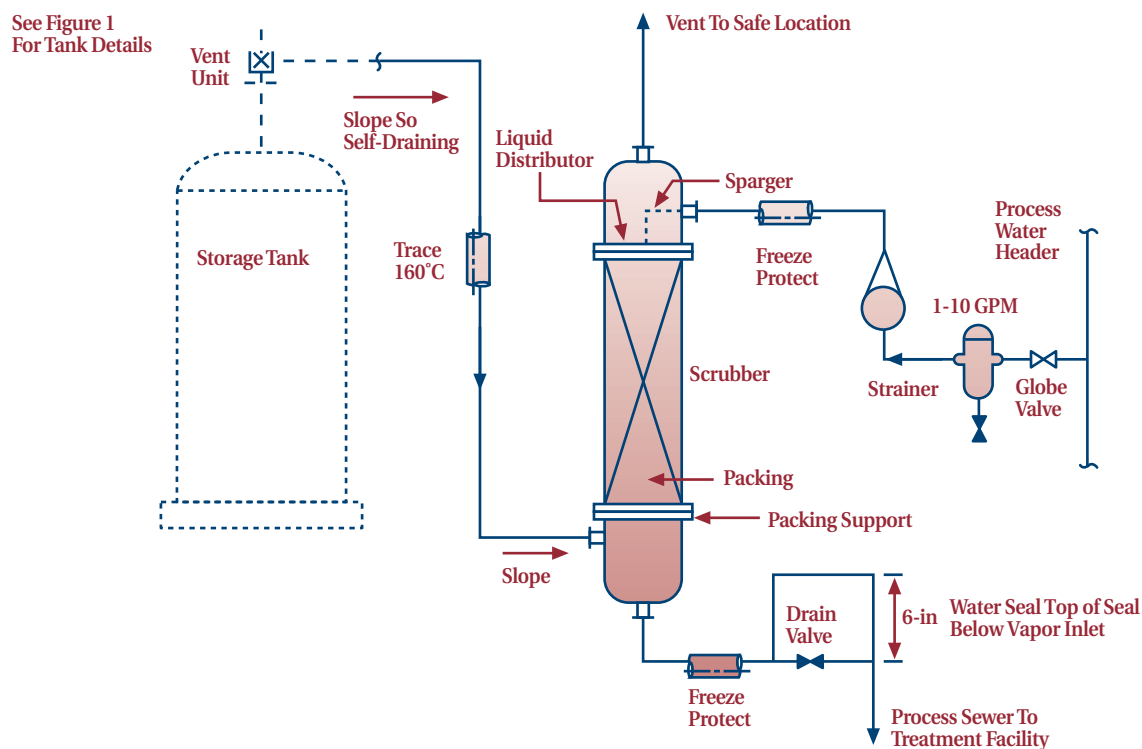
line, and vent line to hold 160°C to decompose amine carbamates in EDA, AEEA, and PIP service. Set pressure 3 oz/in<sup>2</sup> (tank MAWP). Sometimes a separate emergency vent is provided.

**Nitrogen Blanket** – Size to provide nitrogen makeup for worst case vacuum relief: typically, maximum pump-out rate in combination with sudden tank cooling (i.e., hailstorm). If N<sub>2</sub> use rate is excessive, then provide capacity for pump-out only and install a pressure/vacuum breather vent unit with air makeup under hailstorm conditions.

**Heating Coil** – Size based on utility conditions, storage tank size, tank insulation, and target tank temperature. Steam or hot water supply may be interlocked with tank level gauge to shut off heat when product level is below top of coil. (Not required for products stored at ambient temperature.)

**Line Tracing** – 15 psig steam, hot water system, or electrical to maintain desired temperature in pipelines to prevent freezing or limit product viscosity.

➤ **Figure 2** ..... **Vent Scrubber System**



### Typical Equipment Specifications

**Sizing Basis** – Up to 40 actual  $\text{ft}^3/\text{min}$  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/ $\text{in}^2$  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  $\text{ft}^3$ .

**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.

If tanks containing aqueous PIP, HEP, or other aqueous mixtures should freeze, then the product is likely to separate into different composition layers. The tank must be completely thawed and well mixed before transfer to a process.

Since tank heating will cause some product to vent, the tank should be equipped with a vapor conservation relief vent to avoid excessive vapor losses, while also avoiding exceeding the tank design pressure. Transfer lines are typically heated with hot water, low-pressure steam, or electric tracing. Both skin-effect and conventional electric tracing have been used successfully. The tracing system should be designed so that the inside pipe wall temperatures are no more than 30°C higher than the recommended storage temperatures under no-flow, line-empty conditions. This will ensure that the material remaining in the line will not degrade and cause quality problems with the next product transfer.

Aluminum is not often used for transfer lines since fabrication and welding difficulties normally make it more expensive than stainless steel.

➤ **Table 5 ... Storage Conditions**

	Freezing Point, °C	Typical Storage Temp., °C	Vapor Pressure at Storage Temp., mm Hg	Viscosity at Storage Temp., cP
EDA	11	35	24	1.3
DETA	-39	Ambient	<1	7
TETA	-35 <sup>(2)</sup>	Ambient	<0.01	26
TEPA	-46 <sup>(1)</sup>	40	<0.001	30
PEHA	-29 <sup>(1)</sup>	60	<0.001	20
HPA	-32 <sup>(1)</sup>	60	<0.001	35
PIP (68%) <sup>(2)</sup>	48	60	75	10
AEP	-17	Ambient	<0.1	15
AEEA	-45 <sup>(1)</sup>	30	<0.01	70
HEP <sup>(3)</sup>	50-60 <sup>(4)</sup>	80	200-250	11-13

(1) Pour point.

(2) Commercial product has 67-69 wt% PIP, balance H<sub>2</sub>O.

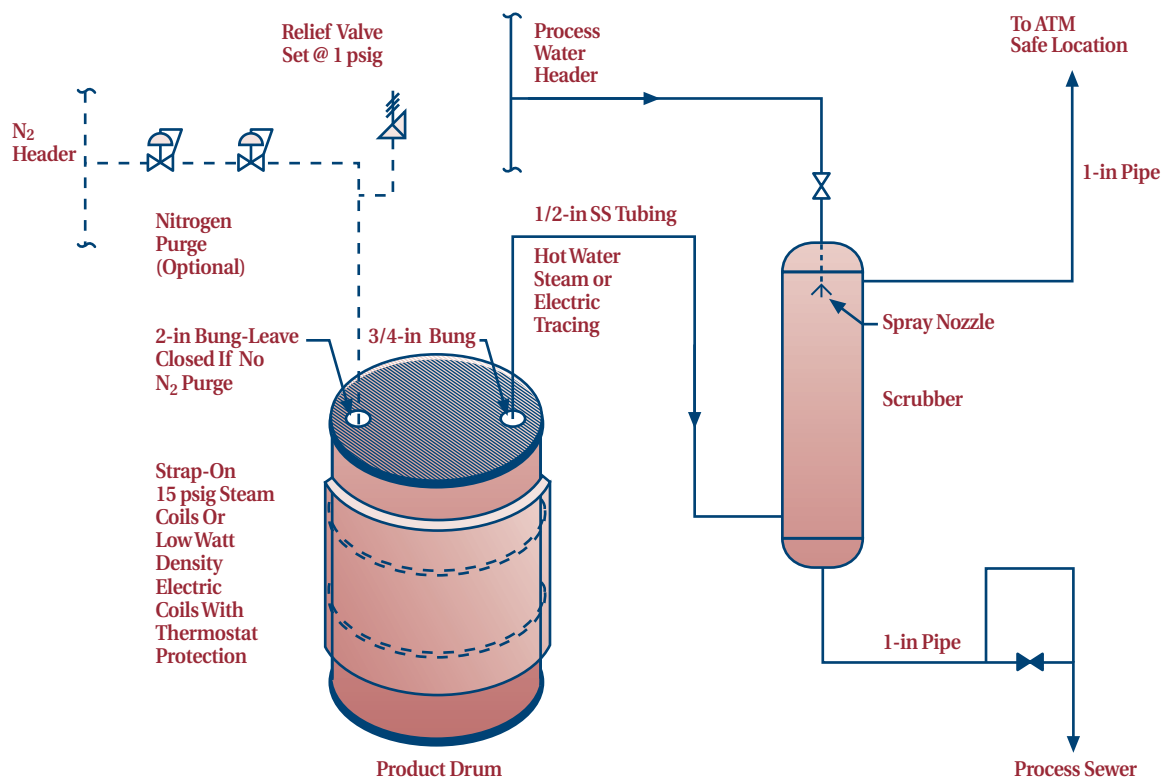
(3) Commercial product is an aqueous solution of 40-45 wt% HEP, 13-19 wt% PIP, 18-25 wt% H<sub>2</sub>O, and 18-23 wt% Dihydroxyethylpiperazine. Properties will vary somewhat, depending on composition.

(4) Exhibits supercooled behavior; can layer-out on freezing.

## Drum Thawing

Customers who receive drum shipments of ethyleneamines that are prone to freezing at ambient temperatures will occasionally need to thaw a drum. This is best done by storage in a “hot room” with a temperature 20 to 30°C above the freezing point. Alternatively, electric, low-pressure (15 psig) 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 open cup flash point (39°C) if heated somewhat above its freezing point (11°C). Drums must be vented to a safe location while heating to prevent pressure buildup. EDA, AEEA, PIP, and DETA may fume while being heated and should be be vented to a small scrubber. Figure 3 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 3** ..... **Drum Thawing**



### Typical Equipment Specifications

**Scrubber** – 4-in diameter, 3-ft long Schedule 40 steel pipe.

**Spray Nozzle** – Size for water supply pressure and 2 GPM full cone spray. Typical Specification: Schutte and Koerting Co. Fig 661-S nozzle, 3/8-in size, 3.0 mm orifice (if water is available at 40 psig) stainless steel construction.

This scrubbing system is to be used for EDA, AEEA, DETA, and PIP drum thawing.

## 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 is not recommended because of the high potential for personnel exposure. Closed sampling systems at ethyleneamine sample points are recommended. EDA is a Volatile Organic Chemical and the U.S. Environmental Protection Agency requires closed sampling systems or other provisions to minimize releases when sampling.

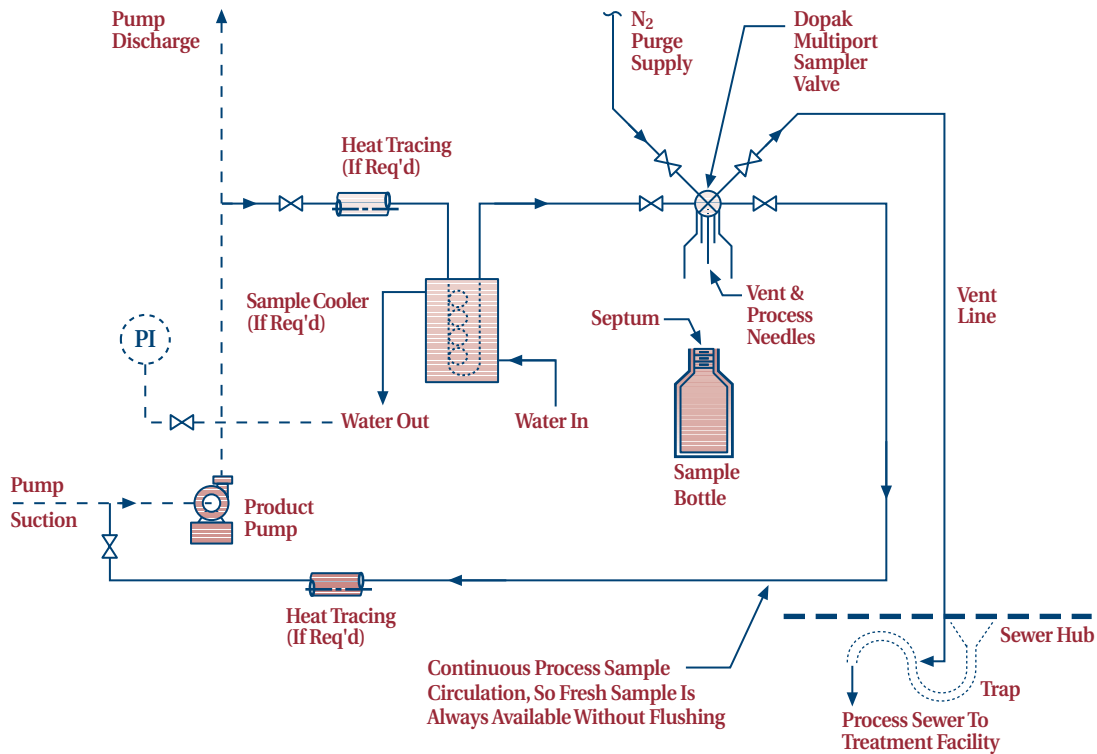
We use the Dopak sampling system (DOPAK, Inc., 666 Plainsboro Road, Plainsboro, NJ 08536-0748), which utilizes a sample bottle with an elastomer septum plug. The bottle is placed against a special valve assembly. Two hollow needles pierce the septum, one for a vent and the other for the sample. A valve with several positions is adjusted to purge the bottle with nitrogen; then the sample is charged while venting the displaced vapor to a safe place. After filling, the bottle is removed and the needle punctures in the septum reseal. In the laboratory, samples for analytical tests are drawn with a syringe, again by puncturing the septum, so that laboratory personnel are not exposed to the product. While still sealed, the bottle with any unused product sample can be disposed of in a safe manner.

Bottles with TFE-coated rubber septums have worked well in ethyleneamines service. Heated sample stations are recommended for EDA and PIP service because of their high freezing points.

Figure 4 (pg. 23), shows a typical sample arrangement. The process is set up to continuously flow through the sample point so that a current, fresh sample is always available. Nitrogen is supplied for purging, and a vent line (that also serves as a liquid overflow if the bottle is overfilled) is routed to a compatible process sewer hub. If necessary, the process lines may be traced to prevent freezing. Small sample coolers may be needed to sample hot process streams. Three-eighths inch stainless steel tubing works well for the sample and vent lines.

Sampling transportation equipment is difficult to do without some risk of exposure. The best procedure is to examine our product quality report; 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, such as that described above. Once the product is confirmed, unloading may commence.

➤ **Figure 4 ..... Closed Sampling System**



### Special Considerations

Several special considerations should be taken into account when handling ethyleneamines:

**Fuming Vents** - Ethyleneamine vapor vents will 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 heavier ethyleneamines can act similarly if heated to high enough temperatures. This smoke or haze can accentuate occupational health concerns because the solids tend to settle rather than disperse away from normal working levels. The carbamate may then be breathed into the lungs where it will be hydrolyzed back to the amine, causing symptoms identical to those which would be expected from the inhalation of the original amine. We recommend that all amine vents be routed to safe locations and vents that exhibit “smoking” be routed to water scrubbers, as described previously.



**Vent Fouling** - 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 overvacuum. Vent fouling can be reduced by using nitrogen blankets on storage tanks to prevent drawing air into tanks and thereby excluding atmospheric CO<sub>2</sub>. Also, vent units may be steam-traced to maintain 160°C, which causes the carbamates to decompose to CO<sub>2</sub> and the ethyleneamine, making fouling unlikely. From a practical standpoint, we have found that 4-in and larger vent units on large field storage tanks do not require tracing to prevent carbamate fouling if:

- The tank has a nitrogen blanket that excludes air entry under any operating conditions.
- The ethyleneamine does not freeze at the coldest ambient temperature.
- The ethyleneamine vapor pressure does not exceed 1 mm Hg at storage conditions.

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.

Any tank in ethyleneamine service that does not have a nitrogen blanket or 160°C tracing on the vent line is vulnerable to amine carbamate fouling of the vent. **Vents must be inspected!** Even the absence of fouling for several years is not a guarantee because the carbamate is very stable at ambient temperatures and can gradually accumulate and clog the line.

**EDA Storage at Flash Point** - EDA freezes at 11°C and has an open cup flash point of 39°C (103°F). Often storage tanks are set to hold temperatures at 20°C above the freezing point; as a result, typical storage temperature may approach or exceed the product's flash point. If the customer utilizes a nitrogen blanket on the tank and also routes the tank vent to a scrubber, then the potential hazard of EDA storage at its flash point is minimized.

**Color Buildup in Traced Pipelines** - When traced and insulated transfer lines are inactive, temperatures can become quite warm and discoloration may be observed in the product remaining in the line. This is due to the high surface-to-volume ratio of the pipe, but can be reduced by the following actions:

- Use only the heat required to keep the product liquid.
- Use stainless steel, preferably 316 stainless steel, for transfer line construction.
- Limit steam pressures to 15 psig or, preferably, utilize hot-water tracing or temperature-controlled traps.
- Blow lines clear with nitrogen after transfers when the lines will remain inactive for long periods.

Note that if lines are blown clear, some venting will inevitably result and possibly require or affect scrubber design. Do not use air to blow lines clear because the oxygen remaining in the line will rapidly discolor the film of product remaining, causing a color problem the next time the line is used and possibly enhancing corrosion of the line.

**Thermal Relief for Traced Lines** - 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. The safety valve is usually set at the line pressure rating.

We have also used metal bellows thermal expansion compensators (i.e., Magnilastic Hydropads, Flexicraft Industries Inc., 2315 Hubbard St., Chicago, IL 60612) 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.

As mentioned in the previous section, it is best to routinely clear traced lines when not flowing in order to prevent product quality degradation.

**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 (such as those in the Kamlok line of the Dover Corporation/OPW Division) that include a valve with the connection hub, so spill volume is small. 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 as described in the section on Product Handling (pg. 31) is essential.

**Nitrogen-Blanketing** - Under normal conditions ethyleneamines are considered to be thermally stable molecules. However, they are sufficiently reactive that upon exposure to adventitious water, carbon dioxide, nitrogen oxides, and oxygen, trace levels of byproducts can form and increased color usually results. As such, nitrogen-blanketing is recommended.

## Product Unloading

The transportation equipment we use 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.

### Unloading System

Figure 1 (pg. 18) shows how the tank transfer pump may also be utilized to unload the container if the pump is located close to the unloading spot. However, if the unloading spot is remote from the 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 can 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 eyebath 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. The pump is driven by a hydraulic or mechanical connection to the truck tractor engine. Your Dow representative can discuss this option.

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

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 psig) 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. EDA and PIP cars will fume while being thawed, and we recommend vent scrubbers for these cars, similar in design to the tank vent scrubbers.

PIP and HEP tanks 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 local and Federal regulatory agencies for mandatory spill containment measures that may apply. Drainage to a process sewer and some provision for flushing the unloading area with water are necessary.

After unloading, hoses are usually blown clear with nitrogen and the connections are broken. Some product will remain in the hose and some minor spillage is likely. Proper personnel protective equipment, discussed later, 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 from exposure to CO<sub>2</sub> in the air.

## Shipping Vessel Descriptions

**Tank Cars** - Tank cars for transfer of ethyleneamines are generally 20,000-U.S. gallon capacity and are constructed of either carbon steel or aluminum, 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 set for 75 psi on the carbon steel cars and 35 psi on the aluminum cars. Typically, these cars have a 4-in bottom outlet valve which is reduced to a 2-in screwed outlet connection. 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 offload 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 DOT 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** - 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 2- to 4-in bottom screwed or flanged outlet, an approximately 18-in diameter top manway, and an approximately 1.5-in screwed or flanged nitrogen gas inlet. Most portable tanks use metric standard fittings. Adapters to ANSI flanges or US NPT threaded connections will be required.

### General Unloading Procedures

The following procedure is a good general guideline for unloading ethyleneamines from tank cars, tank trucks, and portable tanks.

Specific operating procedures should be developed to deal with the particular unloading hardware and site conditions. All Department of Transportation (DOT) requirements must be followed for unloading.

1. Obtain necessary personal protective equipment, including (at least) coverall eye goggles 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 (see Vent Scrubbers, pg. 17, and Figure 2, pg. 19); crack the dome lid or open the vent for other products; connect low-pressure steam or hot water to the coils. 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 which 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. 22-23, and Figure 4, pg. 23). 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 Department of Transportation regulations.
  12. Remove chocks and blue flag. Derailed and release the vessel.
-

## Product Handling

### Personal Protective Equipment

Impervious gloves are required for the safe handling of all ethyleneamines. Consult the Material Safety Data Sheets for more information.

Emergency Eye Bath and Safety Showers should be located near work sites where exposure to the product is likely. These areas would include unloading locations, hose connection switching stations, and near processing equipment, among others. Procedures should require coverall eye goggles and gloves when undertaking operations that could result in a spill or vapor emission, such as breaking a hose connection.

Since we strive to eliminate personnel exposure to ethyleneamines, we utilize well-ventilated workplaces and very low emission processes as opposed to accepting situations that require breathing apparatus for employees. Face masks with cannisters are not used by our employees since there is no method of detecting when the absorbent is saturated. Where conditions preclude low vapor concentrations, only full-face, fresh-air-supplied masks are used for employees who must enter the area.

To restrict employee exposure to the product, only closed processing equipment is suitable for ethyleneamine handling. Open vats or tanks are not employed. High ventilation rates and segregation of personnel from the equipment are necessary for container filling operations. Operations such as manually dumping filters should be conducted only after the equipment is well washed with water. As previously mentioned, in order to avoid a pressure buildup, drum thawing must be done only when the drum is vented.

Contaminated gloves and other clothing should be properly disposed of, consistent with local regulations. Such gloves and clothing should not be taken home. Clothes which are reusable should be laundered and stored separately from street clothing.

### Industrial Hygiene Air Monitoring

Dow has developed two methods to be used by qualified Industrial Hygiene personnel for monitoring workplace exposure to ethylenediamine. Both methods collect and detect ethylenediamine and the carbamates formed when ethylenediamine reacts with carbon dioxide in the workplace environment. The methods may also be used to monitor for other ethyleneamines and their carbamates.



### Firefighting

For large fires, alcohol-type or all-purpose-type foams should be applied according to the manufacturer's recommended techniques. CO<sub>2</sub> 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.

### 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 should 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 should 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 waste water must be disposed of in a manner complying with local and Federal regulations.

## Environmental Considerations

Ethyleneamines are water-soluble and may be initially resistant to biodegradation in a biological waste treatment plant. Biological waste treatment facilities can handle significant waste water loadings once they are acclimated to the product. Cyclic ethyleneamines, such as PIP and AEP, and heavy ethyleneamines, such as HPA, are less readily degraded. Sudden loadings to a nonacclimated waste treatment biomass should be avoided.

Ethyleneamines in waste water 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. It is best to flush the spill to a process sewer with copious amounts of water. Alternatively, dry absorbents may be used to soak up most of the spill. 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). 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.

Empty ethyleneamine drums should be triple-washed with water, resealed, and all labels should be removed. Drums may then be offered for recycling, reconditioning, or crushing and disposal in accordance with federal and state regulations.

EDA has a high enough vapor pressure to be classified as a Volatile Organic Chemical; hence, it is subject to the U.S. Environmental Protection Agency regulations for equipment design in the Synthetic Organic Chemicals Manufacturing Industry (40CFR Part 60 Subpart VV). Among the specific requirements are:

- Pump design provisions to minimize seal leakage (e.g., dual seals, canned pumps, magnetic drives, etc.).
- Closed sampling systems.
- Routine monitoring for leaks for equipment and piping components.

Users of EDA should review the specific regulations as they apply to storage and handling systems to assure legal compliance.

## Product Safety

When considering the use of any Dow products in a particular application, you should review our 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 Dow representative. 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.

Dow requests that the customer read, understand, and comply with the information contained in this publication and the current Material Safety Data Sheet(s). The customer should 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 comply with this information.

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