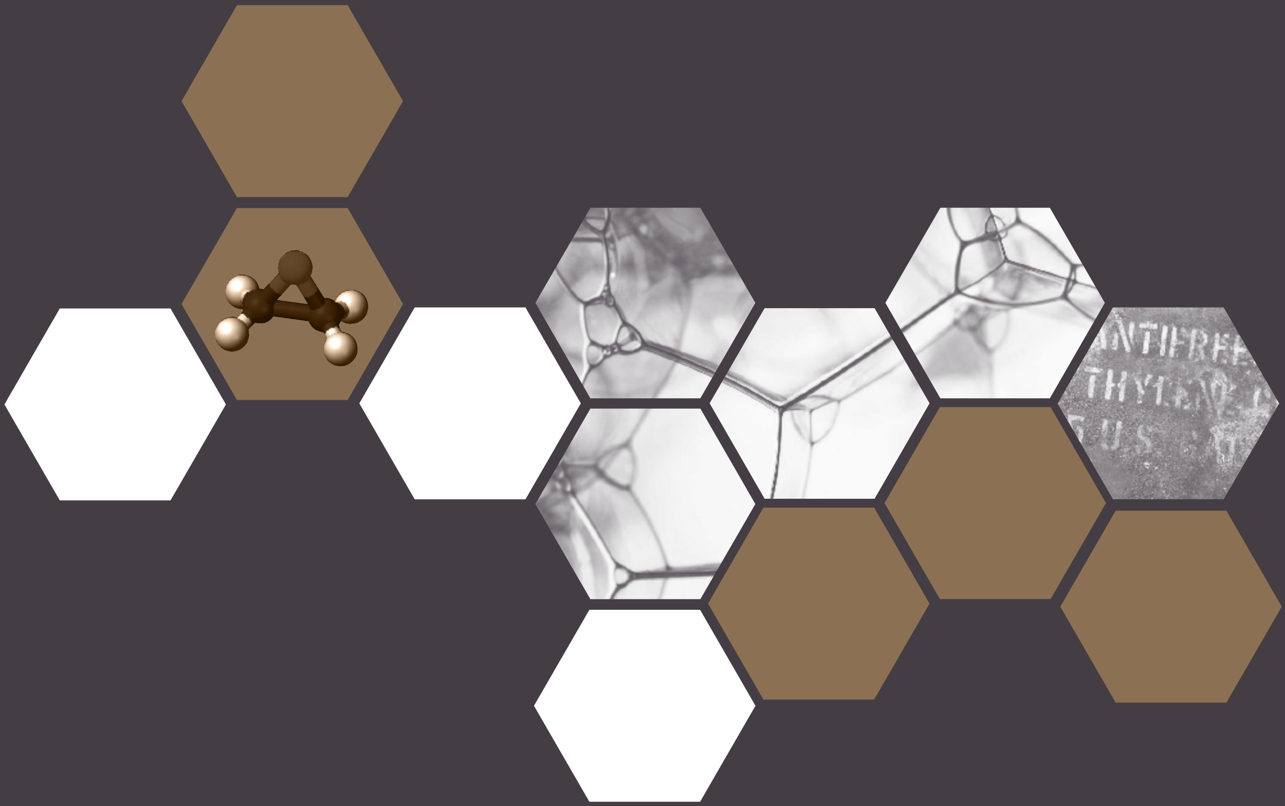
ethyleneoxide

third edition



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To the Reader

Manual Preparation

As members and affiliated companies of the American Chemistry Council, we support efforts to improve the industry's responsible management of chemicals. To assist in this effort, the American Chemistry Council's Ethylene Oxide/Ethylene Glycols Panel supported the creation and publication of this manual. The Panel is comprised of the following companies:

Balchem Corporation/ARC Specialty Products

BASF Corporation

Bayer Material Science LLC

Celanese Ltd.

Champion Technologies

Croda, Inc.

The Dow Chemical Company

Eastman Chemical Company

Honeywell

Shell Chemical LP

The development of this manual was led by the Panel's Ethylene Oxide Safety Task Group (EOSTG), a group comprised of producers and users of ethylene oxide. The EOSTG functions to generate, collect, evaluate and share information to support product stewardship with regard to ethylene oxide. The EOSTG formed a manual work group, chaired by Keith Vogel of Lyondell Chemical Company, to lead the development of this document. The following work group members provided significant contributions:

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Many others contributed to the development and editing of this manual, all of whom cannot be listed here; however, the manual work group would like to thank the following individuals for their significant contributions to this publication:

Ralph Gingell	Shell Chemical LP
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Karl Loos	Shell Chemical LP
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1.0 Introduction

1.1 Purpose and Use of Manual

This manual has been developed for use by producers and industrial users of ethylene oxide. The purpose of this product stewardship document is to provide the reader with a better understanding of how ethylene oxide is used to produce products that play important roles in our lives. It is also our intent to address the health, safety and environmental aspects associated with manufacturing, distributing, using and disposing of ethylene oxide and the bulk of the material presented emphasizes these topics.

This information is provided as a resource in the development of producers' and users' design, operation, maintenance, training and emergency response practices. References to applicable regulations, industry practices are made in tables and text. Contact your supplier for further information as necessary.

Note that a separate, independent group of ethylene oxide producers previously produced two editions of an ethylene oxide guidance manual: Ethylene Oxide User's Guide, First (1995) and Second (1999) Editions. It is the intention of those producers that this manual supercedes the Ethylene Oxide User's Guide, First and Second Editions.

Manual Availability and Updates

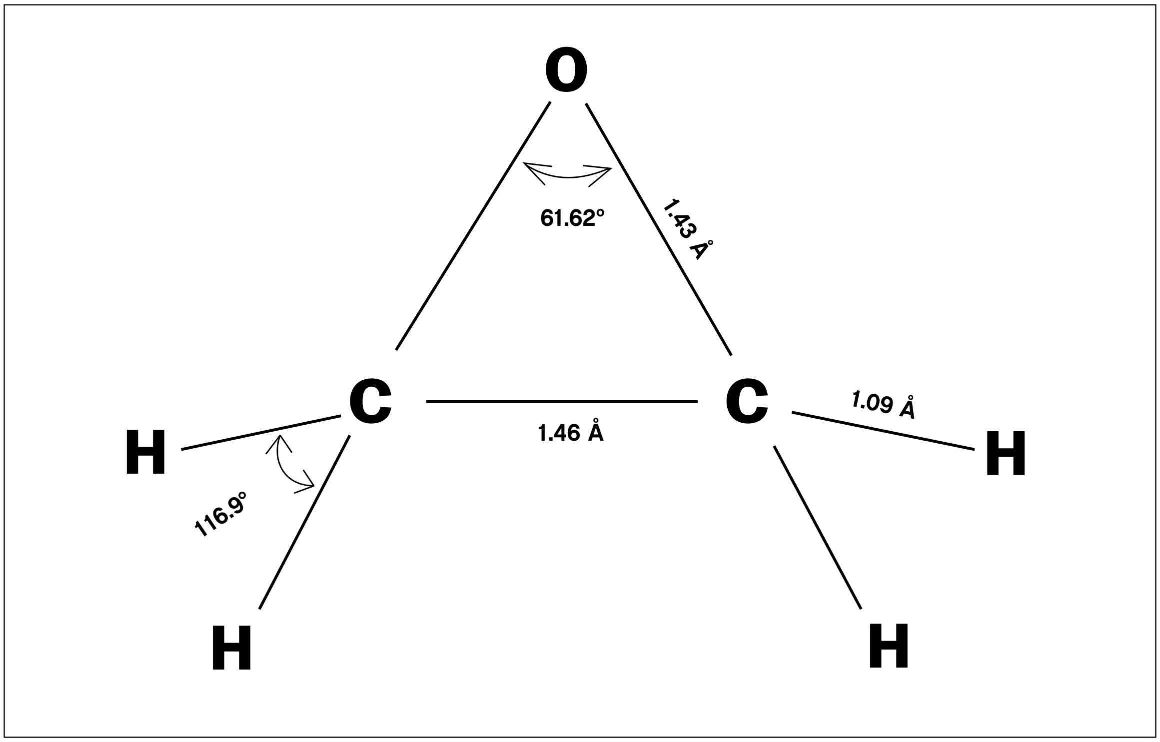
This document is available through your supplier in hard copy and is available on a password-protected Web site hosted by the Panel at **www.ethyleneoxide.com**. This document may be updated. Interim updates may occur on the Web site posting of this document only. Readers should consult the Web site for the most recent version of this manual. Readers should also stay abreast of new developments and information about ethylene oxide, including but not limited to physical properties, handling technology, and regulatory requirements that occur after the date of publication of this document.

Contact your supplier to obtain the most current version of this manual, if you have questions or to get more information about any information presented in this document. We encourage comments on the content of this document and a more in-depth dialogue concerning the issues presented.

2.0 Properties of Ethylene Oxide

2.1 Introduction

Figure 2.1 The Ethylene Oxide Molecule



Ethylene Oxide (EO), sometimes referred to as oxirane, is the simplest cyclic ether. It is a colorless gas or liquid and has a sweet, etheric odor. The structure of an EO molecule is shown in Figure 2.1 above. The C-C bond is short and the bond angles strained [1]. Because its highly strained ring can be opened easily, EO is highly reactive.

EO was first prepared in 1859 by Wurtz [2] using potassium hydroxide solution to eliminate hydrochloric acid from ethylene chlorohydrin. The chlorohydrin process developed from Wurtz's discovery and industrial production of EO began in 1914. The direct catalytic oxidation of ethylene, discovered in 1931 by Lefort [3], has gradually superseded the chlorohydrin process. Currently, EO is produced by direct oxidation of ethylene with air or oxygen.

Virtually all EO produced is further reacted (Section 2.4) to derivative products. Its most important derivative is ethylene glycol, which is used for the manufacture of polyester and in automotive antifreeze. Other EO derivatives include surfactants, solvents, amines and poly(ethylene) glycols. EO also has several direct uses, including use as a sterilant and the treatment of spices and other foodstuffs. United States production of EO in 2004 was 8,315 million (8.3 billion) pounds, according to National Petrochemical & Refiners Association's (NPRA) Petrochemical Surveys 4 Quarter 2003 (published January 27, 2005), highlighting its role as an important industrial chemical.

The highly reactive nature of EO, which helps make it a versatile and commercially important chemical intermediate, also underlies some of the main hazards of EO – in particular, its flammability, reactivity, explosive vapor decomposability and toxicity. Understanding the properties of EO is important to managing its use.

2.2 Physical Properties

Important physical properties of EO are summarized in Table 2.1, below.

Table 2.1 Physical Properties of Ethylene Oxide

Ethylene Oxide		
Chemical Abstracts Name:	Oxirane	
Chemical Abstracts Number:	75-21-8	
PSUID Code:	1441	
UN CODE:	1040	
IUPAC Name:	Oxirane	
Synonyms:	Ethylene Oxide	1,2-Epoxyethane
	Dihydrooxirene	Oxacyclopropane
	Dimethylene Oxide	Oxidoethane
	Epoxyethane	EO, ETO
Other Names: Ethene oxide; Oxane; Oxirene, Dihydro-; Oxyfume; Oxyfume 12; T-Gas; Aethylenoxid; Amprolene; Anprolene; Anproline; ENT-26263; E.O.; 1,2-Epoxyaethan; Ethox; Ethyleenoxide; Etylenu tlenek; FEMA No. 2433; Merpol; NCI-C50088; a,b-Oxidoethane; Oxiraan; Oxiran; RCRA waste number U115; Sterilizing gas ethylene oxide 100%; C2H4O [37]		
Structural Formula:	CH_2OCH_2	

Property	SI Units	Engineering Units	Note(s)/ [References]
Molecular Weight	44.053	44.053	
Critical Temperature	469.15°K	384.8°F	
Critical Pressure	7,191 kPa	1,043 psia	
Critical Volume	0.00319 cu m/kg	0.051 cu ft/lb	
Critical Compression Factor	0.2588	0.2588	AIChe DIPPR (r) Database
Melting Point	160.65°K	-170.5°F	
Triple Point Temperature	161.46°K	-169.1°F	1
Triple Point Pressure	0.0078 kPa	0.00113 psia	
Normal Boiling Point at 101.325kPa (1atm)	283.6°K	50.8°F	AIChe DIPPR (r) Database
Liq. Sp. Gr. 20°C/20°C (68°F/(68°F)	0.875	0.875	
Liq. Volume @ 25°C (77°F)	0.00113 cu m/kg	0.018 cu ft/lb	2
Coefficient of Cubical Expansion, at 20°C (68°F)	0.00158/°K	0.00088/°F	[37]
Heat of Vaporization	579.5 kJ/kg	249.2 BTU/lb	
Entropy of Vaporization	2.04 kJ/kg*°K	0.488 BTU/lb*°F	[37]
Heat of Formation – Ideal Gas	-1,194.8 kJ/kg	-514 BTU/lb	[37, 58, 59]
Heat of Formation – Liquid	-1766.5 kJ/kg	-760 BTU/lb	[59]
Gibbs Energy of Formation – Ideal Gas	-300.3 kJ/kg	-129.15 BTU/lb	4
Gibbs Energy of Formation – Liquid	-267 kJ/kg	-115 BTU/lb	3
Absolute Entropy – Ideal Gas	5.52 kJ/kg*°K	1.319 BTU/lb*°F	[37, 59]
Absolute Entropy - Liquid	3.494 kJ/kg*°K	0.835 BTU/lb*°F	3 [59]
Heat of Fusion at Melting Point	117.5 kJ/kg	50.52 BTU/lb	[37]

(continued on page 4)

Table 2.1 *(continued from page 13)*

Property	SI Units	Engineering Units	Note(s)/ [References]
Entropy of Fusion	0.73 kJ/kg*°K	0.175 BTU/lb*°F	[36]
Standard Heat of Combustion, Liquid HHC (HHV) (to water condensed)	-29,076 kJ/kg	-12,509 BTU/lb	5
Standard Heat of Combustion, Gas LHC (LHV) (to water as vapor)	-27,649 kJ/kg	-11,895 BTU/lb	5
Standard Heat of Combustion, Gas HHC (HHV) (to water condensed)	-29,647 kJ/kg	-12,755 BTU/lb	5
Heat of Solution in Water	-142.7 kJ/kg	-61.35 BTU/lb	
Acentric Factor	0.197	0.197	
Radius of Gyration	1.937E-10 m	6.355E-10 ft	
Dipole Moment	6.3E-30 C*m	1.889 Debye	
Liq Dielectric Const at 0°C (32°F)	14.5	14.5	
Vapor Dielectric Const at 15°C (54.5°F)	1.01	1.01	[10]
Electrical Conductivity (liq)	4E-06 Siemens/m	4E-08 mhos/cm	
van der Waals Volume	5.485E-04 cu m/kg	0.008785 cu ft/lb	
van der Waals Area	7.492E+06 m sq/kg	3.658E+07 ft sq/lb	
Refractive Index, n_D at 6.8°C (44.3°F)	1.3597	1.3597	
Flash Point	<255.16°K	<0°F	
Flammability Limits	2.6-100 vol.%	2.6-100 vol.%	
Fundamental Burning Velocity, Pure EO	0.027m/s	0.089 ft/s	[58]
Autoignition Temp (in Air)	718.15°K	833°F	[60]
Decomposition Temp (at 760 mm Hg)	~773°K	~932°F	6, [17]

NOTES:
1. Estimated to be equal to the melting point temperature.
2. Determined at the normal boiling point.
3. Estimated from CRC 1994 Handbook of Thermophysical and Thermochemical Data.
4. Calculated from the enthalpy of formation and the absolute entropy.
5. Calculated from heats of formation.
6. Decomposition temperature affected by pressure, container surfaces, volume, and geometry. Decomposition temperature has been reported as low as 842°F (723.2°K) and as high as 1060°F (844°K)

WARNING: FLAMMABILITY LIMITS ARE DETERMINED AT 77°F (298°K) AND 1 ATMOSPHERE. HIGHER TEMPERATURES AND/OR HIGHER PRESSURES WILL LOWER THE LOWER LIMIT.

Graphs and tables of selected temperature-dependent properties of EO are provided in Appendix A.

Ethylene Oxide Water Mixtures

Table 2.2 on the next page shows some of the properties of aqueous EO solutions. Of particular note are the relatively high melting points, which are due to hydrate formation [4]. Hydrates consist of organic molecules enclosed by water molecules in a cage structure. The highest melting point observed is 52°F (11.1°C) and corresponds to a hydrate composition of $C_2H_4O \cdot 6.89\ H_2O$ [5].

Liquid EO and water are completely miscible in each other in all proportions, but due to differences in density, may not initially mix in the absence

Table 2.2 Physical Properties of Aqueous Ethylene Oxide Solutions [9,10]

EO Content wt%	Melting Point °F (°C)	Bubble Point °F (°C)	SG at 50/50°F (10/10°C) Flash Point	°F (°C)
0	32 (0)	212 (100)	1.0000	
0.5				107 (41.5)
1	31.3 (-0.4)			88 (31)
2				37 (3)
3	29.7 (-1.3)			
5	29.1 (-1.6)	136.4 (58)	0.9977	28 (–2)
10	42.1 (5.6)	108.5 (42.5)	0.9944	
20	50.7 (10.4)	89.6 (32)	0.9816	-6 (-21)
30	52 (11.1) max	80.6 (27)	0.9658	-18 (-28)
40	50.7 (10.4)	69.8 (21)	0.9500	-31 (-35)
60	46 (7.8)	60.8 (16)	0.9227	-49 (-45)
80	38.7 (3.7)	55.4 (13)	0.9005	-63 (-53)
100	-169 (-111.7)	50.7 (10.4)	0.8828	-71 (-57)

of any agitation (i.e., it is possible to have two separate phases if one is added beneath the surface of the other without mixing). EO/water mixtures are highly non-ideal and do not follow Raoult's Law. Raoult's Law deviation factors for EO/water mixtures are shown in figures 14 and 15 in Appendix A.

Solubility of Ethylene Oxide Gas

The solubility of EO gas in various compounds has been measured and reported at atmospheric pressure and 72–74°F (22–23°C) by Chaigneau [41]. These compounds include water, alcohols, hydrocarbons, oils, chlorocompounds, esters and waxes.

Solubility of Gases in Ethylene Oxide

The solubility of gases in liquid EO vary, increasing in the order nitrogen, argon, methane and ethane. Increasing temperature tends to increase the solubility. The Henry's Law Constants for these gases in EO at different temperatures are given in Appendix A [7].

2.3 Reactive and Combustive Properties

Understanding the reactivity and combustion properties of EO is important to managing its use. As described in Chapter 5, serious incidents have occurred during the processing, storage, and transportation of ethylene oxide.

Combustion/Flammability

EO is a flammable, explosible chemical. Its fire and explosion characteristics are system-dependent. Some of the characteristics for EO/air mixtures are as follows.

- The minimum value cited for the lower flammable limit of EO air mixtures is 2.6% [20].
- The upper flammable limit is typically stated to be 100% because pure EO can violently decompose with a significant release of heat in the absence of air or oxygen.
- Accordingly, the flammable range of EO-air mixtures is 2.6–100%.

Table 2.3 Heat of Reaction of Various Ethylene Oxide Reactions at 25°C

	kJ/kg	BTU/lb	Note [Reference]
Combustion			
Liquid HHC (to water condensed)	-29,076	-12,509	1
Gas LHC (to water as vapor)	-27,649	-11,895	1
Gas HHC (to water condensed)	-29,647	-12,755	1
Decomposition	-3,051 -3,013	-1,312 -1,296 (calc from gas heats of formation)	[59]
Isomerization to acetaldehyde	-2,621	-1,127	
Polymerization	-2,324	-1,000	[13, 17]
Hydrolysis	-2064	-887	[46]

NOTE:
1. Calculated from heats of formation.

- The autoignition temperature of EO in air at 14.7 psia is 833°F (445°C) [21].

This temperature can be lower with the presence of certain impurities such as water, acetaldehyde, and rust.

Figures 2.2 and 2.3 illustrate the flammable limits for EO, air and either nitrogen or carbon dioxide ternary mixtures at atmospheric (14.7 psia) pressure (101.325kPa) [39]. The literature also indicates some variability in the boundary concentration demarcation separating the flammable and non-flammable regions. [38, 39, 59]. Also, it is important to recognize that mixture pressure also affects the flammability characteristics. Figure 2.4 illustrates the effects of pressure on the flammability region for EO/Nitrogen/Air. Thus, more or less dilution with an inerting gas may be required to maintain a non-flammable condition depending on whether the pressure is greater or less than atmospheric pressure.

The flammable limits of other mixtures of EO with various gases and air can be found in the literature. See Appendix D for examples: EO with H_20 [22]; N_2 [23], [22]; N_2-H_20 [24]; $C0_2$-H_20 [24]; CH_4 [15]; $C0_2$ [6], [22], [25]; C_3H_6 [26]; C_4H_9 [26]; N_2-air [6]; CH_4-air [6]; CO_2-air [20]; CF_2Cl_2-air [27], [28]; CO_2-air, N_2-air, R12-air, R134a-air [39]; CO_2-air, N_2-air, Steam-air [24]; MeBr-air [24].

Flammability of Ethylene Oxide and Water Mixtures

Due to the flash characteristics of EO/water mixtures, it can be difficult to extinguish fires of these liquid mixtures until the EO reaches a certain dilution. In closed systems such as sewers, 100 to 1 water to EO dilution ratios (vol/vol) may be required to produce a mixture, the vapor of which will not support combustion. In open systems, such as around an atmospheric spill, water/EO mixtures of less than 22 to 1 (vol/vol) can generate sufficient vapors to support combustion.

Ignition Energy and Static Electricity

Liquid EO is an electrically conductive fluid that cannot accumulate static electricity charges in metal containers having internal parts properly bonded and grounded (see NFPA 77 Static Electricity Guide). Bottom filling is therefore generally not needed unless there are isolated internal areas that might accumulate a charge. If containers have non-conductive linings, such as glass or plastic, use of an uncoated grounded metal device in contact with the contained liquid at all times provides effective grounding of the liquid.

At standard conditions and in the absence of air, pure EO vapor minimum ignition energy (MIE) is about 1000 mJ [9]. While this minimum EO ignition

Figure 2.2 Flammable Region of Ethylene Oxide/Nitrogen/Air Mixtures

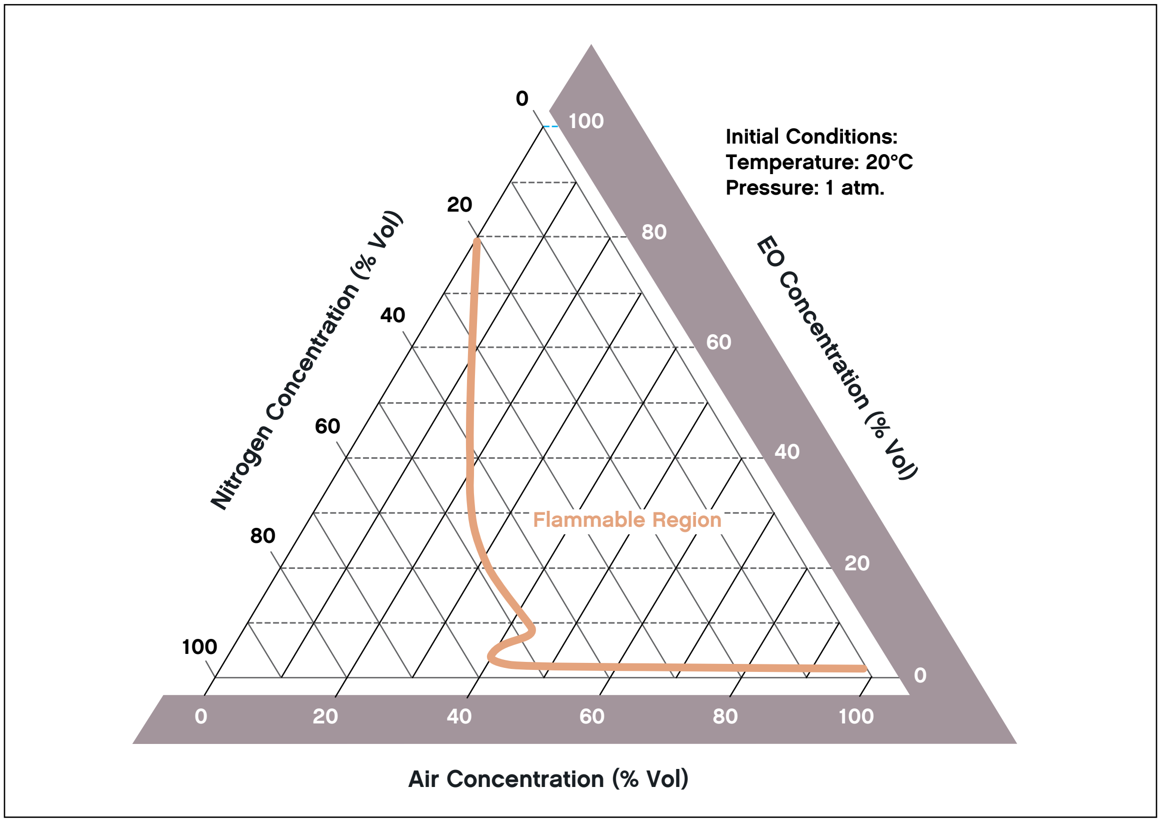


Figure 2.3 Flammable Region of Ethylene Oxide/Carbon Dioxide/Air Mixtures

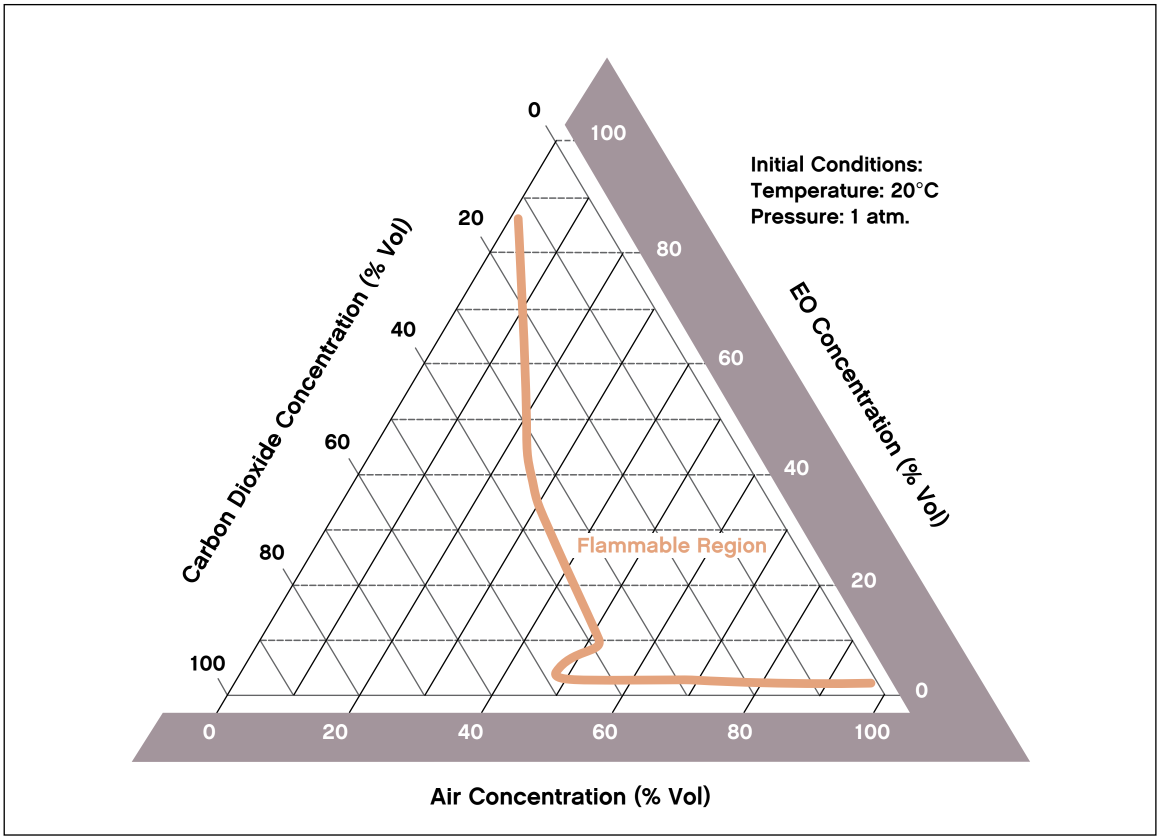
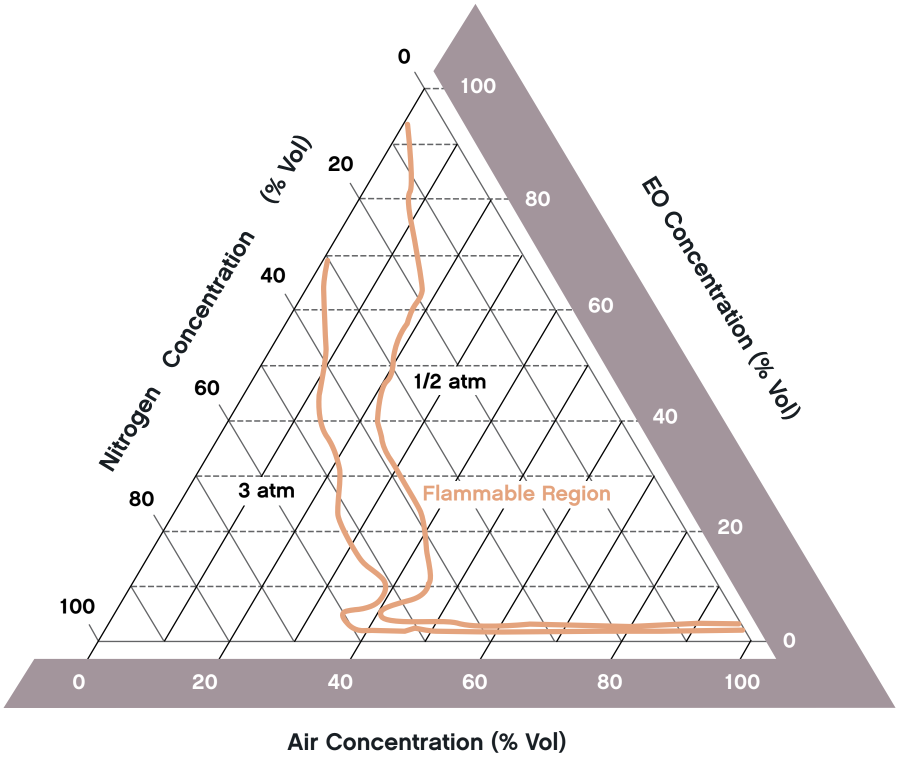


Figure 2.4 Effects of Pressure on Flammable Region of Ethylene Oxide/Nitrogen/Air Mixtures



energy decreases with increased temperature and pressure, a static energy discharge is much lower than the MIE and is not a significant hazard under normal liquid storage and handling conditions. EO liquid discharged into the vapor space of a properly inerted storage tank in the absence of oxygen will not carry sufficient energy to ignite the vapor.

At standard conditions and in the presence of air, the MIE of EO is in the range of 10,000–100,000 mJ at just above the lower flammable limit (2.6 mol%) and is about 1000 mJ at the upper flammable limit (100 mol%) [58]. However, between these upper and lower flammable limits, the ignition energy follows a “skewed parabolic” contour with changes in composition that reaches a minimum value of 0.06 mJ at about 10.4 mol%. Comparing minimum ignition energies, EO in air at these concentrations has a minimum ignition energy less than gasoline vapor (0.24mJ), and only somewhat greater than hydrogen (0.01-0.02mJ). (Routine movement of a person can typically initiate static discharge energy in the range of 1-50 mJ, while the energy from ordinary spark plugs is ca. 20-30 mJ [31]. Note that people cannot usually feel sparks carrying less than about 2 mJ.) Thus, various mixtures of EO vapor and air can be easily ignited by a static spark, even by the low discharge levels that might be generated by a person. EO in air also has a much wider flammability range (2.6-100%) than either gasoline (1.4-7.6%) or hydrogen (4.0-75%). Consequently, static discharge is a very important consideration in the design and operation of equipment. See Eichel [32] for a discussion of electrostatic calculations.

The NFPA 77 Static Electricity Guide provides guidance for bonding and grounding equipment in EO service. In general, the NFPA Guide provides that flanged connections do not need external bonding wires, but that users should consider using external bonding wires where electrical continuity might appear questionable (for example, where specially coated bolting materials are in use, in areas near swivel joints, or if a non-conductive item of equipment is placed in a line). For static grounding, the NFPA Guide notes that all metal parts should have a resistance to ground of 1M Ω or less.

To minimize the potential for static buildup, samples or small quantities of EO are generally obtained using grounded metal portable containers with conductive linings. Use of non-conductive plastic bottles and pails should be performed only with great caution. If circumstances, such as laboratory settings, necessitate their use, the container should be bottom filled (submerged) using a grounded conductive dip tube resting on the bottom of the container to minimize splashing and turbulence. Where a transparent sample container is required (such as for clarity inspection), use of a glass container helps minimize static charge buildup. Avoid rubbing or cleaning the container immediately prior to filling or emptying as another means of avoiding buildup of static charge. (See Section 6.9 for further discussion of sample system design.)

Decomposition

Pure EO vapor or EO vapor mixed with air or an insufficient amount of inert gases can decompose explosively. The primary decomposition reaction is expressed by the following equation:

$$\text{EO } (C_2H_4O) \rightarrow CO + CH_4 + 1312 \text{ BTU/lb}$$

The reaction can also produce ethane, ethylene, hydrogen, carbon and acetaldehyde [10, 17].

At atmospheric pressure, thermal decomposition of pure EO vapor occurs at 932°F (500°C) [17]. Both lower and higher gaseous EO decomposition temperatures have been reported – indicating that decomposition temperature is affected by pressure, surface characteristics, volume and geometry. EO can also ignite and decompose explosively below atmospheric pressures, down to a pressure of around 4.8-5.8 psia, but at greater than 932°F (500°C).

Once the decomposition reaction has been initiated, it can be propagated from the ignition source through the gas phase as a flame (i.e., reaction zone) and, under certain conditions, may be explosive. It is important to understand that this reaction can occur in the absence of air or oxygen. (Note that a number of sources consider a flame a region of combustion, whereas combustion is defined as the oxidation of a fuel source.)

High pressure can be generated by decomposition of EO. The maximum theoretical explosive pressure is about 10 times the initial pressure but this can increase to 20 times the initial pressure if liquid EO is present. This phenomenon occurs because liquid EO evaporates and participates in the decomposition reactions which take place in the vapor phase [15].

EO liquid mists will decompose explosively similarly to EO vapor. The decomposition of these two-phase mixtures yields greater pressures and rates of pressure rise than the vapor alone [17]. Liquid EO can participate in a decomposition that starts in the vapor phase. Explosion of liquid EO, initiated by a strong ignition source within the liquid, was first described in 1980. It is thought that the ignition source vaporizes liquid EO and the decomposition reaction takes place in the gas phase.

It has been reported in the literature that pure EO vapor, when ignited in a closed-end system, can undergo a transition from decomposition flame to a detonation shock wave with a propagation speed of approximately 1 mile (1,600 meters) per second [47]. This phenomenon, which destroyed a 12-inch (0.3 meter) pipe test apparatus, can generate overpressures that are orders of magnitude greater than the maximum theoretical overpressure. The progression of a decomposition flame front to a detonation shock wave can result in a highly destructive event. The literature cited above concluded that certain specific conditions of equipment size, pressure, and temperature were necessary for a deflagration to transition to a detonation. See Chapter 5 for more information and illustrative incidents.

Mixtures of EO with nitrogen, carbon dioxide and methane will not decompose over certain concentration ranges; thus, the risk of vapor decomposition can be minimized by dilution with a suitable inert gas. Nitrogen is most commonly used for dilution, although other inert gases and methane have been used on occasion. Note that carbon dioxide is not typically used as a dilutent due to its high solubility in EO. The dilution quantity depends on temperature, pressure and the expected ignition source and duration [9]. The most thorough discussion of the EO decomposition process is presented in Reference [17]. The minimum total pressure for inert blanketing is important [9, 10], and Section 6.5 presents information relevant to the inerting of EO in storage and handling systems. Chapter 9 provides information concerning the inerting of transportation containers. Inerting of vapor spaces of reactors using EO as feeds or reagents is discussed in Section 6.6.

Deflagration and Detonation of Ethylene Oxide in Piping

Unpublished work by Union Carbide performed in 1956 provided some information on the topic of EO vapor decomposition flame propagation, suggesting that at pressures up to 75 psia, EO decomposition flames would not be expected to propagate indefinitely through vented, horizontal pipe with a diameter of less than 2 inches.

In the late 1990s, the American Chemistry Council's Ethylene Oxide Industry Council (now the Ethylene Oxide/Ethylene Glycols Panel), sponsored work to revisit earlier Union Carbide data and to obtain specific information in two areas: (1) decomposition flame speeds and the extent of flame propagation in long lengths of 2-inch diameter pipe containing pure EO vapor; and (2) maximum flame speeds in long lengths of 12-inch pipe containing pure EO vapor.

This work was completed and results published in 2001[47]. The study showed:

- Indefinite propagation of a slow deflagration flame can occur in 2-inch pipe under certain handling conditions. Flames may fail to propagate under adverse flow conditions or if the flame is forced to propagate downward; however, 2-inch pipe cannot be considered a barrier to indefinite flame propagation.
- A decomposition flame can accelerate from a deflagration to a detonation in 12-inch pipe. Results of the study observed the decomposition flame velocity to have exceeded 3900 ft/sec (1200 meters/sec), but the authors noted that, due to study limitations, the flame front velocity was likely to have been substantially higher at the far end of the pipe. The transition from deflagration to detonation has the potential to create significantly higher pressures than if a direct detonation occurred.

Ethylene Oxide Disproportionation Reactions

Investigation of a major industrial incident that occurred in a North American EO manufacturing facility during the 1990s indicated that EO vapor in contact with high surface area metal oxides, such as the gamma form (Fe_2O_3) of iron oxide, can undergo disproportionation reactions that can raise local temperatures above the decomposition temperature of EO.

In this particular incident the disproportionation reaction occurred within the tubes of a distillation column reboiler, in the presence of a deposit of high surface area rust embedded in an EO polymer matrix, when flow through the reboiler was reduced by a process upset. The loss of reboiler circulation allowed for rapid heat buildup in the vicinity of the iron oxide/polymer deposit, accelerating the disproportionation reactions which then progressed into localized temperatures reaching the EO thermal decomposition temperature. The result was an explosion that destroyed the distillation column [42].

A similar incident occurred at a Gulf Coast EO manufacturing facility in 2000 [43], resulting in internal column damage.

Reference 42 provides the following information with regard to this type of reaction:

> "The disproportionation of ethylene oxide ... was previously unknown... and not reported in the open literature. It consists of several simultaneous reduction/oxidation reactions.... All three of the stoichiometric reactions ... below were observed experimentally."
>
> $$4\ EO \rightarrow 3 \rightarrow C_2H_4 + 2CO_2 + 2H_2$$
>
> $$5\ EO \rightarrow 4 \rightarrow C_2H_4 + 2CO_2 + H_2O + H_2$$
>
> $$6\ EO \rightarrow 5 \rightarrow C_2H_4 + 2CO_2 + 2H_2O$$
>
> The disproportionation produces ethylene and carbon dioxide, which reduces the vapor-phase EO concentration. As the reference notes, "In order for a propagating decomposition of ethylene oxide to occur, the hot spot temperature must reach the ethylene oxide autodecomposition temperature of about 500°C (932°F) while the vapor phase contains above about 40% EO."

As the reference points out, the disproportionation reactions have higher activation energies than polymerization. Although disproportionation reactions release approximately the same heat as the polymerization reaction, the disproportionation reaction rates are much faster at higher temperatures. The heat release rates are thus proportionately higher in disproportionation reactions and this mechanism can form a localized hot spot:

> "… heat release profiles from the reaction of ethylene oxide with the gamma form (Fe_2O_3) of iron oxide [differ] at … different temperatures. At 155°C (311°F), EO polymerization occurs, but it occurs over a period of hours so that the maximum heat flow is relatively low. At 200°C (392°F), however, EO disproportionation occurs in minutes, rapidly generating a very high heating rate. In essence, these disproportionation reactions can serve as a chemical ignition source by generating a hot spot within/on the iron oxide containing polymer with a temperature greater than the EO autodecomposition temperature."

The reference concludes:

> "… Small amounts of ethylene oxide polymers are indigenous to ethylene oxide liquid operations. Furthermore, it was found that ethylene oxide polymer binds any metal ions present in the liquid. The key to safe ORS (Oxide Refining Still) operation is to always maintain adequate liquid contact at all heated surfaces, eliminating the possibility of vapor reaching temperatures higher than the boiling point of the equilibrium liquid."

Reactions with Water, Acids, and Bases

The reaction of EO with water (i.e., hydrolysis) to produce high molecular weight glycols is widely practiced within chemical process industries. Hydrolysis of EO to higher molecular weight glycols is also used in the design of EO vent scrubbers where EO absorbed by water is reacted to glycols. Reactions of this type are exothermic and require appropriately sized heat removal equipment. Adding or mixing water to EO inventories in storage vessels or transportation containers has potentially severe consequences.

Rate expressions for EO in water at neutral pH, acid catalyzed and base catalyzed reactions are available in the open literature [9, 51, 52, 53, 54]. These studies are generally based on first order kinetics with 5 wt.% EO in the solution. However, calculated results from these rate expressions do not agree well with experimental data at significantly higher EO concentrations.

Studies designed to better explain kinetics for the reaction of EO with water at neutral pH were initiated by EO producers [46]. These studies examined varying EO concentrations (up to 99%) in water. The data presented, regarding the kinetics, heat of reaction, stoichiometry, physical properties and vapor-liquid equilibrium for various water-contamination reactions of EO and essentially neutral pH water, can assist in sizing pressure relief devices for inadvertent water contamination of vessels containing EO.

Polymerization

EO has a tendency to polymerize. As this section will discuss, formation of EO polymer is a function of temperature, time at temperature and exposure to catalysts or contaminants.

A number of sources have observed thermally driven polymerization initiated at different temperatures. Industrial laboratory tests have shown high purity EO self-polymerization to have occurred at temperatures at 320°F (160°C) in a closed and near-adiabatic system. Additionally, there have been reports that thermal initiation of polymerization can occur at temperatures as low as 212° F (100°C). Polymerization can occur at lower temperatures, including ambient temperature (see discussion about catalyzation by rust at ambient temperature, below), but at ambient temperature the polymerization reaction is considerably slower. The polymerization reaction can also be influenced by contaminants for which the initiation point for polymerization appears to be strongly dependent upon the level and type of trace impurities in the EO.

The polymerization reaction is exothermic, releasing 1,000 BTU per pound of EO reacted [13]. If exposed to water at temperatures greater than 122°F (50°C), the polymer reacts to produce sticky polyethylene glycols.

The usual catalysts for EO reactions, such as strong alkali [18], iron oxide (rust) [19], and other metal oxides accelerate the reaction. When catalyzed by rust at ambient temperature, polymerization can create blockages or plugs in operations, such as pluggage of lines, relief valve inlets, and instrumentation taps. Polymerization can also result in off-specification product. Britton [17] has reported a rust catalyzed heat of polymerization of 1102 ± 121 BTU/lb.

The condition of metal surfaces is extremely important in determining the rate of EO polymer formation. It has been reported [19] that even clean carbon steel catalyzes polymerization, although at a much slower rate than rusty steel. For this reason, stainless steel is often chosen as a material of construction, especially when the surface to volume ratio is high. Some other factors that have been observed to affect the rate of polymerization are:

- Metal surface to volume ratio
- Temperature
- Residence time in equipment

The polymerization reaction has not been found to be auto-catalytic [43]. That is, the presence of a pure EO polymer does not accelerate the polymerization process. However, polymer traps iron oxide particles which is a catalyst for polymerization.

Overheating of EO or contamination of EO with catalysts such as potassium hydroxide (KOH) can lead to runaway polymerization. Reference [18] discusses an EO polymerization (or "polycondensation") incident involving contamination of an EO-containing cylinder with chlorine and alkali. The result was an 8-hour accelerating or "runaway" reaction that ended in an explosion.

Table 2.4 Physical Properties of Ethylene Oxide Polymer [44]

Molecular Weight	Melting Temp.°F (°C)	Density (g/cc)
200	-85 softening (65)	1.127
600	72 softening (22)	
1000	102 (39)	
3400	131 (55)	1.204
10,000	145 (63)	
100,000	150 (66)	1.130
4,000,000	150 (66)	

Properties of EO Polymer

Pure EO polymers have been characterized [44] as clear viscous liquids (molecular weight less than 600) and as opaque white solids (higher molecular weight). However, in industrial settings, EO polymer is often dark brown or black, due to the presence of magnetite iron oxide (Fe_3O_4) inside the polymer matrix. Note that the density of EO polymer is significantly higher than that of EO, so polymer that precipitates inside a storage container will tend to collect on the bottom.

Solubility of EO polymer in various solvents, including EO, is a function of molecular weight of the polymer and temperature. In general, higher molecular weight polymer is harder to dissolve. Solubilities of low molecular weight EO polymer in various solvents are set out in Table 2.5. Note the extremely low solubility in the non-polar solvent heptane.

Polymer samples from EO processing and storage equipment have exhibited molecular weights ranging from a few thousand to over one million atomic mass units (amu). At the upper end of this range, the polymer is quite insoluble in solvents and hot water and must be removed by physical means.

Cold Temperature Polymer Precipitation ("Drop-Out")

There have been reports observing copious amounts of polymer during railcar off-loading in cold climates at temperatures between 20°F - 40°F (-7°C - 4°C), but when these railcars have been returned to warmer climate loading facilities, the polymer is no longer observed. To explore this phenomenon further, an EO producer collected polymer residues from customer sites and plant storage vessels and dissolved the residues in EO. As illustrated in Figure 2.5 below, rapid cooling of the samples, with molecular weights ranging from 50,000-1,000,000, produced an instantaneous dropout temperature that correlated with molecular weight.

Three important observations can be made about the polymer drop-out process.

- First, the polymer fell out as a gel with a volume one hundred times larger than the dry polymer originally placed in the vessel. Thus, reports of copious amounts of polymer appear to be explainable by gel formation.
- Second, the polymer rapidly sank to the bottom upon standing. Therefore, the concentrated and gelled polymer would be expected to be observed at the beginning of the off-loading process.

Table 2.5 Solubility* of Ethylene Oxide Polymer in Various Solvents [45]

Solvent	Mol Wt 500 – 600		Mol Wt 3000 - 3700	
	T=68°F	T=122°F	T=68°F	T=122°F
Water	73	97	62	84
Methanol	48	96	35	S
Acetone	20	S	<1	S
Trichloroethylene	50	90	30	80
Heptane	0.5	.01	<.01	<.01

**Solubility is given in weight percent; S signifies completely soluble*

- Third, the temperatures at which the polymer precipitated in this experiment were lower than the off-loading temperatures of 20°F to 40°F (-7°C to 4°C) where polymer has been observed.

Comparison of “long-term” drop-out temperatures to “instantaneous” ones appears to resolve the discrepancy of the third observation. Figure 2.6 shows that, after about four days exposure to 40°F (4°C), most polymers above 180,000 amu precipitate. It is not uncommon for a railcar shipped to a colder destination to sit for several days before unloading. Since the temperature of the EO in a railcar shipped to a colder climate would be expected to decrease over several days in such conditions, it may be expected for the once-soluble polymer to precipitate out of solution. This analysis helps explain the polymer drop-out phenomenon observed at off-loading temperatures of 20°F to 40°F (-7°C to 4°C).

Low molecular weight polymer of 45,000 amu, however, failed to drop out after three weeks at 40°F (4°C). It appears that there is a region below 180,000 amu where polymer would not be expected to drop out of solution at 40°F (4°C) during routine railcar holding times.

Figure 2.5 Ethylene Oxide Polymer Instantaneous Drop-Out Temperatures [46]

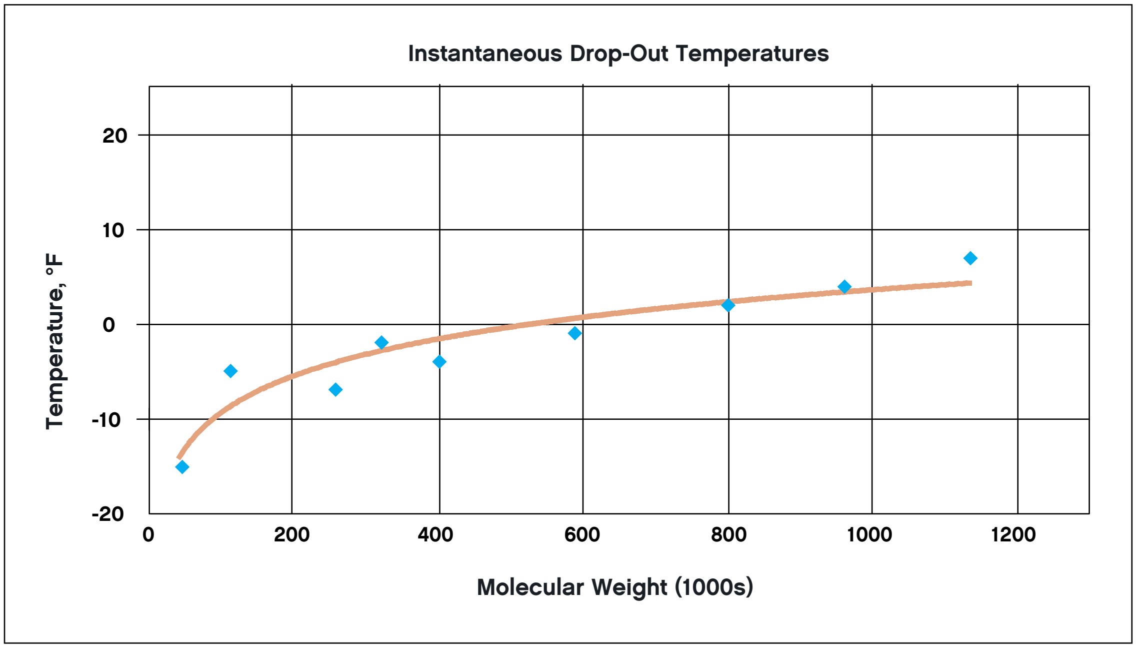
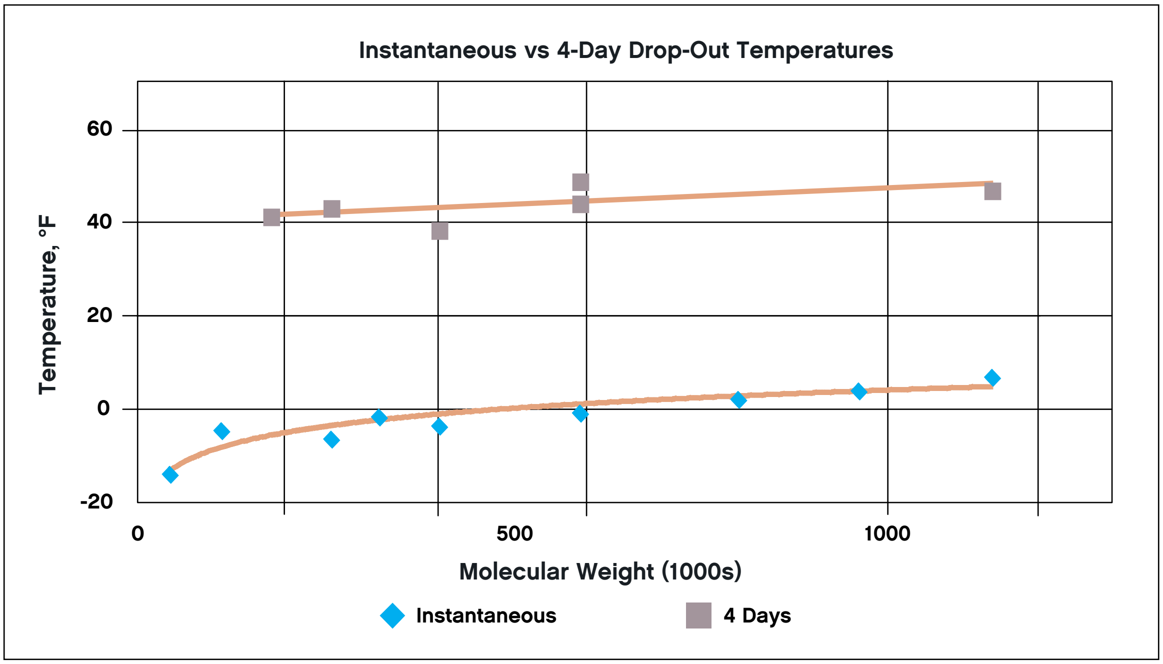


Figure 2.6 Ethylene Oxide Polymer Drop-Out Temperatures after 4 Days [47]



2.4 Commercial Chemistry

EO is a highly versatile molecule. Considerable energy is stored in the ring structure of the EO molecule. Its reactions proceed mainly via ring opening and are highly exothermic. Only a few of the large number of possible reactions are briefly discussed here. More detailed information can be found in references [8]-[14].

Addition to Compounds with a Reactive Hydrogen Atom

EO reacts with compounds containing a reactive hydrogen atom to form a product containing a hydroxyethyl group. Examples of compounds with a reactive hydrogen atom (XH) include: HOH, H_2NH, HRNH, R_2NH, RCOOH, $RCONH_2$, HSH, RSH. ROH, N=CH, and B_2H_6 (R= alkyl or aryl). The reaction is accelerated by acids and bases. All common acids and Lewis acids as well as zeolites, ion exchangers [29], and aluminum oxide are effective catalysts. A detailed discussion of reaction mechanisms and chemistry can be found in references [12] and [30].

The end product of this reaction contains at least one hydroxyl group, so it can react successively with additional EO to produce long chain polyether polymers, which are sometimes called poly-oxyethylene-glycols. The molecular weight distribution of the polymers depends on the reaction conditions, the catalysts employed, and the ratio of reactants.

This type of reaction is commercially important because the reaction of EO with water produces ethylene glycols. The production of poly(ethylene) glycols by this route is also of commercial importance.

When used with starting materials other than water (e.g., phenols, ammonia, fatty amines, fatty alcohols and fatty acids), the resulting reaction, often referred to as ethoxylation, is used to produce the bulk of the other commercially important EO derivatives.

Addition to Double Bonds

EO can add to compounds with double bonds, such as carbon dioxide, to form cyclic products. EO also adds to other double bond systems, e.g., to $R_2C=O$, SC=S, $O_2S=O$, RN=CO, and OS=O.

Catalytic Isomerization to Acetaldehyde

Aluminum oxide (Al_2O_3), phosphoric acid and phosphates, iron oxides, and, under certain conditions, silver, catalyze the isomerization of EO to acetaldehyde.

Other Reactions

EO reacts with many other compounds such as hydrogen (catalytic reduction to ethanol); hydrogen sulfide and mercaptans; Grignard reagents; halides; hydrogen cyanide; dimethyl ether; and compounds with active methylene or methyne.

2.5 Uses of Ethylene Oxide

Products derived from EO have many different uses. Some of these products (or uses) include:

- **Monoethylene Glycol:** Antifreeze for engines, production of polyethylene terephthalate (polyester fibers, film, and bottles), and heat transfer liquids and deicing of aircraft and runways.
- **Diethylene Glycol:** Polyurethanes, polyesters, softeners (cork, glue, casein and paper), plasticizers, gas drying and solvents.
- **Triethylene Glycol:** Polyurethanes, lacquers, solvents, plasticizers, gas drying and humectants (moisture-retaining agents).
- **Poly(ethylene) Glycols:** Cosmetics, ointments, pharmaceutical preparations, lubricants (finishing of textiles and ceramics), solvents (paints and drugs) and plasticizers (adhesives and printing inks).
- **Ethylene Glycol Ethers:** Brake fluids, detergents, solvents (paints and lacquers), and extractants for SO_2, H_2S, CO_2 and mercaptans from natural gas and refinery gas.
- **Ethanolamines:** Chemicals for textile finishing, cosmetics, soaps, detergents and natural gas purification.
- **Ethoxylation products of fatty alcohols, fatty amines, alkyl phenols, cellulose, poly(propylene glycol):** Detergents and surfactants (nonionic), biodegradable detergents, emulsifiers and dispersants.

EO also has direct uses as a sterilizing agent for medical devices and equipment and as a fumigant for spices. In sterilization applications, it is sometimes referred to as EtO.

3.0 Health Effects of Ethylene Oxide

3.1 Introduction

This Chapter provides a brief overview of information pertaining to potential health hazards associated with exposure to EO. A comprehensive discussion of health information pertaining to EO is beyond the scope of this manual. For more information, you may want to contact your supplier. Additional health effects information, including first aid information, also may be found in your supplier's Material Safety Data Sheet (MSDS).

The government and other organizations have established standards and recommendations for personnel exposure to EO [1]. These include the National Institute for Occupational Safety and Health (NIOSH), the American Industrial Hygiene Association (AIHA), the National Academy of Sciences (NAS) in conjunction with the U.S. Environmental Protection Agency (EPA), and the Occupational Health and Safety Administration (OSHA). The OSHA standard for EO is located at 29 CFR 1910.1047. It is important to be familiar with these standards and recommendations because they set exposure levels that are designed to be protective of human health. See Chapter 7.0, Personnel Exposure, for a more detailed discussion of these topics and contact your supplier for additional information.

For general information about this topic, users may wish to consult the Concise International Chemical Assessment Document (CICAD #54) on EO published in 2003 [2]. This document, prepared by the World Health Organization's International Programme on Chemical Safety, summarizes sources of EO exposure and potential effects on humans and the environment. The CICAD notes inhalation to be the route of likely greatest exposure for human health effects from EO. The CICAD designates cancer as the critical end-point for risk characterization of EO.

3.2 Acute Inhalation Exposure

EO has a high odor threshold (>250 ppm). Its odor threshold is too high to provide an adequate warning of hazardous concentrations. The effects of inhalation exposure to EO are concentration and time dependent. Concentrations of several hundred ppm may be tolerated for a few minutes without significant immediate health effects; however, similar concentrations may cause severe injury, especially if inhaled for longer periods.

Short-term exposures to EO vapors may cause irritation of exposed surfaces, including eyes, skin, nose, throat and lungs. Irritation of the lungs can lead to secondary infections, which may lead to pneumonia. Short-term exposures may also affect the central nervous system, leading to symptoms such as drowsiness, disorientation, nausea and vomiting. Convulsions and limb weakness may also occur. These symptoms may be expected to reverse within a few days after cessation of acute exposure.

See reference [4] for proposed Acute Exposure Guidance Levels for EO issued by the National Academy of Sciences committee in September 2006; also see discussion in Section 7.3 regarding IDLH, ERPG, and AEGL values and proposed values for EO.

3.3 Skin and Eye Contact

Liquid EO can cause freezing of the skin by evaporative cooling. It is also highly irritating to the eyes and skin and even dilute solutions can cause blistering or severe damage to the skin or eyes. EO liquid and solutions easily and rapidly penetrate cloth, leather and some types of rubber, and can produce blistering if clothing or footwear contaminated with EO is not removed. See Figure 7.2 in Chapter 7.0 for a photograph of a chemical burn to feet which resulted from a dilute EO-water mixture permeating leather work boots.

3.4 Chronic Exposure Hazards

Repeated dermal exposure to EO, or materials treated with EO, may lead to skin sensitization (allergic) reactions. Repeated exposure to high inhalation concentrations may result in respiratory sensitization (asthmatic) symptoms [5]. A possible association with long term exposure to EO and cataract formation has also been reported [3].

Long-term exposure to EO may also result in neurological effects similar to those observed in cases of acute short-term exposure. Many of the effects may be non-specific, including headaches, nausea, lethargy, numbness and memory loss. There may also be a reduced sense of smell and/or taste, and muscle weakness particularly in the legs. The potential short-term and long-term effects of EO on the nervous system are regarded as reversible.

There have been a few epidemiological reports of increased spontaneous abortions in pregnant hospital or dental sterilizer workers exposed for short times to relatively high EO concentrations [6]. However, methodological questions have raised doubts about the conclusions drawn in these studies [7]. Experimental animal studies have shown reproductive effects in rodents exposed to EO. Effects include a decrease in the number and weight of offspring in rats exposed to high levels of EO. The potential effects of EO on male and female reproduction and development have been the subject of research for many years [6-14] and research into this area continues. Contact your supplier for additional information.

Because EO is reactive, it is capable of directly combining with proteins and DNA when absorbed into the body. EO can react with DNA in tissues to form various DNA adducts [5, 15, 16]. Ongoing research is focused on the repair of these DNA adducts and the possible existence of an exposure threshold associated with the formation of DNA adducts and associated repair mechanisms. Contact your supplier for additional information.

The potential for EO to cause cancer, reproductive, developmental or genetic effects has been examined in experiments using laboratory animals and also by studying exposed human worker populations in epidemiological studies [17-23]. Based primarily on animal data and on cytogenetic changes in exposed workers, the International Agency for Research in Cancer (IARC) classified EO as a known human carcinogen [17]. In 2002, the U.S. National Toxicology Program classified EO as “known to be a human carcinogen” based on “sufficient evidence of carcinogenicity from studies in humans [18]. In April 2004, NIOSH issued a worker notification bulletin summarizing the results of several recent human studies [24]. Ongoing research is being conducted by numerous investigators, including some sponsored by the American Chemistry Council’s Ethylene Oxide/Ethylene Glycols Panel, to explore the potential for EO to cause cancer. For more information concerning potential chronic hazards from exposure to EO, contact your supplier.

Examples of cancer classifications established by various governmental entities as of the date of publication of this manual are listed in Table 3.1.

Table 3.1 Carcinogenicity Classifications of Ethylene Oxide

Organization	Classification
International Agency for Research on Cancer (IARC)	Known Human Carcinogen
Environmental Protection Agency (EPA)	Probable Human Carcinogen
National Toxicology Program (NTP)	Known Human Carcinogen
National Institute for Occupational Safety and Health (NIOSH)	Potential Occupational Carcinogen
American Conference on Governmental Industrial Hygienists (ACGIH)	Suspected Human Carcinogen

Table 3.2 Findings of the NIOSH Ethylene Oxide Studies [24]

Summary of the Recent NIOSH Ethylene Oxide Studies	
Purpose	To determine if exposure to EO is related to cancer or other diseases.
Subjects	18,235 men and women exposed to EO from 14 sterilizer plants around the country. Most of these workers used EO to sterilize medical supplies and treat spices. These were the largest studies ever conducted on EO exposure and the risk of disease.
Findings	No overall elevated risk for any type of cancer or other diseases as compared to the general U.S. population. However, among those workers with very high EO exposures, (combination of exposure levels and years worked); there was evidence of an elevated risk for blood cancers among men and breast cancers among women.
Conclusions	Persons exposed to very high levels of EO may be at an increased risk of developing blood cancers among men and breast cancers among women.

4.0 Environmental Effects of Ethylene Oxide

4.1 Introduction

This Chapter provides a brief overview of information pertaining to potential effects of EO to environmental media.

4.2 Properties in the Environment

Because it is highly reactive, EO does not persist indefinitely in the atmosphere, soil or water. EO is characterized by the following properties:

- EO is somewhat persistent in the atmosphere, but evidence indicates that it ultimately degrades by the process of photolysis;
- EO does not readily absorb into sediments or soils and does not persist in soils; if absorbed, soil organisms will over time convert EO to glycols eliminating any persistence in the soil;
- EO has low to moderate aquatic toxicity;
- EO does not persist in water due to conversion to glycol by hydrolysis or degradation of hydrolysis products, by both biotic and abiotic processes;
- EO does not bioconcentrate in environmental media.

Hydrolysis

Ethylene oxide degrades in both air and natural water via radical formation and hydrolysis, leading to the formation of glycols and halogenated alcohols (the latter forming in the presence of sodium chloride), which in turn degrade into simpler molecules such as carbon dioxide and water. Soil organisms may also convert EO to glycols [30].

Chemical hydrolysis is a major removal process for EO. At ambient temperatures and in fresh water, conversion of EO in water to glycols occurs at a slow rate requiring weeks for completion. The rate of EO hydrolysis can be increased by either changes in pH and/or temperature. Acidic conditions, in particular, can have a large positive effect on hydrolysis rates [7]. The data for EO indicates that water temperature will probably have a greater effect on half-life than expected pH differences in natural waters [1]. The hydrolysis product, ethylene glycol, is biodegraded rapidly in the aquatic environment [8].

Recently developed kinetics for EO hydrolysis with water predict similar half-lives as seen in Figure 4.1 [31].

Table 4.1 Environmentally Relevant Parameters of Ethylene Oxide

Parameter	Units	Value	Reference
Water solubility	mg/L	miscible	[2]
Vapor pressure at 20°C	mm Hg	1095	[2]
Atmospheric Boiling Point	°C	10.6	[1]
Henry's Law Constant at 20°C	atm-m^3/mol	1.4×10^{-4}	[1]
Octanol-water partition coefficient (log Kow)	L/kg	-0.30	[3]
Soil-sediment partition coefficient (log Koc)	L/kg	1.2	[18]
Bioconcentration factor (BCF)*	L/kg	0.35	[4][5]
Theoretical oxygen demand (ThOD)	O2/g EO	1.82	[6]

** Calculated using log BCF = 0.76 log Kow – 0.23 ([4], [5])*

Figure 4.1 Neutral EO/Water/Glycol Kinetics - Isothermal Case, Initially EO/Water mixture

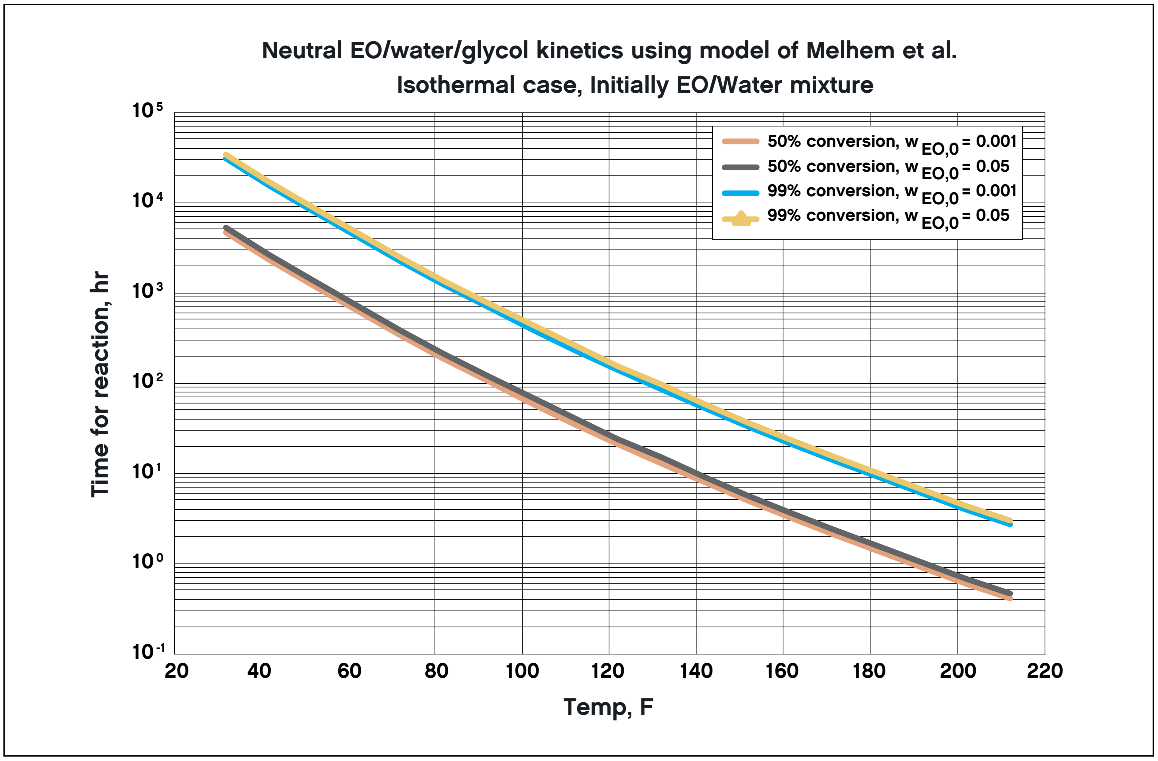
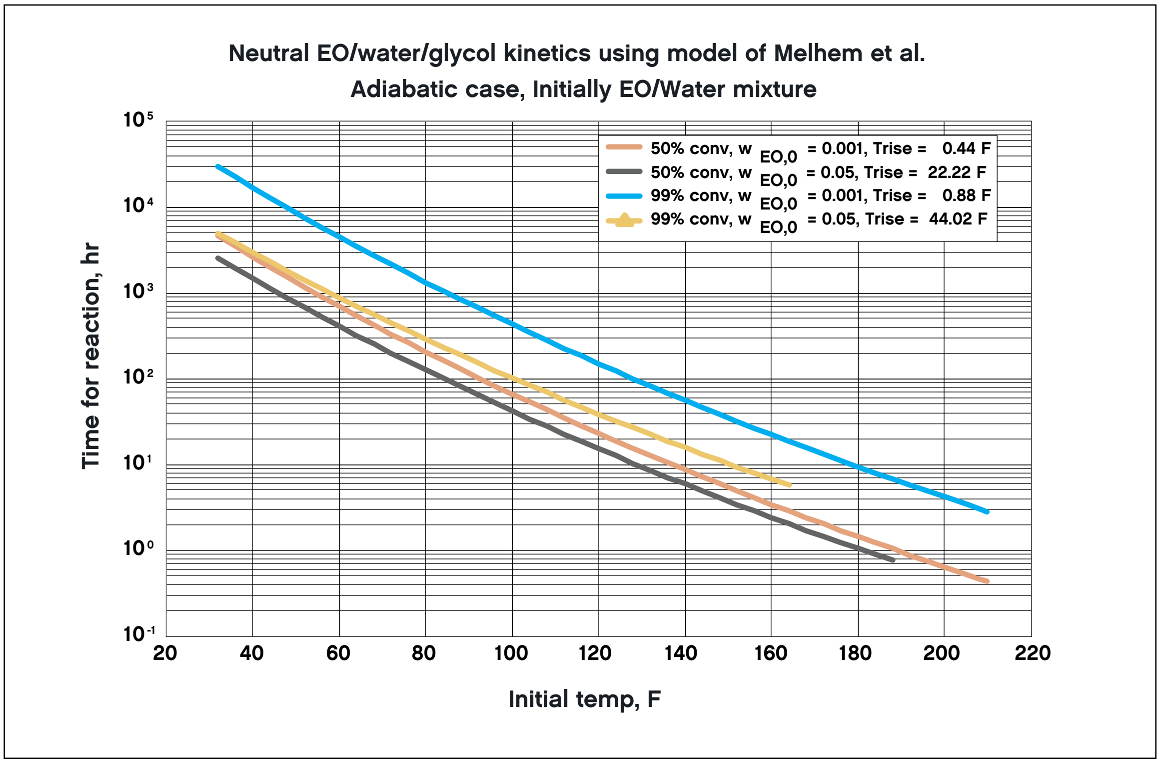


Figure 4.2 Neutral EO/Water/Glycol Kinetics - Adiabatic Case, Initially EO/Water



The half-life for 1000 ppmw in water at 77°F (25°C) is 10 days. Under isothermal conditions, 99% conversion is achieved in approximately 70 days. Figure 4.2 shows conversion data for EO in water assuming adiabatic conditions. At very low EO concentrations, there is little difference in the half-life assuming isothermal or adiabatic conditions. However, at higher EO concentrations, the results may be more significant. Adiabatic conditions may be a more reasonable assumption for spill containment tanks. Comparing adiabatic with isothermal conditions for 5% wt EO in water, the half-life is 6 versus 12 days with a 13°F (-11°C) temperature rise. The time to achieve 99% conversion is 14 versus 76 days with a 25°F (-4°C) temperature rise.

Volatilization

Because of its volatility, EO has a tendency to evaporate from water or soil to the air. The Henry's Law Constant is 1.4×10^{-4} atm-m^3/mole [1]. It has been shown that the transfer rate of EO from natural waters is about 0.36 times that of oxygen under the same conditions [1]. A 4-hour aeration test resulted in 100% removal from water [9], and the volatilization half-lives for removal from a model river and model lake are 5.9 hours and 3.8 days, respectively [10].

Persistence in Air

Earlier studies suggested that EO is not persistent in air due to washout by rain [1] and degradation by chemical processes [11]. However, more recent work has indicated that EO was not readily deposited by rain [12], [13], and the dominant chemical removal process is the reaction with the hydroxyl radical. Based on the most recent determinations of the average atmospheric hydroxyl radical concentration [14] and its reaction rate with EO, [15] the atmospheric half-life of EO is estimated to be 105 days. Under the U.S. Clean Air Act, EO is classified as a toxic air pollutant and regulated as a volatile organic compound.

Biodegradation

A series of biodegradation experiments (biological oxygen demand tests) have been conducted and results are summarized in Table 4.2. These results indicate that EO is rapidly and extensively biodegraded under aerobic conditions. More rapid biodegradation is expected in acclimated systems [16], [17]. Thus, EO will biodegrade in aerobic systems such as rivers, lakes and activated sludge units. However, high concentrations of EO may cause inhibition of bacterial respiration in activated sludge units. The IC50 (concentration that inhibited bacterial growth by 50%) in an activated sludge test (non-acclimated) was in the range of 10-100 mg/L [1].

In testing of a full-scale chemical plant activated sludge unit, EO was shown to rapidly biodegrade to non-detectable levels [17]. Measured EO biodegradation kinetics were determined in this study and were successfully used to predict the measured activated sludge unit EO concentrations [17].

Environmental Partitioning

Environmental partitioning is useful in modeling the transport of EO through environmental media. Fugacity modeling evaluates a scenario in which a chemical is continuously discharged into one of three compartments: air, water, or soil. Following entry into a single environmental compartment, chemicals are redistributed as governed by

Table 4.2 Biological Degradation Data for Ethylene Oxide

Process	Results	Comments	Reference
aerobic	5-d BOD = 20%	standard BOD test	[9]
	10-d BOD = 62%		
	20-d BOD = 70%		
aerobic	5-d BOD = 3%	standard BOD test	[19]
aerobic	20-d BOD = 52%	lightly seeded BOD test	[1]

Table 4.3 Aquatic Toxicity Data for Ethylene Oxide*

Species	Results	Comments	Reference
Fathead minnow	Maximum safe concentration (96-h) = 41 mg/L	no effect concentration	[9]
Fathead minnow	96-h LC50 = 57 mg/L	static; fresh water	[9]
Fathead minnow	24-h LC50 = 86, 90, 274 mg/L 48-h LC50 = 89 mg/L 96-h LC50 = 84 mg/L	static; fresh water	[1]
Goldfish	24-h LC50 = 90 mg/L	static; fresh water	[20]
Daphnia magna	24-h LC50 = 260, 270, >300 mg/L 48-h LC50 = 137, 200, 300 mg/L	static; fresh water	[1]
Brine shrimp	24-h LC50 = 350, 570, >500 mg/L 48-h LC50 = 490, >500, 1000 mg/L	static; salt water	[1]

** Table includes multiple results from separate tests.*

compound-specific physical properties, as well as by advection and dispersion. Chemical concentrations are also simultaneously reduced in the environment by compartment-specific degradation processes. Concentrations in each environmental compartment are calculated when advection, inter-media transfers and degradation are at equilibrium.

Overall distribution of EO in the environment has been characterized in Canada using the ChemCAN Level III fugacity model [18]. The predicted overall persistence was estimated at 3 days with 77% partitioning to air, 23% to water, and less than 1% to soil and sediment. Due to its short overall persistence time, higher EO concentrations were estimated to occur closest to release points.

4.3 Ecotoxicological Effects

EO aquatic toxicity studies have been conducted using fish and crustaceans. The results indicate that EO has low to moderate aquatic toxicity (Table 4.3), with toxicity measurements (LC50 in acute tests) ranging from 57 to 274 mg/L for fish and 137 to 1,000 mg/L for crustaceans.

The effect of EO on the growth and development of plants has also been investigated. Heck and Pires [21] reported that atmospheric concentrations of 10 ppm showed no effects on plants after seven days of exposure, but tests conducted at higher EO concentrations of up to 1000 ppm in air caused death for all of the five plant species studied. EO levels in biota have not been reported [18]. The bioaccumulation potential is expected to be low because of EO's low octanol/water partition coefficient.

4.4 Environmental Evaluation of Ethylene Oxide Spills

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) reportable quantity for a release of EO to the environment is 10 pounds. (40 CFR 302.4.)

Soil

EO is poorly adsorbed to soil. In a spill to soil, much of the EO will be lost to evaporation and the balance will infiltrate the ground. Environmental considerations include downward penetration of EO toward the groundwater table. Some of the EO will convert over time to ethylene glycol through hydrolysis; however, this process is relatively slow. Note that ethylene glycol would biodegrade rapidly (0.2 to 0.9 day half-life) [22].

Once the EO has infiltrated the soil, evaporation will continue but at a reduced rate. Diluting an EO release with water will increase the viscosity of the resulting mixture and will have the net effect of reducing the speed of downward movement in the soil. If the soil surface is saturated with moisture at the time of the release, as might be the case after a rain, the EO will tend to run off or pond and eventually evaporate, hydrolyze or biodegrade.

After a spill, the generator of waste must determine if the material to be disposed of is regulated as a hazardous waste. Although EO is not a listed hazardous waste under U.S. environmental regulations, as a pure substance it exhibits the characteristic of ignitability (D001). Soils and residue from a spill therefore must be analyzed to determine if the materials being disposed meet the criteria for classification as a hazardous waste. Once this determination is made, an appropriate disposal technique can be selected in accordance with federal and state disposal requirements.

Water Systems

When spilled on water, EO will volatilize and simultaneously spread on the surface of and mix with the water. The EO may also simultaneously hydrolyze and biodegrade in bodies of water. EPA has developed models to simulate the fate and transport of chemicals within watershed areas [23]. These models are publicly available on the Internet.

EO Air Dispersion and Sampling

Chemical releases are typically evaluated using computer models. EPA developed ALOHA® software for evaluating an episodic chemical release and the downwind dispersion of the chemical cloud [24]. EPA also developed the SCREEN3 air dispersion model for evaluating chemicals that disperse as a plume from point, area, flare, and volume sources [25]. Both of these screening tools are available for free from EPA.

Other air dispersion modeling software is commercially available. Some of these models may be easier to use than EPA's models; some may offer more modeling options, such as multi-media modeling of releases to air, water, or soil.

Several methods are available to measure EO in ambient air. Real-time field measurements can be made in the 5-10 ppb range using a portable gas chromatograph with a photoionization detector using NIOSH Method 3702 [26]. Additionally, the measurement of lower concentrations (below 1 ppb) has been validated using EPA Method TO-15 and Summa™ canisters for sampling [27]. The method is designed to be similar to Method TO-15 using evacuated canisters and gas chromatography-mass spectrometry (GC-MS). Additional information is available from commercial vendors specializing in air sampling and analysis.

4.5 Fugitive Emissions

Fugitive emissions are those that enter the atmosphere from a source other than a smoke stack, process vent or a storage vessel. Fugitive emissions include equipment leaks, evaporative losses from surface impoundments, spills, and releases from building ventilation systems. EO fugitive emissions are typically calculated rather than measured. In some cases, fugitive emissions can be a large contributor to reported emissions.

Fugitive emissions are subject to federal regulations, but in most states, the primary implementing regulations are state air quality regulations. State requirements vary; however, equipment leaks are typically regulated through leak detection and repair (LDAR) programs. Federal rules cover the frequency and protocol for monitoring valves, connectors, pump seals, compressors and other fugitive emission sources. Emissions can be estimated using field leak concentration data (screening data) in EPA-developed correlation equations [28]. Commercially available software is available to document LDAR compliance and estimate fugitive emissions based on screening data.

Secondary air emissions from wastewater systems are another type of fugitive emissions. Several computer models with varying degrees of sophistication have been developed to estimate secondary emissions. The publicly available EPA WATER9 software estimates air emissions from wastewater collection, storage, treatment and disposal facilities [29]. Proprietary software is also available from commercial vendors. Some modeling issues to consider are how well the modeled emissions agree with field measurements, ability to simulate complex configurations, the number of chemicals in the physiochemical property database and the ease of use of the software.

5.0 Hazards of Ethylene Oxide

5.1 Introduction

EO has been involved in incidents in both EO production plants and EO consuming plants [1] resulting in major plant damage as well as fatalities. EO has also been involved in significant transportation incidents.

One of the best ways for the EO user to understand the hazards of EO is to become familiar with historical incidents. This Chapter reviews some incidents involving EO that are particularly instructive in understanding EO hazards. It is hoped that the lessons to be learned from incidents like these will assist in future plant design as well as in the development of procedures for operations, maintenance, training and emergency response.

5.2 Contamination Incidents

EO is routinely reacted with other chemicals under controlled conditions to produce commercial products. Because EO is reactive with so many other chemicals and the resulting reactions are highly exothermic, contamination is one of the most significant hazards of working with EO.

Contamination of pure EO with waste materials or other chemicals – including water – can lead to uncontrolled reactions producing large amounts of heat. Generation of heat from the reaction of EO and contaminants or from the polymerization of EO can overpressure and rupture the EO-containing vessel. In a contamination incident, the EO-containing vessel typically ruptures long before all the EO has reacted. The sudden depressurization when the vessel ruptures results in the formation of an EO vapor cloud.

EO contamination incidents can be described as “kindling chain” events. A typical description of such a chain of events is as follows: a small contamination of an EO vessel leads to a reaction of EO in the vessel, which leads to an overpressure and rupture of the vessel, which leads to formation of an EO vapor cloud, which subsequently results in a vapor cloud explosion. In many of the contamination incidents discussed below, as well as many of the EO decomposition incidents, most of the resulting damage was due to an EO vapor cloud explosion.

Contamination of Ethylene Oxide with Aqueous Ammonia

In a 1962 incident at an EO production and derivatives plant, an EO storage vessel containing 21 tons of EO was contaminated with aqueous ammonia due to backflow from an ethanolamines unit. The EO and ammonia rapidly reacted in the vessel; the overpressured vessel ruptured; and an EO vapor cloud explosion occurred. (Figures 5.1, 5.2, 5.3, 5.4, 5.5). The primary explosion threw an adjacent EO storage vessel containing 13 tons of EO into another process structure 400 feet away. Numerous vessels in the area of the primary explosion ruptured during the vapor cloud explosion or during the resulting fires at the site.

Figure 5.1 Older View of Plant Before Explosion Showing EO Tanks in Foreground

Figure 5.2 Blast Center after Explosion – EO Vessels No Longer Visible

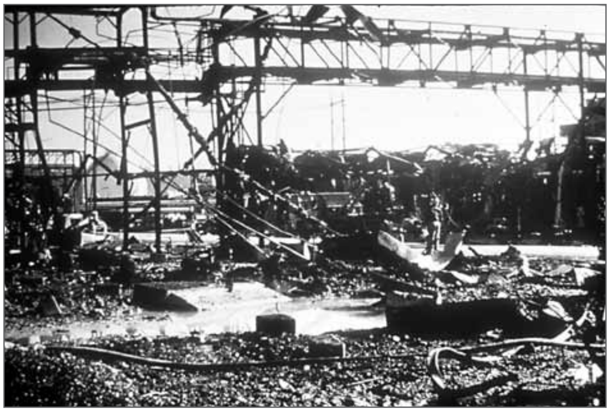


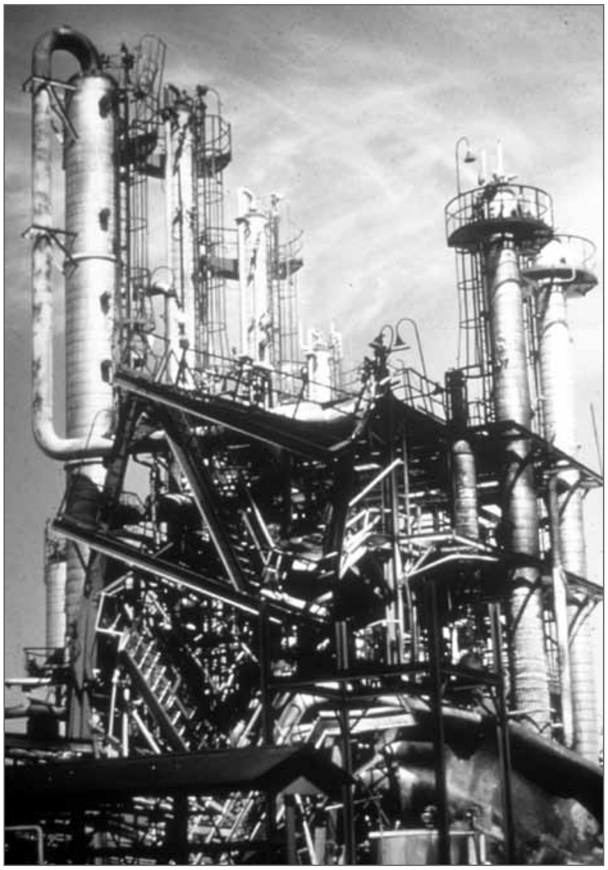
Figure 5.3 Aerial View of the Plant Showing Overall Damage

Ignition of the EO vapor cloud caused extremely heavy structural damage in a radius of 500 feet from the blast center. Implosion damage occurred in a radius of 700 – 1,000 feet from the blast center. Buildings and equipment within a radius of 1,000 feet of the blast center suffered extensive glass breakage and minor structural damage. The explosion could be heard 35 miles away from the plant and evidence of the shock wave from the explosion was noted up to three miles away. The explosion resulted in one fatality, three serious injuries and 18 less serious injuries.

The EO producer's investigation revealed that ammonia backflowed from the EO transfer line into the EO storage vessel. The ammonia passed through several check valves and a positive displacement pump (through its relief valve) before entering the EO vessel [2,3].

Railcar Explosion Due to Reaction Between Residual Ethylene Oxide and Cleaning Water

Figure 5.4 EO Tank Blown Into Process Structure 400 Feet Away



In this incident, an EO railcar was sent to a contractor for cleaning prior to maintenance on the railcar. Unknown to the cleaning contractor, the railcar contained a "heel" of a few thousand gallons of EO. The contractor pumped brackish water into the car and left it in a rail yard overnight. During the night the railcar exploded, causing significant damage to other railcars in the rail yard. (Figures 5.6, 5.7, 5.8). The EO producer's investigation revealed that a major contributing factor to this incident was slow addition of water to the railcar, which helped the EO and water – which have different densities – resist mixing. The EO and water collected in two layers in the railcar, and the formation of these layers meant that there was a large area of interface between high concentration EO and high concentration water. This resulted in a much higher reaction rate than would have occurred if the EO and water had been well mixed. Contaminants in the brackish water may have also contributed to the high reaction rate. The subsequent reaction generated high temperature and pressure in the railcar, resulting in its rupture [4].

Figure 5.5 Plant Laboratory After EO Vapor Cloud Explosion, 300 Feet Away from Explosion Center

Figure 5.6 Remnants of Railcar

Figure 5.7 Remnants of Railcar

Figure 5.8 Damage to Other Railcars from Ethylene Oxide Railcar Explosion

Ethylene Oxide Railcar Contamination with Bentonite Clay

A railcar was returned to an EO producer's plant after cleaning by a contractor. The contractor had put bentonite clay (a drying agent) in the car to reduce rust formation. The EO producer was unaware of the use of clay and did not remove it when the railcar was received at the plant. During loading of the railcar with EO, a fire occurred in the railcar dome. Reaction between the bentonite clay and EO caused an internal ignition and release of burning EO vapor through the railcar's safety relief valve. The fire was initially extinguished with water but it re-flashed. The fire was ultimately extinguished with dry chemical.

Contamination of Railcar with Ammonia

A European EO producer shipped an EO railcar to a customer. The railcar was delivered to the wrong plant and the workers at the receiving plant thought the car contained anhydrous ammonia. They attempted to offload the EO into an anhydrous ammonia vessel. The ammonia vessel was at a significantly higher pressure than the pressure on the EO railcar. During the attempt to offload the EO, a check valve leaked and allowed a small amount of ammonia to backflow into the EO railcar. When the workers at the plant discovered that the car was delivered by mistake, the unloading operation was stopped and the car containing the contaminated EO was sent to its proper destination, 300 kilometers (180 miles) away. The railcar exploded in the middle of the night on a rail siding at the edge of the plant. The explosion destroyed an adjacent warehouse, caused major damage over a 300 meter radius and broke windows up to 5 kilometers (3 miles) away. (Figure 5.9).

Explosion of Railcar Containing Ethylene Oxide Washwater

In an incident occurring in December 1973, an EO producer in the U.S. washed an EO ship loading line and an EO storage sphere with river water and then stored the EO contaminated water in a 22,500 gallon railcar. The railcar contained 8000 gallons of EO at 43°F (6°C) and 5200 gallons of wash water at 63°F (17°C). The railcar was padded with nitrogen at 35 psig. The railcar was stored on a siding during which time it was not monitored for temperature or pressure. After 23 days of storage, the railcar exploded. Prior to the explosion, the railcar's relief valve lifted, and the immediate area was evacuated. The exploding railcar created a large fireball and a crater in the ground. An adjacent operating facility was demolished. Twenty-eight people had minor injuries but there were no fatalities. Based on the damage to the adjacent operating facility, the immediate evacuation most likely prevented a significant number of fatalities.

As illustrated by the incident above, storage of EO/water mixtures can present significant hazards. Storage of EO/water mixtures in railcars, vessels or process equipment should only be practiced with a thorough understanding of the reaction kinetics of EO and water [5]. For more information on EO-water mixtures, see Chapter 2.

Contamination of Ethylene Oxide Plant Nitrogen Source with EO

This incident involves a European EO plant, in which vessels were padded with 5-bar nitrogen from a central line. The equipment for feeding nitrogen consisted of a check valve and a control valve monitored by a differential pressure measurement. The nitrogen feed equipment was installed on the ground level of the plant, which means that it was below the tops of the vessels. Over time, EO and water (from the EO light ends column feed vessel) condensed in the nitrogen line above the control valve. An EO-water mixture gradually built up directly on the outlet of the control valve, on the lower pressure side. Every time the control valve opened, the hydrostatic head forced a small amount of liquid EO and water to the upstream side of the control valve. The nitrogen header became contaminated with liquid EO, EO vapor and water.

Nitrogen from this header was used to purge the EO unit oxygen feed line during a unit shutdown. During the purge, there was a reverse flow

Figure 5.9 Remnants of Railcar (after EO explosion caused by contamination with ammonia)

from the oxygen line into the nitrogen line. An explosion between EO and oxygen occurred in the nitrogen line and a piece of shrapnel from the line penetrated the adjacent ethylene line, releasing ethylene into the pump house. The ethylene release resulted in a second, much larger explosion that blew the door off and caused major damage to the pump house.

5.3 Formation of Ethylene Oxide Vapor Clouds

Release of EO vapors can result in the formation of a vapor cloud. Because the minimum ignition energy of EO in air is extremely low, EO vapor clouds often explode. (See Chapter 2 for more information on EO vapor ignition energy.) Note that in most EO contamination incidents and EO decomposition incidents, the majority of the damage has resulted from an EO vapor cloud explosion. Such incidents can be extremely destructive.

Ethoxylation Plant Explosion

The contents of an ethoxylation reactor were pumped to a neutralization vessel about one half-hour before completion of all the reaction steps. The neutralization vessel was located indoors. The material was pumped to the vessel at a temperature of approximately 390°F (199°C). The vessel contained 100 to 150 pounds of un-reacted EO. The EO rapidly vaporized and escaped from the vessel, mixing with the air in the building. An explosion occurred when an operator entered the building to turn on the ventilation system. The explosion killed the operator entering the building, injured two other operators and destroyed the building housing the ethoxylation reactor and the neutralization vessel. Nearby buildings sustained extensive damage.

5.4 Ethylene Oxide Decomposition Incidents

EO decomposes at a temperature around 932°F (500°C). The incidents listed below illustrate decomposition incidents.

Ethylene Oxide Decomposition Incidents and External Fires

An external fire is one of the most hazardous situations that can occur in an EO plant because of the potential for EO decomposition. Even with water spray systems and well-insulated equipment, flame impingement from an external fire can increase piping and vessel wall temperatures to EO decomposition temperature in a short time period. If this happens, an internal explosion can occur.

Fire Around Distillation Column

An EO producer in the U.S. had a rupture of an EO compressor cylinder. This resulted in a large fire, which engulfed the EO distillation column. The resulting temperature increase on the surface of the column and in the contained EO resulted in an internal explosion and significant damage.

Flange Fire while Plant was Down

A European EO producer experienced a flange leak in the EO distillation section of an EO plant. The plant had been shut down but still contained an inventory of EO. The flange leak resulted in a fire and the flame impinged on a process line containing EO. The heat caused an EO decomposition reaction to be initiated in the line. The decomposition propagated down the line and into a distillation column. The column head was torn off and thrown about 100 feet. Large and small parts of the column jacket were scattered over a 2000 foot radius. Only 7 minutes elapsed from the start of the unit fire to the column explosion.

Pump Seal Leak Fire

A European EO production plant had an EO pump seal leak that was ignited by contact with hot pump parts. The flame from the pump seal fire impinged on an uninsulated minimum flow return line causing evaporation of the EO in that line. Continued heat input from the flame impingement resulted in an EO decomposition in the minimum flow line. The decomposition reaction propagated into the EO purification column reflux drum where an explosion occurred. The reflux drum and its associated distillation column were destroyed. This incident resulted in four fatalities. The plant was heavily damaged and out of operation for four months.

Ethylene Oxide Decomposition Incidents and Mechanical Equipment

Some important considerations regarding pumps and compressors in EO service include the potential for high temperatures if mechanical energy is not dissipated and the potential for a fire due to seal leaks. A good example of nondissipated mechanical energy is a blocked pump discharge. The pump seal leak fire described immediately above is a good example of the potential consequences of a seal leak fire. The two incidents described in this section illustrate potential results of operating an EO pump deadheaded.

Decomposition in Reflux Pump Propagates to Reflux Drum and Tower

The EO purification column reflux pump of a European EO producer had been over-speeding. The producer had also been experiencing instrumentation problems with the level controller on the reflux drum, which caused the reflux control valve on the discharge of the reflux pump to fail while closed. There was no minimum flow recycle or high temperature or low flow safety shutdown system on the reflux pump. (For more information about safety systems on EO pumps, see section 6.7) The reflux pump operated deadheaded against the level control valve, causing the temperature in the pump to rise. The EO vaporized and the EO vapor was heated to its decomposition temperature. The EO in the pump decomposed and the decomposition propagated through the pump suction line into the reflux vessel where an explosion occurred. Shortly afterward the EO purification column exploded. This explosion resulted in four fatalities. The plant was heavily damaged and out of operation for four months [6].

Ethylene Oxide Decomposition in Blocked-in Pump

A U.S. EO producer used high-speed centrifugal pumps to feed EO to two ethylene glycol units. The plant had a common spare feed pump for the two glycol units. The spare pump was typically kept cleared of EO, pressured up with 200-psig nitrogen, and left with the suction and double discharge valves blocked in. A small amount of EO leaked through the two blocked discharge valves into the pump. An electrical system malfunction caused the high-speed centrifugal pump's electric motor to start. The pump ran blocked in for approximately ten minutes until the seal area of the pump reached EO decomposition temperature and the pump exploded. The decomposition of the 0.6 pounds of EO in the bowl of the pump generated over 450,000 pounds of force and caused the failure of twelve, ¾ inch stainless steel nuts and bolts that held the pump together (Figure 5.10). The upper part of the vertical centrifugal pump and the motor (approximately 1000 pounds) were launched 60 feet in the air. The pump and motor landed on the discharge piping of another EO feed pump that was operating at 750 psig, pumping 80 gpm of EO (Figure 5.11). The discharge piping did not fail.

Ethylene Oxide Decomposition in Blocked-in Pump

A U.S. EO producer uses magnetic drive pumps extensively in EO service. At the time of this incident, the magnetic drive pumps were protected from overheating by a safety shutdown system that included shutdown initiators for both high temperature and low flow. During the normal startup sequence for these pumps, the shutdown system must be bypassed for a few seconds to allow the low flow shutdown to be satisfied. To allow the pump to start, the pump start switch was also configured to function as a shutdown system bypass switch while it was depressed. During a normal startup of these pumps, the operator had to hold the start switch down for a couple of seconds to allow the pump to start pumping and satisfy the low flow shutdown.

On the day this incident occurred, an EO tower residue pump had been tripping every few minutes. An operator tried to start the spare pump, but it would not run. The operator then attempted to re-start the pump that had tripped. The operator tried several times, but each time it tripped. In an attempt to keep the EO production unit running, the operator held the start button down for several minutes to keep the pump running without tripping. After several minutes of holding the start button down, the operator noticed that the pump had become very hot and there was a grinding sound from the back of the pump. The operator released the start button. The EO production unit was shut down and the pump was pulled out for repair.

When the pump was opened up for repair, the area between the driven magnet and the containment can was completely packed full of carbon (carbon deposits are sometimes found after an EO decomposition; under EO decomposition conditions, the methane produced in the decomposition can decompose further to form carbon and hydrogen). The containment can had a blue discoloration that indicated that it had been exposed to temperatures over 800°F (426°C). EO had decomposed inside the containment can and around the driven magnet [7]. In this incident, it is believed that the decomposition reaction did not propagate through the small passages inside the pump because the mass of the metal in the pump absorbed enough heat to quench the decomposition flame.

Figure 5.10 High Speed Centrifugal Pump "Launched" by Decomposition of 0.6 Pounds of Ethylene Oxide

Ethylene Oxide Decomposition Incidents and Leaks

Under Insulation

An EO leak into porous insulation can result in reactions of EO with the insulation material or EO with moisture contained in the insulation, which can lead to high temperatures. This may occur with mineral wool, asbestos, fiberglass, calcium silicate, magnesium silicate and other porous insulation materials. Porous insulation can soak up and retain water from the environment, thereby providing a large surface area for EO-water contact. It has also

Figure 5.11 Motor Landed on Operating Ethylene Oxide Pump Discharge Line

been shown that many types of insulation catalyze reactions of EO [8]. These reactions all produce heat, the dissipation of which is inhibited by the insulation itself. An under insulation EO leak can result in a "hot spot" on the wall of the vessel, which can trigger a decomposition reaction of the EO inside the vessel. Use of nonporous insulation, such as cellular glass, reduces the potential for hot spots and still provides a degree of protection from overheating due to fire. See Section 6.3 for a more thorough discussion of insulation.

Ethylene Oxide Leak at an Insulated Manway Flange Results in Tower Explosion

In 1987, a European EO producer had a catastrophic explosion of its EO purification column. The damage to the plant was very extensive. Investigation after the incident revealed that a manway flange leak under mineral wool insulation on the EO distillation column resulted in an external "hot spot" which caused an EO decomposition inside the tower. The decomposition reaction increased both the temperature and the pressure in the tower until it ruptured. The remaining EO in the tower was suddenly released at high pressure and temperature forming an EO vapor cloud, which then exploded. The EO vapor cloud explosion caused more damage to the plant than the initial decomposition reaction (Figures 5.12, 5.13, 5.14, 5.15).

Ethylene Oxide Leak Under Insulation Results in Tower Explosion

In 1989, a catastrophic explosion of an EO purification column occurred at the production plant of a European EO producer. A crack developed where a pipe was attached to the wall of an EO distillation tower. The crack allowed EO to leak into mineral wool insulation. EO reacted with water in the insulation to produce polyglycols. When portions of the insulation and insulation jacketing were removed for maintenance, air flowed into and under the insulation, rapidly oxidizing the polyglycols and producing a high temperature.

Figure 5.12 Ethylene Oxide Distillation Column Reboiler after Explosion

Figure 5.13 Aerial View of Ethylene Oxide Plant after Explosion

Figure 5.14 Remnants of Base of Ethylene Oxide Distillation Column after Explosion

Figure 5.15 Piece of Ethylene Oxide Distillation Column Wall Turned Inside Out by Explosion

The insulation prevented dissipation of the heat and the reaction in the insulation caused the wall temperature of the EO distillation tower to reach EO decomposition temperature. The internal decomposition reaction resulted in vessel failure. In this incident, the EO decomposition reaction initiated in the aldehyde column and propagated through overhead piping to the EO purification column, which also exploded. Like the incident in 1987, most of the damage to the plant in this incident was caused by the EO vapor cloud explosion. Damage to the plant was severe, requiring more than a year for rebuilding (Figures 5.16, 5.17, 5.18).

Ethylene Oxide Decomposition – Ethylene Oxide Disproportionation Reaction in Column Vertical Thermosiphon Reboiler

Ethylene Oxide Redistillation Column Explosion

An EO manufacturer experienced an explosion in an EO redistillation column (Figures 5.19, 5.20). The explosion appeared to have been initiated at the top of the reboiler. There was one fatality and the plant was out of service for more than one year [9]. After the incident, the EO producer's research identified a previously unknown reaction of EO: disproportionation (see discussion in Section 2.3). This reaction can be initiated at significantly lower temperatures than thermal decomposition. In this incident, the reaction occurred

- Inside the tubes of a distillation column reboiler;
- In the presence of a deposit of high surface area rust embedded in an EO polymer matrix; and
- During a period when flow through the reboiler was reduced by a process upset resulting in tube surfaces exposed to vapor only, not liquid.

It was concluded that loss of reboiler circulation allowed for rapid heat buildup in the vicinity of the iron oxide/polymer deposit, resulting in localized EO vapor temperatures reaching the thermal decomposition temperature. The result was an explosion that destroyed the distillation column.

Ethylene Oxide Decomposition – Ethylene Oxide Disproportionation Reaction in a Horizontal Thermosiphon Reboiler

This June 2000 redistillation column incident

Figure 5.16 Aerial View of EO Unit After Explosion

Figure 5.17 EO Plant Burning after Explosion

Figure 5.18 EO Purification After Explosion – Two Towers are Missing

occurred on the shell side of a horizontal thermosiphon reboiler. Damage was limited to the trays in the column and some associated piping. There was no loss of containment and there were no injuries or fatalities. The incident occurred during the startup of the unit and when the following conditions were present:

- There was inadvertent heat input to the reboiler during startup;
- The initial charging of EO to the column during startup was interrupted, exposing the reboiler tube bundle to EO vapor;
- An iron oxide-polymer deposit was present on the reboiler tubes which initiated the disproportionation reaction.

Figure 5.19 Ethylene Oxide Re-distillation Tower Explosion (re-distillation tower is gone and adjacent tower is damaged and leaning)

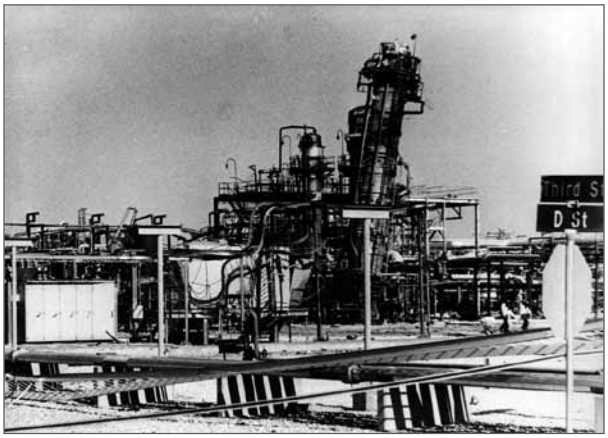


Figure 5.20 Resulting Damage to the Plant

The iron oxide-polymer deposit was wetted and dried during the startup with the interruption of feed to the column. A rapid temperature rise initiated the disproportionation reaction, which in turn led to an EO vapor decomposition reaction. The decomposition reaction propagated from the reboiler into the distillation column. Several of the bottom trays in the column did not have the manways in place. This allowed the velocity of the reaction front and volume of decomposition gases to accelerate to a critical point up to the trays which had the manways properly installed. The remaining trays in the top of the column were propelled upward and wedged in the top of the tower and the vapor overhead line. The pressure wave continued into the column overhead piping damaging several piping supports and several trays in the downstream column. The top trays were forced into the overhead piping of the column. It is believed that the trays compacted into the top of the tower and that overhead piping prevented the decomposition reaction from propagating into the downstream equipment.

Ethylene Oxide Decomposition – Catalyst Residue in the Vapor Space of an Ethoxylation Reactor

An ethoxylation reactor exploded during normal operation while EO was being fed to the reactor. During the investigation of the explosion, pieces of the reactor head were found that had a heavy buildup of potassium hydroxide (KOH) catalyst on the metal. The reactor was not designed for addition of KOH directly into the liquid. The liquid KOH stream was added at the top of the reactor and a KOH residue had built up on the inside of the head. The KOH catalyzed a reaction of the EO in the vapor space of the reactor driving the temperature in localized areas of the reactor head to the decomposition temperature. The vapor space decomposed explosively. The vapor space of the reactor was blanketed with nitrogen, but the nitrogen partial pressure was insufficient to yield a non-decomposable mixture. Refer to Section 6.6 for more information on inerting ethoxylation reactors.

5.5 Ethylene Oxide Transportation Incidents

In both of the following transportation incidents an EO railcar was punctured and a fire resulted. In one incident, the emergency responders controlled the process of burning off the EO. In the other incident, injuries were prevented by evacuation.

Ethylene Oxide Railcar Fire

In July 1981, a full railcar of EO was punctured as a result of a coupler override (this was before double shelf couplers were required by federal regulations) at a railyard in Newark, New Jersey. The leaking EO ignited. The location of the railyard was very close to the Newark International Airport and the New Jersey Turnpike. Both the airport and a four mile section of the turnpike were shut down during the incident. Three unmanned fire monitors were set up to limit the temperature increase in the car and to reduce the likelihood of a “hot spot” in the car shell. Nitrogen was fed into the car through a hose from portable nitrogen bottles to maintain an inert atmosphere inside the car. With input from EO technical specialists, a burn pit was set up approximately 400 feet away from the railcar. Liquid from the railcar was routed to the burn pit and ignited. The contents of the railcar were burned over a three hour period while the leaking EO continued to burn at the railcar. A 1½ inch firewater hose was also connected to allow flooding of the car’s interior when the flaring was complete. The fire was allowed to burn until all liquid EO had been consumed. When the fire went out, the car was filled with water as rapidly as possible to cool the car and to expel unburned EO vapors. No further damage resulted.

Ethylene Oxide Railcar Explosion

In October 1969, a multi-car derailment resulted in the puncture of an EO railcar and a fire. Water was put on the burning railcar and on an adjacent EO railcar that was not leaking. The fire was extinguished after about 12 hours. About five hours after the fire was out, the safety relief valve on the adjacent EO railcar lifted and vapor from the relief valve caught fire. Comments from responders at the scene indicated that the adjacent car “felt cool” after the initial fire was extinguished. At this point, the accident scene was cleared for a radius of ¼ mile. After about 55 hours, the relief valve fire went out for a brief period and then a violent explosion occurred. A large piece of the railcar was blown 5,000 feet through the air. The explosion was attributed to flame propagation back through the safety relief valve or a "hot spot" in the metal near the relief valve that triggered a decomposition reaction.

5.6 Runaway Ethylene Oxide Polymerization Incidents

Polymerization Incidents in Ethylene Oxide Filters

In 1969, a U.S. EO producer had an EO filter explode due to runaway polymerization. The filter had been left full of EO and blocked-in.

In May 1998, runaway polymerization occurred in an EO railcar-loading filter of a U.S. EO producer. The insulated loading filter was normally cooled by continuous circulation of chilled EO. However, circulation in this case had been stopped for over two days due to maintenance on other equipment in the EO tankfarm. During the incident investigation, it was discovered that the filter elements had not been changed in 18 months and were highly loaded with rust. The person formerly responsible for changing the filter elements had retired and this duty had not been reassigned to another employee.

The ambient temperature at the time of the runaway polymerization incident was 100°F (38°C). The combination of the stagnant EO, the high ambient temperature and the rust in the filter elements initiated the polymerization. The filter case did not rupture, but the temperature in the filter case was very high and the pressure was high enough to stretch the bolts on the head of the filter case. The cotton filter elements were found to be carbonized (dehydrated), indicating that the temperature in the center of the filter case exceeded 500°F (260°C) (Figures 5.21, 5.22, 5.23).

5.7 Runaway Reactions in Ethoxylation Units

Delayed Addition of Catalyst

EO was added to an ethoxylation reactor with the circulation cooling line blocked. The circulation line was also used for addition of a KOH catalyst. In order to continue feeding EO to the reactor, the

Figure 5.21 Filter Case after Runaway Polymerization

Figure 5.22 Filter Case after Runaway Polymerization

Figure 5.23 Filter Case after Runaway Polymerization

operator had to reset the high temperature EO feed shutdown. When it was discovered that the circulation line was blocked, the block valve was opened to re-establish cooling, but this action allowed a "slug" of concentrated KOH to enter the reactor and come into contact with EO. Because catalyst was not present when EO feed was started, the EO concentration exceeded normal design levels. The sudden addition of catalyst when the cooling line was opened resulted in a runaway reaction. Subsequently, the reactor ruptured explosively. Metal parts and valves were propelled over a distance of approximately 2,300 feet.

Inadvertent Addition of Reactive Material (Hydrogen Peroxide)

The reactor in a European ethoxylation unit suddenly exploded. The incident investigation revealed that hydrogen peroxide used to bleach the ethoxylate product was inadvertently added during the EO addition phase of the operation. The EO reacted with the hydrogen peroxide and caused the reactor to explode. There was no interlock to prevent addition of hydrogen peroxide when EO was present in the reactor.

5.8 Incidents in Ethylene Oxide Abatement Devices

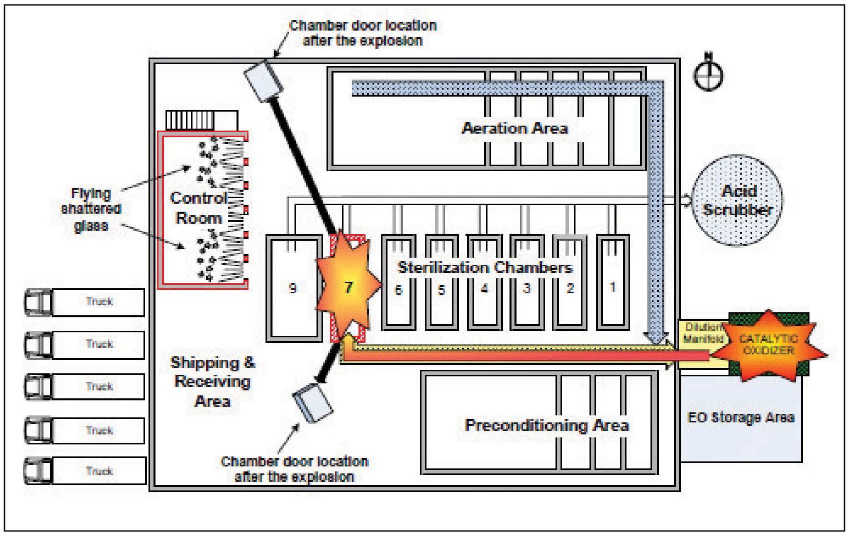
Catalytic and Thermal Oxidizer Incidents

Between 1994 and 1998, EO was involved in 10 explosions at industrial EO sterilization facilities and EO repackaging plants. One of these incidents resulted in a fatality and all of the incidents caused damage to the plants. Most of the facilities involved used oxidizers to control EO emissions. In April 2000, in response to these explosions, the National Institute for Occupational Safety and Health (NIOSH) published a Safety Alert titled "Preventing Worker Injuries and Deaths from Explosions in Industrial Ethylene Oxide Sterilization Facilities." [10] EPA and Industry representatives from the Ethylene Oxide Sterlizers Association (EOSA) collaborated with NIOSH to produce this alert. It warns EO sterilization facility employees and managers about the explosion hazards associated with oxidizers, and it makes comprehensive recommendations for preventing future incidents.

During 1997 and 1998, there were explosions and fires at four large-scale sterilization plants that use EO to sterilize medical devices. There was another explosion at large-scale sterilization plant in 2004. The explosion in 2004 was investigated by the U.S. Chemical Safety and Hazard Investigation Boar (CSB). The CSB produced a report and video on the 2004 explosion, which is available to the public on the CSB website, www.csb.gov.[11]

All of the sterilizer explosions in 1997, 1998 and 2004 were associated with EO abatement devices used for destruction of EO in process vents. Four of the explosions involved catalytic oxidizers and one explosion involved a thermal oxidizers. Each of the explosions either severely damaged or destroyed the EO abatement device and the sterilization chambers. Figure 5.24 is an overview diagram of the 2004 explosion. Figure 5.25 through 5.27 are photos of damage to the sterilization plant. [11]

Figure 5.24 Diagram of Sterilizer Explosion



Two of the sterilizer incidents occurred during the startup testing of catalytic oxidizers. In one of the incidents, there was an explosion with a fireball and the oxidizer system and the building were destroyed. In the 2004 explosion, the doors were blown off of the sterilization chamber and the walls of the chamber itself were bulged outward. [11]

Three common themes in all of these EO abatement device incidents were: (1) the lack of an interlock to prevent opening the chamber door when EO was in the chamber or the ability for the operator to override an interlock, (2) a higher than design concentration of EO at the inlet of the EO abatement device, and (3) the lack of EO concentration monitoring in the sterilization chamber to warn of explosive concentrations. Catalytic oxidizers are designed for conversion of low concentrations of EO in a vent stream to carbon dioxide and water. When the vent system to a catalytic oxidizer has a higher then design EO concentration, the result can be overheating of the catalyst bed and uncontrolled combustion or decomposition of the excess EO due to the high temperature in the catalyst bed.

Overload of Reactive Vent Scrubber

Incidents have also occurred in acid or caustic reactive EO vent scrubbers when a higher than design EO concentration was sent to the scrubber. Sending liquid EO to a reactive vent scrubber can easily overload a scrubber. Reactive vent scrubbers are typically designed to handle low concentrations of EO in a gaseous vent stream. Reactive vent scrubber systems are often designed with acid or caustic recirculation systems. If liquid EO is fed into the bottom of a reactive vent scrubber, it can flow into the acid or caustic vessel and result in a runaway reaction and explosion.

In the early 1990s, operators at an ethoxylates production unit with a sulfuric acid scrubber tried to clear the unit's EO feed line by blowing the liquid EO to the vent scrubber with nitrogen. The liquid EO overloaded the vent scrubber, resulting in a runaway EO hydrolysis reaction in the scrubber. The polypropylene packing in the scrubber melted and the 40 foot tall fiberglass reinforced plastic (FRP) scrubber tower failed and collapsed due to the high temperature produced by the EO hydrolysis in the scrubber. See Section 6.8 for more information on vents and scrubbers.

Figure 5.25 Sterilizer Explosion Damage

Figure 5.26 Sterilization Chamber Damage

Figure 5.27 Damage to the building wall from impact of sterilizer door

6.0 Design of Facilities

6.1 Introduction

The characteristics of EO – including flammability, toxicity and reactivity – are crucial considerations in the design of facilities for the storage, transport, and processing of this material. This Chapter, which summarizes some important issues relevant to EO facility design, addresses not just the chemical and physical characteristics of EO, but also includes discussion of the practical experience of industry. It is particularly helpful to review Chapter 2, Properties of EO, and Chapter 5, Hazards of EO, before reading this Chapter.

Note that risk assessment and hazard analysis, mandated by OSHA Regulations at 29 CFR 1910.119, are an integral part of the initial design of the facility and must also be conducted before making modifications to equipment and procedures.

6.2 Plant Layout and Siting

This section addresses general considerations for siting of EO storage vessels, pumps and piping. Some important considerations in selecting the location of EO storage vessels include:

- Criteria developed for LPG in NFPA [1], [2], [3] and API [4] standards to establish separation distances;
- Distance from operating plants, offices and perimeter fences;
- Distance (and adequate isolation) from fire hazards and potential ignition sources;
- Whether the location is a low fire risk area;
- Accessibility of the vessel to emergency responders (e.g., is it in an "open" area);
- Intended use of the storage vessel for inventory control (e.g., for EO in process feed vessels in the immediate vicinity of the plant, consider the minimum quantity of inventory compatible with the effective control and safe operation of the process concerned);
- Potential impacts of a release on the community; and
- Site security.

EO pumps are potential sources of fire hazard; for example, a mechanical seal failure and EO release, followed by fire. When locating a pump, consider the possible effects of a pump seal fire on surrounding equipment or railcars. Two techniques available to help mitigate potential hazards include pump installation within a diked or curbed area with leaks/spills routed to a secondary containment area and pump installation in a separate containment area from storage vessels.

EO piping is also a potential source of fire hazard. For routing EO piping, some key considerations include:

- Proximity to utility piping and systems essential to plant safety in the event of an EO fire;
- Minimizing EO piping through hazardous plant areas;
- Minimizing EO piping adjacent to higher temperature lines (>400°F/204°C) where there is a possibility of heating the EO in the piping;
- Minimizing EO piping close to lines containing corrosive chemicals that could damage the pipe; and
- Protecting grade-level pipe runs from impact damage, especially if piping is adjacent to road and railways.

Routing EO piping underground increases the possibility of corrosion and makes inspection more difficult. It may, however, reduce or eliminate the need for insulation, and it may significantly reduce or eliminate potential exposure to fire. For EO piping routed underground, installation of a cathodic protection system which is regularly maintained will help protect the EO piping from corrosion.

Electrical equipment in areas that produce, store, use, load or unload EO must conform to National Electrical Code, Class I, Division 1 or 2, Group B (or Group C if conduit seals comply with NEC paragraph 501-5(a)).

6.3 Materials of Construction

Because of the reactivity of EO, materials in contact with EO must be chosen with care.

Metallic Materials (Metals and Alloys)

Equipment for storage and handling of EO is generally fabricated from 300 series austenitic stainless steels or mild carbon steel. Stainless steels have the advantage of minimizing the potential for rust, which can catalyze EO polymerization. Cast iron is not considered suitable for EO use due to the low ductility of the material.

Austenitic stainless steels such as Type 304 and Type 316 are typically used for tubing, small piping, instrumentation and other equipment that cannot be readily cleaned of rust. Use of austenitic stainless steels is also appropriate in areas where EO liquid or vapor is likely to remain stagnant for periods of time.

Note that, depending on location and process conditions, stainless steels can be subject to stress corrosion cracking from naturally occurring atmospheric chlorides. External coating in such circumstances is an appropriate measure to address corrosion potential.

When carbon steels are chosen, it is important that they retain integrity under the full range of temperatures encountered in the specific application. Also note that the presence of rust (iron oxide, in the form of red hematite or black magnetite) on internal surfaces of carbon steel equipment leads to polymerization of EO.

Carbon steels are also susceptible to external corrosion from wet external insulation and wet metal surfaces. These conditions can occur from ingress of rainwater and also by condensation of atmospheric moisture on cold metal surfaces (for example, equipment containing refrigerated EO). Use of a suitable coating on the carbon steel equipment and periodic monitoring of the physical integrity of the coating and equipment, can help minimize the risk of corrosion. Monitoring is conducted in accordance with the plant's mechanical integrity program (required under OSHA Regulations at 29 CFR 1910.119). External corrosion is a concern when the operating temperature of the equipment is below approximately 200°F (93°C) because this temperature range is too low to evaporate water that penetrates under insulation. For example, the typical operating temperatures of EO purification columns make them particularly vulnerable to external corrosion. There have been several cases where carbon steel EO purification columns experienced serious external corrosion above insulation support rings where water was trapped. External corrosion has also been observed in carbon steel EO storage vessels and piping.

Historically, metals such as copper and silver and their alloys have not been used in EO service. This was based on the potential for the formation of metal acetylides, which are explosive. The current EO production technologies in use in North America do not result in the formation of acetylene.

Published literature describing the compatibility of mercury with EO presents an inconsistent view concerning hazards that may result from the contact of these two substances. Some papers suggest that elemental mercury can promote and accelerate the decomposition of EO. Others suggest that the presence of small, trace quantities of acetylenes contained in the EO is the source of the hazard (acetylenes react with the mercury to form explosive mercury acetylides). While the literature does not present a consensus view as to whether elemental mercury may present a potential safety hazard if it comes into contact with EO, limiting the use of mercury in EO service, where appropriate or practicable, may reduce the risk of a reactive hazard.

Non-Metallic Materials

EO rapidly attacks and degrades many of the organic polymers and elastomers that are used to make O-rings, packing material and gaskets. When selecting non-metallic materials of construction in contact with EO, it is important to understand the rate of degradation of the material. A good starting point is to review available test data specific to the EO service being considered. However, because material degradation may be affected by multiple complex factors, industry field testing or field experience with the material may also be extremely useful in helping to inform the selection.

If neither test data nor field experience data is available to help select a material of construction, consider conducting a field test that includes an analysis of consequence of material failure. If a field test is used, additional measures to monitor and evaluate the performance of the material are generally implemented, which may include:

- Testing the material in a limited number of applications;
- Testing the material in a type of application where the consequence of a material failure is minimized (for example, testing only the inboard seal on a double mechanical seal);
- Increasing the frequency of monitoring for EO leaks; and
- Increasing the frequency of inspection of the material being tested.

Gaskets

Design criteria for gaskets include materials of construction, gasket thickness and torque. There may be other gasket design criteria relevant to the specific joint. Once a facility specifies the gasket(s) to be used in EO service, it is useful to adopt a process or system to check that the specified gasket(s) are actually in use. There have been cases in the industry where one gasket was specified but a different gasket was inadvertently installed, resulting in an EO leak.

Asbestos and asbestos-filled materials are not durable in EO service. Industry experience has shown that asbestos gaskets are attacked by EO and have failed catastrophically without any prior warning. (Figure 6.1)

Polytetrafluoroethylene (PTFE) is chemically resistant to EO at temperatures as high as 400 - 500°F (204 - 260°C). Virgin (non-filled) PTFE, exhibits cold flow behavior at all temperatures and does not work well as a gasket material in most conventional applications. Several EO operations have experienced cold flow incidents with virgin PTFE (non-filled) gaskets resulting in EO releases. (Figure 6.2) At least one of these incidents was followed by ignition and significant damage to the facility. In well-confined applications (such as valve packing and tongue and groove joints), virgin PTFE can be used successfully.

Because of its tendency to cold flow, PTFE for gasket applications is typically filled with glass fibers or ceramic particles to increase its dimensional stability. Glass and ceramic filled PTFE may absorb EO. If this occurs, the EO polymerizes within the PTFE-filler matrix and the resulting EO

Figure 6.1 Degradation of Compressed Asbestos Valve Bonnet Gaskets by Ethylene Oxide

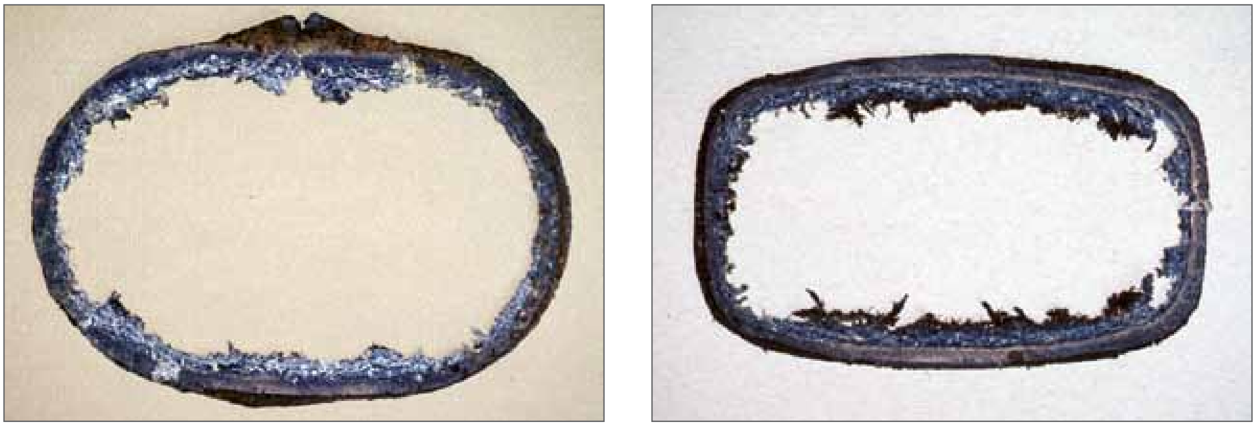
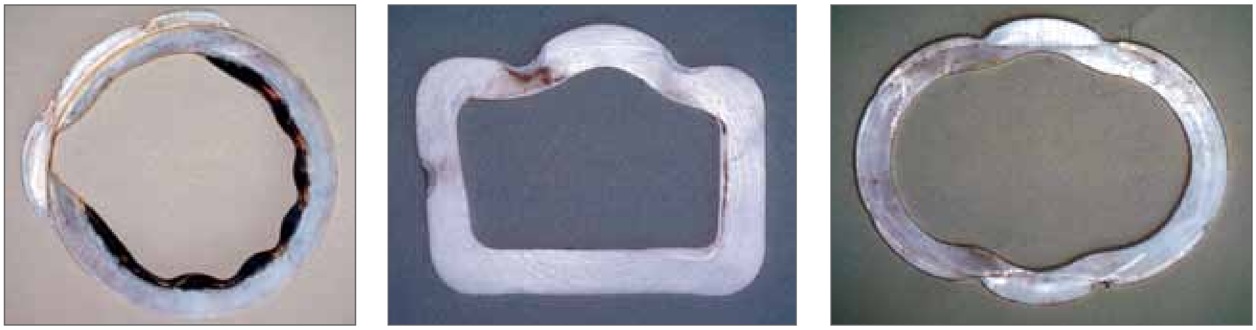


Figure 6.2 PTFE Gasket Failures in EO Service Due to Cold Flow



polymer causes swelling and failure of the gasket. Glass and ceramic filled PTFE gaskets have failed in many applications in EO service, especially at higher temperatures (Figure 6.3)

Spiral wound gaskets with stainless steel windings and virgin PTFE or graphite filler have been successfully used to seal raised face flanges and valve bonnets in EO service. However, there have also been many incidents where EO permeated between the windings and the filler material and polymerized. If EO permeates this space, EO polymer can swell and generate enough force to cause deformation or unwinding of the gasket (Figure 6.4). Inner and outer retaining rings will help avoid unwinding of the spiral wound gasket in the event that EO polymer forms within the windings. In isolated instances, polymer formation may deform the gasket windings even with inner and outer retaining rings (Figure 6.4, 6.4a) When installing spiral wound gaskets, compressing the gasket evenly will help reduce the possibility of gasket failure due to EO permeating between the windings and filler. Proper gasket placement, flange alignment and torquing procedures have been used effectively to achieve even compression.

High purity (98% or higher), flexible compressed graphite is a commonly used gasket and packing material in EO service. This material has no fillers or binders and is chemically compatible for use with EO. High purity, flexible compressed graphite is available in flat sheet form as well as crinkled tape for valve packing. The sheet form of flexible graphite is somewhat fragile, so for gasket applications the sheet is typically used as filler for stainless steel spiral wound gaskets. (Figure 6.5)

In EO service applications where spiral wound gaskets cannot be used, laminated flexible compressed graphite gaskets are often used. Several manufacturers produce gaskets from two layers of flexible compressed graphite laminated to a 0.004” tang (perforated) stainless steel sheet. Because the graphite is laminated to tang stainless steel sheet, there are no adhesives used in the lamination process. (Figures 6.7 and 6.8) If a laminated gasket is used, it is important to specify a tang stainless steel sheet rather than flat stainless steel sheet. Tests have shown that EO will attack some adhesives that are used to bond flexible graphite to flat stainless steel sheet (Figure 6.8).

Figure 6.3 **Glass Filled PTFE Gasket Failure Due to EO Polymerization in PTFE-Glass Matrix**

Figure 6.4a **Deformation of a Spiral Wound Stainless Steel-PTFE Gasket Due to EO Permeation and Polymerization**

Figure 6.4b **Deformation of a Spiral Wound Stainless Steel-PTFE Gasket**

Figure 6.5 Spiral Wound Gasket with Stainless Steel Windings, Flexible Compressed Graphite Filler, and Inner and Outer Retaining Rings

Figure 6.6 Laminated Gasket Made of Polycarbon Sigraflex™ BTCSS Flexible Compressed Graphite – Laminated on Stainless Steel Tang Sheet

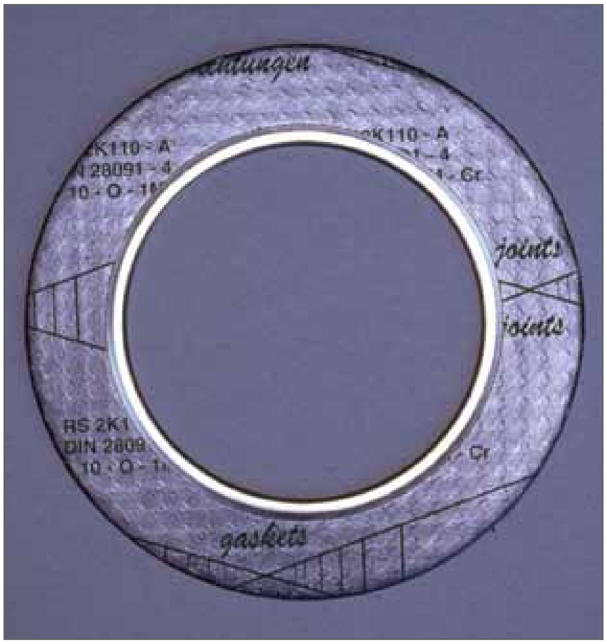


Figure 6.7 Laminated Gasket Made of UCAR Grafoil GH™ E Flexible Compressed Graphite – Laminated on Stainless Steel Tang Sheet

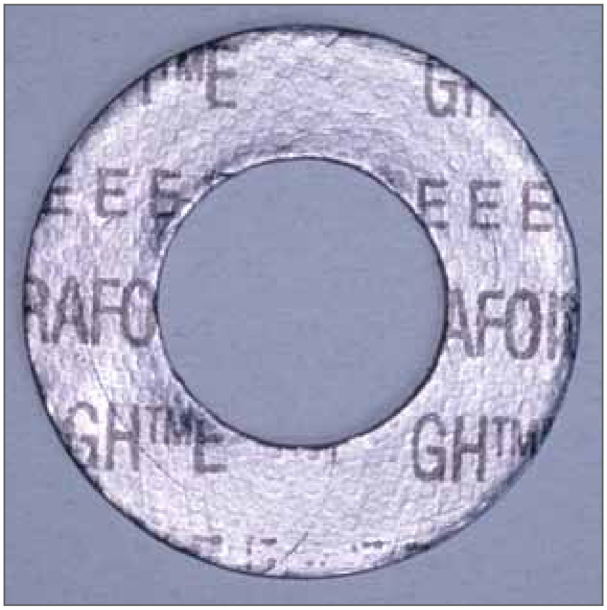
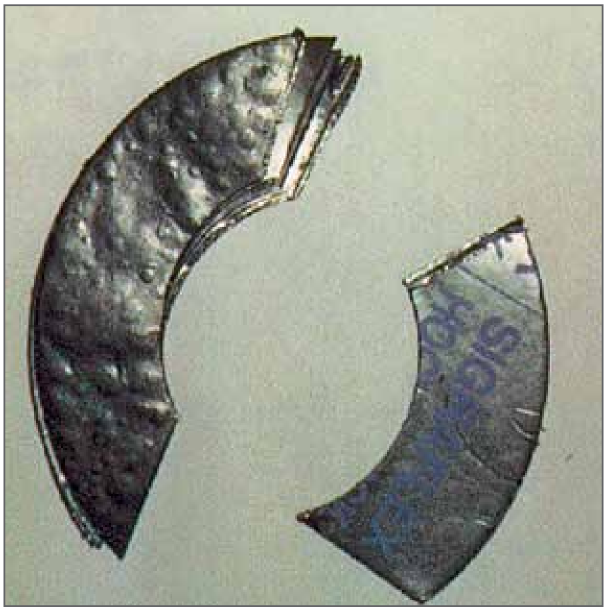


Figure 6.8 Gasket Test Showing Failure of Compressed Graphite Gasket, Laminated on Flat Stainless Steel Sheet with an Adhesive



O-Rings

Elastomers, which are most commonly used to make O-rings, often will degrade in EO service. Experience within the EO industry has shown only a few elastomers to perform well in EO service. Note that elastomers that have performed well in EO service may not perform well in applications that involve with mixtures of EO and other chemicals. For example, industry experience has shown that even though some elastomers perform well in applications in pure EO service, they will degrade in high temperature EO/water mixtures. (Figures 6.9, 6.10, 6.11)

The following is a list of elastomeric O-ring materials that laboratory tests have shown to be compatible with EO (refer to Appendix B for test methods and results):

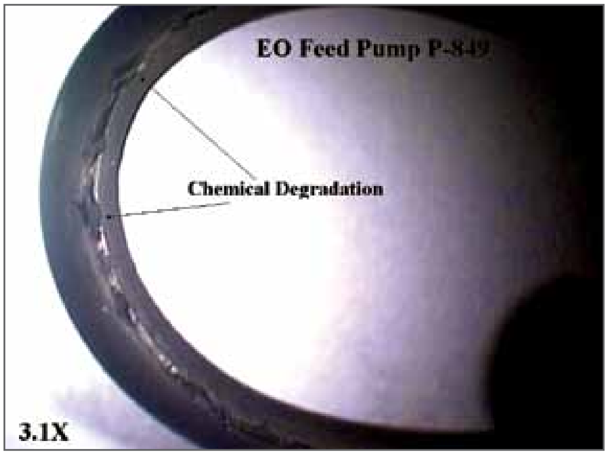
Chemraz® 505
Kalrez® 2035
Kalrez® 6375
Parker EPDM-740-75
Parker EPDM-962-90
Parker E-515-8-EPM

The following elastomers are commonly used O-ring materials in many non-EO applications in the chemical industry. Laboratory test results show that these materials are not compatible with EO.

Kalrez® 1050 LF
Viton® 2F (V1163-75 FKM75A)
Nitrile (N304-75 LT Nitrile 75)
Butyl Rubber (Bu-70)

Figure 6.9 Butyl Rubber O-Ring Before and After Exposure to EO for 30 days

Figure 6.10 Example of Degraded O-ring Attacked by EO



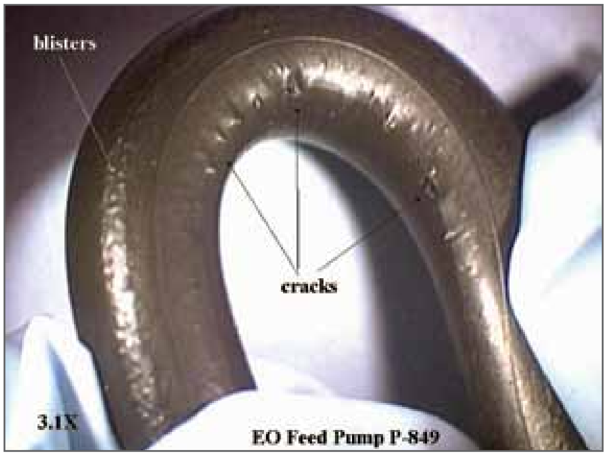


Figure 6.11 Example of Severely Degraded O-ring in High Temperature EO-water Service

Packing (Valves)

Both flexible graphite and PTFE have been successfully used as packing materials in EO service. Corrugated, flexible, compressed, high purity (98%) graphite ribbon and virgin PTFE rings or chevrons, are examples of typically used packing materials.

Durability of non-metallic materials in EO service varies with the material used and with the process conditions. An inspection program can help determine the durability and required change-out frequency for the materials selected for a given application.

Insulation

Insulation provides a degree of protection for metal walls of vessels, piping and other equipment from being heated to EO decomposition temperature by external flames. Selection of insulating materials for EO service takes into consideration many factors.

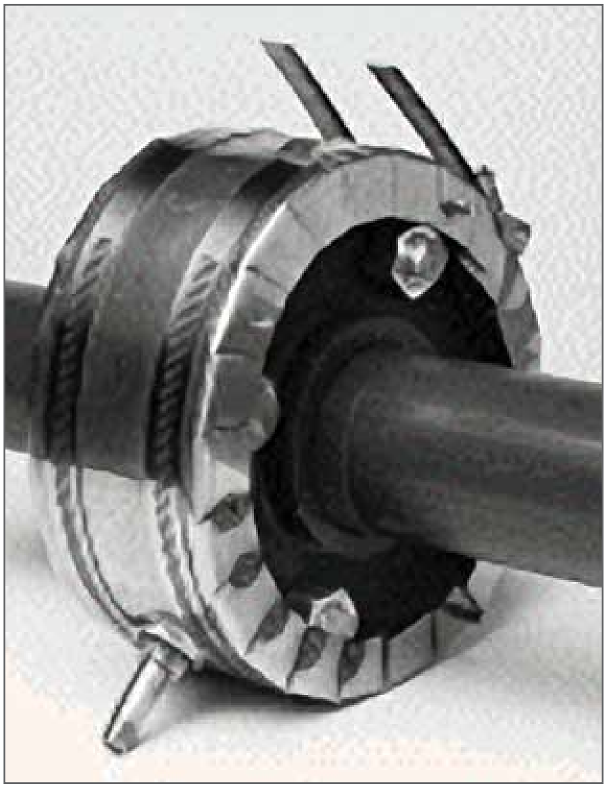
Use of closed cell non-combustible insulation materials, such as cellular glass, reduces the potential for water absorption and for exothermic reactions in the event of an EO leak under insulation. Porous insulating materials such as magnesium silicate, calcium silicate, fiberglass, mineral wool, or asbestos can absorb moisture from the environment and retain EO, which may have leaked from gaskets, pinhole leaks, or elsewhere. If water is also contained in the insulation, the EO will react with the water to form polyglycols in a highly exothermic process, creating heat in and under the insulation. The heat of reaction is trapped by the insulation, resulting in high surface temperatures. In addition to the heat generated by the exothermic polyglycol formation, the polyglycols act as a fuel reserve. With air ingress into the insulation, polyglycols can spontaneously combust at temperatures of less than 212°F (100°C), depending on the liquid loading, insulation type, thickness, and rate of air ingress. EO leaks under porous insulation resulting in hot spots and internal ignition have been implicated in major industrial incidents. Two such incidents are discussed in Chapter 5.

Note that although polyurethane foam is a non-porous insulation material, it is combustible and will not provide insulation protection in a fire scenario. Loss of insulation in a fire scenario can result in an EO decomposition.

Aluminum insulation jacketing (sometimes called sheathing) and banding have a relatively low melting point. In a fire scenario, insulation can be lost when aluminum sheathing and bands melt or burn. Stainless steel or galvanized carbon steel jacketing and banding has superior fire resistance to aluminum.

For insulated flanges, it is helpful to install leak detection tubes at the flanges. Sealed stainless steel bands installed around the flange can help prevent transport of liquid along the piping. (Figure 6.12) In horizontal lines, pre-formed snap-on insulation boxes can be adapted so that in the event of leakage the liquid will be drained.

Figure 6.12 **Example of Flange Seal Band with Leak Detection Drip Tube**



6.4 Unloading Facilities – Bulk Receipt of EO

Design consideration for EO unloading facilities seeks, among other things, to minimize the potential for contamination of EO. One mechanism to achieve this is to design a system dedicated exclusively to EO.

Backflow of process contaminants into an unloading EO railcar can contaminate the EO, so facility design will seek to avoid the potential for backflow. Intermediate storage vessels downstream from the offloading facility are commonly used to avoid backflow, but other engineering controls have been successfully used.

Locate the EO unloading area with sufficient separation from inventories of flammable materials and with sufficient space to allow movement of railcars. Provide sufficient space in the unloading area for vehicle access.

Acceptable means of transfer from a railcar or intermodal (IM) portable tank into the storage facility include pressurization with nitrogen gas and pumping. If pressurization is used, design considerations include controlling the pressure applied to the railcar and adopting an appropriate means for venting off excess pressure. If EO railcars are pressure off-loaded with excessive nitrogen pressure, the relief valve O-rings may be damaged by premature weeping of the relief valve (75 psig safety valve setting per DOT requirements). Off-loading at pressures no greater than 50-55 psig greatly reduces this potential.

Because of the flammability and reactivity hazards of EO, pressurized transfer by heating is not an acceptable practice.

Typical layouts for a pressure transfer facility and a pump transfer facility are shown in Figures 6.13, 6.14, and 6.15.

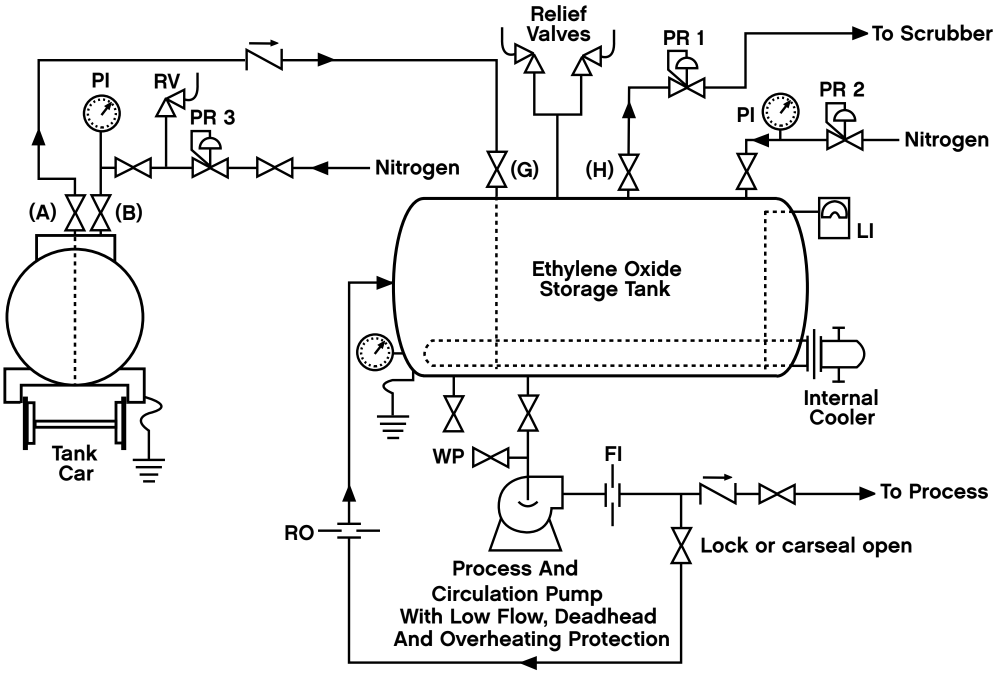
Design of unloading facilities also takes into consideration adequate electrical grounding, which prevents dangerous differences in electrical potential developing between the carrying vessel, body of the vehicle, piping, and ground or earth while unloading the shipping vessel. If a manual grounding system is used, consider including a ground indication light and/or interlocks.

Installation of a water deluge system and fire monitors at the unloading site can help support on-site fire fighting, enhance the ability to "knock down" EO vapors, and provide water for the dilution of EO that might pool in the unloading area in the event of a release. Water deluge systems that can be activated manually (either at the unloading site or at a remote location); by combustible gas detectors; or by high temperature sensors are available for use in EO service.

Facility design considerations also include mechanisms to access the railcar dome while unloading. DOT regulations require protection against inadvertent movement of the railcar during connection of the loading/unloading hoses. Use of an elevated rack for railcar dome access is an appropriate approach.

Figure 6.13 **EO Unloading Facilities**

Figure 6.14 Representative layout of Ethylene Oxide unloading facilities – Pressurized transfer



SAMPLE PROCEDURE FOR UNLOADING WITH INERT GAS

(1) Check pressure, temperature, inventory of storage vessel, and all piping line-ups before unloading the EO railcar or IM portable tank. While unloading, system pressure always remains in the inert region as determined by railcar and storage vessel temperatures (Figure 6.16 can be used as a guide for sites to establish minimum pressure(s) for unloading operations and onsite storage).

(2) Verify valve H is open

(3) Open liquid valves A, G

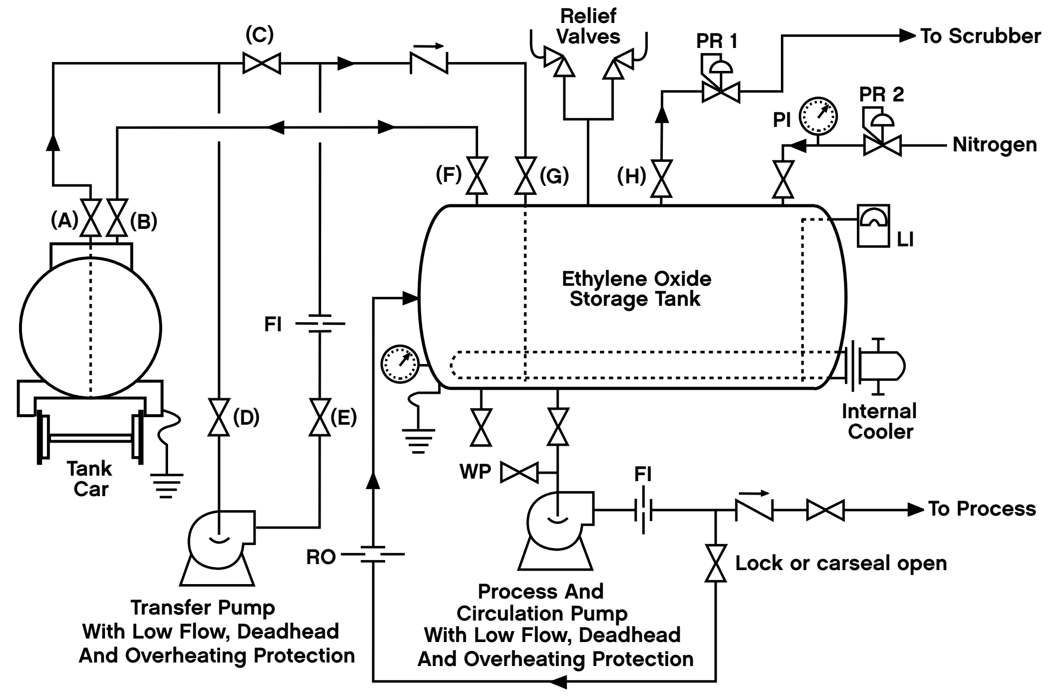
(4) Open vapor valve B and apply nitrogen pressure

NOTE: Figure 6.14 and the sample procedure are provided for illustration purposes only. Specific system design should be made following consultation with appropriately qualified engineers or experts.

NOMENCLATURE

RO — Restrictive orifice
TI — Temperature indicating device
PI — Pressure indicating device
PR 1 — Pressure regulator –35 psig setting min.
PR 2 — Pressure regulator –35 psig setting min.
PR 3 — Pressure regulator –60 psig setting max.
RV — Safety valve set to open at 70 psig or below (Note: nominal set pressure for EO railcar relief valves is 75 psig as specified by the US DOT, with an acceptable range of 72-78 psig before opening)
LI — Level indicating device
WP — Wash point valve
FI — Flow indicator

Figure 6.15 Representative layout of Ethylene Oxide unloading facilities – Pump transfer



SAMPLE PROCEDURE FOR UNLOADING WITH TRANSFER PUMP –

(1) Check pressure, temperature, inventory of storage vessel, and all pipe line-ups before unloading the EO railcar. While unloading, system pressure always remains in the inert region as determined by railcar and storage vessel temperatures (Figure 6.16 can be used as a guide for sites to establish minimum pressure(s) for unloading operations and onsite storage).

(2) Open liquid valves A, D, E, G

(3) Close liquid valve C

(4) Open vapor valves B, F

(5) Check that the transfer pump is properly primed and not vapor bound

NOTE: Figure 6.15 and the sample procedure are provided for illustration purposes only. Specific system design should be made following consultation with appropriately qualified engineers or experts.

NOMENCLATURE

RO — Restrictive orifice
LI — Level indicating device
TI — Temperature indicating device
WP — Wash point valve
PI — Pressure indicating device
FI — Flow indicator
PR 1 — Pressure regulator –35 psig setting min.
PR 2 — Pressure regulator –35 psig setting min.
PR 3 — Pressure regulator –60 psig setting max.
RV — Safety valve set to open at 70 psig or below (Note: nominal set pressure for EO railcar relief valves is 75 psig as specified by the U.S. DOT, with an acceptable range of 72-78 psig before opening)

6.5 EO Storage

EO Storage Vessels – Types

A variety of EO bulk storage vessels have been successfully used by industry. Considerations for vessel type selection include site location, size of space available, and regulatory requirements, as well as the features of the types of vessels noted as follows:

- Aboveground and free standing vessels (three types):
  - **Cylindrical (vertical)**. Advantages: minimum flame impingement; ease of monitoring inventory; less potential for accumulation of polymer.
  - **Cylindrical (horizontal)**. Advantages: less exposure to flying debris in the event of an incident.
  - **Spheres**. Advantages: less potential for accumulation of polymer.
- Mounded (vessels at grade level covered with sand or soil) and buried vessels.
  - **Advantages:** passive fire protection and protection against impact.
  - **Disadvantages:** unable to readily detect leaks if not double walled; top take off eliminates the need for underground flange connections but increases potential for polymer accumulation in the sump; it can be difficult to inspect external shell condition, sometimes necessitating internal entry to verify shell integrity.

Selection of storage vessel type will be dependent on company philosophy, plot space, and regulatory requirements. Long-term and extended storage of EO should be made in storage vessels designed or appropriately managed for this purpose.

Design Considerations – EO Storage Vessels

Vessel capacity is a relevant design consideration for storage vessels. Providing sufficient vessel capacity to allow unloading of an entire railcar in one continuous operation will minimize railcar connection/disconnection operations and the potential for EO release and personnel exposure.

NOTE: EO in railcars is not as readily monitored for temperature or pressure increases as in specially designed storage vessels. Railcars have no capability for external heat removal in case of EO polymerization or reaction with a contaminant. EO railcar relief valves are generally sized for fire conditions and not for reaction scenarios.

Diking and containment are other important considerations when designing an EO storage area. Locating above-grade EO storage vessels within a diked area, or an area otherwise designed to contain vessel leaks or spills, can help prevent other product spills from entering the EO storage area. Protection of an EO storage vessel from possible exposure to a pool fire should be a major consideration when designing an EO storage area. A pool fire under an EO storage vessel is a very hazardous situation that can lead to an EO decomposition. If diking is used, it is very important to design the EO storage area with an adequate grade under the storage vessel and in the storage vessel dike area so that any liquid release will drain away from the vessel and cannot form a pool beneath or adjacent to the vessel. Another containment option is the use of a drainage system under EO storage vessels that routes liquid to a secondary containment area located well away from the EO storage vessel. This approach can be used to contain both EO spills and firewater or dilution water.

Fire Protection Systems

Fire protection measures are also considered in the design process. Passive fire protection, such as insulation, can provide additional fire protection for those vessels located above grade and not mounded or buried. Remotely operated, fire-resistant valves allow isolation of the storage vessel in the event of an emergency. Additionally, excess flow check valves can be used at the vessel inlet and outlet lines to minimize releases in the event of downstream piping and equipment failure.

NFPA 58 and API 2510 and 2510A may apply to the design of fire protection systems for EO storage and processing areas. These codes describe fire protection systems with passive (insulation) and active (deluge/sprinkler) systems. Areas appropriate for deluge protection can be identified using process hazards analysis methods that examine the severity of the consequences of a fire scenario.

A fire protection system takes into consideration whether fire water supplies are located so as to be readily available and sufficient in volume so as to adequately dilute a spill. Drainage design for the system includes the capacity to retain emergency water whether used for cooling, fire fighting, or dilution purposes.

Storage vessel design pressure and inerting of storage vessels

A primary consideration in vessel design is vessel pressure. Consult the current ASME Code for Unified Pressure Tanks for the minimum design working pressure consistent with process requirements, including consideration of the blanket inert gas pressure needed to maintain a non-decomposable vapor space.

Understanding pressure is extremely important due to the potential for pure EO vapor to decompose explosively. Refer to Section 2.3 for more information. EO vapor spaces can be rendered non-decomposable by dilution with the appropriate concentration of an inert gas. In practice, vessels are most often inerted with nitrogen and are maintained in the non-decomposable region by controlling pressure and temperature.

> **CAUTION: Carbon dioxide is generally not used as an inerting gas. CO2 exhibits very high solubility in liquid EO (approximately ten times that of nitrogen).**

Based on existing published data, Figure 6.16 illustrates the storage pressure needed in fixed storage vessels to achieve a non-decomposable EO vapor space, as a function of liquid storage temperature. (Refer to Chapter 9 and Appendix C for pressurization of railcars.) The figure assumes use of nitrogen as the inerting gas. The graph is a useful tool for calculating an appropriate storage temperature for EO facilities and operations. In selecting an inerting pressure, a key consideration is to maintain the vapor space in the non-decomposable or inert range over the full range of EO storage temperatures. Calculating the inerting pressure required in the event of loss of cooling can be factored into the storage vessel design process.

Storage vessel contamination, backflow and inerting

Contamination of EO in storage vessels can lead to an uncontrolled runaway reaction with serious consequences if facility design does not include measures to prevent or mitigate such incidents. Possible sources of storage vessel contamination include:

- Backflow from other process areas
- Incorrect vessel line-ups, allowing other materials to enter the storage vessel
- Contaminants in the inerting gas
- Contaminants such as water, cleaning solutions and other materials inadvertently remaining after maintenance

Backflow of process fluids into EO storage vessels from other process areas, such as reactors, can result in an extremely rapid, exothermic reaction. Be aware that storage vessel emergency relief valve /device sizing and cooling system capacity (if so equipped) may not consider runaway reactions as a design case. Consequently, system engineering is critical to prevent or minimize backflow from occurring.

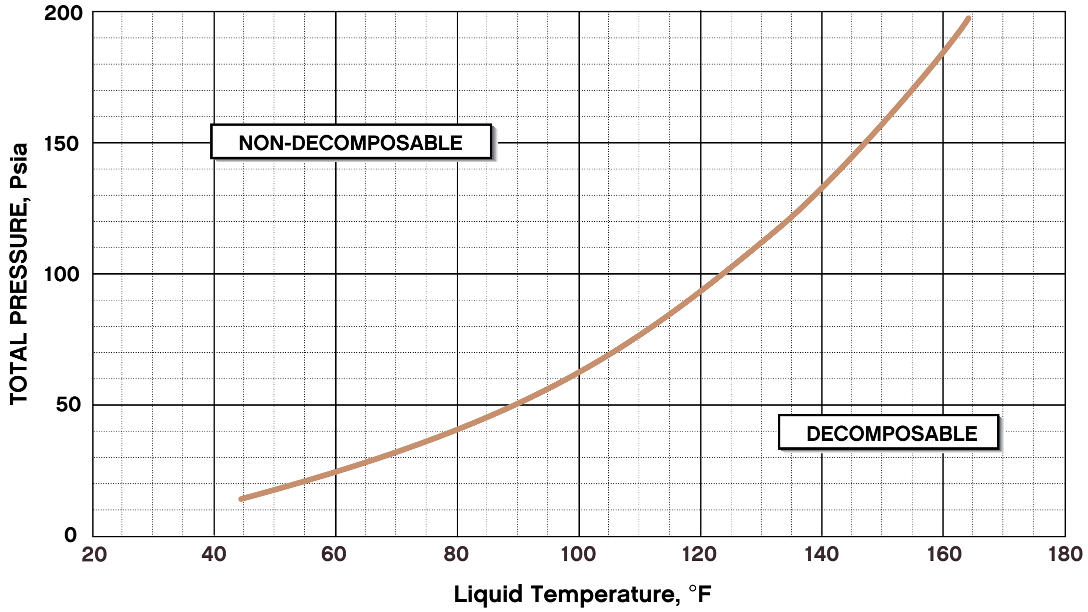
Engineered backflow prevention systems can provide a reliable and robust system to prevent backflow of process fluids into EO pipeline and storage facilities. See discussion on *Prevention of Backflow in Reactors* in Section 6.6, Reaction Systems, for more information.

Historically, check valves have been used as part of an overall system to prevent backflow of process fluids into EO supply pipeline and storage systems. Industrial experience has shown that a single check valve alone may not be an adequate backflow prevention device. Multiple check valves of the same type may experience common mode failures. Consider multiple check valves of different types and/or automatic isolation valves to protect against backflow.

EO users should be aware that inerting systems are themselves potential sources of contamination. Systems used to prevent inert gas contamination include:

- Dedicated sources of inert gas, such as high-pressure cylinders, or liquid nitrogen storage and vaporizers.

Figure 6.16 Total pressure required to inert vapor above Ethylene Oxide with nitrogen diluent



Based on "Prediction of decomposition limits for ethylene oxide-nitrogen mixtures", J.L. Brockwell; Plant Operations Progress, vol. 9, 98-102, April 1990

- Area knockout pots with high liquid level alarms or interlocks on nitrogen supply lines. This design can prevent contamination of EO with other chemicals while also preventing the contamination of other plant systems with EO.
- Continuous analyzers (for contaminants) on inerting systems.
- On a high pressure nitrogen supply pipeline – (1) the EO user uses nitrogen first, ahead and upstream of all other users and/or (2) there are backflow prevention systems at each point of nitrogen withdrawal, for each user (a single check valve is not relied on as the sole means of preventing inert gas contamination).

Incorrect vessel and pipeline manifolding can also lead to contamination of the EO storage vessel, resulting in the potential for violent reaction. Dedicated EO storage and piping systems are used from off-loading to storage to reduce the potential for contamination. Clearly marked and identified EO pipelines, especially in the receiving area, have been used to prevent unloading an incompatible fluid into an EO vessel.

Storage vessel pressure relief systems

Pressure relief devices are sized to relieve pressure developed by the controlling contingency identified for that process. A safety analysis of the process is conducted to define the characteristics of the controlling contingencies. Pressure relief devices, however, are not designed to provide relief in cases such as explosive decomposition of EO. Additional information about proper sizing of relief systems can be found at:

- API Recommended Practices #520-521 (addresses sizing of pressure relief valves; these practices do not cover reaction scenarios)
- NFPA 58: Liquefied Petroleum Gas Code (pressure relief guidelines)
- ASME Code for Unfired Pressure Vessels (design standards for relief protection).

Uncontrolled releases can be minimized by setting an adequate margin between ordinary operating pressure and the design pressure of the storage vessel to minimize such uncontrolled releases.

With regard to the routing of relief valve discharges, some systems are designed to vent to the atmosphere, while other systems are designed to feed into a flare or scrubber. If routing to a scrubber, consider the pressure drop across the scrubber and the possibility of plugging or damage in the scrubber in the design. If vented to atmosphere, discharges from pressure relief devices are designed with adequate height and discharge velocity to prevent contact of flammable vapor clouds with potential ignition sources. Addition of steam to the relief valve outlet piping, manually or automatically, can improve dispersion and reduce flammability of the EO plume. Relief valve discharge piping routed to the atmosphere is also designed to minimize potential for human exposure. See Section 6.8 for additional information on design considerations for controlling vent emissions.

Atmospheric discharge from safety valves and vents can result in a fire or an explosion. In some incidents, flames from ignited vent streams were found to have impinged on vessel walls or piping. Directing vents and safety valve discharges of EO and other flammables well away from equipment or piping containing EO is therefore an important design step.

Rupture disks on EO storage vessels should not be used for pressure relief because they will not reseat. Use of a rupture disk in conjunction with a pressure relief valve for control of fugitive emissions may, however, be appropriate.

In EO pressure relief system nozzles, blockage by polymerization has been observed in both EO liquid and vapor service (in EO vapor service, the EO condenses and polymerizes). This condition can be minimized or avoided by a number of different approaches, including, but not limited to:

- Locating pressure relief devices as close to the vessel shell as possible. Stagnant vapor in long lengths of dead-ended pipe may promote polymer formation.
- Bursting/rupture disks can be placed on the upstream side of the pressure relief valves to help prevent accumulation of polymer in the pressure relief valve. (Non-reclosing bursting/rupture disks are generally not used as a method of emergency relief; such devices would allow the continued escape of EO from the storage vessel.) If equipped with a bursting/rupture disk upstream of the pressure relief valve, a method of indicating failure of the disk, such as a pressure gauge between the disk and pressure relief valve, might be considered.
- Introducing a small nitrogen stream into the nozzle upstream of either the bursting disk or relief valve to sweep away EO and prevent polymer formation in the nozzles. If the discharge is in to a header system, a nitrogen sweep downstream of the relief valve may be warranted.
- Using stainless steel as a material of construction for piping, isolation valves, and relief valves.

Note that the lifting of a storage vessel relief valve or similar action by other pressure relief devices is not considered to be a routine pressure management event for EO service. These devices are intended to function as emergency venting devices and not as a part of routine pressure control practices.

Instrumentation

EO storage instrumentation is designed to provide accurate level measurement, accurate temperature measurement and sufficient data to determine that the storage vessel is inerted at an adequate pressure to stay out of the decomposable region. Consider the following when designing instrument systems for EO storage:

- Remote monitoring and trending of EO storage instrumentation.
- Installation of multiple, independent level measurements (a level measurement with an independent high level alarm).
- Installation of multiple, independent temperature measurements and alarming on high temperatures.
    - Multiple temperature measurements might include, especially for larger storage vessels, temperature monitors at different liquid levels to differentiate between potentially stratified EO layers that could represent isolated areas of reaction.

  - Monitoring and alarming on rate of rise of storage temperature. Changes in the rate could indicate intensification of a contamination reaction and help signal the need for corrective actions or emergency response.
- Monitoring of pressure, with alarms for both high and low pressure (low pressures indicate loss of inerting gas).

The use of stainless steel tubing for instrument impulse lines in EO service will reduce the likelihood of polymer formation and plugging. Also note that the use of remote diaphragm, sealed differential pressure transmitters, "bubbler" dip tubes, ultrasonic level devices, vessel radar or nuclear level indicators can reduce the potential for erroneous level indication caused by polymer formation. Gauge glasses are typically not used because they have the potential to be damaged and/or leak. As mentioned above, plugging from polymer formation can result in false gauge level indications.

Although the use of mercury in instrument systems has declined considerably in the past few decades, instances do occur where elemental mercury may be present within an instrument system or device. See the *Metallic Materials* discussion in Section 6.3 for more information about the use of mercury in EO service.

Refrigeration

EO can be stored in refrigerated or non-refrigerated storage vessels. Refrigerated storage has the following benefits:

- Lower temperatures decrease the rate of EO polymerization, reducing the potential for polymerization-related difficulties such as vessel nozzle plugging.
- If the EO is contaminated, refrigeration systems can remove all or part of the heat of reaction. In some cases, this substantially assists in control of the reaction; in others, it slows the reaction, providing more time to implement control or disposal measures.
- Lower EO storage temperature allows a lower inert gas pressure to maintain the vapor space in the non-decomposable region.
- Lower temperatures will result in a smaller fraction of EO being vaporized in the event of a leak. The hazard of a pool of EO liquid may be mitigated more successfully than that of a vapor cloud.

One possible drawback of refrigeration, especially at low temperatures, is a reduction of the solubility of EO polymer, which may cause the precipitation of polymer that has already formed. This can cause plugging of instrument tubing and plugging of transfer lines.

Another issue that must be considered with refrigerated EO storage is detection of a reaction in the storage vessel. If a reaction occurs in an EO storage vessel and the refrigeration system is controlling the EO temperature, the refrigeration system will remove the heat of reaction until the refrigeration system capacity is exceeded. In this scenario, the operator may not be aware a reaction is occurring until the reaction has been going on for quite a while. If refrigeration is used for EO storage, consider installing instrumentation to calculate the heat load on the refrigeration system and include an alarm on high heat load and increasing heat load.

Reference [5] is a useful study of the relative risks of storing EO at moderate temperature and pressure versus low temperature and pressure.

EO storage refrigeration designs can incorporate refrigerated coils within the storage vessel, an external vessel cooling jacket, or an external heat exchanger and circulation pump. Internal coils can offer better heat removal in the event of an exothermic reaction within the storage vessel. Internal coils, however, can potentially contaminate the storage vessel if a leak occurs. Depending on the coil configuration, heat transfer area for internal and external coils may be less at lower levels in the vessel as the coils are not in contact with the liquid. Heat transfer fluids such as water or glycols could react with the EO in the vessel. External heat exchangers may also contaminate the vessel contents due to leakage, but the leak can be readily isolated for a more timely and expeditious repair. External vessel cooling jackets minimize the potential for contamination but may be less effective at heat removal.

Maintaining the refrigeration system coolant pressure below that of the storage vessel reduces the potential for contamination of the vessel contents in the event of an exchanger leak. In such a case, a leak can be identified by routinely monitoring the coolant for EO.

In practice, storage temperatures range from 20°F to 80°F (-6°C to 26°C), with a typical range of 40°F to 60°F (4°C to 15°C). Operating with temperatures in the lower end of the range can result in precipitation of EO polymer. The consequence of this can be reduced by operating at EO storage temperatures comparable to those of the EO supplier.

Consider incorporating alarms in the refrigeration system design to alert individuals in the event the system shuts down or begins to lose cooling capacity.

Emergency Disposal of Vessel Contents

Design of an EO storage system includes provisions for the disposal of EO inventory in the event of a contamination reaction. The objective is to safely dispose of storage system contents before the rate of temperature increase becomes too rapid and/or the concentration of EO in the vapor phase approaches or enters the non-inert region. Options in current practice include:

- Reacting the EO to glycols or other derivatives by feeding to downstream users (under emergency disposal conditions, a rapid rate of consumption is the goal of the reaction)
- Depressuring the storage vessel. Examples include discharge into a scrubber, flare system, or to an elevated discharge point. Depressuring can be a highly effective response because evaporation of the EO during this procedure provides an auto-refrigeration effect, which cools the vessel contents. See section 6.8 for the EO-specific design considerations for a flare system.
- Transferring to a holding system and diluting with water. If the transfer is to a body of water such as a pond, the volume of the pond must be sufficiently high to allow a dilution ratio of at least 22:1 volume/volume water to EO to limit the flammability of the vapor above the resultant mixture. In fresh water, EO hydrolyzes to ethylene glycol very slowly, with a measured half-life of 14 days. Acids or bases can be directed to the pond to catalyze the water – EO reaction and speed the conversion of EO into glycol. During conversion EO vapor will continue to be evolved.

EO users must carefully consider the effects of any of these actions on the health and safety of their workers and communities and on the environment. These actions should only be taken as part of a well-defined, site-specific emergency response plan that has addressed environmental and worker safety regulatory requirements. See also the discussion in Chapter 10 regarding emergency response and the discussion of personal protective equipment selection in Chapter 7.

6.6 Reaction Systems

Consider the following elements in the design of EO reaction systems:

- Prevention/minimization of backflow from reactors into EO storage vessels.
- Prevention/minimization of build up of unreacted EO.
- Prevention/minimization of explosive mixtures in reactor vapor space.
- Heat duty requirements.
- Catastrophic failure modes.
- Materials of construction.

More details about these elements are discussed below.

Prevention of Backflow from Reactors

Catalysts in widespread use in EO reaction systems, such as KOH, have the capability to initiate EO polymerization and accelerate other reactions if they backflow into EO storage vessels. These reactions are exothermic and can result in uncontrolled heat release and vessel rupture. Note that storage vessel emergency relief sizing does not normally consider runaway reaction as a design case. Likewise, storage vessel cooling systems are ordinarily designed to remove heat gain from ambient sources or to remove temperature after unloading a railcar. Storage vessel cooling systems are generally not designed to address the extremely rapid reaction rate of EO and its highly exothermic nature, so it is important that engineered systems be employed that prevent backflow from occurring. Examples of engineered systems for backflow prevention include:

- Triple block and double bleed automatic valves activated by three independent inputs;
- Double block and single bleed automatic valves activated by two independent inputs;
- Double block and single bleed automatic valves activated by one independent input; and
- Multiple high performance check valves (single check valves are generally not considered a reliable means, by themselves, to prevent EO backflow).
- Combinations of automatic block valves and check valves

Historically, check valves have been used as part of an overall system to prevent backflow of process fluids into EO supply pipeline and storage systems. Industrial experience has shown that a single check valve alone may not be an adequate backflow prevention device. Multiple check valves of the same type may experience common mode failures. Consider multiple check valves of different types and/or automatic isolation valves to protect against backflow.

The operation of an engineered backflow prevention system should be checked on a regular basis. For instrumented systems, consider the need for redundancy of the sensing element, logic solver and final control element to provide a robust protection system. Diversity in sensing elements is often used in engineering design, such as pairing a low flow sensor with a differential pressure meter across the EO feed valves. Setting the EO feed pump discharge pressure higher than the reactor safety valve set pressure is a common practice to minimize the potential for backflow.

Prevention of Buildup of Unreacted EO

Accumulation of unreacted EO in a reaction system can result in a runaway reaction exceeding the designed heat removal and relief capacity of the system. The rate of reaction is almost always dependent upon the concentration of EO present; thus, by controlling the EO feed rate and the reaction temperature, the reaction rate is also controlled. Establishing automatic EO feed shut down points based on maximum allowable feed rates at a minimum reaction temperature or on analyzed unreacted EO concentration present in a reactor are common protection methods. On-line analyzers are another means of continually monitoring unreacted EO levels.

Some conditions that can lead to an accumulation of unreacted EO include:

- EO addition rate higher than design limits
- Poor mixing of reactants and catalysts
- Low concentration or lack of catalyst
- Low reaction temperature

If the control parameters are outside the design limits, automatic shutdown of EO feed is typical.

Possible indications of unreacted EO include:

- High reactor pressure
- High EO concentration in EO vapor space
- Lack of heat of reaction

An additional hazard occurs if reactor product contains significant quantities of unreacted EO. This can result in release of EO vapor from product storage vessels. Not providing sufficient reaction time can contribute to such a condition. See Section 5.3 for a discussion on a release of unreacted EO.

Prevention of Explosive Decomposition of EO in Reactor Vapor Space

The amount of diluent required to provide a non-decomposable mixture in the reactor vapor space varies with temperature and EO concentration. The reactor pressure control system should be designed to provide adequate diluent pressure to prevent decomposable mixtures over the expected range of reactor operation. Parameters to be considered when determining decomposability limits include:

- Temperature operating range
- Pressure operating range
- Reactor mechanical design (for example, batch, semi-batch, CSTR, plug flow, or circulating loop reactor)
- Solubility of nitrogen or other diluent employed in the reaction mixture

Some reaction system designs allow decomposable EO concentrations in the vapor space. These designs have typically eliminated sources of ignition such as mechanical agitators. In such designs, it is important to eliminate external sources of heat such as hotspots in the insulation.

Figure 6.17 illustrates the molar nitrogen concentration at the EO decomposable limit versus temperature for several total system pressures as measured by June and Dye. [6]. All data is for the nitrogen-EO binary system. The presence of other materials may invalidate these predictions. This graph differs from Figure 6.16 in that it addresses EO concentrations at saturation and below. Figure 6.16 is applicable only to systems containing both liquid and vapor EO in equilibrium. For systems such as vessels and reactors where no liquid EO is present, Figure 6.17 may be used as a tool to assist in the determination of the nitrogen pressure required to have a non-decomposable composition. An alternate way of representing the data that may be more useful if the vapor oxide concentration is being measured is to plot mole% EO versus total system pressure as is presented in Figure 6.18.

Unless a process specifically requires oxygen for the process chemistry, all air or oxygen should be excluded from the reactor space. The presence of oxygen reduces the lower decomposable concentration of EO and reduces the minimum ignition energy for EO. See Section 2.3 for further discussions on the combustion properties of EO.

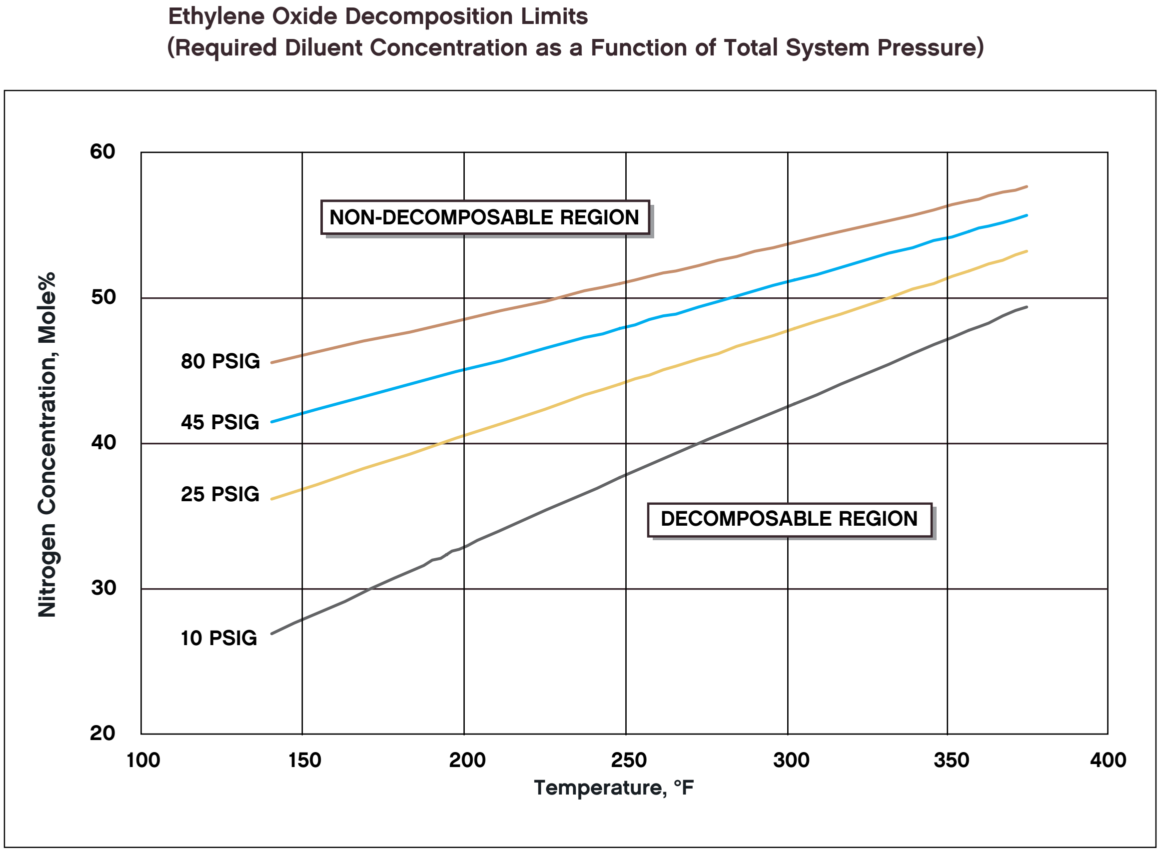
Reactor Design and Instrumentation

Consider designing reactor cooling systems with excess capacity to remove the heat generated by the onset of a runaway reaction. Since designing to remove 100% of the heat generated in a runaway reaction scenario may not be practical, automatic EO feed shutdowns are often utilized to restrict the magnitude of incidents.

Consider designing reactor control systems to stop EO addition in the event of the following:

- Excess rate of EO feed
- Failure to add other reactants

Figure 6.17 EO Decomposable Limits versus Molar Nitrogen Concentration



- Failure to add catalyst
- Loss of mixing or agitation
- High reactor temperature
- Low reactor temperature
- Loss of cooling
- High reactor pressure
- Low reactor pressure
- Loss of utilities such as electricity
- High EO concentration in vapor or liquid

If practicable, reactor vent and/or safety valve capacity can be sized to help mitigate upset conditions.

Process analyzers can be used to monitor EO concentration in the reactor vapor space to maintain operation below the decomposable limit. When process analyzers are used as part of a safety system, continuing maintenance is important to maintaining high reliability. Analyzer cycle time is a consideration in the design of safety systems. Redundancy and on-line error detection are common features when analyzers are used as part of reaction shut down systems.

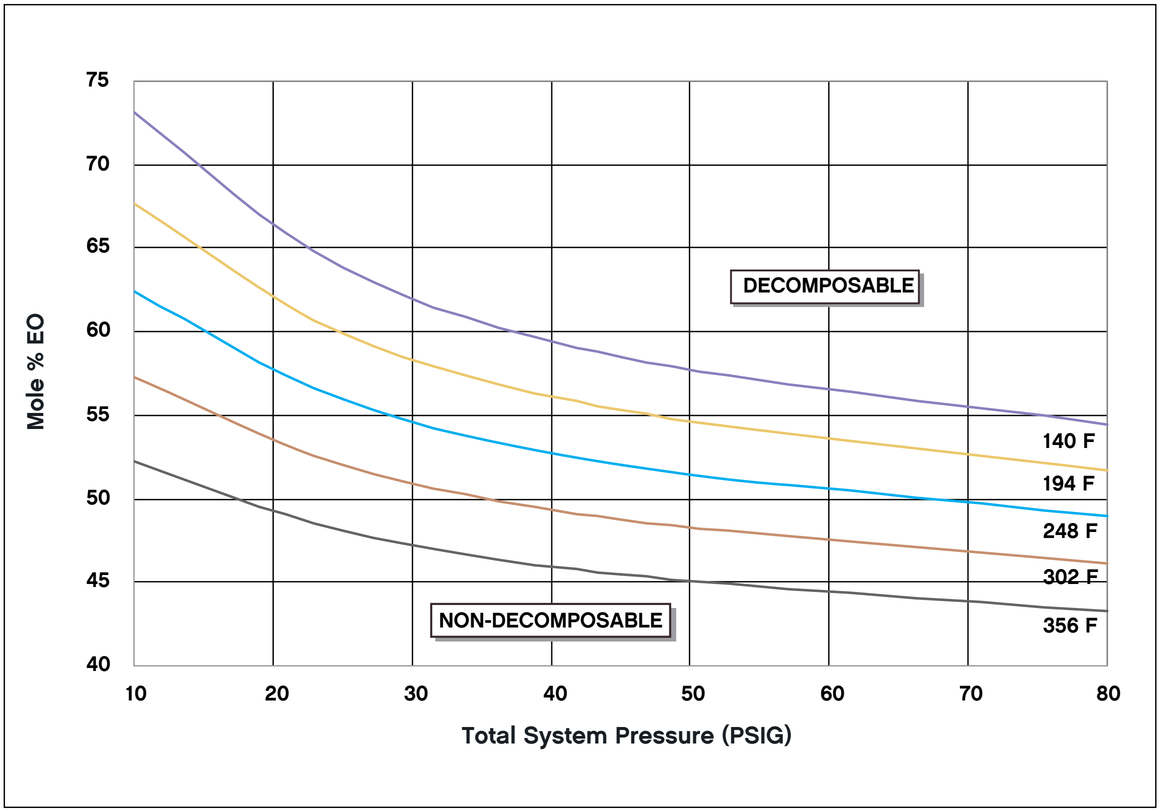
6.7 Piping and Pumps

Piping Systems

Carbon and stainless steel are suitable materials for EO service piping. Piping constructed of non-metallic materials has limited fire resistance, can be subject to chemical attack, and is not considered suitable for EO service. Stainless steel piping systems retard the development of rust, so these systems may eliminate the need to remove rust from the interior of the piping prior to initial service and after outages where the interior of the pipe is exposed to the atmosphere. Carbon steel systems, on the other hand, may require significantly more service over their lifetimes to remove rust.

Figure 6.18 Decomposition Limit of Mole % EO versus Total System Pressure

EO Decomposition Limits
(Mole % EO versus Total Pressure for EO-N_2 Binary System



Proper installation and maintenance of insulated piping is especially important because moisture can infiltrate under the insulation, damaging the pipe's protective coating and reducing metal thickness and strength. Carbon steel systems are more susceptible to water-initiated external corrosion than stainless steel systems, but regardless of the type of steel used, it is important to periodically remove insulation and verify the integrity of piping systems.

EO polymerization is a design consideration for EO piping systems due to the relatively high amount of surface area of the piping system. Polymerization, once begun, can continue over extended periods of time in a piping system. Construction of piping systems to minimize the number of low points and dead spots ("stagnant areas") helps avoid or slow polymerization. Designing piping lines to be as short as possible with gravity drainage to points at which contents can be purged from the system with nitrogen is another useful technique. In areas where emptying stagnant EO lines is not feasible — for example, a long EO charging line to a batch reactor — a pipe loop that circulates back to the storage vessel may be considered as a design option. Chilled tracing of lines that may sit idle can also reduce the polymerization potential.

Welded and/or flanged construction is generally used in EO piping systems because it is considered to have less leak potential than threaded joints. For instrumentation connections, consider using welded or flanged construction up to the instrument/instrument tubing isolation valve. The design process should seek to minimize the number of flanges because each flange represents a potential leak source (including fugitive emissions). Where flanges are necessary, they should utilize gasket materials suitable for EO service.

Preventing or minimizing introduction of contaminants into the system is a critical design element for an EO piping system. Some key considerations are:

- Operating EO piping as dedicated piping for EO product only;
- Minimizing valves in EO piping that can be used to connect/introduce foreign products into the piping system;
- Providing clearly visible, permanent labels on EO piping; and
- Minimizing permanent connections to water, steam, or other substances that are reactive with EO.

Use of Hoses in EO Service

Hoses are generally not used for process line applications in EO service because they cannot be effectively insulated for fire protection. In an external fire situation, a hose containing EO is very vulnerable to EO decomposition.

There are four applications where hoses are commonly used in EO service. The first three are 1) EO sample systems; 2) EO loading or off-loading connection to railcars; and 3) hoses for blowing EO equipment clear of EO with nitrogen. For these three applications, the hoses are used for a limited time period and then blown clear of EO with nitrogen. The fourth application where hoses are commonly used in EO service is in filling and unloading small EO containers such as EO drums or cylinders. In this type of application, hoses are often in continuous use, but they are also well protected with deluge systems and blown clear of EO with nitrogen after use. When hoses are used in EO service, larger hoses are typically corrugated stainless steel with a stainless steel braid outer jacket with welded fittings. For small sampling hoses, PTFE hoses with stainless steel outer braid are sometimes used. Note that the crimped or banded-type end fittings often used in conjunction with PTFE hoses may be more susceptible to end connector separation than welded-type end connections.

It is extremely important to note that loading arms or hoses used for loading and off-loading EO railcars cannot be insulated for fire protection. For this reason, consider the use of deluge systems and/or fire monitors to protect the hoses and arms.

Thermal expansion protection in liquid piping systems

EO has a high coefficient of thermal expansion. Heating (ambient heating or otherwise) of a closed or isolated system containing EO can result in high pressures in a short time period, leading to gasket failures, or in more severe cases, line or equipment rupture. For this reason, liquid EO is not confined in lines closed at both ends unless this is otherwise unavoidable. Where the confining of liquid EO is unavoidable, lines are equipped with adequate relief valves to address potential high pressures. EO discharged from the relief valves is then captured and either returned to an appropriate location in the process or disposed of in accordance with applicable plant requirements and regulatory provisions.

Diaphragm-type surge suppressors providing a vapor space that can be displaced by expanding liquid have been utilized for EO systems on a limited basis with varying levels of success. A key issue with this type of device is proper material selection for the diaphragm. Suppressor protection devices of this type are routinely inspected and maintained so that the device will perform as needed. Consult the manufacturer for more information to select a design appropriate to facility needs.

Surge suppressors without diaphragms that provide an inert compressible vapor space in direct contact with EO (commonly known as nitrogen snubbers) have also been used in EO service to accommodate thermal expansion. Because nitrogen is soluble in EO, it is important to periodically verify the inert gas volume needed to maintain the effectiveness of the nitrogen snubber. Some nitrogen snubbers have a small, continuous nitrogen make-up flow.

Two alternate means of addressing thermal expansion are to install chilled water tracing, or install a continuous circulation loop on piping that may be susceptible to thermal expansion.

In piping systems without the surge suppressors described above or without pressure relief systems, consideration can be given to displacing a portion of the liquid EO in a piping system with an inert compressible gas prior to isolating the liquid system. A high purity nitrogen supply is generally appropriate for this type application. System and atmospheric conditions are monitored by qualified personnel in order to determine the proper volume of inert gas required.

Valves

The potential for trapped EO in valve cavities is an important consideration in valve design, as well as in facility design. EO trapped in valve cavities can polymerize and render the valve inoperative, or create an undesirable pressure buildup due to thermal expansion. To address this issue, valve designs can be selected that minimize trapping of EO. Gate valves, globe valves, and high-performance butterfly valves have all performed well in EO service. Ball valves and plug valve designs have also been successfully used in EO service, although some have the potential to trap EO liquid when the valve is in the closed position.

Controlling fugitive emissions is also an important consideration in valve design and selection.

Decomposition Flame Arrestors

Control and avoidance of ignition sources and the use of an inert gas diluent are available mechanisms used to help avoid decomposition events. Where process conditions prevent the use of these mechanisms, consider the use of decomposition flame arrestors. Flame arrestors function by preventing the passage of a decomposition “flame” in one part of the process from propagating to an area with a large inventory of material. The use of flame arrestors may be considered in EO lines entering or leaving an EO storage or processing area where large inventories may be present. “In-process” flame arrestors can also complement the use of vapor (EO) compressors or air-cooled heat exchangers. “Off the shelf,” conventional flame arrestors are not likely to be designed for the high propagation speed of EO decomposition flame fronts. A general disadvantage of flame arrestors is their high surface area and small passages, which makes them susceptible to plugging if EO polymerization occurs.

One example of a simple flame arrestor design that has been used packs a bundle of half-inch diameter tubes into a pipe shell. Limited testing suggested that this design might be effective in EO service. Research has indicated that the diameter and length of the tubes are critical to an effective design. However, there are to date no published data on the effectiveness of flame arrestors for EO service to help guide design considerations.

Pumps

Carbon steel, stainless steel or ductile iron are appropriate materials for pump bodies in EO service. The brittle nature of cast iron makes its use inappropriate for EO systems.

Pump Designs

Centrifugal-type pumps are commonly used in a wide range of EO service conditions. Diaphragm-type pumps are also used but their use is generally limited to situations where process conditions favor this type of pump (e.g., high pressure, low flow) over centrifugal designs. Other types of pump designs are not widely used in EO service; before using another design type, consult with qualified engineering personnel.

Pumps with double or tandem mechanical seals and sealless pumps are commonly used for purposes of reducing fugitive emissions in compliance with applicable regulatory requirements. In the event of seal or pump failure, these pumps may result in a lower volume of EO being released (reducing potential personnel exposure and fire and explosion hazards) than single seal designs.

Pumps with Double or Tandem Seals

Pumps with double or tandem mechanical seals are widely used in EO service. Double seal systems using a pressurized seal fluid introduce small volumes of seal fluid into the process across the inboard seal; an important criterion, therefore, in the selection of a seal fluid is its relative non-reactivity while in contact with EO. Tandem seals with an unpressured seal fluid system greatly reduce the potential for introducing seal fluid into the process, but require a suitable disposal system for collecting and disposing of EO vented from the seal system. Consider including the following components in a seal fluid system:

- Local or remote monitoring of seal pot level with low and high level alarms;
- Instruments/remote alarms capable of warning of excessive seal pot pressure resulting from a seal failure; and
- Safety relief device(s) on pressure seal pots.

A bypass flush of EO from the pump discharge to the inner seals removes frictional heat.

Seal fluids successfully used on double and tandem mechanical seal systems include 50% aqueous solutions of ethylene glycol, pure ethylene glycol, and/or pure diethylene glycol. Note that a properly functioning double mechanical seal/pressurized seal fluid system continuously adds small volumes of seal fluid into the EO product being pumped. This generally does not have product quality implications and is considered acceptable for pumping applications where the pumped EO is continuously consumed or converted to other products; it may therefore be less acceptable for pumps loading transportation containers or feeding EO into storage vessels with long product turnover time intervals.

Dry gas (nitrogen) seal systems use nitrogen as the seal purge material. These seals allow a very small, continuous flow of nitrogen into the process. Dry gas seals have been successfully used in EO service. When dry gas seals are used, it is important to monitor the nitrogen pressure and the flow and alarm on low pressure and high flow. A low nitrogen pressure or a high nitrogen flow indicates a seal failure.

Sealless pumps

Sealless pump designs such as magnetic drive pumps and canned motor pumps have also been successfully used in EO service. An advantage of these types of pumps is the elimination of fugitive emissions because of the elimination of an external seal system on the pump shaft between the impellor and driver.

Design considerations for these types of pumps include:

- EO without foreign particles or polymer is used to lubricate pump bearings. Evaluate the need for a filtering system (magnetic or element type) to remove particles and polymer from the EO in the suction line feeding these types of pumps. Magnetic filters are commonly used on pumps with magnetic couplings.

- Sealless pumps are more susceptible to damage caused by low suction pressure than some other pump designs. Consult the pump manufacturer's net positive suction head (NPSH) requirements with regard to the suction line.
- Entrained gases in EO such as nitrogen can impede pump operation; two such examples are reduced or lost suction or reduced pump bearing lubrication. Removal of entrained gases from EO used to lubricate bearings will help maintain effective pump operation. If necessary, equipment can be installed to remove entrained gases from liquid before it enters the pump.
- Damage to the containment shell can result in a flammable toxic release. A double containment shell design can reduce the likelihood of a release .

If a rotor on a magnetic drive pump locks up, the magnets decouple and the driver continues to run, then the pump contents will experience a rapid temperature rise due to the magnetic flux. Consequently, the response time available to prevent pump failure and decomposition of pump contents may be significantly less than the response time likely to be available in a similar incident with a conventional centrifugal pump. Consider the use of high and low power meter monitoring and shutdown to address this issue.

Pump Hazard Mitigation

Physical Facilities

Locating pumps within an impervious containment area provides protection against spills or leaks leaving the plant site or spreading to other process areas inside the plant. This type of protection is commonly provided by locating pumps inside curbed areas constructed of concrete or other materials suitable for containing EO liquid.

Because EO spills may ignite, creating the potential for flame impingement on nearby equipment, locate pumps and any associated containment areas an appropriate distance from process equipment, transportation container loading/unloading areas, and storage vessels. Equipping pump areas with fixed firewater spray systems and/or remote firewater monitors provides additional spill ignition protection. If water spray systems are used, many are available that are capable of remote activation, such as by heat-sensitive devices, combustible gas detectors, and/or personnel.

Combustible gas detectors (CGD) or EO-specific sensors/alarms can be installed in the immediate vicinity of the pump. Consider using CGDs/EO-specific sensors to activate pump area water spray systems.

Pumps can be located an adequate distance from a road to address possible damage from a vehicle collision. If a pump is located in close proximity to a road, consider additional facility designs to protect the pump, such as placing a physical barrier at the edge of the roadway or adding additional physical protection around or to the pump.

Pump Instrumentation

EO overheating — which can lead to a violent decomposition – is a primary safety focus in the design of EO pumping systems. There are many possible sources of additional heat to pumped EO, including: operation of EO pumps in a dead-headed or non-flow condition; improper pump operation; undetected pump mechanical damage; or inadequate cooling of recycle streams. For examples of specific protective measures to address EO overheating in pumps, refer to Figure 6.19

Redundant sensors and multiple shutdown initiators are valuable tools in EO pump safety systems for identifying and responding to overheating scenarios, but before selecting a sensor/shutdown system, it is helpful to conduct a thorough process hazard analysis of the system with the support of appropriately qualified engineers. The decision regarding the number of alarms and shutdown initiators to install in a specific system considers the potential severity of and opportunity for an EO incident with regard to the pumping system under consideration.
EO pumping systems have been successfully protected by alarms and shutdowns with systems using two sensors where one sensor is triggered (1 out of 2 initiation). Additional sensors can be

added with alarms/shutdowns triggered by a group of sensors (2 out of 3 initiation). In certain circumstances, it may also be appropriate to set alarms/shutdowns to trigger when all sensors reach their initiation point (2 out of 2 or 3 out of 3 initiation), but this approach is generally not used without complete review and approval in advance from qualified personnel.

Maintaining minimum flow through a recycle line can be used to prevent pump deadheading when forward flow is shut off. Minimum flow can either be constant (through a fixed orifice) or automated (through a control valve when forward flow is lost). Two mechanisms to control the heat of the EO in the recycle line are to equip the recycle line with a cooler or to return the recycle line to a large heat sink, such as a large storage vessel or process vessel.

Additional protective measures may be necessary for pumps operating above 3600 rpm. Consult with the pump manufacturer regarding these types of operations.

Where EO pumping systems are connected to large inventories of material such as in storage vessels or rail cars, failed pumping systems are isolated as quickly as possible. Design considerations include measures to rapidly isolate the pump, such as use of remotely activated isolation valves on pump suction piping and discharge piping.

Filter Systems

Filter systems are designed to trap and remove solid particles from EO. EO can be filtered before it is delivered to the customer; before it is delivered to storage; before it is loaded into transportation containers; before delivery to a pump; or at other points in the process. Both magnetic-type filters and removable element-type filters have been successfully used by industry.

Magnetic-type filters are designed to attract and remove iron and iron oxide particles from the EO. These materials are not present in the EO product initially, but can enter the EO as it comes into contact with carbon steel, such as that in piping or equipment.

Removable filter elements are designed to remove iron and iron oxide as well as polymer that may have formed and precipitated from the product as it moves through the process.

A large variety of removable filter elements and filter designs may be applicable for EO service operation. Cotton and polypropylene are two materials that

Table 6.1 EO Pump Shutdown and Alarm Considerations

Pump Type	Potential Hazard	Typical Protection Systems
Centrifugal, magnetic drive, or canned	EO decomposition resulting from high temperature	Minimum flow recycle (automated or always open)
		Low flow shutdown
		High discharge temperature shutdown
		Delta temperature across pump shutdown
		Pump motor low power shutdown
		Pump motor high power shutdown
		Low Level in pump suction vessel
Canned	EO release/ EO decomposition	Rotor thrust displacement shutdown
Centrifugal - double seal	EO seal failure release	Seal pot low pressure alarm
		Seal pot low level alarm
Centrifugal - tandem seal	EO seal failure release	Seal pot high level alarm
		Seal pot high pressure

have been successfully used in EO service.

Bear in mind the possibility of thermal expansion occurring when filters are not operated with continuous flow. Iron oxide particles inside filter vessels and filter elements have the ability to catalyze EO polymerization reactions if stagnant EO is present for extended periods of time. Periodic removal of these particles and periodic changing or cleaning of filters elements (not leaving filters in place with stagnant EO for extended periods of time) will minimize the potential for the initiation of a polymerization reaction. There have been multiple incidents of runaway reactions in EO filters due to rust catalyzed EO polymerization. See Section 5.6 for a discussion of EO filter incidents.

6.8 Handling of Vents and Effluent

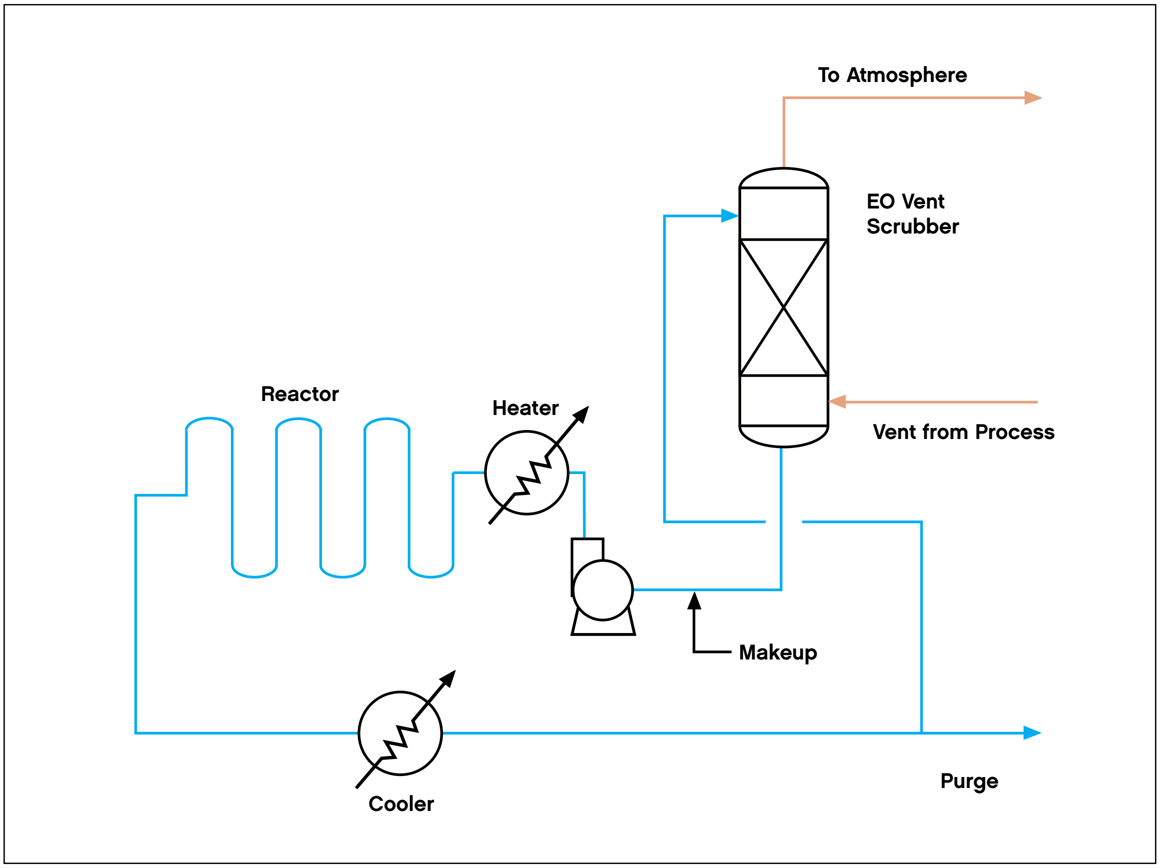
Vent Scrubbers

Aqueous systems for absorbing EO in process vents are in widespread use in industry. These systems can be designed for very high efficiency of EO removal. Vent gas is typically fed to a scrubber column filled with random packing such as Pall rings. EO is absorbed by an aqueous stream running countercurrent to the vent gas. EO absorption efficiency improves with lower temperature and/or higher absorbent flow rate. EO/water mixtures are highly non-ideal, so in scrubber design, Raoult's Law deviation factors are applied. Scrubbed gas can usually be discharged to the atmosphere in accordance with applicable environmental regulatory requirements.

A recirculation system using pumps, solution heat exchangers/reactors, and storage vessel(s) are required in some but not all applications.

The absorbed EO in the aqueous effluent can be recovered in the manufacturing process or can be converted to glycol in a separate reaction system. Design of the system for recovering EO through the manufacturing process is specific to the user and is not discussed here. For many EO users, the EO is reacted to glycol. Although thermal hydrolysis has been used to react EO to glycol (Figure 6.19), acid and base reactions are more commonly used. Either strong base or acid is added to the

Figure 6.19 Ethylene Oxide Vent Scrubber System



absorbent stream as a hydrolysis reaction catalyst (acids are more effective EO hydrolysis catalysts than bases). Phosphoric acid, sulfuric acid, and caustic soda are commonly used for this purpose. Hydrochloric acid is typically not used for glycol reaction systems due to the potential to form chlorohydrins. Hydrochloric acid has, however, been used in scrubber systems where the EO and dilute acid solution are consumed in the manufacturing process.

It is important to take appropriate steps to avoid contamination of the process due to backflow from the scrubber systems, especially if acid or base solutions are used. Likewise, liquid EO entering the scrubber system can result in large exothermic reactions, especially in the presence of catalysts such as acids or bases. There have been multiple incidents where fiberglass EO scrubbers and polypropylene scrubber packing were melted due to overload of an acid catalyzed EO scrubber with liquid EO.

Design considerations and equipment configuration are specific to the relevant process. Scrubber design may be different for intermittent processes (for example, filling a storage vessel from a railcar) and continuous processes. Reactor venting accommodates the vessel pressure let down during normal operation and also allows for overpressure releases during a process upset. A process hazard analysis covering both the process and the scrubber (including interlocks) can be a valuable tool in support of safe operation.

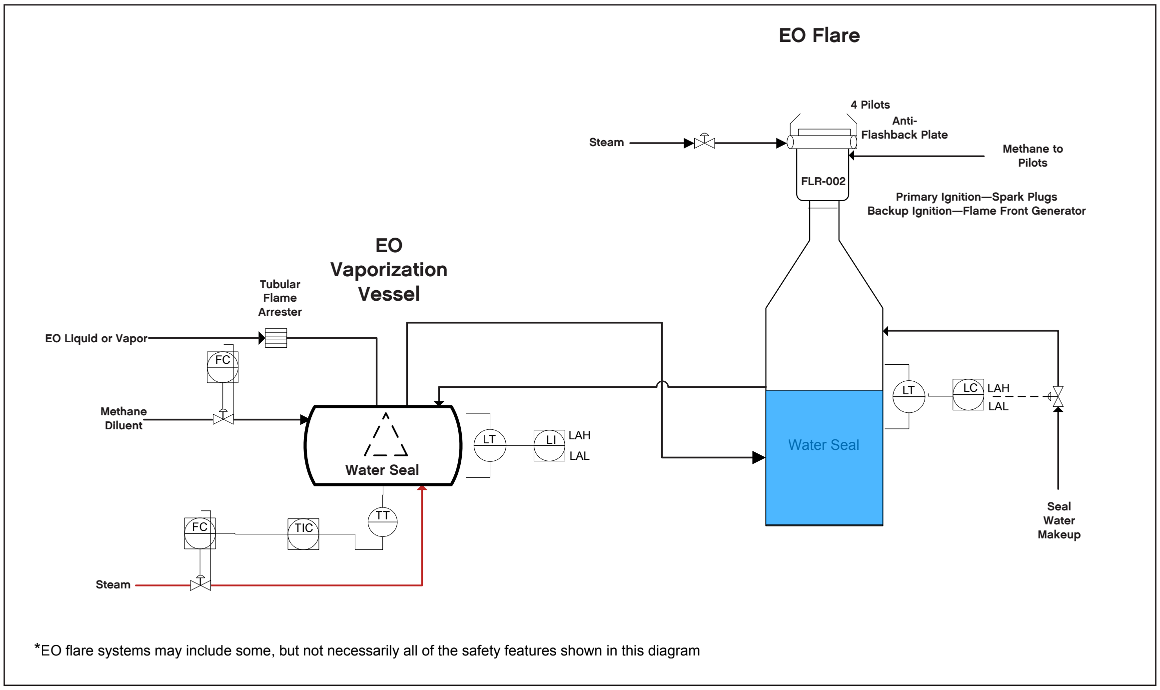
An EO scrubber system may shut down due to hardware failure or conditions outside the normal operating range. Plant design and operating procedures anticipating shut down scenarios can include instrumentation or response practices to minimize EO emissions.

Flares

Several EO producers and users successfully use flares to handle EO containing vents. A critical design consideration for such flares is the prevention of decomposition flame propagation backward from the flare tip into the flare header system (flashback). The flame velocity of an EO decomposition flame can be very high. The decomposition flashback velocity is, among other things, dependent on the system geometry as well as the temperature and composition of the gas mixture. Because an EO decomposition flame can transition from a deflagration to a detonation, the decomposition flame velocity greatly exceeds the normal EO combustion flame velocity, and can be much greater than sonic velocity. Because of the high velocity of the decomposition flame, the typical forward velocity in a flare header will not protect against reverse propagation of a decomposition flame. To address this, consider installing additional layers of protection in waste gas systems connected to down stream combustion equipment. Such additional design options for flare systems can include primary safeguards, such as the velocity section at the flare tip, flame arrestors and redundant safeguards, such as IR instrumentation and liquid seals, as described below:

- **Dilution:** EO to a flare can be diluted with methane into a non-decomposible mixture. By using methane instead of an inert gas like nitrogen, the heating value of the stream can be maintained to meet regulatory requirements. Dilution reduces the likelihood of a decomposition flame in the header, and is typically a “primary” level of protection for an EO flare system.
- **Velocity section:** The velocity section is a device used to prevent flashback initiated at the flare tip or in the combustion chamber of a thermal oxidizer. This device is located directly at the ignition source or at the inlet of the waste gas to the flare or thermal oxidizer. The distance between the velocity section and the flare or the thermal oxidizer is minimized. In case there is flashback, the outgoing speed required to exceed the flashback velocity is maintained by addition of a monitored flow of an inert gas or methane into the waste gas pipe. When this flow falls below a set operational minimum, a gas stream (at a flow greater than the operational minimum flow) is introduced into the waste gas pipe. The performance of a velocity section depends on the forward speed of the waste gases exceeding the flashback velocity of the flammable gases.
- **Flame arrestor:** A flame arrestor prevents propagation of the flame for a limited period of time. Rapid cooling of the flare header can result in the backflow of air from the

Figure 6.20 Schematic of Typical Flaring System



*EO flare systems may include some, but not necessarily all of the safety features shown in this diagram

atmosphere into the flare system and possible formation of a flammable mixture capable of ignition by the flare pilot. Properly designed flare tips and flame arrestors are designed to prevent this hazard scenario from occurring. If an ignition occurs, however, the flame arrestor can only prevent propagation of the flame for a limited period of time (the gap width of the flame arrestor is smaller than the limiting gap width of the flammable gas). If continuous combustion heats a flame arrestor, it may lose its effectiveness with regard to flashback; therefore, the temperature at the flame arrestor is monitored. When the permissible temperature is exceeded, an inert gas is introduced into the waste gas pipe. The design basis for the inert gas flow rate is set so the flame at the flame arrestor will be extinguished.

Ignition of a non-inerted EO vapor mixture inside a flare system can result in an EO decomposition. The flame front generated by a decomposition travels at a very high velocity and may not be quenched by a flame arrestor designed for a combustion flame (conventional flame arrestor). In such cases, consider testing the specific device with regard to EO decomposition flame propagation.

- **IR instrumentation:** IR instrumentation is placed in the waste gas pipe upstream of the flare or thermal oxidizer. When the IR instrumentation senses a flashback, it activates the feed of inert gas into the waste gas pipe to extinguish the flame. The length of the waste gas pipe between the IR-instrumentation and the inert gas inlet is set at a distance sufficient to extinguish a flashback. IR instrumentation is generally implemented as a redundant safeguard together with a velocity section or a flame arrestor.
- **Liquid seal:** When the waste gas is introduced into the liquid seal, it is distributed into individual bubbles to prevent a continuous pathway between the inlet and the outlet streams (hence avoiding a flow path for a flashback). Water or water mixtures are typically used as a sealing medium. Continuous makeup or level control is often used to maintain design liquid level. Because of the potential for losing a liquid seal (for example, blowing the seal out or loss of liquid level), this option provides less robust protection against flashback than the other options discussed in this section. Liquid seals are therefore generally used as redundant safeguards in conjunction with the use of a velocity section or a flame arrestor.

Thermal and Catalytic Oxidizers

Thermal and catalytic oxidizers have been used to control EO emissions from some processes. There have, however, been serious incidents involving several thermal and catalytic oxidizers used at sterilization facilities for control of EO emissions. During 1997, there were explosions at three plants that use catalytic oxidizers for destruction of EO in process vents. Each of the explosions either damaged or destroyed the catalytic oxidizer. One of the three incidents occurred during startup testing of the oxidizer. In another of the three incidents, there was an explosion with a fireball, and the oxidizer system and the building were destroyed. Subsequent government investigations concluded that in all three cases, overfeeding of the oxidizer emission control devices resulted when a high concentration of EO was inadvertently sent to the devices. [7]

Sewer Systems and Waste Disposal Facilities

If EO is drained (or could inadvertently be drained) to a sewer system, the potential exists for EO emissions to occur in the sewer system and treatment facility, and for accumulation of flammable vapors in the sewers, lift stations, and waste water storage vessels. Installation of online analyzers, nitrogen purges, and emission control devices may be appropriate in such cases. Because of the combustibility of EO vapors in air, there is significant potential for an explosion in a closed sewer system. Consider using a design with open flumes and/or open top wastewater vessels in order to minimize the potential for fire or explosion. (The potential for fire exists if the EO is not diluted with water with a ratio of greater than 100:1.)

Wastewater containing low concentrations (less than 1000 ppm) of EO has been successfully disposed of in biological waste treatment facilities after proper acclimation of the system. Check applicable environmental regulatory requirements before sending EO to a disposal facility. See Section 4.2 for a discussion of biodegradation of EO.

6.9 Miscellaneous

Electrical Equipment

Electrical area classification Class I, Division 1, Group B or Class I, Division 2, Group B (National Electrical Code [3]) are used where atmospheres contain or may contain EO under normal or abnormal conditions. Group C may be used if conduit seals comply with National Electrical Code paragraph 501-5(a). Chapter 5 of the National Electrical Code [3] deals with hazardous atmospheres, classifications, and equipment requirements. Additional references for area classification can be found in API RP500 [4] and NFPA 497A [2].

The National Electrical Code requires other equipment, such as lighting fixtures, resistors, and solenoid coils to have normal operating surface temperatures that do not exceed the ignition temperature of EO. See Section 501 of the National Electrical Code [3] for further details.

Leak Detection Systems

Fixed-point combustible gas detectors are often used in petrochemical processing plants. These can be calibrated specifically for EO and are often used to trip deluge systems in plants. Note, however, that these detectors are generally not designed for monitoring for industrial hygiene purposes. The low concentrations of allowable exposure and the low Reportable Quantity for environmental releases make more sensitive leak detection equipment desirable for EO processes. Gas Chromatograph-based leak detection systems sensitive to 1 ppm EO are in use both in process plants and laboratories where EO may be present. These systems generally have multiple fixed sample locations connected to a single analyzer. Electrochemical sensors have also been used, but are not EO specific and are subject to interference from other chemicals.

Sampling Systems

There are a number of design considerations for EO sampling systems. Minimizing EO leaks or personnel exposure is an important starting point. An effective system design allows capture of a representative sample of EO without releasing EO to the environment or exposing the sample collector. Potential for personnel exposure to EO during sample preparation and analysis can be minimized by use of a laboratory hood. Dry-disconnect tubing fittings can also be used for the connection from the sample tubing to the cylinder.

Residual EO in the sample cylinder can be managed by purging the sample connection with nitrogen and depressuring the sample system to a vent collection system. Using a vacuum water jet system to evacuate the sample cylinder prior to disconnecting is another effective technique.

A well-designed system seeks to avoid overfilling the sample cylinder with liquid. Overfilling results in the potential for cylinder overpressure from liquid expansion. For this reason, typical EO sample cylinders are stainless steel with an internal dip tube to prevent overfilling with liquid. The cylinder is filled while positioned vertically with the dip tube at the top, and only the valve with the dip tube connects to the sample system.

To reduce the temperature of the EO in the sample cylinder, store cylinders under refrigeration (before and during sample analysis) until the remaining EO is returned to process use or disposed of in accordance with applicable environmental regulatory requirements.

Figure 6.21 EO Sampling System

7.0 Personnel Exposure

7.1 Introduction

This Chapter provides an overview of issues related to personnel exposure to EO including selection of personal protective equipment for use in EO service. This Chapter focuses on the requirements of the OSHA EO standard published in the Federal Register on June 22, 1984, and amended on April 6, 1988. The regulation, 29 CFR 1910.1047, should be consulted for specific requirements.

7.2 OSHA Standard for Ethylene Oxide

Coverage

The OSHA regulation applies to any worker who may be exposed to EO. Operations associated with the production, use, transportation, storage, loading or unloading of EO are covered under this regulatory standard. The only exception to this coverage is the processing, use, or handling of products containing EO where objective, reasonably reliable data demonstrates that the product is not capable of releasing EO in airborne concentrations at or above the action level under expected conditions of processing, use, or handling. Records of the objective data must be maintained if the exemption is used.

Exposure Limits

OSHA's Permissible Exposure Limits, or PELs, are the following:

- 1 ppm in air as an 8-hour time weighted average (TWA) concentration
- 5 ppm in air as a 15-minute time weighted average (TWA) concentration - excursion limit (EL)

There is also an action level (AL) at 0.5 ppm as an 8-hour TWA, which triggers certain compliance activities such as exposure monitoring, medical surveillance, and training. The excursion limit is 5 ppm.

7.3 Other Exposure Standards/ Recommendations for Ethylene Oxide

Immediately Dangerous to Life and Health

The National Institute for Occupational Safety and Health (NIOSH) has quantified exposures to approximately 400 toxic chemicals that could be "Immediately Dangerous to Life and Health" (IDLH). The IDLH exposure value for EO is 800 ppm. The official definition of IDLH is given in 30 CFR 11.3. The IDLH concentration represents an estimate of the maximum concentration of a substance in air from which healthy workers can escape without loss of life or irreversible health effects under conditions of a maximum 30-minute exposure time.

Emergency Response Planning Guidelines

The American Industrial Hygiene Association (AIHA) has recommended Emergency Response Planning Guidelines (ERPGs) for a number of substances. For EO, AIHA has recommended an ERPG-3 of 500 ppm, which is "the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing life threatening health effects."[1]

The ERPG-2 of 50 ppm for EO is "the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action." [1]

There is no specified ERPG-1 for EO, the "maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor."

Acute Exposure Guideline Levels

Acute Exposure Guideline Levels (AEGL) for EO were proposed by a National Academy of Sciences committee in September 2006, as set out in Table 7.1 below.

Table 7.1 AEGL Values for Ethylene Oxide

Classification	10 minute	30 minute	1 hour	4 hour	8 hour	Endpoint
AEGL-1 (Nondisabling)	No values derived					
AEGL-2 (Disabling)	80 ppm (144 mg/m^3)	80 (144)	45 (81)	14 (25)	7.9 (14)	Developmental toxicity and neurotoxicity
AEGL-3 (Lethal)	360 ppm (648 mg/m^3)	360 (648)	200 (360)	63 (113)	35 (63)	Lethality

AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects, or an impaired ability to escape.

AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Data were available for deriving AEGL-2 and -3 values. Values for AEGL-1 were not derived because the odor threshold and concentrations causing mild sensory irritation would be above the AEGL-2 levels causing "disabling effects." [2]

Exposure Monitoring

Initial monitoring is required to determine airborne concentrations of EO to which employees are exposed. If concentrations are above the OSHA action level of 0.5 ppm, periodic monitoring is also required. Additional monitoring may be required if there are changes in process, production, control equipment, personnel, or work practices that may result in new or additional exposures. The OSHA regulation requires employees to be notified of any monitoring results within 15 days of receipt of the results.

Regulated Areas

Regulated areas must be established wherever occupational exposure may exceed the PELs. Those areas must be marked and access limited to authorized persons. Warning signs must be posted around regulated areas stating:

Figure 7.1 OSHA Warning for EO Regulated Areas

Methods of Compliance

Where the TWA or excursion limit is exceeded, the employer must establish and implement a written program to reduce employee exposure to or below the TWA and to or below the excursion limit by means of engineering and work practice controls, as required by paragraph (f)(1) of Section 1910.1047, and by the use of respiratory protection where required or permitted under this Section.

The compliance program must include a schedule for periodic leak detection surveys and a written plan for emergency situations as specified in paragraph (h)(i) of the OSHA regulation.

OSHA recognizes that engineering controls are generally not feasible for certain activities, including loading and unloading of railcars, vessel cleaning, and maintenance and repair activities. In cases where engineering controls are not feasible to prevent exposure above either of the PELs, NIOSH-approved respirators must be worn. See the Respiratory Protection discussion in Section 7.5 below for more information on respirator selection.

Medical Surveillance Program

The employer must provide annual medical surveillance for employees who are or may be exposed to EO at or above the Action Limit, without regard to the use of respirators, for at least 30 days during the year. Specific requirements for surveillance and medical record retention are included in the OSHA standard [3].

Training

Information and training must be provided to any personnel who are potentially exposed to EO at or above the action limit or excursion limit. Topics for training are specified in the OSHA standard.

Product Exemptions

Products made from EO or containing EO are exempt from the standard if objective data shows they will not release EO at or above the action level during normal handling or use.

Written Emergency Plan

An emergency plan must be developed for each workplace where there is a possibility of an emergency. The employer must have a means of promptly alerting affected employees of an emergency occurrence.

Recordkeeping

The standard contains requirements for retention of medical and exposure records. Other provisions of the standard also contain recordkeeping requirements.

7.4 Measuring Exposure

A number of methods are available for monitoring exposure to EO. Many of these involve the use of charcoal tubes and sampling pumps, followed by analysis of the samples by gas chromatography. There are also indicator tube systems specific to EO that do not require subsequent analysis, with detection limits in the low ppm range. Portable electrochemical EO detector/alarms and passive badge-type monitors for EO exposure are also available.

Appendix D of the OSHA EO standard describes available methods of sampling and analysis. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under the employer's field conditions.

7.5 Personal Protective Equipment

Ethylene Oxide Exposure

When there is potential for exposure to EO vapors or liquid, it is important to use the proper protective equipment. EO can be trapped against the skin and can cause severe chemical blistering and burns, which take a long time to heal. When released, EO liquid will quickly change to vapor. If protective clothing with open sleeves and legs is worn, this vapor can readily get underneath the clothing and result in burns. EO can also penetrate protective clothing seams, so it is important to consider suit construction as well.

Even dilute EO solutions can result in severe chemical burns if the skin remains exposed to the solution. Figure 7.2 shows a chemical burn resulting from 90 minutes of exposure to a dilute EO-water mixture absorbed into leather shoes.

Figure 7.2 Chemical Burn Resulting from Low Concentration of EO in Water

Eye Protection

Splashes of EO into the eye can cause severe eye irritation with corneal injury. The OSHA EO standard recommends wearing goggles at all times in those areas where there is a risk of splashes from liquid EO. Face shields (visors) provide additional protection when performing any activity in which there is a risk of splashes from liquid EO.

In the non-mandatory Appendix A of the standard, OSHA recommends that contact lenses not be worn where EO exposure potential exists. Where contact with EO can occur, consider the use of contact lenses carefully in the context of overall personal protective equipment policies and practices.

Protective Clothing

There are many important factors to consider when selecting appropriate personal protective equipment. These can be broadly grouped into two categories: material chemical resistance and material physical properties.

- Material chemical resistance: ideally, the chosen material(s) resists permeation, degradation, and penetration by the respective chemicals.
    - Permeation breakthrough time is the most important factor used to assess material chemical compatibility. The rate of permeation is a function of several factors such as chemical concentration, material thickness, humidity, temperature, and pressure.
    - Degradation involves physical changes in a material resulting from chemical exposure, use, or ambient conditions (such as sunlight). The most common observations of material degradation are discoloration, swelling, loss of physical strength, or deterioration.
    - Penetration is the movement of chemicals through zippers, seams, or imperfections in a protective clothing material.
- Physical properties: other factors to consider include evaluating the material for its
    - Strength, such that it can withstand the physical tasks at hand
    - Resistance to tears, punctures, cuts, and abrasions
    - Durability in light of repeated contamination and decontamination
    - Flexibility/pliability to allow users to perform needed tasks
    - Heat/cold resistance, such that the material maintains its protective integrity and flexibility under hot and cold extremes
    - Flame resistance/ability to self extinguish where a fire hazard may be present (such as in the event of a flash fire). For EO service, consider whether a flash oversuit or an EO resistant suit incorporating flash protection may be appropriate.
    - Seam quality, such that that garment seams in the clothing are constructed to provide the same physical integrity as the garment material

Many protective clothing materials in common use are permeable to or attacked by EO. Clothing contaminated by EO must either be discarded or decontaminated before reuse. Clothing must be discarded if it has been degraded or has absorbed EO. It is also important to note that EO and aqueous mixtures permeate leather, including leather boots (see Figure 7.2 above). Accordingly, leatherwear contaminated with liquid EO must be discarded because decontamination is not practical.

Materials proposed for use in protective equipment that are not known to be EO-resistant should first be tested to establish their suitability. Test data may be generated from a number of sources, such as materials manufacturers, equipment manufacturers, EO producers or users, researchers, contract laboratories, or others. Published, peer-reviewed data is also available to help evaluate the suitability of the material for EO use.

When evaluating test data, be aware that data may be of varying quality or reliability. Whether the data is well-documented or published, derived from multiple sources, has been subject to repeated testing, has been generated from an independent testing agency, and is recent or updated are all factors to consider. If an ASTM test method is available, there may be data obtained from tests performed in accordance with standard ASTM methods. Note that qualitative ratings of"poor," "good," or "excellent" give little to no indication of how a material may perform against various chemicals and with regard to the specific needs of EO service.

EO permeation data for clothing, glove, and boot materials are presented in Tables 7.3, 7.4, and 7.5 below.

Respiratory Protection

If the presence of EO in excess of exposure limits is expected or detected, OSHA regulations dictate that respiratory protection consisting of a NIOSH-approved respirator must be used. The OSHA EO standard, 29 CFR 1910.1047, provides minimum standards for respiratory protection for airborne EO (Table 7.2).

Table 7.2 **OSHA Minimum Standards for Respiratory Protection for Airborne Ethylene Oxide**

Airborne EO Concentration or Condition of Use	Minimum Required Respirator Type
Less than or equal to 50 ppm	Full facepiece with EO-approved canister, front or back mounted
Less than or equal to 2,000 ppm	(A) Positive-pressure supplied air equipped with full facepiece, hood or helmet, or (B) Continuous-flow supplied air (positive pressure) equipped with hood, helmet or suit
Above 2,000 ppm or unknown (such as in emergencies)	(A) Positive-pressure self contained breathing apparatus (SCBA), or (B) Positive-pressure full facepiece supplied air respirator equipped with an auxiliary positive-pressure self-contained breathing apparatus
Firefighting	Positive-pressure self-contained breathing apparatus (SCBA), equipped with full face-piece
Escape	Any respirator described above

IMPORTANT NOTE for Tables 7.3, 7.4, and 7.5: Data and characterizations of performance are provided as reported by materials manufacturer, from published literature or government sources, or from other databases. Data entered as "EOIC 1990 Data" is from materials permeation testing sponsored by the Ethylene Oxide Industry Council (now the Ethylene Oxide/Ethylene Glycols Panel) and published by Stull, Pinette, and Green (1990). The data displayed is for information purposes only; the data displayed does not constitute an endorsement or recommendation of any particular material of construction or PPE manufacturer. Note that some materials have been tested more than once by more than one party, as indicated by multiple results. Manufacturers may change materials selection or formulation at any time which may change breakthrough times and other performance characteristics of the PPE. Before making any PPE selection, contact the supplier for specific product information, suitability for use in EO service, and current information on test data regarding the manufacturer's products. "NS" means not specified in test data. PPE names and/or descriptions may be trademarked by the manufacturer.

Table 7.3 Ethylene Oxide Permeation Data for Clothing

MATERIALS - PROTECTIVE CLOTHING
Permeation Breakthrough Time: >480 minutes
(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data[1]	Materials/PPE Manufacturer Data[2]	Gov't Data	
Barricade® (DuPont®)	Gas	>480			No longer manufactured
	Liquid	>480			No longer manufactured
Challenge 5100®(ChemFab®)	Gas		>950		
Chemrel Max® (Chemron UK)	NS	>480			The personal protective suit is now manufactured by Draeger.
CPF-3® (Kappler/ DuPont®)	Gas	>480	>480		
	Liquid (11°C, 0°C)		>480		
CPF-4® (Kappler/ DuPont®)	Gas	>480	305		
	Liquid (11°C, 0°C)		>480		
Responder® (Kappler/DuPont®)	Gas	>480	>480		
Responder®/Blue Max (LifeGuard/MSA)	Gas	>480			

(continued on page 74)

Table 7.3 **Ethylene Oxide Permeation Data for Clothing** *(continued from page 73)*

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Responder CSM® (Kappler/DuPont®)	Gas		>480		
Responder Plus® (Kappler/DuPont®)	Gas	>480			
Trellchem® HPS (Trelleborg)				>480	www.cdc.gov/niosh/ncpc/ecpc.html In supplement to NIOSH Guide to Chemicals.
Tychem® 9400 (DuPont®)	Gas	>480			No longer manufactured
	Liquid	>480			No longer manufactured
Tychem® 10,000 (DuPont®)	Gas	>480			No longer manufactured
	Liquid	>480			No longer manufactured
Tychem® BR and Tychem® LV (DuPont®)	Gas		>480		
	Liquid (0°C)		>480		
Tychem® Reflector (Kappler /DuPont®)	Gas		>480		
	Liquid		>480		
Tychem® Responder (Kappler/DuPont®)	Gas		>480		
Tychem® TK (DuPont®)	Gas		>480		
	Liquid (0°C)		>480		
	Mixture: 10% EO in HCFC 124		>480		

(continued on page 75)

Table 7.3 Ethylene Oxide Permeation Data for Clothing *(continued from page 74)*

MATERIALS – PROTECTIVE CLOTHING
Permeation Breakthrough Time: 60 - <480 minutes

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
4H®			>240		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Butyl rubber			>240		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Cloropel™ – Blue CPE (ILC Dover)	NS	2) 118, 375	Rated by manufacturer as excellent (Little or no effect)		ILC Dover Chemical Compatibility Chart.
CPE® (Kappler/ DuPont®)	Gas	80			
MSA BETEX Butyl/ Neoprene	NS	165			No longer manufactured
PE/EVAL (4H®-Safety 4 Company and SilverShield®-Siebe North Company)			>240		www.cdc.gov/niosh/ ncpc/ecpc.html
Responder Plus® (Kappler/DuPont®)	Liquid	>180			
TeamMaster – Umex (Draeger)	NS		>60 to 120		
TeamMaster Pro –Himex® (Draeger)	NS		>60 to 120		
Tychem® F (DuPont®)	Gas		65		
Tychem®Responder (Kappler/DuPont®)	Liquid (11° C, 0°C)	>180	>180		
Tychem® TK (DuPont®)	Liquid (-70°C)		>180		

(continued on page 76)

Table 7.3 Ethylene Oxide Permeation Data for Clothing *(continued from page 75)*

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Ultra-Pro Commander (Mar-Mac Manufacturing Inc®)	Gas	>180			Ultro Pro was replaced with TK500 series, now manufactured by DuPont.
WorkMaster – Umex (Draeger)	NS		>60 to 120		
WorkMaster – Himex ® (Draeger)	NS		>60 to 120		

MATERIALS – PROTECTIVE CLOTHING
Permeation Breakthrough Time: Immediate - <60 minutes

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Butyl rubber (LifeGuard)	Gas	44-52			
Challenge® 5200 (ChemFab)	NS	27-35			
CPF® –2 (Kappler / DuPont®)	Gas		Immediate		
Fairprene® Neoprene	NS	51,158			No permeation data available from the materials manufacturer.
N-44 Neoprene (Pioneer-acquired by MAPA® Professional)	NS	31			
Natural rubber			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Neoprene (DuPont®)			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.

(continued on page 77)

Table 7.3 Ethylene Oxide Permeation Data for Clothing *(continued from page 76)*

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Nitrile rubber			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Polyethylene			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Polyurethane (ILC Dover)	1) NS 2) NS	2) 29, 65	1) Not recommended by materials manufacturer for EO use (severe effect)		ILC Dover Chemical Compatibility Chart.
Polyvinyl chloride			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Saranex™ (Dow Chemical Company)			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.
Saranex™ NS			6		
Tychem® 7500 (DuPont®)	Gas	53 minutes	75		
Tychem ®QC (DuPont®)	Gas/Vapor		Immediate (less than 10 minutes)		
Tychem® SL (DuPont®)	Gas/Vapor	Immediate	Immediate		
Tyvek®-Polyethylene coated (DuPont®)	NS	Immediate (<1)			
Viton® (DuPont® Dow Elastomers®)			<60		Forsberg, K et al. Quick selection guide to chemical protective clothing. 3rd edition. Van Nostrand Reinhold 1997.

Table 7.4 Ethylene Oxide Permeation Data for Gloves

MATERIALS - PROTECTIVE GLOVES
Permeation Breakthrough Time: > 480 minutes

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Butyl Rubber (North® Safety Products)	Gas	>480			
Silvershield®(North® Safety Products)	NS/Gas	>480	>480		

MATERIALS – PROTECTIVE GLOVES
Permeation Breakthrough Time: 60 - < 480 minutes

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
4H® (Ansell Occupational Healthcare®)	Gas	>240			No longer manufactured
878 Butyl® (Best®)	Gas	189	189		
A-15 Nitrile (Pioneer – acquired by MAPA® Professional)	NS	195, >315			
Butyl Chemical Protective – Styles CP-7, CP7F, CP-14, CP-14R, CP-25, IB-35 (Guardian Manufacturing®)	NS		173		
Barrier (Ansell Occupational Healthcare®)	Gas		234		
Silver Shield®/4H® (North® Safety Products)	NS - 21°C		>240		
Tychem® TK (DuPont®)	Gas		>180		

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Table 7.4 Ethylene Oxide Permeation Data for Gloves *(continued from page 78)*

MATERIALS – PROTECTIVE GLOVES
Permeation Breakthrough Time: Immediate - < 60 minutes

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
65NFW Natural Rubber (Best®)	Gas	1			
6780 Neoprene (Best®)	Gas	21	21		
890 Viton® (Best®)	Gas	48	48		
CHEM-PLY™/N-440 neoprene (MAPA® Professional)	NS		45		
Composition 29-865 neoprene, 37-145 nitrile (Ansell Occupational Healthcare®)					Not tested by manufacturer for use in EO service.
Hustler™ 725R PVC (Best®)	Gas	1	1		
N-44 Neoprene (Pioneer-acquired by MAPA® Professional)	NS	31			
Natural Rubber Surgical (Dayton®)	NS	3, 5			
Neoprene Chemical Protective (Guardian Manufacturing®)			40		
Neoprene Ultraflex 32 (Best®)	Gas		Degradation rating over time -operations use; excellent at 5 min, 30 min, 60 min, 240 min). Permeation data: 7 minutes, (heavy exposure) Not tested in limited exposure.		

(continued on page 80)

Table 7.4 Ethylene Oxide Permeation Data for Gloves *(continued from page 79)*

Material (Manufacturer)	Gas/Liquid	Breakthrough Time (Minutes)			Additional Comments
		EOIC 1990 Data	Materials/PPE Manufacturer Data	Gov't Data	
Nitrile (Ansell Occupational Healthcare®)	(1) Gas; (2) Splash Gas	(1) minimal splash protection for routine tasks; (2) 60-84 minutes; (3) <4 to 4	(4) Not tested by vendor for use with EO		
Nitri-Solve® 727 Nitrile (Best®)	Gas	17	17		
Nitty Gritty® 65NFW (Best®)	Gas		1 minute		
PVC Model G3112 (North® Safety Products)	Gas	4-8			Not tested by manufacturer for use in EO service.
Stansolv® A-14 nitrile (MAPA® Professional)	NS		32 (non-normalized breakthrough)		
Stansolv® AK-22 (MAPA® Professional)			No test data available from vendor		
Stanzoil®/Milled Neoprene (Pioneer-acquired by MAPA® Professional)	Gas	28-38			
Ultraflex 22R Nitrile (Best®)	Gas	12	12		

Table 7.5 Ethylene Oxide Permeation Data for Boots

MATERIALS – PROTECTIVE BOOTS

(See Important Note for Tables 7.3, 7.4, and 7.5, above)

Material (Manufacturer)	Gas/ Liquid	Breakthrough Time (Minutes)			Additional Comments
		Materials Manufacturer Data	Boots Vendor Data	Gov't Data	
Rubber Bunker Boots, vulcanized, hand-crafted ozone resistant (FireTech™- a division of LaCrosse® Safety and Industrial)					Manufacturer notes it meets NFPA 1971 Standard on Protective Ensemble for Structural Fire Fighting, 2000 Edition.
Firewalker (Ranger™- Total Fire Group™)					According to manufacturer there is no EO permeation data available for the fabric that is used as a liner.
Hazmax™ (OnGuard Industries)	NS		180 minutes		Tested to meeting the NFPA 1991, 2005 Edition Boot Requirements
Steel Toe Neoprene Chemical Resistant Boots (Tingley Rubber Corporation)					Manufacturer notes "Chemical Resistance: Animal fats and blood, oils, certain acids, alcohols, alkalies, and certain solvents."
Neoprene (Tingley Rubber Corporation)					Manufacturer notes "Chemical Resistance: Fats, certain acids, hydrocarbons, caustics, and other chemicals."
HazProof® (Tingley Rubber Corporation)	NS		Actual breakthrough time: >60 minutes; Normalized breakthrough time: >60 minutes		
Triple Dipped Neoprene (Servus Fire)					Manufacturer notes NFPA 1971 (2000 edition) certified.

[1] *Gathered from American Chemistry Council, Ethylene Oxide Industry Council sponsored research by Stull, Pinette, and Green (1990).*

[2] *Collected from the Material manufacturer or PPE manufacturer.*

8.0 Equipment Preparation and Maintenance

8.1 Introduction

When equipment in EO service must be opened for testing, inspection or repairs, facility requirements applicable to handling of flammable and toxic liquids and gases are strictly observed. All EO is removed from the system and either returned to the process or disposed of in accordance with federal, state, and local regulations.

Storage tanks and lines are thoroughly cleaned and purged with dry nitrogen before equipment is placed in or returned to EO service. Contaminants such as oxygen, water, and cleaning chemicals are completely removed to avoid dangerous reactions.

8.2 Preparation for Inspection or Maintenance

Preparations for Entry

Where applicable, the user must follow the requirements of the OSHA confined space standard (29 CFR 1910.146). Equipment is cleaned and purged of EO before beginning any maintenance work. If it is impractical or not possible to reduce airborne concentrations in and around the equipment below 1 ppm, OSHA regulations require that appropriate personal protective equipment be worn. See Section 7.5 for further discussion. The use of a gas detector for measuring ppm ranges of EO is required by federal regulations to verify that equipment is free of EO before allowing personnel to enter equipment. [29 CFR 1910.146 (OSHA confined space entry regulation) and 29 CFR 1910.1047 (EO-specific OSHA regulation)].

An important prerequisite to maintenance work on EO equipment is the development and use of a robust safe work plan that educates all affected personnel regarding applicable hazards. An effective work plan also includes other relevant components, such as an explanation of the importance of using proper personal protective equipment, of observing applicable safety precautions in each work task, and of observing other measures appropriate to working with EO.

Equipment being worked on is thoroughly drained and blown free of liquid EO with nitrogen. The equipment is then washed with cool water to remove residual liquid EO and drained to an appropriate wastewater treatment system. If EO polymer is present, refer to the discussion below, “Special Issues with Ethylene Oxide Polymer.” Care should be taken that hydrates are not formed during the water washing, since the melting points of EO/water mixture can be as high as 52°F (11.1°C) (see Table 2.2 in Chapter 2). Dispose of rinse water in accordance with applicable regulatory requirements and in a manner that is protective of personnel. (It should be noted that even dilute solutions of EO in rinse water have caused severe chemical burns. See Chapter 7). Once equipment is substantially free of liquid EO, steam purging can be used to remove traces of EO to allow for equipment entry. While steam purging, sudden condensing of steam may produce a vacuum in equipment that is not rated for vacuum service.)

Prior to entry, the equipment is isolated from the process and from potential sources of hazard. Atmosphere is tested for the presence of EO. Levels of EO must be low enough so personnel can safely enter. Persons entering equipment, vessels, or any confined space that has been in EO service are equipped with appropriate respiratory protection (see Section 7.5) unless it is demonstrated that the atmosphere inside the equipment, vessel or confined space does not present a hazard and measured EO levels do not otherwise require respiratory protection under OSHA.

Special Issues with EO Polymer

In systems storing pure EO, it is common for polymer to form and to accumulate gradually, especially where the EO is relatively stagnant. Polymer can retain EO after washing, and the polymer can gradually release the retained EO even after the equipment initially tests free of EO. To address this scenario, one effective practice is to wait several hours after the initial purging and rinsing steps and retest before opening the storage system to the atmosphere.

Low molecular weight polymer can generally be removed from EO by steaming or washing with hot water. Before using hot water or steam – both of which would be reactive with EO – to further decontaminate equipment, the equipment should be substantially free of EO. Adequate isolation of EO systems to be cleaned will help prevent introduction of water or steam into other equipment still containing EO.

High molecular weight polymer is generally removed by physical means, such as high pressure water blasting.

Polymer residues can contain residual EO. The residues may be flammable and may present a health hazard, and EO may continue to evolve from polymer. If polymer cannot be removed by warm water washing, personnel entering a vessel to undertake physical cleaning should be provided with appropriate personal protective equipment. OSHA regulations require respiratory equipment if free EO levels cannot be reduced to less than 1ppm.

Mothballing

Equipment which has been in EO service, but is being removed from service, is decontaminated by washing or steam cleaning to less than 1 ppm of EO. Before washing or steam cleaning, such equipment is disconnected or blinded from "live" equipment. Consider maintaining carbon steel equipment under a nitrogen blanket to prevent rust formation.

8.3 Preparation of Internal Surfaces

Foreign material on internal surfaces of EO-containing equipment can cause slow self-polymerization of EO, resulting in a buildup of the polymerized material on those surfaces. This self-polymerization can be minimized by removing foreign matter such as welding slag, loose debris, and rust on internal surfaces prior to putting equipment into service.

Cleaning can be accomplished by shot or grit blasting, or by chemical methods. Shot blasting creates dust and debris, which is then removed. It is helpful to maintain a dry air purge during blasting. Purging the equipment as soon as possible after the blasting helps prevent rust formation. Where equipment surfaces, such as pipework, are inaccessible to blast cleaning, chemical methods may be used.

Chemical cleaning may involve the use of hazardous materials, and it may damage equipment if not properly specified and performed. The use of a qualified cleaning specialist is helpful in making such specifications and in performing the cleaning. A variety of chemical cleaning processes are available for preparing metal surfaces for EO service depending on what surface contaminants are present, including:

- Alkaline or detergent degreasing, followed by thorough rinsing.
- Acid cleaning, if the metal is carbon steel. The presence of both carbon and stainless steel creates complexities that suggest the use or consultation with appropriately qualified engineers before undertaking acid cleaning. Acid cleaning is followed by thorough rinsing of the equipment.

Acid-based cleaning often uses EDTA or citric acid. It may or may not be preceded by a degreasing step. If the system to be cleaned contains mild steel, a neutralization and passivation step is performed. Sodium nitrite is typically used for passivation. The system is thoroughly flushed with water (oxygen-free, if available) and dried by blowing with dry, hot nitrogen. Equipment is left under nitrogen pressure until ready to receive EO. Failure to adequately passivate or to keep material under nitrogen blanket will result in significant rust formation.

CAUTION:

EO is highly reactive. It is extremely important to remove all residues of cleaning chemicals because EO may react violently with them after the equipment is returned to EO service.

The effectiveness of a particular chemical cleaning procedure can be evaluated in advance using a test sample of the same metal as the surfaces to be cleaned.

8.4 Leak Repair Clamps

Clamp-on or bolt-on, split body style leak repair clamps have been used for temporary mitigation of small EO leaks from piping, valves, and vessels. Leak repair clamps can often be obtained "off-the-shelf," or they can be engineered to fit, depending on the application. The user must evaluate the relative risk of using clamps. Many common leak repair sealants are not suitable for use in EO service due to the potential for chemical reactivity.

Prior to the use of a sealant in a leak repair clamp, determine its potential reactivity with EO. This can be effectively accomplished by testing for reactivity with EO in a calorimeter. If a sealant is reactive with EO, there is the potential to generate a hot spot due to the heat of reaction, which could initiate an EO decomposition reaction. Because EO can be an aggressive solvent, the effectiveness and long-term durability of leak repair sealants to be used in EO service should be determined before use. Testing can help make this determination.

As with any moving stem valve, valves in EO service may experience fugitive emissions leaks. It is generally preferable to avoid leak repairs while a system is online. If an EO valve packing gland has to be repaired by drilling, tapping, and installing a sealant injection fitting for injection of a sealant, carefully control the localized frictional heat generated during the drilling on the valve body to help prevent approaching the decomposition temperature of EO.

8.5 Preventive Maintenance

A routine preventive maintenance program for EO equipment helps achieve proper operability of the system. Key components for internal inspections include checking the integrity of monitoring equipment and detecting polymer formation in the system. Other areas of focus for an inspection program are no flow or low flow zones in a piping network and small bore instrumentation tubing, both of which have the potential for polymer buildup. Nozzles for instrumentation and inlets to pressure relief valves are also generally included as areas for inspection as part of a routine maintenance program.

To help prevent polymer formation, include consideration of purging spare and offline piping and equipment as part of the maintenance program.

8.6 Equipment Commissioning

Before returning equipment to service after maintenance, leak testing is conducted. This is commonly done by closing, capping, and plugging all bleed valves with all flange covers tight. Equipment and piping is pressurized with nitrogen to a pressure at or near the normal operating pressure of the equipment. All new or disturbed flange connections and other fittings can be leak tested while holding the pressure for an appropriate period.

Some techniques commonly used to detect leaks before putting EO equipment into service include:

- Soap test
- Helium leak test using a portable mass spectrometer
- Vacuum test (on equipment rated for vacuum service)

Detected leaks are repaired before introducing EO into the system. After introducing EO into the system, all flange connections are rechecked as soon as possible using a gas detector capable of detecting EO at ppm levels.

9.0 Transportation and Unloading Operations

9.1 Introduction

This Chapter provides a basic overview of transportation and unloading operations for EO.

Note that the use of dedicated EO unloading facilities is extremely important to help avoid contamination of EO with other chemicals.

9.2 Emergency Response Telephone Numbers

In the event of an emergency involving an EO shipment, contact the emergency response telephone number found on the shipping papers or the emergency assistance numbers provided in the shipper's MSDS. CHEMTREC® (Chemical Transportation Emergency Center) was established as a public service hotline for fire fighters, law enforcement personnel, and other emergency responders to obtain information and technical assistance for emergency incidents involving chemicals and hazardous materials. CHEMTREC provides a 24-hour emergency telephone number on shipping documents that can be called in the event of an emergency involving hazardous materials.

For additional assistance or information within the United States call CHEMTREC: (800) 424-9300 or (202) 483-7616.

For additional assistance or information within Canada, call: CANUTEC at (613) 996-6666, collect (or *666 via cellular phone within Canada). For additional information regarding shipment to and from Canada see Section 9.8.

9.3 Ethylene Oxide Classification

EO is classified by the U.S. Department of Transportation (DOT) as a primary poison gas hazard (Division 2.3) with a subsidiary hazard of a flammable gas (Division 2.1), and must be placarded accordingly. Further, it carries the materials poisonous by inhalation (PIH) designation by the DOT. See also Chapter 11, Selected Regulations.

9.4 Railcars

Design – General

DOT requires that EO be transported in Class 105-J tank cars. All tank cars used in EO service must have a tank pressure rating of at least 300 psig by July 1, 2006, at the latest. Most EO tank cars in service already meet this requirement.

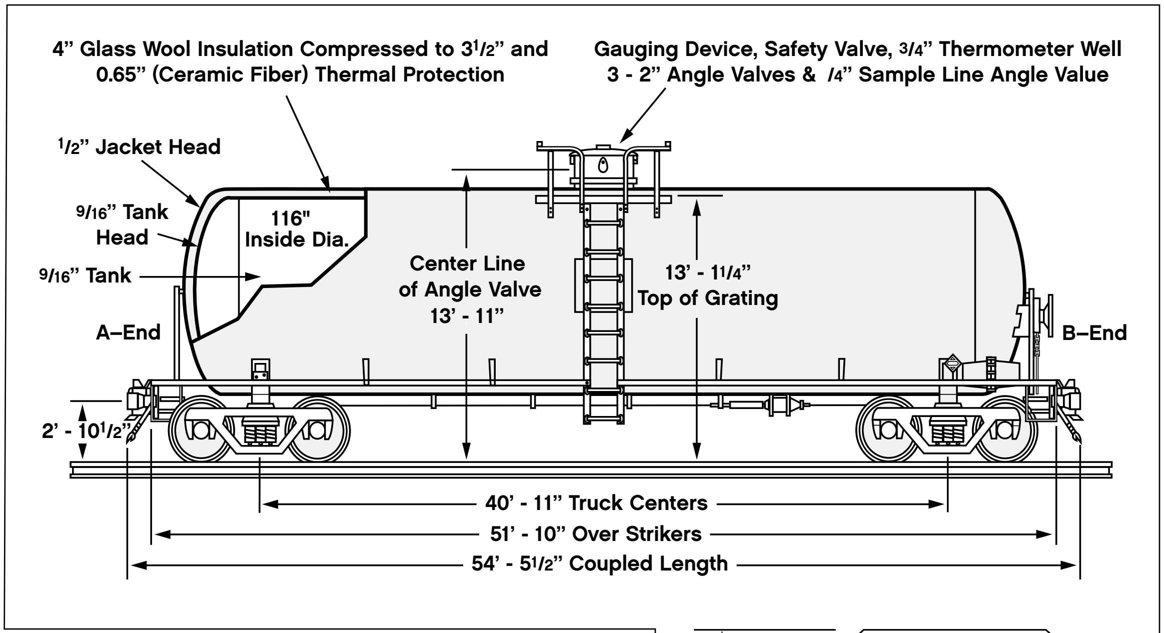
Regulations also require EO tank cars to have a reclosing pressure relief device set to function at 75 psig. These requirements are specified in 49 CFR 173.323. DOT class 105-J railcars meeting the required 300 psi tank test pressure are constructed from fusion welded carbon steel with 9/16" minimum plate thickness, and must have an approved thermal protection system.

An EO tank car is designed for loading and unloading from the top only with no bottom fittings. The potential for leakage from damaged tank fittings is greatly reduced in a transportation incident when protected top fittings and no bottom fittings are used. An EO railcar (Type DOT 105-J) is equipped with two eduction pipes/unloading connections, one vent for loading or vapor connection, a gauging device, a reclosing pressure relief device (safety valve), and a thermometer well (thermowell). All railcars are equipped with a sump for the eductor or discharge tubes. Some railcar tank bottoms are designed to slope towards the sump. The sump aids in minimizing the remaining EO heel after the railcar is unloaded.

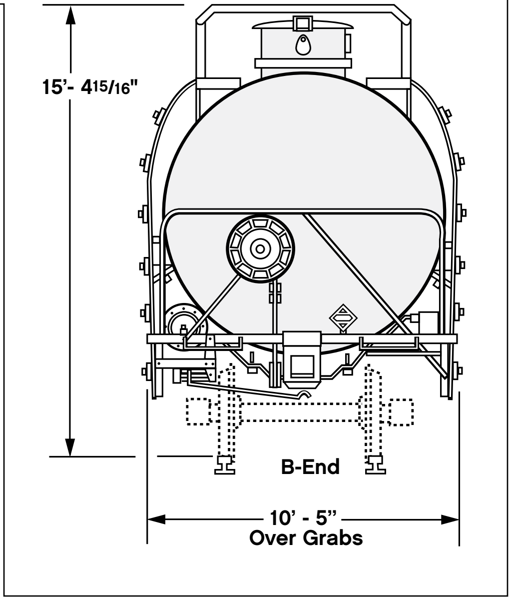
Design – Insulation

A typical insulation system found for an EO railcar consists of 0.65 inches of ceramic fiber surrounding the tank shell, covered with 4-inches of glasswool fiberglass insulation compressed to 3-1/2 inches by an outer metal jacket. The ceramic fiber section also provides additional protection to prevent an external fire from raising the temperature of the tank metal to a point at which it loses strength. The outer metal jacket is 11 gauge (about 1/8 -inch) carbon steel, except at the ends of the car where tank puncture resistance is provided by 1/2 -inch headshields. Such insulation systems have been used for EO railcars for a number of years and are credited as a major factor in the record of transportation safety achieved by this product.

Figure 9.1 **DOT 105-J railcar for transporting Ethylene Oxide**



The dynamics of an EO railcar engulfed in flames are complex. For a more detailed discussion, consult Chapter 10.



Design – Pressure Relief

DOT requires that railcars in EO service must be provided with one or more pressure relief devices. The regulations also require that pressure relief devices must be of a type that will resist dynamic forces including liquid surge. The pressure relief device is to be set to open at a pressure of 75 psig (5.2 barg). It should be noted that the pressure relief device may begin to weep at approximately 10 percent below pressure. Once the pressure relief device opens, it does not reseat bubble tight until 60 psig.

Design – Excess Flow Check Valves

EO tanks are equipped with float type excess flow check valves underneath each liquid load/unload valve and vapor valve. This is a safety precaution as the valve is designed to shut off the flow of liquid or vapor if the valves are “sheared” from the cars pressure plate during an accident. An excess flow valve is not designed to, and will not, shut off flow in the event of minor or slow leaks from valves, hoses, or flanges.

If a liquid or vapor valve is opened too rapidly or if an excessive unloading rate occurs, the excess flow check valve may close, cutting off the flow of liquid or vapor prior to its design shut off flow of 120 gpm. If the excess flow check valve closes, the pressure needs to be equalized to force the internal plug back to the open position. Equalizing the pressure can be performed by closing the load/unload valve on the liquid line. In extremely unusual circumstances, the vapor valve can get stuck closed if there is EO polymer present in the vent line. Nitrogen pressure may have to be supplied on the downstream side to force the internal plug in the valve back to the open position.

Be aware that the vapor line excess flow check valve can close if the car is depressurized too

Figure 9.2 Dome Arrangement of a DOT 105-J Railcar for Ethylene Oxide Service

rapidly. If the excess flow check valve closes, a false reading of railcar pressure can occur, as pressure is measured in the line downstream of the car loading/unloading valve.

If the excess flow check valve has inadvertently closed, the railcar could be mistakenly over-pressured and lift the pressure relief device set at 75 psig. Again, by closing the load/unload valve, the pressure can equalize on both sides of the excess flow check valve and gravity should drop the float back into position.

Significant problems experienced with loading and unloading operations such as malfunctioning equipment, running gear, or loading appliances should be reported to the EO supplier. Other than emergencies, repairs should only be performed with supplier approval in order to maintain material quality, equipment function, and design requirements. Emergency repairs should be reported to the supplier before putting the car in transportation.

Preparation for Unloading

Persons unloading a railcar or offering an unloaded railcar for transportation have had general training with respect to general safety awareness and railcar operation; function-specific requirements; and safety/emergency response. 49 CFR 172.704 requires refresher training at intervals (at least every 3 years).

Remember that EO in a railcar is constantly maintained under an atmosphere of an oxygen-free, inert gas. Air (oxygen) is not allowed to enter railcars or other transportation containers when in EO service, whether filled or unloaded. A vapor environment with an oxygen level of less than 1% has been generally considered "oxygen-free."

Dry nitrogen has been successfully and widely utilized as an inerting gas for railcars and other transportation containers. It has limited solubility in liquid EO.

CAUTION:

Carbon dioxide is generally not considered suitable as an inerting gas for railcars and other transportation containers. CO2 exhibits very high solubility in liquid EO (approximately ten times that of nitrogen), allowing the cargo (or heel) of EO to absorb a significant quantity of carbon dioxide from the railcar vapor space. This inherent property of CO2 to readily dissolve into EO can result in a sizeable depression of both the CO2 partial pressure and total pressure within the void space of a railcar. As a consequence, the pressure within the railcar could fall precipitously to a sufficiently low level to be rendered non-inert, and susceptible to hazardous decomposition reactions.

Other general considerations include:

- EO is highly reactive.
- The use of dedicated EO unloading facilities is extremely important to help avoid contamination of EO with other chemicals.
- The unloading area should be well ventilated and away from sources of ignition.
- OSHA requires that exposures not exceed either 1 ppm averaged for an 8-hour period or 5 ppm over a 15 minute period (excursion level).
- Use appropriate respiratory protection (see Section 7.5) when making/breaking connections, and during EO product sampling.
- Know where safety showers and eye wash facilities are located in the railcar unloading area.
- Know the location, in the unloading area, of fire fighting equipment (extinguishers, fire monitors, hose reels, deluge systems) and know how to use these.

- Consider checking or replacing any fire extinguishers with broken seals before commencing unloading.

It can be useful to develop and provide to unloading personnel a detailed site-specific procedure and checklist specifying each step of the unloading operation and the precautions to be observed. Consider maintaining an operator unloading log to record key information for both the railcar and the receiving storage tank or vessel, such as:

- Railcar and storage vessel temperature
- Railcar and storage vessel pressure
- Storage vessel level
- Railcar numbers
- Seal numbers

Consider recording and monitoring the temperature of EO railcars from time of arrival on-site up through railcar unloading. The presence of higher than normal temperature or a temperature rise not explained by ambient conditions may indicate the presence of contamination and the potential for reaction in the railcar. Consider maintaining records of all previous cars received at that site to understand the normal temperature of EO. See Chapter 5 for a discussion of the hazards of contamination and Chapter 10 for emergency response.

DOT requires that the DOT car specification number on the car must be 105-J300W. “Ethylene Oxide” and “Inhalation Hazard” must be stenciled on opposing sides of the railcar. Check the dome for an intact seal. If the seal is not intact, check for signs of tampering and monitor railcar temperature and verify as stable before unloading. Notify the EO supplier if the seal is not intact.

If the temperature is not stable or contamination is suspected, initiate emergency procedures as described in Chapter 10 of this manual.

Typical steps for unloading EO follow, along with a series of photographic illustrations.

The DOT requires placement of blue signs that read “Stop — Tank Car Connected” or “Stop — Men at Work” at appropriate spots.

Figure 9.3 DOT “Stop—Tank Car Connected” Sign

- Locking track switches and utilizing a derail mechanism to prevent collisions with other cars.

Typical steps for unloading (photographic illustrations);


1

- Setting the hand brake (DOT requirement).


2

- Chocking the car front and back of at least one wheel (DOT requirement).

3

- Grounding the railcar on its bolster or on the top working area. Because corrosion between bolted and riveted parts on railcars can serve as insulators between the ground clamp and the tank, continuous continuity checks are helpful when grounding the railcar as shown in the photo above. Regardless of where the grounding clamp is applied, maintain metal-to-metal contact between the clamp and the selected railcar hardware.


4

- Raising the dome cover. Note how the personnel are inspecting the area under the dome carefully - use caution, as valves and devices under the dome could leak.


5

- Measuring and recording the temperature of the EO in the railcar by lowering a thermocouple or thermometer into the thermowell (allow several minutes for the temperature measurement to stabilize).

Figure 9.4 Canister Mask with Ethylene Oxide-Specific Canister

Figure 9.5 Positive Pressure "Hoseline" Type Respirator

Experience has shown that it is difficult to meet the 1 ppm exposure limit when connecting or disconnecting EO railcars. If the 1ppm exposure limit is not met, OSHA-compliant respiratory protection is available for operator use when making or breaking connections on EO railcars. Supplied air breathing devices exist for both normal operations/maintenance activities and emergencies. Check with manufacturer for details..

Unloading

Typical steps for the transfer/unloading of the EO from the railcar to the receiving storage vessel are noted here. The sequence of procedures or procedures used may vary by company; the steps provided here are for illustration purposes only.

- Wear proper PPE. Experience has shown that it is difficult to meet the 1 ppm exposure limit when connecting or disconnecting EO railcars. If the 1ppm exposure limit is not met, operators should wear OSHA compliant respiratory protection when making or breaking connections on EO railcars. Supplied air breathing devices are suitable for both normal operation/maintenance activities and emergencies. Canister masks are generally protective for limited concentration levels. Check with manufacturer for details.
- Check the valves, flanges and relief device in the dome for leaks. Leak detection procedures that are commonly practiced include use of a soap solution and detection with monitoring devices (flammable gas detectors or EO-specific detectors). A leak could result in several hazards:
  - Reduction of the pressure within a railcar resulting in a vapor space that is not inert. Additional nitrogen injection into the railcar will restore the inert atmosphere.
  - Presence of flammable vapors around the railcar.
  - Potential for exposure above OSHA levels.

  (Note: in addition to flammable vapor around the leak, railcar leaks could result in a railcar vapor space that is not inert, requiring additional nitrogen injection into the railcar to restore the inert atmosphere.)

Typical steps for the transfer/unloading of the EO from the railcar to the receiving storage vessel.

1

- Remove plugs in both vapor and liquid valves.

2

- Insert pipe extensions into the valves so that connections can be made outside the dome of the car. Be sure that pipe extensions do not interfere with operation at the valve operating mechanism.

3

- Attach the unloading line to the liquid valve extension.
- Off-loading can be accomplished by either pressuring or pumping EO from the railcar. In either case, (a) nitrogen and/or (b) vapors displaced from the tank receiving the EO are needed to replace the liquid and to maintain railcar pressure.
- Check for leaks on hose connections prior to introducing EO.
- Either (a) attach nitrogen, or (b) line up the vapor balance return line to the railcar vapor line to provide for maintenance of the railcar nitrogen pad.

4

- Purge lines with nitrogen to remove any air that might be present.
- Install a pressure gauge on the vapor line. Measure and record pressure. Refer to Figure 6.16 in Chapter 6 (Design of Facilities) for guidance on selecting proper nitrogen pressure to maintain a non-explosive EO vapor content while unloading EO.
- Monitor temperature and pressure throughout the unloading process.

- Carefully open the vent and liquid valves. If utilizing a pump to unload the EO, check the unloading pump to prevent deadheaded or vapor-bound operation.

- If sampling is part of the procedure, sample and obtain laboratory verification before unloading the railcar. Grounding of the sample cylinder is recommended to prevent static sparks.

  NOTE: Polymer has a tendency to build up in the railcar sampling line in cars equipped with a sampling valve. Sampling from the offloading line reduces potential for plugging.

- Maintain the railcar pressure in non-explosive region during unloading by adding either (a) nitrogen or (b) displaced vapors from the receiving vessel via the railcar vapor line as the inventory of EO in the railcar is depleted.

Minimizing the heel remaining in an EO railcar after unloading is a very important consideration when developing unloading procedures.

Unloading procedures that utilize vapor balancing typically employ pumps to transfer EO from the railcar to the storage vessel. Such facilities and procedures should be designed to prevent a premature stop in the unloading process, possibly resulting in a large heel of EO remaining in the railcar. Unloading practices might include blowing vapor through the railcar and losing liquid flow from a pump as a method of minimizing remaining liquid heel. However, operating a pump without flow for any duration of time could result in an EO vapor decomposition. Refer to Section 6.7 on piping and pumps for more information.

Detecting the loss of liquid flow can be achieved by such means as a flow switch or ultrasonic device in the liquid line. In some cases, the use of a properly designed sight glass (e.g. “bullseye”) may be appropriate.

The excess flow check device consists of a float that becomes buoyant at high flow. Once closed, the excess flow check valve will not reopen until the pressure differential on both sides of the valve is equalized. Remember that the railcar pressure monitor is downstream of the vapor check valve and therefore will not read car pressure if the excess flow check valve is closed.

Inerting the Unloaded Railcar for Return

Unloading a tank or a shipping container of liquid EO does not remove the danger of vapor decomposition because unloaded railcars contain a residual heel of EO liquid. The heel results in the continued presence of EO vapor. As long as EO vapor remains in a vessel, the railcar needs to be pressurized to maintain an inert atmosphere using either pure nitrogen, or in the alternative, vapors displaced from the EO storage tank into which the railcar is discharged. Railcar pressurization is a DOT requirement found at 49 CFR, Chapter 1, Part 173.323 (f).

After the cargo of EO is unloaded, the transfer lines to EO storage are blown with nitrogen. Once nitrogen flow is evident in the receiving tank or vessel, the liquid unloading line is closed and secured.

The composition of the vapor space within a railcar can be significantly affected by temperature and vaporization of the remaining heel. As a consequence, railcar inerting requirements differ significantly from those defined for storage tanks and are dependent on the source of the inerting gas.

EO railcars are designed to leave minimal volumes of residual liquid (typically less than 50 gallons) after the cargo is discharged. Tables 9.1 and 9.2 illustrate railcar pressurization for a 50 gallon heel.

The data in Tables 9.1 and 9.2 are valid for a 50 gallon heel. Higher minimum pressures are used for larger heels to achieve proper inerting and lower maximum pressures are used to prevent lifting of the relief valve.

In Tables 9.1 and 9,2, it is assumed that the inert atmosphere will be maintained up to a temperature of 105°F (as required by DOT) while maintaining the railcar pressure below the 75 psig setpoint of the pressure safety valve. This illustration addresses pressurization with either pure nitrogen or tank vapors from an EO storage tank inerted with nitrogen.

This illustration addresses potential vaporization of EO into the vapor space that might occur during the time interval required for unloading, pressuring, and securing the railcar. (See Appendix C for additional information.)

Table 9.1 Illustration – Pressuring Unloaded Railcars with Pure Nitrogen (Assuming 50 Gallon Ethylene Oxide Liquid Heel)

Pure Nitrogen Makeup			
50 GALLON EO LIQUID HEEL			
Railcar Temperature Range –°F		Railcar Pressure – PSIG	
From	To	Minimum[1]	Maximum[2]
25	30	20	50
31	35	20	50
36	40	20	51
41	45	20	52
46	50	20	53
51	55	20	53
56	60	20	54
61	65	20	55
66	70	20	55
71	75	20	56
76	80	20	57
81	85	20	58

[1] *Minimum is set to meet DOT requirement for a non flammable vapor space at 105°F.*

[2] *Maximum is designed to reduce likelihood of potential release from relief valve in transit should the railcar reach or exceed a temperature of 105°F.*

Pressuring unloaded EO railcars by vapor balancing (EO receiving tank vapors) for return to the supplier is slightly more complex, because the level of pressurization is dependent on the starting temperature of the EO tank from which the vapors are directed to the railcar. Supplementary pure nitrogen may need to be added to the railcar if the balance tank vapors cannot provide the necessary pressure level required to achieve an inert vapor space as dictated by DOT regulations.

Table 9.2 Illustration – Repressuring Unloaded Railcars – Vapor Balancing (50 Gallon Ethylene Oxide Liquid Heel)

VAPOR BALANCING			
LESS THAN 50 GALLON EO LIQUID HEEL			
Balance Tank Temp. Range –°F		Railcar Pressure – PSIG	
From	To	Minimum[1]	Maximum[2]
25	30	20	50
31	35	20	50
36	40	20	50
41	45	20	50
46	50	21	52
51	55	24	53
56	60	28	53
61	65	31	53
66	70	35	53
71	75	39	53
76	80	43	53
81	85	46	55

[1] *Minimum is set to meet DOT requirement for a non flammable vapor space at 105°F.*

[2] *Maximum is designed to reduce likelihood of potential release from relief valve in transit should the railcar reach or exceed a temperature of 105°F.*

9.5 IM Portable Tanks (Intermodal/Iso-Containers)

Although movement of EO in IM Portable Tanks (Intermodal/Iso Containers) is practiced in various regions of the world and also is approved as a mode of transportation in North America, IM Portable Tanks are not typically utilized for EO service in North America.

More information concerning rules and regulations for IM Portable Tanks in EO service are found in the Code of Federal Regulations Title 49—Transportation. EO is considered a hazardous, liqueified compressed gas by the U.S. DOT. The following sections of CFR Title 49 specifically address the use of IM Portable tanks for EO and other hazardous, liquified compressed gases (other regulatory sections may also apply):

- 172.101-102;
- 173.32;
- 173.323;
- 178.245 -1 through 7; and
- 178.272-276

9.6 Non-Bulk Packaging for High Purity Ethylene Oxide

EO can be shipped in small quantities in cylinders and drums. It is a violation of federal law to use a cylinder or drum of EO in a manner inconsistent with its labeling. Only qualified EO handling facilities, with appropriate safeguards and properly trained personnel, following applicable local, state, and federal laws, should fill non-bulk EO containers.

The most common use of EO in non-bulk packaging is for the sterilization of medical devices and reduction of microbial load in spices. These activities must comply with EPA's regulation of pesticides under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA) at 40 CFR Subchapter E and FDA's Quality Systems Regulation (21 CFR 820).

The following discussion addresses EO in DOT specification cylinders and UN 1A1 Drums. Transportation-specific comments apply to shipments that fall under the DOT hazardous materials table (49 CFR 172.101) description "Ethylene Oxide with Nitrogen." This section applies only when EO is the primary component in the container, apart from the nitrogen inerting gas, and that the contained EO is in the liquid phase. Specific regulations cited here may not apply to users of EO in other non-bulk packaging.

Design – General

EO in non-bulk packaging must meet the requirements of 49 CFR 173.323 (b). Cylinders must meet DOT Specification Cylinder Requirements of 49 CFR 173.40 and UN 1A1 Drums must comply with 49 CFR 178.504. Commonly used non-bulk containers are:

- 400 Pound 1A1 Drum
- 175 Pound 4BW240 Cylinder
- 20 Pound 4BW240 Cylinder

Figure 9.6 Commonly Used Non-bulk Containers

All non-bulk packaging of EO must be labeled in accordance with federal regulatory requirements. DOT hazard labels for both the primary (2.3) and subsidiary (2.1) hazards must be properly affixed to the containers and any outer packaging. OSHA Hazard Communication requirements (29 CFR 1910.1200) and applicable EPA FIFRA (40 CFR 156) labeling requirements must be met. Note that OSHA also has an ethylene oxide-specific standard that should be consulted (29 CFR 1910.1047).

Non-bulk containers must be equipped with insulation of sufficient thermal resistance and provided with adequate pressure relief devices to prevent rupture when exposed to fire. Cylinders and drums are equipped with fusible relief devices with yield temperatures of 157°F to 170°F (69°C to 77°C). Cylinders and drums have a pressure relief device that relieves at 75 psig. Refer to 49 CFR 173.323 and CGA Pamphlets S-1.1 and C-14.

EO in containers or cylinders is padded with dry nitrogen at sufficient pressure to render the vapor space non-flammable (e.g., up to 41°C (105°F)). Nitrogen is typically padded to a pressure of 50 psig.

EO may be shipped in UN 1A1 insulated steel drums of no more than 61 gallons (231 liters) capacity. Packing Group I performance standards are set out at Title 49 of the Code of Federal Regulations, Part 178.600 et seq.

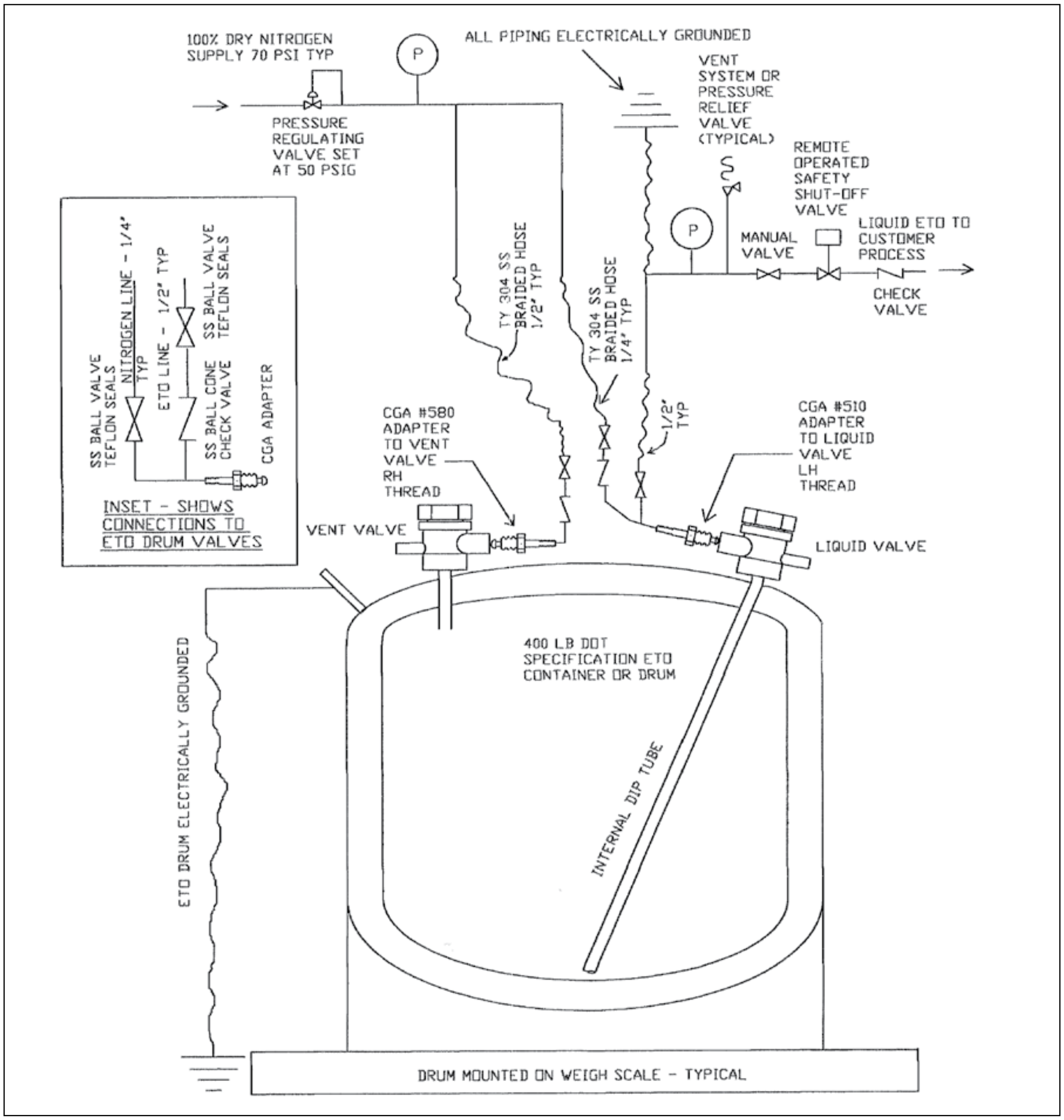
Federal regulations require UN 1A1 drums to be of all welded construction with a non-removable head. “The inner, pressure-containing shell must have a minimum thickness of 0.068 inches (1.7-mm), and the outer shell a minimum thickness of 0.095 inches (2.4 mm). Drums must be capable of withstanding a hydrostatic test pressure of 100 psig (690 kPa). Openings for filling, unloading and venting in the bodies or heads of non-removable head (1A1) drums may not exceed 3 inches (7.0 cm) in diameter. Closures for openings in the bodies and heads of drums must be designed and applied so that they will remain secure and leakproof under normal conditions of transport.

Regulations also require cylinders over 1 gallon (4 liters) capacity to have pressurizing valves and insulation. Eductor tubes must be provided for cylinders over 5 gallons (19 liters) capacity. Cylinders must be seamless or welded steel (not brazed) with a nominal¡ capacity of no more than 30 gallons (115 liters). Each cylinder must be equipped with a fusible-type relief device with yield temperature of 157°F to 170°F (69°C to 77°C). The capacity of the relief device and the effectiveness of the insulation must be sufficient to prevent a charged cylinder from exploding when tested by the method described in CGA Pamphlet C-14 or other equivalent method.

There are two valves commonly used in drum and cylinder service: a nitrogen valve and a liquid valve with an attached dip tube. A nitrogen valve (CGA 580) is used to pressurize the container with nitrogen. This valve has a spring activated relief which is set at 75psig by CGA requirements, and can only operate when the valve is open. This valve provides relief to protect the package from over-pressurization while in use only. If the relief is activated, it will reset once pressure is reduced below 75 psig. This valve has a CGA 580 right-hand internal thread connection with a silver handle.

A liquid valve (CGA 510) is used to unload the contents of the container. There is a dip tube threaded into the valve that extends to the bottom of the container which is used for liquid unloading. This valve has a CGA 510 left-handed internal thread connection with a red handle.

Figure 9.7 Typical Drum Connections



Preparation for Unloading Containers from Transport Vehicles

Federal regulations require all persons offering EO for transportation to be trained with respect to general awareness and familiarization; function-specific requirements; safety - emergency response; and hazardous material security. 49 CFR 172.704. Refresher training must be conducted at intervals not exceeding 3 years. See also Chapter 11, Selected Regulations.

Users of drums and cylinders may also wish to consult CGA Pamphlets P-1 (Safe Handling of Compressed Gases in Containers) and PS-7 (Position Statement on the Safe Transportation of Cylinders in Vehicles).

There are several National Fire Protection Association (NFPA) standards that may be applicable to a particular use: NFPA 55 (Compressed & Liquefied Gases in Cylinders) and NFPA 560 (Standard for Handling, Storage, Use of EO for Sterilization/Fumigation). Other standards may be applicable.

Advance arrangements for transportation of drums and cylinders are generally made by the supplier of the EO. If the end user chooses to return emptied containers, transporters/carriers should have any necessary regulatory approvals for transporting or handling hazardous materials, and should be sufficiently familiar with the properties and hazards of EO to transport the materials safely. The DOT requires all carriers and end users of EO to be registered as handlers of hazardous material and to comply with the DOT security rule. Note that suppliers often request or require that they be contacted before unloaded EO non-bulk containers are returned to them.

Unloading Drums and Cylinders from Transport Vehicles

After the vehicle carrying drums or cylinders arrives at its delivery destination, the engine is generally shut off (unless needed to remain on for a particular purpose, such as to operate a lift gate) to minimize risk of ignition. Chocking the wheels and using the handbrake of the truck or other motorized vehicle will help prevent the truck from moving and keep it stable during the unloading process.

All areas for unloading or storage of EO are considered Class 1, Division 2, and Group B as defined by the National Electrical Code. The NEC prohibits open flames, smoking, or other combustion sources in the vicinity of the vehicle being unloaded. Give consideration to providing adequate ventilation in the unloading area during the unloading process, and in trucks or other motorized vehicles before and during the unloading process.

Use caution when entering a trailer or other transport vehicle that may contain the drums or cylinders of EO; in this regard, the use of area or portable EO-specific detection devices can be a very useful tool. During the unloading process, check the containers for damage and leaks. If a leak is suspected or any containers are damaged, initiate appropriate emergency response procedures and contact the supplier.

Unloading drums and cylinders must be performed with care. Puncturing or damaging the drums is to be avoided, as is exposing them to heat or fumes. Select unloading equipment that will avoid or minimize damage to drums and cylinders. Using a handtruck or pallet jack, as appropriate, will help avoid rough handling of the drums (rolling, dragging, or sliding them), which can damage them, and also helps avoid the risk of damage from the use of powered equipment (such as motorized forklifts). Also note that some cylinders and drums are equipped with caps to help protect valves from damage; having these caps in place during all times except when needed to access the valve helps protect the cylinders and drums.

Full and unloaded drums are also stored with care. They are generally designed to be stored upright, in a well-ventilated area. Damage to an eductor tube can occur to a cylinder stored on its side. It is desirable to store the drums in a manner that avoids heat build up, so consider controlling the temperature of the storage area and sheltering the drums to avoid direct sunlight or other sources of heat. Give consideration to the location of the pressure relief devices (ability to vent without obstruction or other safety considerations) while the drums are stored. Store drums in a manner to provide adequate protection from physical damage, and provide an adequate schedule of checking for cracks, leaks, faulty valves, or other circumstances to be addressed.

Unloading (Discharging) Drum and Cylinder Contents

The information provided in this section is intended to introduce information and general principles of safe handling with regard to the receipt, use and return of cylinders and drums containing EO. The end user should request detailed instructions from the EO supplier concerning specific types of cylinders or drums.

Considerations while unloading drums and cylinders include:

- Cylinder or drum fittings are inspected for wear or possible damage. (Where damaged cylinders/drums are identified, contact the supplier for further instructions).
- The threaded connections and valve are inspected for dirt, grease, or obstructions. Note that some threaded connections may be designed to work without lubricants, and the use of lubricants on such threadings may impede performance.
- Use of a check valve or other backflow prevention device in the discharge line will help prevent backflow and entry of contaminants into the EO cylinder or drum.
- Use of spark-resistant tools can help minimize the risk of sparking.

At all times during unloading, the container is properly secured. This helps avoid unintentional movement or fall of the container. When selecting a storage area, consider locations that will minimize inadvertent contact that could lead to a puncture; for example, storage areas well away from traffic lanes. Note that drums and cylinders may be designed for valve protection, such as cylinder caps valve plugs, to be kept in place and secured at all times when the container is not being loaded or unloaded.

Nitrogen is used to maintain cylinder and drum pressure and to discharge the EO from the container. (The valve located at the discharge connection of the drum or cylinder is useful for throttling and regulating the flow of EO from the container and also for providing the required backpressure to maintain the container vapor space within the non-flammable inert region.) The nitrogen is at a high enough pressure to maintain the container vapor space within the non-flammable or inert region. Follow the supplier's instructions regarding appropriate pressure to achieve inerting. With the drum and cylinder designs discussed in this manual, a pressure of about 50 psig has been used in practice for pressuring and unloading a cylinder or drum. Note that the use of a backpressure control valve or regulator can help prevent overpressuring the EO drum or cylinder.

Securing the Unloaded Drum or Cylinder for Return to Supplier

An emptied drum or cylinder may contain residual quantities of EO, which can pose a danger of vapor decomposition. Due to possible residual EO, these containers are handled very carefully.

DOT regulations require that any unloaded cylinder or drum containing the residue of a hazardous material be transported in the same manner as when it previously contained a greater quantity of that hazardous material. DOT requires containers to be returned to the supplier as a hazardous material. Packages must retain DOT Hazard markings 2.3 and 2.1 (Poison Gas placard and Flammable Gas placard). DOT regulations require the shipper to ensure that any truck carrying EO is appropriately placarded.

9.7 Ethylene Oxide Shipping Data

Table 9.3 Temperature/Density/Vapor Pressure for Shipping Ethylene Oxide

Temperature	Density (lb/gal)	Vapor Pressure (psia)
20°F	7.59	7.1
40°F	7.47	11.6
60°F	7.34	18.0
80°F	7.21	26.9
100°F	7.08	39.1
105°F	7.05	42.7

According to DOT federal regulations (49 CFR 173.24b), EO railcars and portable tanks must be loaded to ensure that a 5% outage exists at a temperature of 105° F.

9.8 Shipments of Ethylene Oxide between the U.S. and Canada

Canada has established regulations for the Transportation of Dangerous Goods (TDG) within Canada. Canada identifies EO as a dangerous good subject to TDG rules. This section provides a brief overview of Canadian requirements; the user should consult the regulations for more information.

Canadian TDG regulations require that the importer of record for EO into Canada must have an approved emergency response assistance plan (ERAP) on file with Transport Canada. Part 7 of the TDG Regulations outlines this requirement and Column 7 of the dangerous goods list provides the ERAP Index.

Shipments of EO from within the U.S. to, or through Canada

TDG Regulations allow shipments of EO that originate from within the United States to be transported into or through Canada under the classification, marking, labeling, placarding and documentation requirements of Title 49 of the US Code of Federal Regulations (49 CFR).

More details concerning *Transportation of Dangerous Goods from the United States into or through Canada* can be found in the Canadian Government's Transport of Dangerous Goods Regulations, Sections 9.1 and 10.1, and other referenced sections, for the shipment of EO by either road or rail, respectively.

Shipments of EO from within Canada to, or through the U.S.

The U.S. DOT has established provisions for EO shipments originating within Canada that terminate within the United States, or which travel through the United States to a Canadian or foreign destination. These regulations also apply to the return to Canada of any unloaded bulk packages containing residues of hazardous materials that were originally imported into the United States.

Shipments of EO originating within Canada that are properly marked, labeled, placarded, described on a shipping paper, and packaged in accordance with the Transportation of Dangerous Goods (TDG) Regulations issued by the Government of Canada may be transported to or through the United States by railcar or tankwagon / road vehicle, provided that:

- Shipping papers contain the words “Toxic Inhalation Hazard” or “Poison Inhalation Hazard” or “Inhalation Hazard”; and
- A label or placard that conforms to the specifications in the TDG Regulations for a “Class 2.3” label or placard may be substituted for the POISON GAS or POISON INHALATION HAZARD label or placard, and
- The containers used for shipping EO as authorized by the TDG Regulations correspond to the USDOT specification or UN packaging specifications for EO.

Details concerning the shipment of hazardous materials originating from within Canada can be found in the U.S. Code of Federal Regulations, Title 49, Part 171.12a, Canadian Shipments and Packaging.

10.0 Emergency Response

10.1 Introduction

Every emergency situation will be different. It is not the intent of this manual to address every potential situation; it is intended to help producers, users, and others as a resource in the development of their own emergency procedures for EO.

Emergency responders must be properly trained and equipped in accordance with OSHA standards on emergency response and emergency fire protection (29 CFR 1910.38, 1910.120 and Subpart L). The first priority in responding to an emergency situation is the safety of the emergency responders, employees, and people in the surrounding community. The second priority is to determine the incident's impact on the surrounding environment, and to set a strategy to stabilize the situation and minimize the impact. The third priority is the conservation or protection of equipment and property.

Downwind evacuation should be considered if EO is leaking but not on fire. For large spills, DOT recommends "first isolate in all directions at least 200 feet." DOT further recommends protecting persons downwind during the day at least 0.3 miles and during the night at least 1.1 miles. In case of small spills, DOT recommends first isolating for 100 feet and protecting downwind persons for at least 0.1 miles.

If a tank or rail car is involved in a fire, isolate and consider initial evacuation for one mile in all directions. If the fire is prolonged or uncontrollable, or if a container is exposed to direct flame, consider evacuation for one mile in all directions for protection from flying debris if the container should rupture violently. [1]

10.2 Potential Hazards

For more information on potential hazards attendant to EO emergency response and selection of PPE, see also Chapter 3, Health Effects of Ethylene Oxide, and Chapter 7, Personnel Exposure.

Health Hazards

- Liquid EO and EO/water solutions:
  - Are extremely irritating to skin and eyes
- Can cause blistering and severe chemical burns
  - Easily penetrate cloth, leather and some types of rubber. Leather cannot be decontaminated.
- EO vapor can be absorbed by wet or sweaty skin with potential for serious chemical burns.
- Odor thresholds are much greater than permissible exposure limits; overexposure occurs before the odor can be detected.
- Inhalation of EO vapors:
  - Can irritate exposed surfaces (eyes, nose, throat and lungs).
  - Potential effects on central nervous system include drowsiness, nausea, convulsions and limb weakness.
- IARC (International Agency for Research on Cancer) classifies EO as Class 1 — carcinogenic to humans[2].
- Water contaminated with EO evolves EO vapor and can be a source of exposure.

Fire Hazards

See also Chapter 2, Properties of Ethylene Oxide.

- Volatile flammable liquid with heavier than air vapors that may travel considerable distance to a source of ignition.
- Lower Flammable Limit: 2.6% in air. Upper Flammable Limit: 100% in air.
- Fire impingement on EO-containing equipment can result in explosive decomposition, which can rupture the vessel and result in an EO vapor cloud explosion.
- Water/EO mixtures can support combustion if water/EO ratio is less than 22:1 (vol/vol) in open areas.
- In closed systems such as sewers, water/EO mixtures with a ratio of less than 100:1 (vol/vol) can potentially flash.
- May polymerize violently in container if exposed to heat.
- Often a secondary vapor cloud explosion resulting from a primary event could cause more damage than the primary event itself.

Hazards of Contamination

- Reacts with water, evolving heat. In closed containers, reaction may be self accelerating, resulting in container rupture.
- Contamination with acidic or basic materials accelerates reactions with water.
- Contamination of pure EO with acidic, or basic materials; metal oxides, metal chlorides, or active catalyst surfaces may cause explosive polymerization.

10.3 Fire Response

Special considerations for EO-containing equipment exposed to flames or with flame impingement:

- In almost all cases, EO decomposition will result in overpressure and equipment failure
- EO decomposition initiation temperature decreases as pressure increases
- Polymerization can occur with flame impingement leading to loss of containment. Depending on the scenario, the reaction can go very quickly or take many hours to build to a point to lose containment.
- Maintain water on any equipment exposed to flames particularly uninsulated parts
- Relief valves are not designed for decomposition or polymerization
- Keep personnel at an appropriate distance

Extinguishing Materials

- Carbon dioxide or dry chemical fire extinguishers are suitable for small fires only.
- Water fog or spray is more suitable for larger fires. In general, more water is beneficial because it will cool the equipment, extinguish the fire, dilute the EO release to the atmosphere and reduce the potential for a vapor cloud.
- Water dilution for EO spills should be at least 22:1 (vol/vol) in open areas, and at least 100:1 (vol/vol) in closed areas where vapors might be trapped (e.g., storm sewers).
- Alcohol resistant foams (ATC type) are suitable for fighting EO fires. General-purpose synthetic foams (including AFFF) or protein foams may function, but much less effectively because these foams are less stable.

Extinguishing Techniques

- Stay upwind.
- Avoid physical contact with product.
- Wear self-contained breathing apparatus (SCBA) and appropriate protective clothing. Wear full chemical protective suit if contact with material is anticipated.
- For a large fire or a fire where there is flame impingement on EO containing equipment, use unmanned hose holders or monitor nozzles. Focus on minimizing the transfer of heat from the fire to piping and equipment containing EO to minimize the possibility of decomposition reactions.
- Where the fire is not impinging or heating EO-containing equipment, consider letting the EO burn (controlled burn) as in a hydrocarbon fire. Focus on minimizing the potentials for a vapor cloud explosion.
- Withdraw immediately in case of prolonged venting of safety device or discoloration of equipment.
- Keep fire-exposed containers and nearby equipment cooled using water spray. Minimum 500 gpm/point of flame impingement.
- The addition of warm water (above 51°F/11°C) to pools of liquid EO may temporarily increase vapor evolution.

If there is potential for runaway internal reaction, or flame impingement that can result in explosive decomposition and container rupture, consider evacuation for a one mile radius according to DOT recommendations.

Considerations Whether to Extinguish a Fire

Flame impingement on EO-containing equipment can result in explosive decomposition. Because of this, a responder should strongly consider extinguishing a fire if there is a potential for flame impingement on EO-containing equipment, even if the source of the hydrocarbon feeding the fire has not been stopped. After the fire has been extinguished, continue to apply large volumes of water on the leak to dilute the EO, which will minimize the potential for re-ignition of the impinging fire or the potential for a vapor cloud explosion.

10.4 Spill Response

General Information

- Proceed with caution.
- Restrict access to spill area.
- Keep unprotected personnel upwind of spill.
- Monitor EO vapor concentrations in area.
- Avoid contact with spilled product.
- Wear SCBA and a full chemical protective suit.
- Eliminate ignition sources. (Minimum ignition energy for EO/air mixtures is very low, comparable to hydrogen and ethylene.)
- Prevent liquid EO and contaminated runoff water from entering sewers and confined spaces (unless adequately diluted to 100:1 vol/vol)
- Notify proper authorities as required by regulations.
- If spill has the potential of entering a waterway, notify downstream users of potentially contaminated water.
- Only equipment approved for use in flammable atmospheres should be employed in the vicinity of an EO spill.
- Be cognizant of the extremely volatile, flammable, and heavier than air nature of EO while planning the response.

Air Release

Techniques for responding to releases to the atmosphere include:

- Evacuate and monitor local and downwind areas as conditions warrant to prevent exposure of personnel and to allow vapor to dissipate.
- Knock down vapor with water fog or spray. Water fog or spray applied to EO vapors or fumes will absorb a substantial amount of EO.
- When using water spray, small quantities may actually worsen conditions because of acceleration of vaporization. Large quantities of water are necessary to effectively knock down EO vapor and dilute spills. (See Section 10.7 for additional information.)
- Alcohol resistant foams applied to the surface of liquid EO spills may slow the release of EO vapors into the atmosphere. Alcohol-resistant foams (ATC-type) function well; general-purpose synthetic foams (including AFFF) or protein foams function less effectively because these foams are less stable in EO.

10.5 Emergency Response to Temperature Rise

A temperature rise in EO storage or an EO railcar may be due to a variety of factors, including:

- Loss of cooling in EO storage
- Off-loading railcar containing EO that is warmer than EO in storage
- Ambient conditions (typical rise in a railcar under summertime conditions is less than 2°F per day)
- Reaction in storage vessel or railcar due to contamination

A reaction in a storage vessel or railcar could result in catastrophic failure of the vessel. Pressure relief valves on EO railcars and storage vessels are not typically sized to protect against an uncontrolled reaction.

Figure 10.1 illustrates the temperature profile for a reaction of an EO/water mixture (neutral pH) with a high concentration of EO. The analysis assumes adiabatic conditions with no external cooling such as from cooling coils or autorefrigeration resulting from the lifting of a relief valve. The timeline is not shown because it is highly dependent on EO concentration, starting temperature, and other types of contaminants. Some key observations from the graph:

- Pressure increases and temperature increases can both indicate that a reaction is occurring.
- The temperature rise is slow initially and then increases exponentially.
- It is important to record the temperature with enough frequency to track the rise in temperature.
- In a non-vented system, such as a railcar or a storage tank without pressure control, pressure rise is less effective than temperature rise in providing an early warning of a reaction.

- In a vented storage tank, pressure is even less effective as an indicator of a reaction because the pressure control valve will maintain constant pressure in the vessel until the valve capacity has been exceeded.
- Refrigeration systems on EO storage vessels can delay the detection of a reaction by maintaining temperature until the capacity of the refrigeration system has been exceeded. Monitoring the heat load on a refrigeration system may be used for early detection of a reaction.
- The time from the point of contamination to the point that the reaction is beyond control can vary from hours to several days, depending on the type and concentration of contaminant and the initial temperature.
- Sustained temperature rises can signal an uncontrolled reaction. See, e.g., Figure 10.1. As with any exothermic reaction, the greater the temperature rise over time, the shorter the reaction time available to prepare for and respond to an incident. For example, if the temperature rise is approximately 1°F per hour, the time to respond could be less than a few hours; if the temperature rise is greater than 2°F / hour, time to respond could be shorter than 1 hour before vessel failure could occur due to overpressure.
- If contamination is suspected, proceed with an emergency response plan for contamination in vessel or railcar. See Section 10.6 for further discussion.
- If contamination of a railcar is suspected, notify the supplier immediately.

  CAUTION: DO NOT RETURN THE RAILCAR IF CONTAMINATION IS SUSPECTED WITHOUT FIRST DISCUSSING WITH THE SUPPLIER AS THERE MAY BE A RUNAWAY REACTION INSIDE THE RAILCAR.

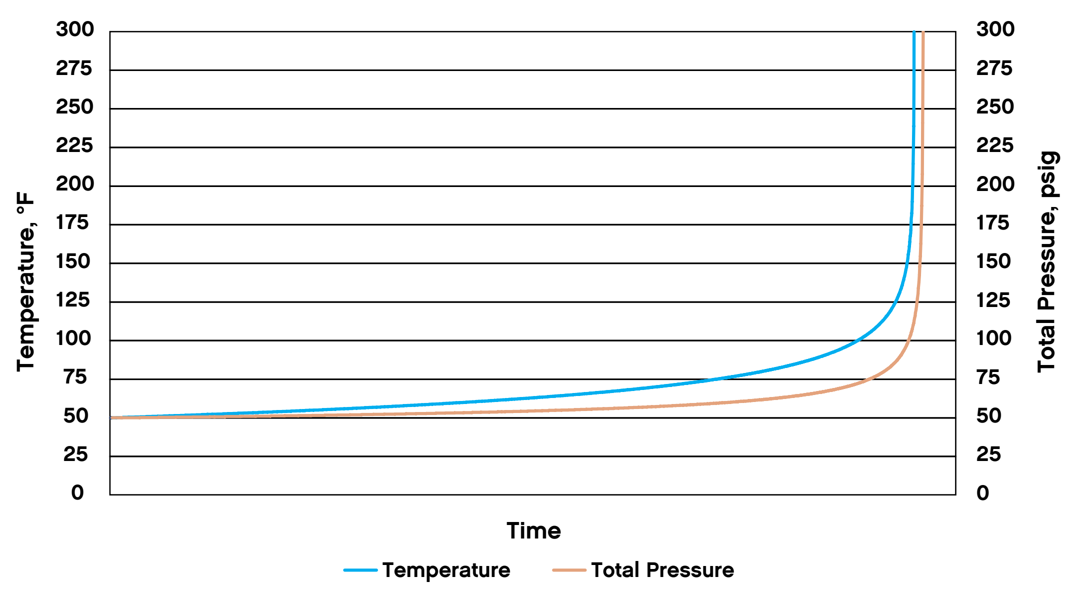
10.6 Emergency Response Plan to Temperature Rise

Elements of an emergency response plan to address rising temperature of EO in storage or in a railcar might include, as appropriate:

- Increase frequency of measuring and recording the temperature of the EO in the vessel or railcar.

Figure 10.1 Ethylene Oxide / Water (Neutral) Reaction Temperature Profile

EO / Water (Neutral) Reaction Temperature Profile
(Graph for illustration only)



- Slow temperature rise by removing heat such as with a sprinkler system, cooling coils or water deluge. Sprinkler systems or deluge water have little effect on insulated vessels or railcars (EO railcars are insulated). Be sure the cooling medium temperature is lower than the temperature of the EO in storage.
- Dispose of contaminated material as quickly as possible by feeding to downstream processors. This might include charging a water/caustic or water/acid solution to a batch reactor, then charging EO to convert the EO to glycols in the reactor. (The reaction rate for hydrolysis of EO to glycols may be much faster than the normal process reaction.) Evaluate the design of the reaction system for this scenario (heat removal, metallurgy, shut down systems, control systems, pressure relief systems, etc).
- Transfer contaminated material to a designated holding pond or tank with water. (The volume of water should provide at least a 22:1 vol/vol dilution ratio.)
- Reduce reaction rate by venting to a properly designed EO flare or safe location (venting results in auto-refrigeration of the contained EO). Discharge should be designed for dispersion of EO vapors to avoid vapor cloud explosion and to minimize personnel exposure.
- Plan for evacuation of the unit, the plant, and the surrounding community.

10.7 Use of Water in Emergencies

Be aware of the following when considering the use of water in an EO emergency response scenario:

- Water can be useful for extinguishing EO fires and cooling equipment subject to fire impingement.
- EO and water are completely soluble in each other, and a water spray can be useful in knocking down EO vapors. However, a water spray directed on a pool of liquid EO will increase evolution of EO vapors until significant mixing and dilution of the liquid EO have occurred.
- Water/EO mixtures of less than 22:1 ratio can support combustion in open areas. In closed systems such as sewers, water/EO dilution ratios up to 100:1 are required to eliminate combustion potential.

From the above points it can be concluded that a significant volume of water should be applied in many EO emergency scenarios. In many cases, this may be the maximum amount of water available. Having available at least 30,000 gallons of water per hour to fight a fire allows for 500 gpm water flow per point of impingement for 60 minutes. This consideration is especially important in remote areas where water might not be readily available; in such cases, consider carefully whether to adopt an evacuation strategy to an appropriate distance.

EO also reacts with water. At ambient conditions, the EO/water reaction occurs over days and months for dilute EO concentrations. The responder should not hesitate to apply water in situations where EO has been released to the environment, since the hazard of fire and personnel exposure is far more significant than the hazard of an EO/water reaction.

In a closed container, the heat release from the EO/water reaction can increase the temperature, leading to an accelerating or “runaway” reaction and loss of containment. This potential exists unless the EO in the container can be rapidly purged out or diluted to a few weight percent. See discussion above in Section 10.5.

11.0 Selected Regulations

11.1 Introduction

This Chapter is provided solely as background information and is not intended to substitute for up-to-date research should a specific legal question arise. It also is not intended to be a statement of legal requirements when using or handling EO. Please consult with qualified experts regarding compliance with all applicable laws and regulations. Although this Chapter is believed to be accurate, no warranty, expressed or implied, is made concerning the contents.

The following federal regulations are not represented as inclusive of all U.S. federal regulations that apply to manufacturing and handling EO. The list specifically does not include:

- Federal regulations promulgated after the Chapter was updated; and
- State and local regulations.

11.2 Regulations — Numerical with Subject Listed

Internal Revenue — Internal Revenue Service

26 CFR Part 52 — Environmental taxes.

.4682-3 — EO/CFC-12 is included on the list of imported taxable products. The EO/CFC-12 mixture is used in example 3 of this Section.

Labor — Occupational Safety and Health Administration (OSHA)

29 CFR Part 1910 — Occupational safety and health standards.

.19(h) — Applies the standards in 29 CFR Section 1910.1047 to the exposure of every employee to EO in every employment and place of employment covered by Sections 1910.12 (construction work), 1910.15 (shipyard employment), and 1910.16 (longshoring and marine terminals), in lieu of any other EO exposure standard that would otherwise be applicable.

Appendix A to Section 119 — List of highly hazardous chemicals, toxics and reactives. The appendix contains a listing of toxic and reactive highly hazardous chemicals that present a potential for a catastrophic event at or above the threshold quantity (TQ). EO is listed, and the TQ is 5,000 pounds.

.178(c)(2)(i) — Prohibits use of power-operated industrial trucks in atmospheres containing hazardous concentration of EO.

.1000 —

Table Z-1 — Lists limits for air contaminants and refers to 29 CFR Section 1910.1047 for EO limits.

.1047 —

(a) Specific regulation covering all exposure scenarios to EO except those below the action level (still requires retention of objective data for exempted operations).

(b) Establishes action level of 0.5 ppm, 8-hour time-weighted average (TWA).

(c) Establishes permissible exposure limits of 1 ppm, 8-hour TWA and 5 ppm excursion limit (15-minute average).

(d) Requires exposure monitoring, including initial, periodic, and termination samples, and periodic sampling every 3 or 6 months, depending on exposure levels. Also includes standards for accuracy of monitoring and employee notification of monitoring results.

(e) Requires establishment of regulated areas where EO concentrations may exceed 8-hour TWA or EO concentrations exceed or can reasonably be expected to exceed the excursion limit.

(f) Delineates methods of compliance with exposure requirements including engineering controls (preferred) and personal protective equipment (PPE). Where the TWA or excursion limit is exceeded, requires employer to establish and implement compliance program.

(g) Outlines approved respiratory protection and PPE.

(h) Requires written emergency response plan, including employee alerting procedures, for each workplace where there is a possibility of an emergency.

(i) Outlines mandated medical surveillance plan; required for all employees who are or may be exposed at or above the action level (0.5 ppm) for 30 days or more per year, without regard to respiratory protection, and for any employees exposed during an emergency event. Exams must be done prior to assignment to the work area, annually, at termination or reassignment, after an emergency exposure, and where symptoms of over-exposure exist or when the employee requests medical advice concerning the effects of current or past exposure on reproductive capabilities.

(j) EO hazards communication requirements include signs at demarcation zone, precautionary labels on containers, developing MSDSs as required, and initial and annual employee training programs.

(k) Recordkeeping requirements include objective data to support exempted operations (retained as long as employer relies on the data), exposure measurements (30-year retention period) and medical surveillance records (duration of employment plus 30-year retention period).

(l) Permits employee or designated representative to observe any monitoring of employee exposure.

(m) Lists effective dates. All requirements took effect by December 6, 1988.

(n) Appendices A, B, C, and D provide non-mandatory samples of an EO MSDS, technical guidelines, medical surveillance guidelines, and sampling and analytical methods, respectively.

29 CFR Part 1915 — Occupational safety and health standards for shipyard employment.

.1000 — Refers to 29 CFR Section 1910.1047 for EO limits.

.1047 — Applies the standards in 29 CFR Section 1910.1047 to shipyard employment.

29 CFR Part 1926 — Safety and health regulations for construction.

.55 —

Appendix A — 1970 American Conference of Governmental Industrial Hygienists' Threshold Limit Values of Airborne Contaminants. EO is included on the list, which refers to 29 CFR 1926.1147 for EO limits.

.64 —

Appendix A — List of highly hazardous chemicals, toxics and reactives. The appendix contains a listing of toxic and reactive highly hazardous chemicals which present a potential for a catastrophic event at or above the TQ. EO is listed and has a TQ of 5,000 pounds.

.1147 — Applies the standards in 29 CFR Section 1910.1047 to the construction industry.

National Defense — Department of the Army

32 CFR Part 627 — The Biological Defense Safety Program, technical safety requirements.

.31(d)(6) — The PPE requirements for gloves state that sterilization of nondisposable gloves either before use or before reuse is usually done with EO or formaldehyde gas. Sterilized gloves must be aerated in flowing sterile (filtered) air at 21°C or higher for a minimum of 24 hours prior to use to prevent skin burns and irritation from residual decontaminants.

.33(e) — Provides requirements for using vapors and gases as a method of decontamination. States that formaldehyde, EO, peracetic acid, betapropiolactone, methyl bromide, and glutaraldehyde have all been used successfully as space sterilants where they can be employed in closed systems and with controlled conditions of temperature and humidity. Of these, methyl bromide, beta-propiolactone, and glutaraldehyde are not recommended because of their toxic properties. Peracetic acid can readily decompose with explosive violence in a concentrated state and must be used only in a diluted state and with extreme care. Formaldehyde and EO are both regulated by OSHA for their potential human carcinogenicity, but do have permissible exposure levels (unlike beta-propiolactone, for example) and can be used safely under controlled conditions.

(2) Provides specific requirements for EO. EO sterilization will only be conducted in a sterilizer designed for that purpose and designed to maintain potential exposure levels below the current OSHA standard. EO is effective against all microorganisms, including spores, molds, pathogenic fungi, and highly resistant thermophilic bacteria. All materials to be used in contact with human skin (for example, clothing, shoes, masks and adhesive tape) must be aerated for at least 24 hours after sterilization and prior to use. Concentrations of 500 to 1000 ppm are required for sterilization. Specific OSHA requirements for the use of EO are found in 29 CFR Section 1910.1047.

Navigation and Navigable Waters — U.S. Coast Guard (USCG)

33 CFR Part 126 — Handling of dangerous cargo at waterfront facilities.

.3 — Defines dangerous cargo to include all hazardous materials listed in 49 CFR Parts 170 through 179, which includes EO. Topics addressed by Part 126 include the designation of waterfront facilities, permits required for handling dangerous cargo, supervision and control of dangerous cargo, and conditions for conducting welding and hotwork.

33 CFR Part 127 — Waterfront facilities handling liquefied natural gas (LNG) and liquefied hazardous gas.

.1209 — Requires each waterfront facility handling LNG to provide respiratory protection equipment for each employee in the marine transfer area for LNG during the transfer of EO. The equipment must protect the wearer from EO's vapor for at least 5 minutes.

33 CFR Part 154 — Facilities transferring oil or hazardous material in bulk.

.105 — Defines hazardous material to include all hazardous materials listed in 49 CFR Parts 170 through 179, which includes EO. Requirements for facilities including operations manual and procedures, equipment requirements, facility operations, vapor control systems, and response plans for facilities.

33 CFR Part 160 — Ports and waterways safety — general.

.109 — District Commander or Captain of the Port may direct the handling, loading, unloading, storage, and movement (including the emergency removal, control and disposition) of explosives or other dangerous articles and substances on any structure on or in the navigable waters of the United States, or any land structure or shore area immediately adjacent to those waters. Also allows District Commander or Captain of the Port to conduct examinations to assure compliance with the safety equipment requirements for structures. Applies to DOT hazardous material, which includes EO.

Protection of Environment — U.S. Environmental Protection Agency (EPA)

40 CFR Part 52, Subpart O — Illinois.

.741 —

Appendix A — List of chemicals defining synthetic organic chemical and polymer manufacturing. Includes EO.

40 CFR Part 60 — Standards of performance for new stationary sources.

Subpart VV — Standards of performance for equipment leaks of volatile organic compounds (VOC) in the synthetic organic chemicals manufacturing industry (SOCMI).

.489 — Includes EO on list of chemicals that are produced, as intermediates or final products, by process units covered under this subpart. The applicability date for process units producing one or more of these chemicals is January 5, 1981.

Subpart III — Standards of performance for VOC emissions from the SOCMI air oxidation unit processes.

.617 — EO is included on the list of chemicals affected by Subpart III.

Subpart NNN — Standards of performance for VOC emissions from SOCMI distillation operations.

.667 — EO is included on the list of chemicals affected by Subpart NNN.

Subpart RRR — Standards of performance for VOC emissions from SOCMI reactor processes.

.707 — EO is included on the list of chemicals affected by Subpart RRR.

40 CFR Part 61 — National emissions standards for hazardous air pollutants (NESHAP).

.01 — Lists substances that, pursuant to Section 112 of the Clean Air Act (CAA), have been designated as HAPs. EO is listed and the *Federal Register* citation for the EO listing decision is 50 Fed. Reg. 40286 (Oct. 2, 1985).

40 CFR Part 63 — NESHAPs for source categories.

Subpart D — Regulations governing compliance extensions for early reductions of HAPs.

.74(f), Table 1 — List of high-risk pollutants. EO is listed with a weighting factor of 10.

Subpart E — Approval of state programs and delegation of federal authorities.

.99 — Lists the specific source categories that have been delegated to the air pollution control agencies in each state, including the following for EO: Alaska (EO sterilizers); Arizona (EO sterilization facilities); Idaho (EO sterilizers); Louisiana (EO sterilizers); Nevada (EO sterilization facilities); New Mexico (EO sterilizers); Oklahoma (EO sterilizers); Oregon (EO sterilizers); and Washington (EO sterilizers).

Subpart F — National emission standards for organic HAPs from the SOCMI.

Table 1 — Synthetic Organic Chemical Manufacturing Industry Chemicals. Lists EO in Group I.

Table 2 — Organic Hazardous Air Pollutants. Lists EO.

Table 4 — Organic Hazardous Air Pollutants Subject to Cooling Tower Monitoring Requirements in Section 63.104. Lists EO.

Subpart G — National emission standards for organic HAPs from the SOCMI for process vents, storage vessels, transfer operations, and wastewater.

Table 9 — Organic HAPs Subject to the Wastewater Provisions for Process Units at New and Existing Sources and Corresponding Fraction Removed (Fr) Values. EO is listed with an Fr value of 0.98.

Table 34 — Fraction Measured (Fm) and Fraction Emitted (Fe) for HAP Compounds in Wastewater Streams. EO is listed with a Fm value of 1.00 and a Fe value of 0.50.

Table 36 — Compound Lists Used for Compliance Demonstrations for Enhanced Biological Treatment Processes. EO is included on List 2.

Subpart O — EO emissions standards for sterilization facilities.

.360 — All sterilization sources using one ton EO in sterilization or fumigation operations are subject to the emissions standards in Section 63.362, except as specified. Subpart O does not apply to EO sterilization operations at stationary sources such as hospitals, doctors' offices, clinics, or other facilities whose primary purpose is to provide medical services to humans or animals.

.361 — Defines sterilization facility as "any stationary source where ethylene oxide is used in the sterilization or fumigation of materials."

.362 — Provides standards for EO commercial sterilizers and fumigators for sterilization chamber vent, aeration room vent, and chamber exhaust vent.

.363 — List the compliance and performance provisions for owners and operators of sources subject to the EO emissions standard. Facilities must demonstrate continuous compliance with each operating limit and work practice standard required under this section, except during periods of startup, shutdown, and malfunction.

.364 — Lists monitoring requirements. Provides specific requirements for sterilization facilities using acid-water scrubbers, catalytic oxidation or thermal oxidation, or through the use of another control device. Requires computation of a 24-hour average daily and requires installation, calibration, operation, and maintenance of a monitor to measure EO.

.365 — Lists test methods and procedures for performance testing, efficiency determination at the sterilization chamber vent, concentration determination, efficiency determination at the aeration room vent (not manifolded), determination of baseline parameters for acid-water scrubbers, and compliance demonstration.

.366 — List reporting, construction and reconstruction, and notification requirements.

.367 — Owners or operators of a source subject to Section 63.362 must comply with the recordkeeping requirements in Section 63.10(b) and (c). All records required to be maintained must be maintained so that they can be readily accessed and are suitable for inspection. The most recent two years of records must be retained onsite or be accessible to an inspector while onsite. The records of the preceding three years, where required, may be retained offsite. Records may be maintained in hard copy or computer-readable form including on paper, microfilm, computer, computer disk, magnetic tape, or microfiche.

.368 — EPA or authorized authority, such as the applicable state, local, or tribal agency, can implement and enforce this Subpart.

Subpart U — NESHAPs: Group I polymers and resins.

.482 — "Epichlorohydrin elastomer" is defined as an elastomer formed from the polymerization or copolymerization of epichlorohydrin (EPI). The main epichlorohydrin elastomers include epi-ethylene oxide (EO) copolymer. Epoxies produced by the copolymerization of EPI and bisphenol A are not epichlorohydrin elastomers.

Table 5 — Known organic HAPs emitted from the production of elastomer products. Table provides elastomer products/subcategories for listed chemicals, including EO.

Subpart DD — NESHAPs from off-site waste and recovery operations.

Table 1 — EO is included on the list of HAPs, with a Method 305 fraction measure factor (fm 305) of 1.0.

Subpart JJ — National emission standards for wood furniture manufacturing operations.

Table 2 — List of volatile HAPs (VHAP). EO is included.

Table 4 — Pollutants excluded from use in cleaning and washoff solvents. EO is listed.

Table 6 — VHAP of potential concern. EO is listed with 0.09 tons per year de minimis value.

Subpart GGG — National emission standards for pharmaceuticals production.

Table 2 — Lists EO as a partially soluble HAP.

Table 8 — Lists 1.0 as the fraction measured (F_m) for EO in wastewater streams.

.1423 —

> "Epoxide" is defined as a chemical compound consisting of a three-membered cyclic ether. Only emissions of epoxides listed in Table 4 of this Subpart, including EO, are regulated by the provisions of this Subpart (Subpart PPP, Sections 1420-1439).
>
> "Extended Cookout (ECO)" is defined as a control technique that reduces the amount of unreacted EO and/or propylene oxide (epoxides) in the reactor. This is accomplished by allowing the product to react for a longer time period, thereby having less unreacted epoxides and reducing epoxides emissions that may have otherwise occurred.

Subpart PPP — Known organic HAPs from polyether polyol products.

Table 4 — Lists EO as a known organic HAP from polyether polyol products.

Subpart EEEE — NESHAPs: Organic liquids distribution (non-gasoline).

Table 1 — Lists EO as an organic HAP.

Subpart FFFF — NESHAPs: Miscellaneous organic chemical manufacturing.

Table 8 — Lists EO as a partially soluble HAP.

Subpart UUUU — NESHAPs for cellulose products manufacturing.

.5480 — Lists EO as one of the HAPs emitted in greatest quantity from cellulose products manufacturing operations.

.5610 —

> "Cellulose ether process" is defined to include a manufacturing process that includes the following process steps: (i) reaction of cellulose with sodium hydroxide to produce alkali cellulose; (ii) reaction of the alkali cellulose with a chemical compound(s), such as EO, to produce a particular cellulose ether; (iii) washing and purification of the cellulose ether; and (iv) drying of the cellulose ether.

"Extended cookout (ECO)" is defined to include as a cellulose ether process change that reduces the amount of one of several unreacted chemicals, including EO, leaving the reactor. This is accomplished by allowing the product to react for a longer time, thereby leaving less unreacted EO and reducing emissions of EO that might have occurred otherwise.

Subpart XXXX — NESHAPs: Rubber Tire Manufacturing

Table 16 — EO is listed as a selected HAP.

Subpart GGGGG — NESHAPs: Site remediation

Table 1 — EO is listed with an f_{m305} (fraction measure factor in Method 305, 40 CFR Part 63, Appendix A) of 1.0.

Subpart HHHHH — NESHAPs: Miscellaneous coating manufacturing.

Table 7 — EO is included on the list of partially soluble HAPs in wastewater that are subject to management and treatment requirements

40 CFR Part 68 — Chemical accident prevention provisions.

.130 —

Table 1 — List of regulated toxic substances and TQs for accidental release prevention. EO is listed with a TQ of 10,000. EO was listed based on the following:

(a) Mandated by congress; and

(b) On EHS list, vapor pressure 10mm Hg or greater.

Table 2 — List of regulated toxic substances and TQs for accidental release prevention. EO is listed with a TQ of 10,000. EO was listed based on the following:

(a) Mandated by congress; and

(b) On EHS list, vapor pressure 10mm Hg or greater.

Appendix A — Table of toxic endpoints. EO is listed with toxic endpoint of 0.09 mg/L.

40 CFR Part 180 — Tolerances and exemptions from tolerances for pesticide chemicals in food.

.151 — Establishes tolerances for residues of the "antimicrobial agent and insecticide" EO, when used as a postharvest fumigant in or on copra coconut, whole spices, and black walnuts. EO may be safely used as a fumigant for the control of microorganisms and insect infestation in ground spices and other processed natural seasoning materials, except mixtures to which salt has been added, in accordance with prescribed conditions.

.910 — Residues of listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest. Inert ingredients include mixtures produced using EO, and mixtures containing EO.

.920 — Listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to growing crops only. Inert ingredients include mixtures produced using EO, and mixtures containing EO.

.930 — Listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to animals. Inert ingredients include mixtures produced using EO, and mixtures containing EO.

.940 — Lists pesticide chemicals that, when used as ingredients in an antimicrobial pesticide formulation, may be applied to dairy processing equipment, and food-processing equipment and utensils. Pesticide chemicals include mixtures produced using EO, and mixtures containing EO.

.960 — Residues resulting from the use of the listed polymers as inert ingredients in a pesticide chemical formulation are exempted from the requirement of a tolerance, if such use is in accordance with good agricultural or manufacturing practices. EO is included as a substance used to create a listed polymer.

.1001 —

(c) Residues of the listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest. Listed inert ingredients include mixtures produced using EO, and mixtures containing EO.

(d) Listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to growing crops only. Listed inert ingredients include mixtures produced using EO, and mixtures containing EO.

(e) Listed materials are exempted from the requirement of a tolerance when used in accordance with good agricultural practice as inert or occasionally active ingredients in pesticide formulations applied to animals. Listed inert ingredients include mixtures produced using EO, and mixtures containing EO.

40 CFR Part 261 — Identification and listing of hazardous waste.

.33(f) — EO is listed as U115 (U list waste).

Appendix VIII — EO is included on the list of hazardous constituents list.

40 CFR Part 266 — Standards for the management of specific hazardous wastes and specific types of hazardous waste management facilities.

Appendix V — Risk specific dosages (risk specific doses (10^{-5}). EO is listed with a unit risk of 1.0E-04 m^3/·g and an RsD of 1.0E-01 ·g/ m^3.

Appendix VII — Nonmetals: Residue concentration limits. EO is listed with a concentration limit for residues of 3xE-04 mg/kg.

40 CFR Part 268 — Land disposal restrictions.

.40 — Lists treatment standards for hazardous wastes. Includes waste code, waste description and treatment/regulatory subcategory, regulated hazardous constituent, and concentrations in wastewater, and nonwastewater. EO is listed as follows:

Under waste code F039 as a regulated hazardous constituent, with a concentration of 0.12 mg/L in wastewater; and

Under waste code U115 with technology codes (WETOX or CHOXD) fb CARBN or CMBST, or concentration 0.12 mg/L in wastewater, and technology codes CHOXD or CMBST in nonwastewater.

.48 — Lists universal waste treatment standards. Includes EO, and the listed wastewater standard is a concentration of 0.12 mg/L in wastewater.

40 CFR Part 302 — Designations, reportable quantities and notification requirements for CERCLA hazardous substances.

.4 — Lists EO as a hazardous substance under CAA Section 112 and Section 3001 of the Resource Conservation and Recovery Act (RCRA) with a final reportable quantity of 10 pounds.

Appendix A — Sequential CAS Registry Number list of CERCLA hazardous substances. Includes EO.

40 CFR Part 355 — Emergency planning and notification.

Appendix A — The list of extremely hazardous substances and their threshold planning quantities. EO is listed with a reportable quantity (RQ) of 10 pounds and a threshold planning quantity of 1,000 pounds. There is a note for EO: "Chemicals on the original list that do not meet toxicity criteria but because of their high production volume and recognized toxicity are considered chemicals of concern ('Other chemicals')."

Appendix B — The list of extremely hazardous substances and their threshold planning quantities. EO is listed with an RQ of 10 pounds and a threshold planning quantity of 1,000 pounds. There is a note for EO: "Chemicals on the original list that do not meet toxicity criteria but because of their high production volume and recognized toxicity are considered chemicals of concern ('Other chemicals')."

40 CFR Part 372 — Toxic chemical release reporting: Community right-to-know.

.65 — EO is listed effective January 1, 1987.

40 CFR Part 414 — Organic chemicals, plastics, and synthetic fibers.

.60(a) — EO is included on list of aliphatic organic chemicals.

40 CFR Part 721— Significant new uses of chemical substances.

.3680 — SNUR requirements for EO adduct of fatty acid ester with pentaerythritol. The significant new use is release to water.

.3700 — SNUR requirements for fatty acid, ester with styrenated phenol, EO adduct. The significant new uses are the hazard communication program and release to water.

.3800 — SNUR requirements for formaldehyde, condensated polyoxyethylene fatty acid, ester with styrenated phenol, EO adduct. The significant new uses are the hazard communication program and release to water.

.7000 — SNUR requirements for polymer of disodium maleate, allyl ether, and EO. The significant new uses are the hazard communication program and industrial, commercial, and consumer activities.

Shipping — USCG

46 CFR Part 150 — Compatibility of cargoes.

Table 1 — The alphabetical list of cargoes includes chemical name, group number, footnote, CHRIS code, and related CHRIS codes. EO is included on the list, and is in group 0, with footnote 1, and CHRIS code EOX. EO, propylene oxide mixture is also listed, and it is in group 16, footnote 1, CHRIS code EPM.

Table 2 — This table lists the grouping of cargoes. EO is included in group 0, unassigned cargoes. EO, propylene mixtures are included in group 16, alkylene oxides.

46 CFR Part 151 — Barges carrying bulk liquid hazardous material cargoes.

Table 151.05 to Subpart 151.05 — Summary of Minimum Requirements. The Table lists requirements for cargo identification, hull type, cargo segregation tank, tanks, cargo transfer, environmental control, fire protection, special requirements in 46 CFR Part 151, electrical hazard class and group, temperature control installation, and tank internal inspection period. EO is included in the Table.

.50-10(a) — For the purpose of this part, alkylene oxides are considered to be EO and propylene oxide.

.50-10(q) — The special requirements for EO contained in Section 151.50–12 must also be observed.

.50-12 —

(a)

(1) EO shall be carried in fixed, independent, pressure vessel type cargo tanks, designed, constructed, arranged and, if necessary, equipped with machinery to maintain the cargo temperature below 90°F except as otherwise provided for in paragraph (a)(3) of this section.

(2) EO shall be loaded at a temperature below 70°F.

(3) When EO is to be transported at or near atmospheric pressure, the Commandant may permit the use of alternate methods of storage which are consistent with the minimum requirements of this subpart.

(b)

(1) All cargo tanks shall be constructed of a carbon steel or stainless steel acceptable to the Commandant. Impurities of copper, magnesium and other acetylide-forming metals shall be kept to a minimum. The chemical composition of all steel used shall be submitted to the Commandant for approval prior to fabrication. Aluminum, copper and other acetylide-forming metals, such as silver, mercury, magnesium, and their alloys shall not be used as materials of construction for tanks or equipment used in handling EO.

(2) Cargo tanks shall meet the requirements of Class I pressure vessels.

(3) Cargo tanks shall be designed for the maximum pressure of vapor or gas used in discharging the cargo but in no case shall the design pressure of such tanks be less than 75 pounds per square inch gauge. The tank shell and heads shall not be less than 5/16-inch thick.

(c)

(1) Cargo tanks shall be located below deck in holds or enclosed spaces with the domes or trunks extended above the weather deck and terminating in the open. Provisions shall be made to maintain the

watertightness of the deck by means of watertight seals around such domes or trunks. The holds or enclosed spaces, in which the EO tanks are located, shall not be used for any other purpose. However, in open hopper type barges of a suitable design approved for such service, the weatherdeck may not be required to be watertight.

(2) All cargo tanks shall be installed with the manhole openings and all tank connections located above the weatherdeck in the open.

(3) Tanks shall be electrically bonded to the hull.

(4) No welding of any kind shall be done on cargo tanks or supporting structure unless authorized by the Commandant.

(d) All cargo tanks, piping, valves, fittings, and similar equipment which may contain ethylene oxide in either the liquid or vapor phase, including the vent risers, shall be insulated. Flanges need not be covered, but if covered, a small opening shall be left at the bottom of the flange cover to detect leaks. Insulation shall be of an approved incombustible material suitable for use with EO, which does not significantly lower the autoignition temperature and which does not react spontaneously with EO. The insulation shall be of such thickness as to provide a thermal conductance of not more than 0.075 B.t.u. per square foot per degree Fahrenheit differential in temperature per hour.

(e)

(1) When cooling systems are installed to maintain the temperature of the liquid below 90°F, at least two complete cooling plants, automatically regulated by temperature variations within the tanks shall be provided; each to be complete with the necessary auxiliaries for proper operation. The control system shall also be capable of being manually operated. An alarm shall be provided to indicate malfunctioning of the temperature controls. The capacity of each cooling system shall be sufficient to maintain the temperature of the liquid cargo at or below the design temperature of the system.

(2) An alternate arrangement may consist of three cooling plants, any two of which shall be sufficient to maintain the temperature of the liquid cargo at or below the design temperature of the system.

(3) Cooling systems requiring compression of EO are prohibited.

(f) In addition to the shutoff valve required, all tank connections larger than one-half inch inside pipe size, except safety relief valves and liquid level gauging devices, shall be fitted with either internal back pressure check valves or internal excess flow valves in conjunction with a quick closing stop valve operable from at least two remote locations. The quick closing stop valve shall be of the "fail safe" type acceptable to the Commandant and shall be equipped with a fusible plug designed to melt between 208°F and 220°F, which will cause the quick closing valve to close automatically in case of fire. The quick closing valve shall be located as close to the tank as possible.

(g) Piping systems intended for EO service shall not be used for any other product and shall be completely separate from all other systems. The piping system shall be designed so that no cross connections may be made either through accident or design.

(h) Each safety relief valve shall be set to start to discharge at not less than 75 pounds per square inch gauge, nor more than the design pressure of the tank.

(i) The filling density shall not exceed 83 percent.

(j)

(1) The cargo shall be shipped under a suitable protective inerting gas system, such as nitrogen. When nitrogen gas is used, the gas inerting system shall be so designed that the vapor space above the liquid cargo will be filled and maintained with a gas mixture of not less than 45 percent nitrogen. Other gases proposed for inerting use may be given consideration by the Commandant. Original charging only of protective inerting gas at the loading facility is not

considered adequate. A sufficient amount of spare inerting gas as approved by the Commandant shall be provided on the vessel in order to maintain the proper concentration of the gas in the event of normal leakage or other losses.

(2) Any inerting gas selected should be at least 98 percent pure and free of reactive materials, such as ammonia, hydrogen sulfide, sulfur compounds, and acetylene.

(k) Prior to loading, a sample from the cargo tank will be taken to insure that the pad gas will meet the requirements of paragraph (j) of this section and that the oxygen content of the vapor space will be not more than 2 percent maximum. If necessary, a sample will be taken after loading to insure the vapor space meets this requirement.

(l) The cargo piping shall be inspected and tested at least once in each two calendar years.

(m) In those cases where the cargo transfer hose used is not part of the barge's equipment, the person in charge of the transfer operation shall determine that the provisions of Section 151.50–10(k) have been met before using this hose. A certificate of test, supplied by the transfer facility, will be considered as adequate for this determination.

(n) The provisions of Section 151.50–10 shall be complied with as a requirement for shipping EO.

(o) A hydrostatic test of 11⁄2 times the design pressure shall be made on the cargo tanks at least once in each four years at the time the internal examination is made and at such other times as considered necessary by the Officer in Charge, Marine Inspection.

46 CFR Part 154 — Safety standards for self-propelled vessels carrying bulk liquefied gases.

.7 —

"Flammable cargoes" is defined to include several liquefied gases, including EO, from Table 4 (follows Section 154.1872).

"Toxic cargoes" is defined to include several liquefied gases, including EO, from Table 4 (follows Section 154.1872).

.22(a)(8) — To obtain an endorsed Certificate of Compliance to meet Section 154.1802(a) for a foreign flag vessel, whose flag administration issues IMO Certificates, and an endorsement for the carriage of EO, an application must be submitted to the USCG that includes a classification society certification that the vessel meets the requirements of Section 154.1725(a)(4), (5), and (7).

.1705(a) — EO must be carried in an independent tank type C that meets Section 154.701(a).

.1710 — When a vessel is carrying EO, the master must ensure that air is purged from the cargo tanks and associated piping before the cargo is loaded. The mast must also ensure that the air is excluded after the cargo is loaded by maintaining a positive pressure of at least 13.8 kPa gauge (2 psig) by either introducing a gas that is not reactive; is not flammable; and does not contain more than 0.2percent oxygen by volume; or by controlling the cargo temperature.

.1720 — A refrigeration system that is used to cool EO must be an indirect refrigeration system that does not use vapor compression.

.1725 —

(a) A vessel carrying EO must:

(1) Have cargo piping, vent piping, and refrigeration equipment that have no connections to other systems;

(2) Have valves, flanges, fittings, and accessory equipment made of steel, stainless steel, except types 416 and 442, or other material specially approved by the Commandant (G–MSO);

(3) Have valve disk faces, and other wearing parts of valves made of stainless steel containing not less than 11 percent chromium;

(4) Have gaskets constructed of spirally wound stainless steel with teflon or other material specially approved by the Commandant (G–MSO);

(5) Not have asbestos, rubber, or cast iron components in the cargo containment system and piping;

(6) Not have threaded joints in cargo piping;

(7) Have a water spray system under Section 154.1105 that protects the above deck cargo piping; and

(8) Have a nitrogen inerting system or on board nitrogen gas storage that can inert the vapor space of an EO cargo tank for a period of 30 days under the condition of paragraph (e) of this section.

(b) The cargo hose used for EO must:

(1) Be specially approved by the Commandant (G-MSO); and

(2) Be marked "For (Alkylene or Ethylene) Oxide Transfer Only."

(c) EO must be maintained at less than 30°C (86°F).

(d) Cargo tank relief valves for tanks containing EO must be set at 539 kPa gauge (78.2 psig) or higher.

(e) The vapor space of a cargo tank carrying EO must be maintained at a nitrogen concentration of 45 percent by volume.

(f) A vessel must have a method for jettisoning EO that meets the requirements of Sections 154.356 and 154.1872.

.1730 —

(a) The master must ensure that before EO is loaded into a cargo tank:

(1) The tank is thoroughly clean, dry, and free of rust;

(2) The hold spaces are inerted with an inert gas that meets the requirements of Section 154.1710(b)(1); and

(3) The cargo tank vapor space is inerted with nitrogen.

(b) EO must be off loaded by a deepwell pump or inert gas displacement.

(c) EO must not be carried in deck tanks.

.1872(d) — When EO is carried, the master must ensure that the emergency jettisoning piping with associated pumps and fittings is on-line and ready for use for an emergency.

Table 4 — Provides summary of minimum requirements for several cargoes, including EO.

Transportation — Research and Special Programs Administration

49 CFR Part 172 — Hazardous materials table, special provisions, hazardous materials communications, emergency response information, and training requirements.

.101 — Hazardous materials table. This table lists the proper shipping name, hazard class or division, identification number, packing group, label code, special provisions, packaging requirements, quantity limitations, and vessel stowage requirements for hazardous materials. The table includes EO and carbon dioxide mixture with more than 87 percent EO; EO and carbon dioxide mixtures with more than 9 percent but not more than 87 percent EO; EO and carbon dioxide mixtures with not more than 9 percent EO; EO and chlorotetrafluoroethane mixture with not more than 8.8 percent EO; EO and dichlorodifluoromethane mixture, with not more than 12.5 percent EO; EO and pentafluoroethane mixture with not more than 7.9 percent EO; EO and propylene oxide mixtures, with not more than 30 percent EO; EO and tetrafluoroethane mixture with not more than 5.6 percent EO; EO or EO with nitrogen up to a total pressure of 1MPa (10 bar) at 50 degrees C.

Table 1 to Appendix A — List of hazardous substances and RQs. EO is included, and the RQ for EO is 10 pounds (4.54 kg).

.102 — List of non-refrigerated liquefied compressed gases subject to portable tank code T50. Includes EO with nitrogen up to a total pressure of 1MPa (10 bar) at 50°C; EO and carbon dioxide mixture with more than 9 percent but not more than 87 percent EO; EO and dichlorodifluoromethane mixture with not more than 12.5 percent EO; EO and chlorotetrafluoroethane mixture, with not more than 8.8 percent EO; EO and pentafluoroethane mixture, with not more than 7.9 percent EO; and EO and tetrafluoroethane mixture, with not more than 5.6 percent EO.

49 CFR Part 173 — Shippers— general requirements for shipments and packagings.

.304a(a) — Liquefied gases (except gas in solution) must be offered for transportation, subject to the requirements in this section and Sections 49 CFR Sections 173.301 and 173.304, except that no DOT 4E or 39 packaging may be filled and shipped with a mixture containing EO, unless specifically authorized in this Part.

.323 —

(a) For packaging EO in non-bulk packagings, silver mercury or any of its alloys or copper may not be used in any part of a packaging, valve, or other packaging appurtenance if that part, during normal conditions of transportation, may come in contact with EO liquid or vapor. Copper alloys may be used only where gas mixtures do not contain free acetylene at any concentration that will form copper acetylene. All packaging and gaskets must be constructed of materials which are compatible with EO and do not lower the auto-ignition temperature of EO.

(b) EO must be packaged in one of the following:

(1) In 4G fiberboard boxes with inner glass ampoules or vials. Total quantity of EO may not exceed 100 grams (3.5 ounces) per package. The completed package must be capable of passing Packing Group I performance tests.

(2) In 4G fiberboard boxes constructed with top and bottom pads and perimeter liner. Inner packagings must be aluminum receptacles of no more than 135 g (4.8 ounces) capacity cushioned with incombustible material. No more than 12 receptacles may be packed in one box, and no more than 10 boxes may be overpacked under the provisions of Section 173.25 of this part. Each completed package must be capable of passing Packing Group I performance tests.

(3) In 4C1, 4C2, 4D or 4F wooden boxes or 4G fiberboard boxes with inner metal receptacles of no more than 340 g (12 ounces) capacity. The metal receptacle must be capable of withstanding no less than a 1241.1 kPa (180 psig) burst pressure. No more than 12 receptacles may be packed in one box, and each receptacle may not be liquid full below 82°C (180°F). Each inner receptacle must be insulated and equipped with a relief device of the fusible plug type with yield temperature of 69°C to 77°C (156°F to 171°F). The capacity of relief device and insulation must be such that the charged receptacle will not explode when tested by the method described in CGA Pamphlet C–14 or other equivalent method. Each completed package must be capable of passing all Packing Group I performance tests.

(4) In specification cylinders, as authorized for any compressed gas except acetylene. Pressurizing valves and insulation are required for cylinders over 4 L (1 gallon) capacity. Eductor tubes must be provided for cylinders over 19 L (5 gallons) capacity. Cylinders must be seamless or welded steel (not brazed) with a nominal capacity of no more than 115 L (30 gallons) and may not be liquid full below 82°C (180°F). Before each refilling, each cylinder must be tested for leakage at no less than 103.4 kPa (15 psig) pressure. In addition, each cylinder must be equipped with a fusible type relief device with yield temperature of 69°C to 77°C (157°F to 170°F). The capacity of the relief device and the effectiveness of the insulation must be such that the charged cylinder will not explode when tested by the method described in CGA Pamphlet C–14 or other equivalent method.

(5) In 1A1 steel drums of no more than 231 L (61 gallons) and meeting Packing Group I performance standards. The drum must be lagged, of all welded construction with the inner shell having a minimum thickness of 1.7 mm (0.068 inches) and the outer shell having a minimum thickness of 2.4 mm (0.095 inches). Drums must be capable of withstanding a hydrostatic test pressure of 690 kPa (100 psig). Lagging must be of sufficient

thickness so that the drum, when filled with ethylene oxide and equipped with the required pressure relief device, will not rupture when exposed to fire. The drum may not be liquid full below 85°C (185°F), and must be marked "THIS END UP" on the top head. Before each refilling, each drum must be tested for leakage at no less than 103 kPa (15 psig) pressure. Each drum must be equipped with a fusible type relief device with yield temperature of 69°C to 77°C (157°F to 170°F), and the capacity of the relief device must be such that the filled drum is capable of passing, without rupture, the test method described in CGA Pamphlet C–14 or other equivalent method.

(c) When Section 172.101 of this subchapter specifies that a hazardous material be packaged under this section, only the following bulk packagings are authorized, subject to the requirements of subparts A and B of this part, the special provisions specified in column 7 of the Section 172.101 table, and paragraphs (d) through (j) of this section:

(1) Tank cars. Class DOT 105J tank cars: Notwithstanding the requirements of Section 173.31(c), each tank car must have a tank test pressure of at least 20.7 Bar (300 psig) no later than July 1, 2006.

(2) Cargo tanks. Specification MC 330 and MC 331 cargo tank motor vehicles.

(3) Portable tanks. DOT 51 portable tanks.

(d) The pressure relief devices must be set to function at 517 kPa (75 psig). Portable tanks fitted with non-reclosing devices made and in use prior to December 31, 1987, may continue to be used in EO service.

(e) In determining outage, consideration must be given to the lading temperature and solubility of inert gas padding in EO as well as the partial pressure exerted by the gas padding.

(f) Each tank, loaded or empty, must be padded with dry nitrogen or other suitable inert gas of sufficient quantity to render the vapor space of the tank nonflammable up to 41°C (105°F). The gas used for padding must be free of impurities which may cause the EO to polymerize, decompose or undergo other violent chemical reaction.

(g) Copper, silver, mercury, magnesium or their alloys may not be used in any part of the tank or appurtenances that are normally in contact with the lading.

(h) Neoprene, natural rubber and asbestos gaskets are prohibited. All packing and gaskets must be made of materials which do not react with or lower the autoignition temperature of the lading.

(i) Each tank must be insulated with cork (at least 10 cm (4 inches) thick), or mineral wool, fiberglass or other suitable insulation material of sufficient thickness so that the thermal conductance at 16°C (60°F) is not more than 0.075 Btu per hour per square foot per degree F. temperature differential. Portable tanks made and in use prior to December 31, 1987, equipped with fusible plugs instead of a pressure relief valve or rupture disc, must have sufficient insulation so that the tank as filled for shipment will not rupture in a fire. The insulation on portable tanks or cargo tank motor vehicles must be protected with a steel jacket at least 2.54 mm (0.100 inch) thick, or as required by the specification. (j) Tank car tanks built after December 30, 1971, must be equipped with a thermometer well.

Appendix A Figures and Tables

Figure 1 Ethylene Oxide Liquid Density

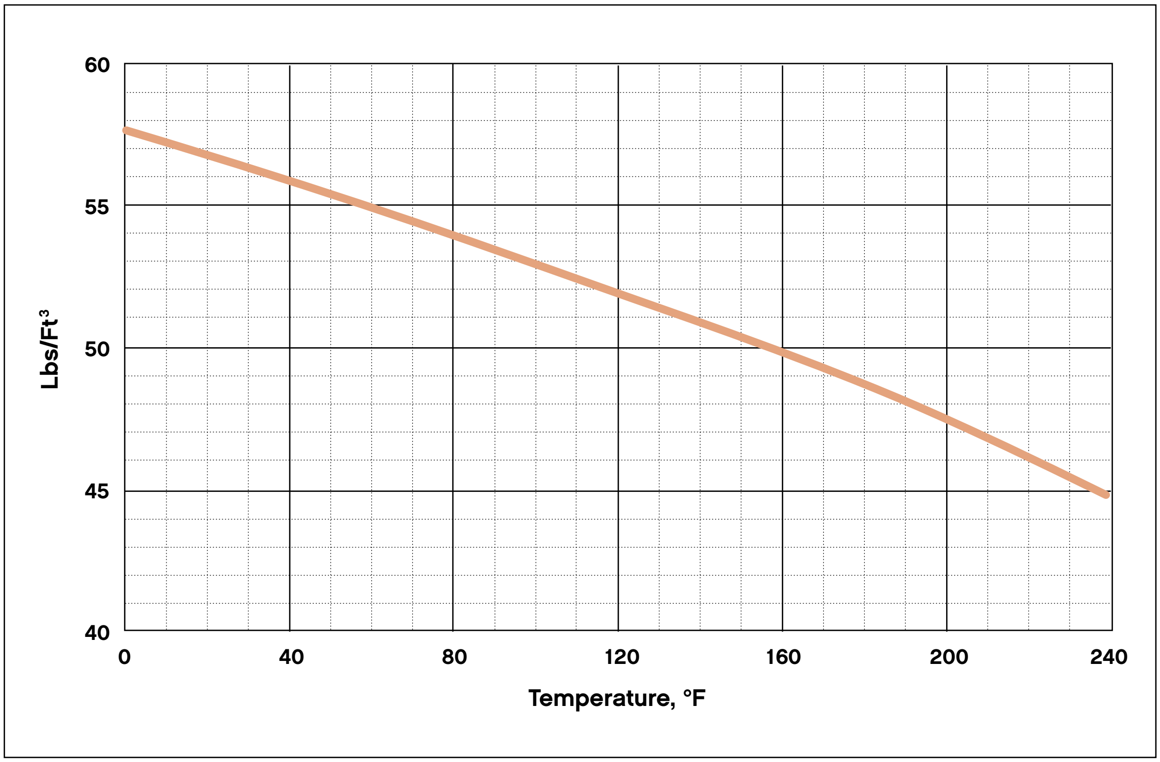


Figure 2 Ethylene Oxide Vapor Pressure

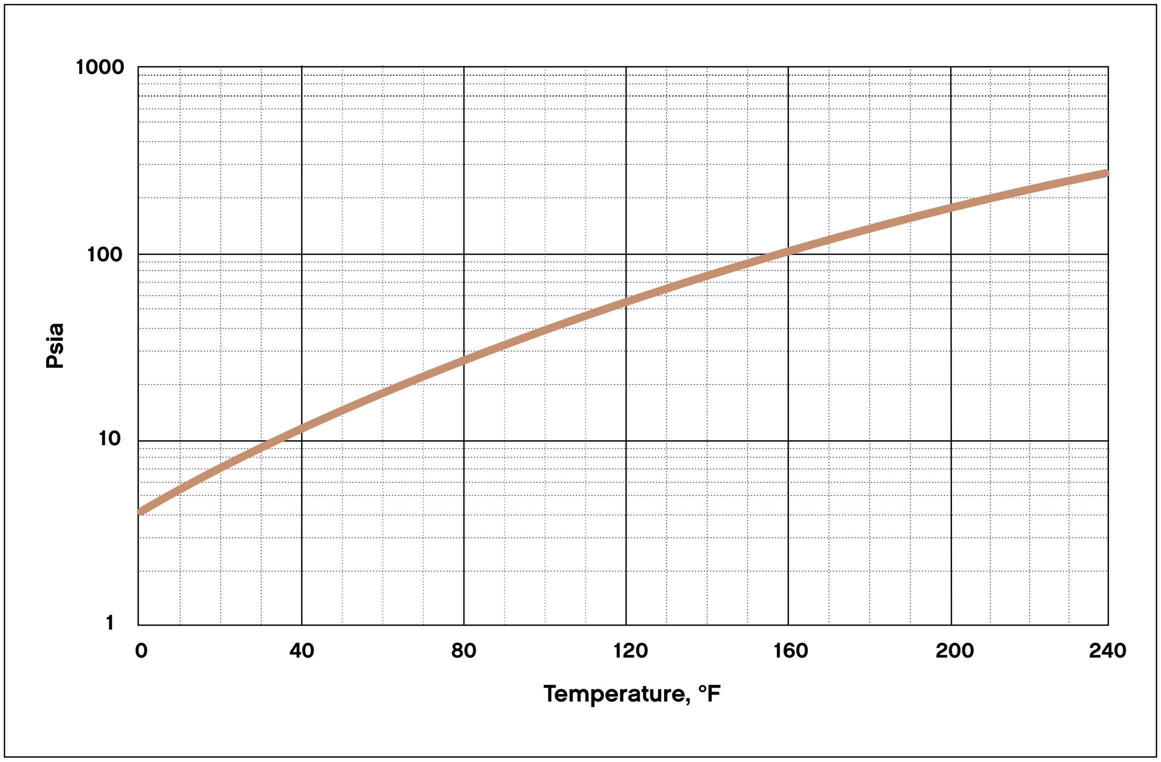


Figure 3 Ethylene Oxide Liquid Heat Capacity

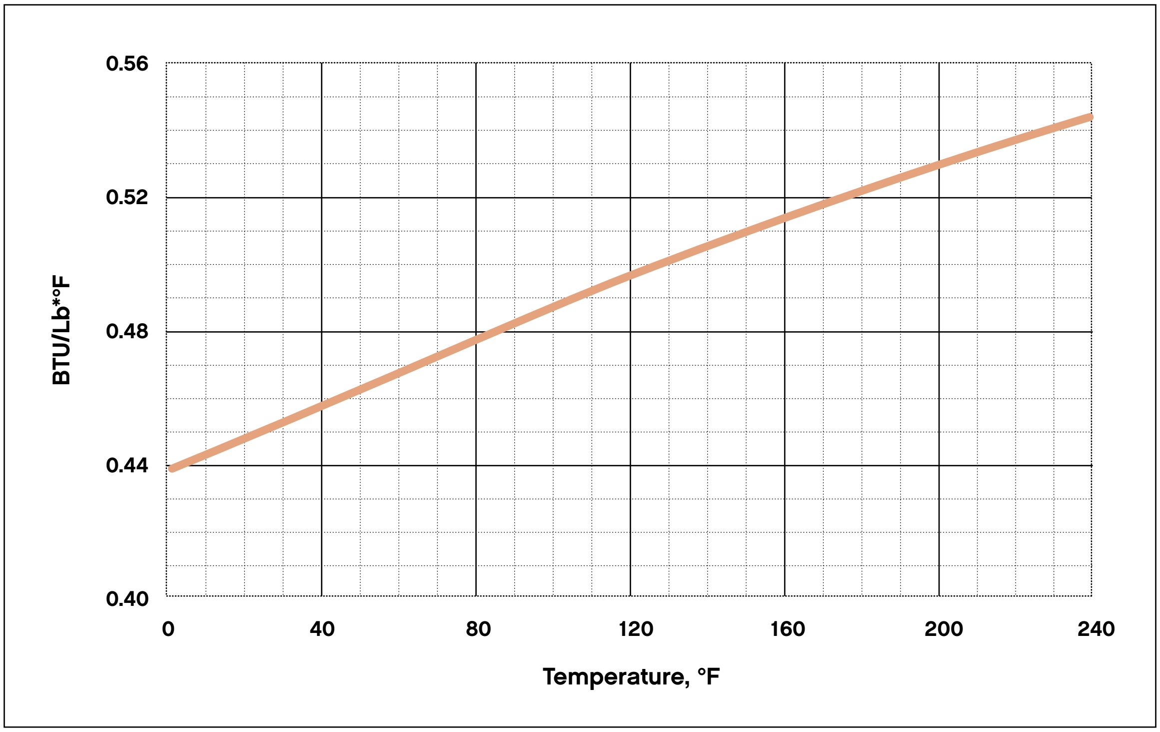


Figure 4 Ethylene Oxide Liquid Viscosity

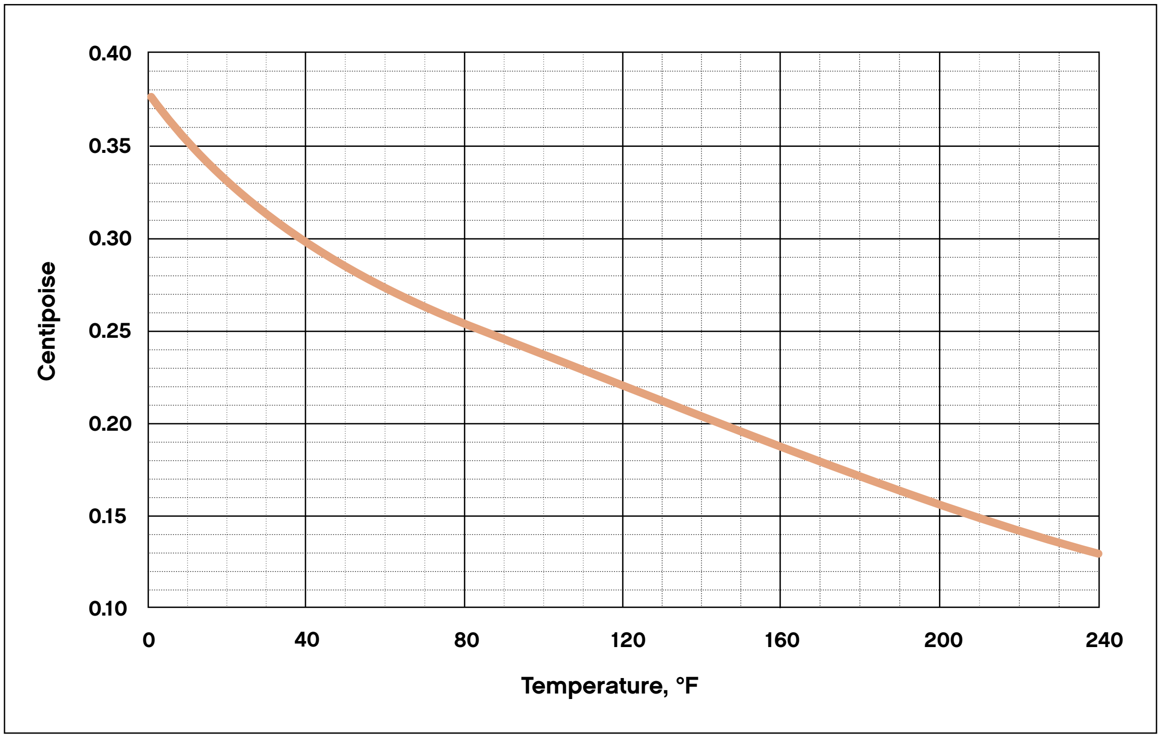


Figure 5 Ethylene Oxide Liquid Thermal Conductivity

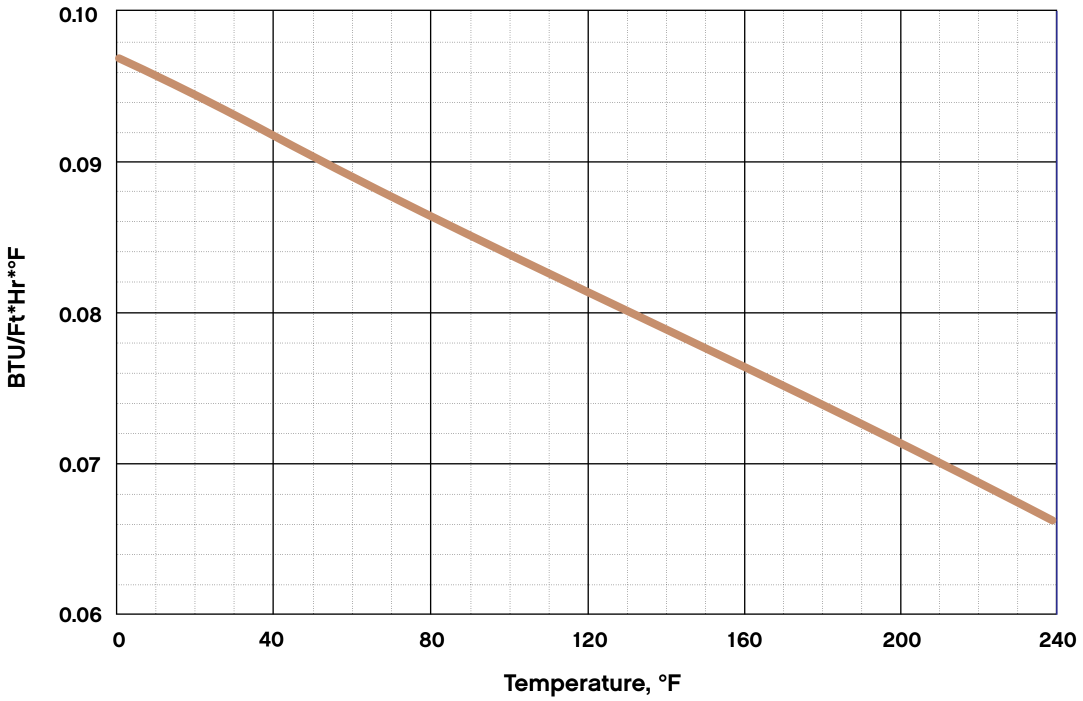


Figure 6 Ethylene Oxide Heat of Vaporization

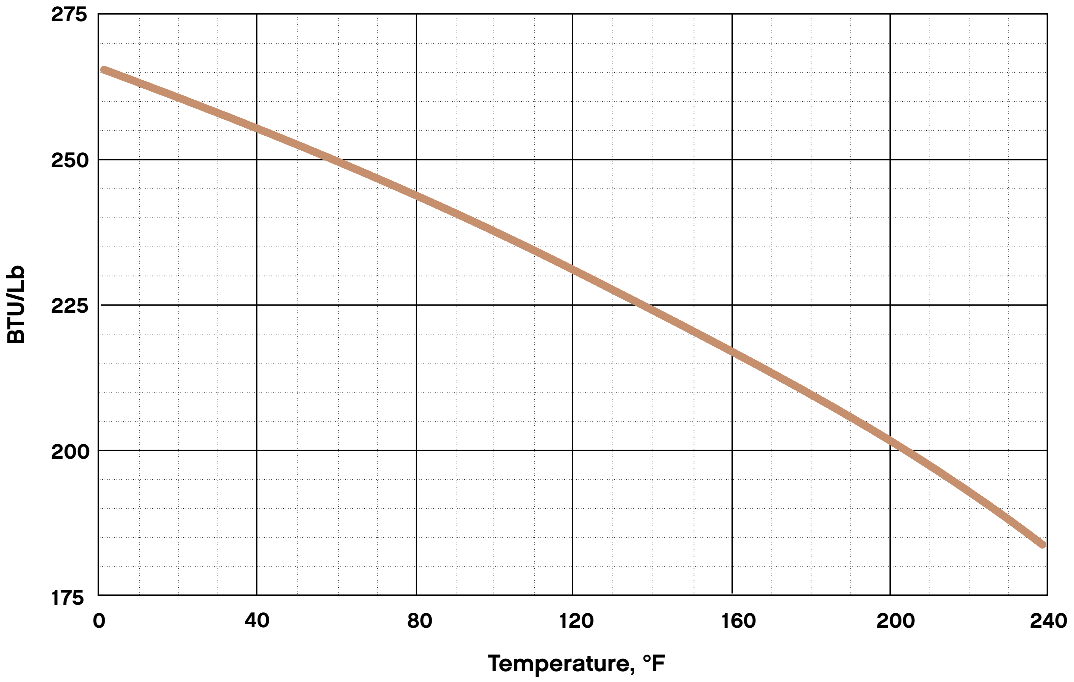


Figure 7 Ethylene Oxide Vapor Heat Capacity

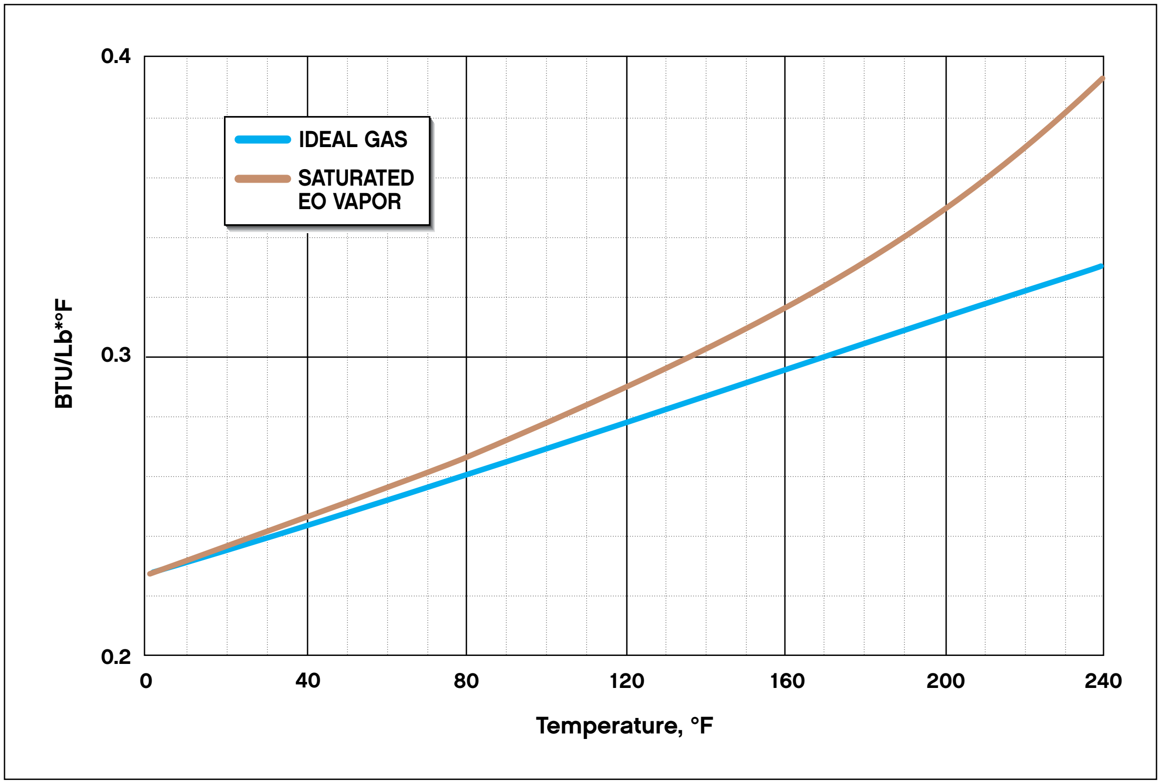


Figure 8 Ethylene Oxide Vapor Viscosity

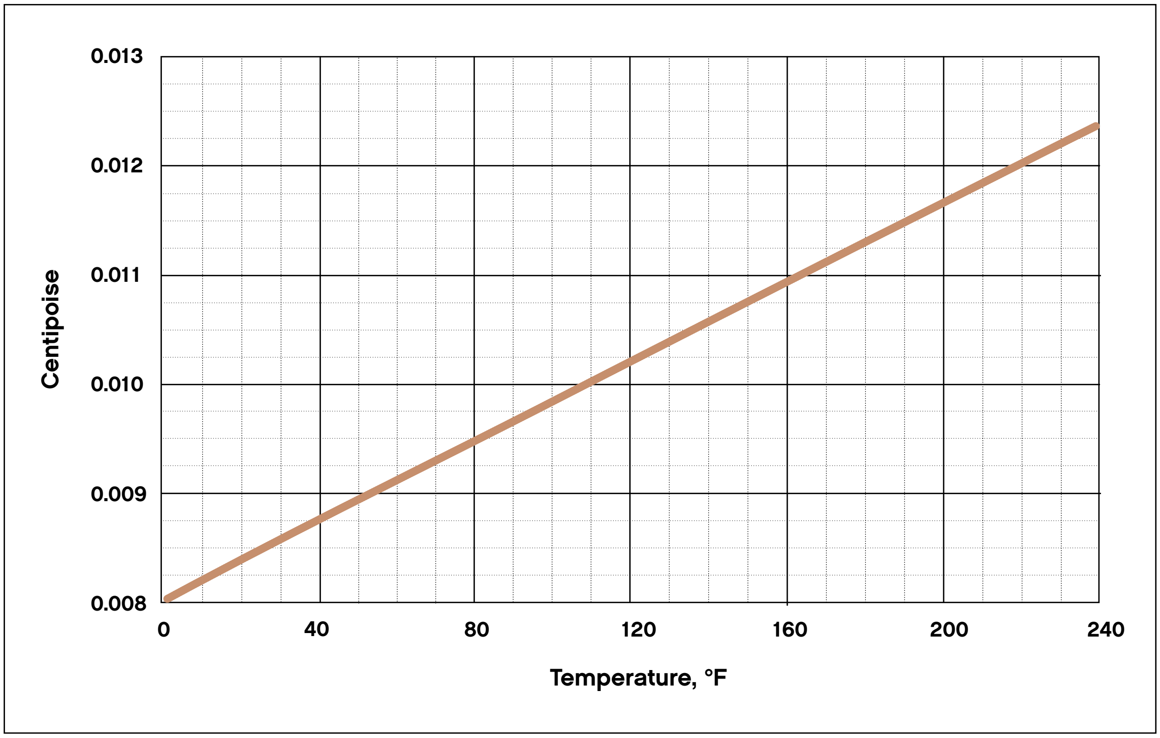


Figure 9 Ethylene Oxide Vapor Thermal Conductivity

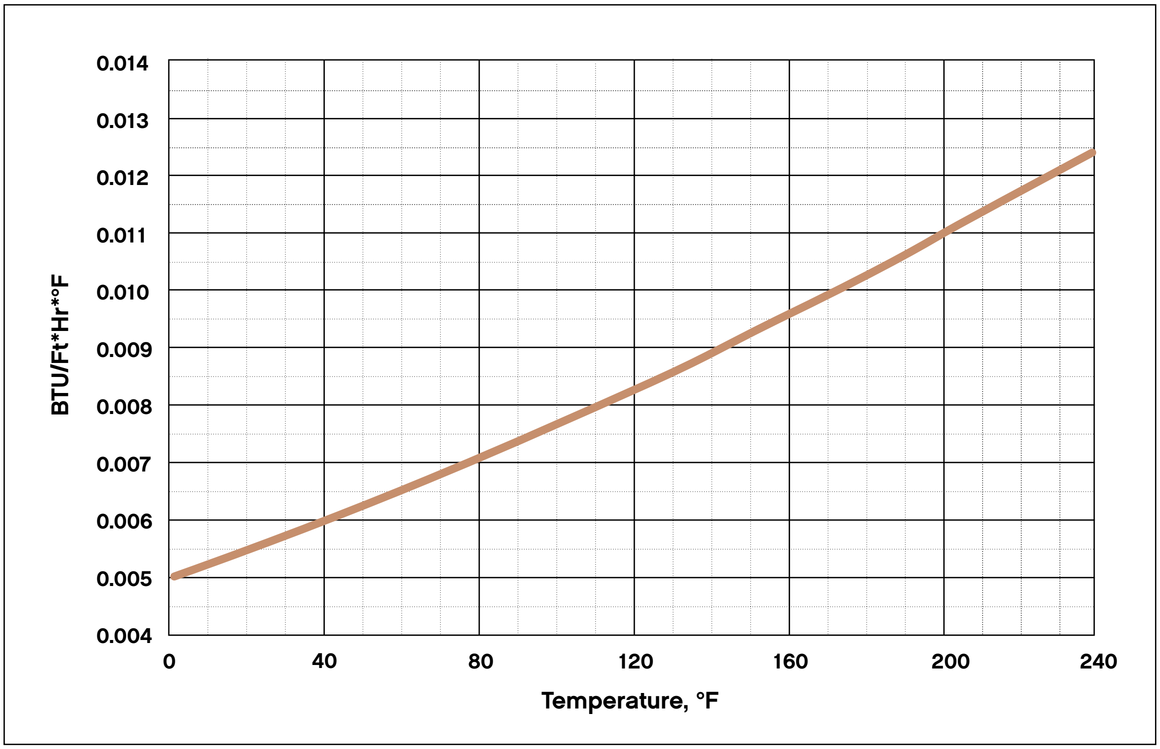


Figure 10 Freezing Points Ethylene Oxide/Water Mixtures

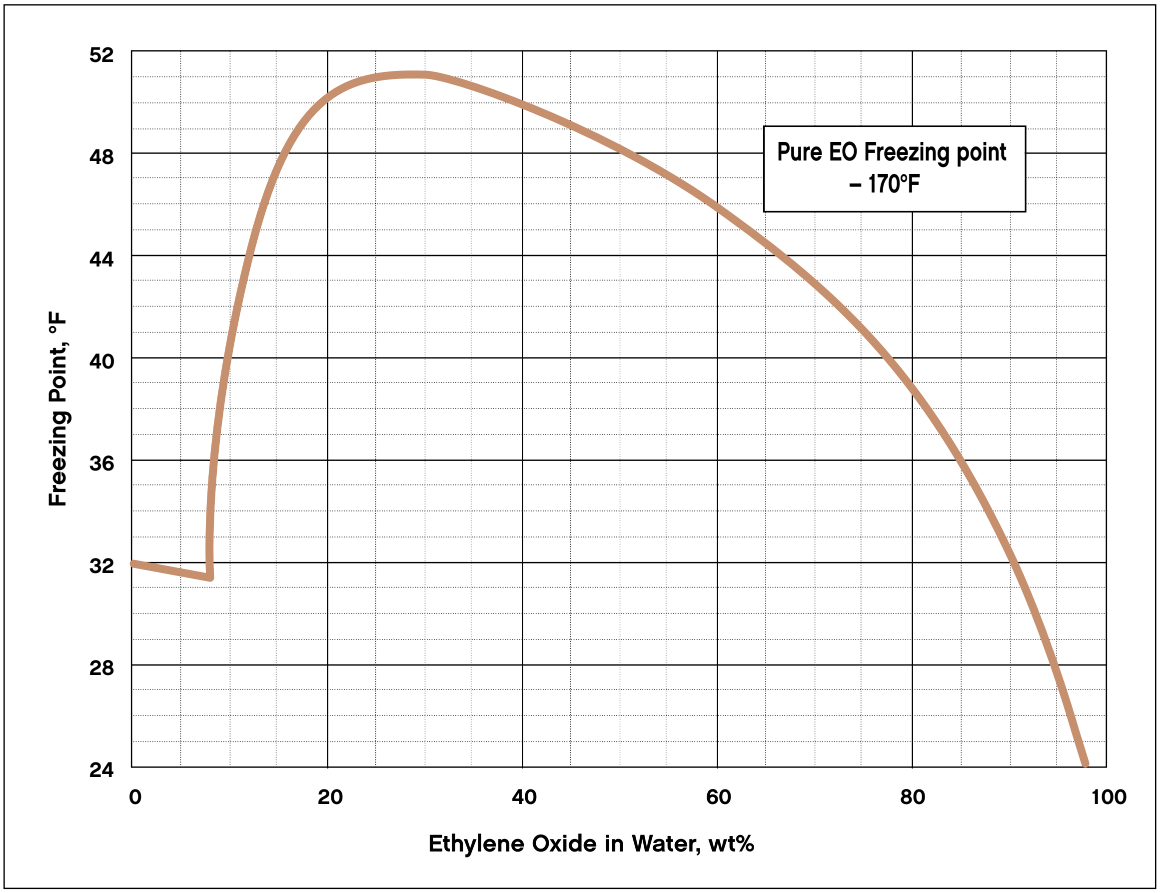


Figure 11 C_p/C_V For Saturated Ethylene Oxide Vapor

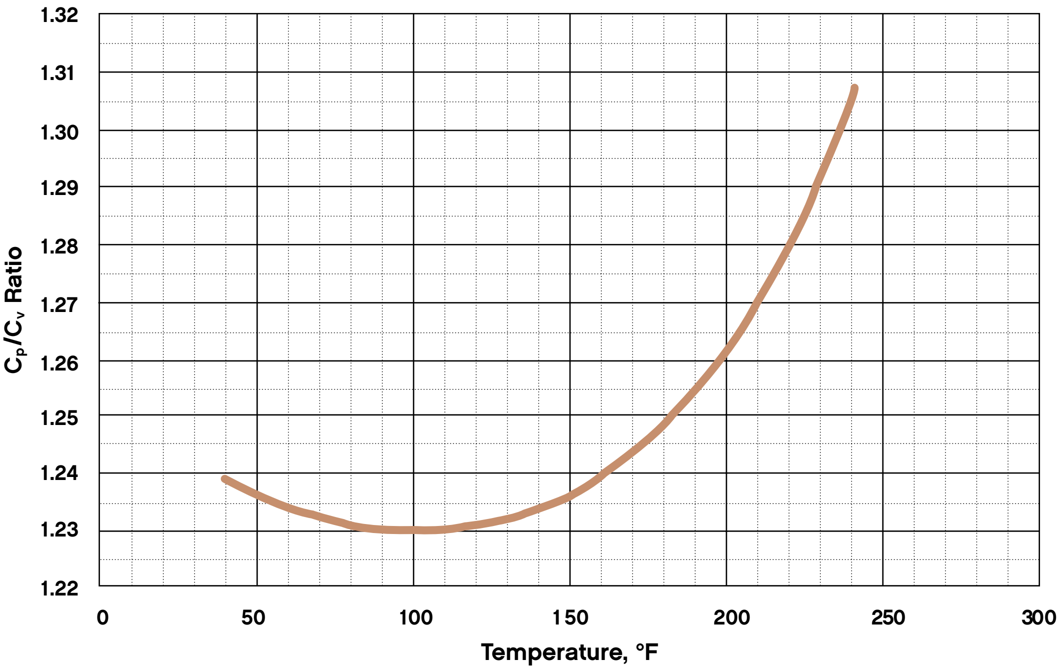


Figure 12 Ethylene Oxide Vapor Density

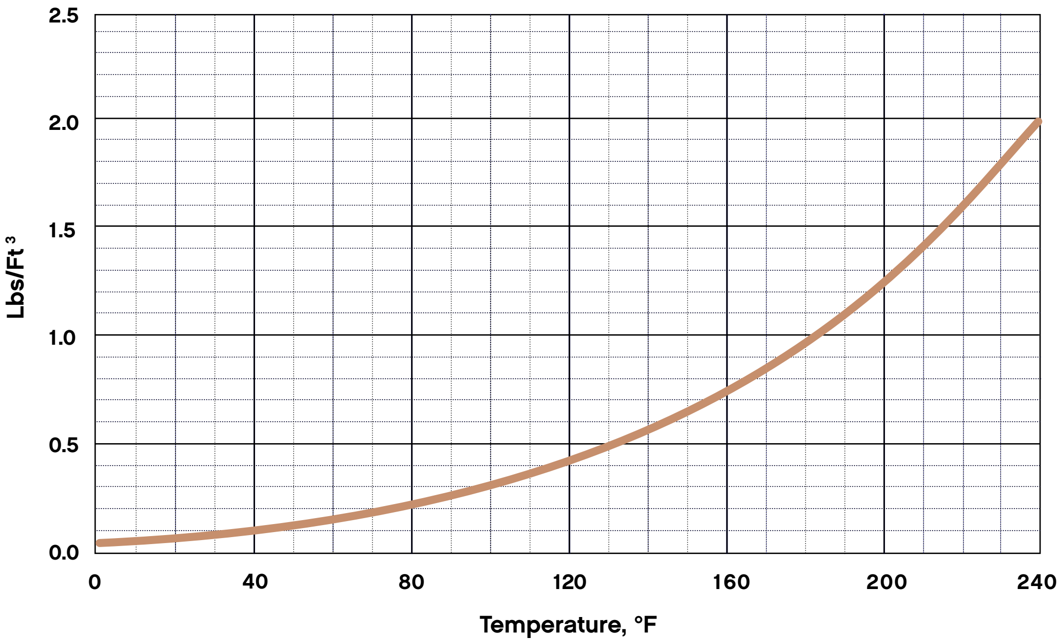


Figure 13 Ethylene Oxide Coefficient of Cubic Expansion

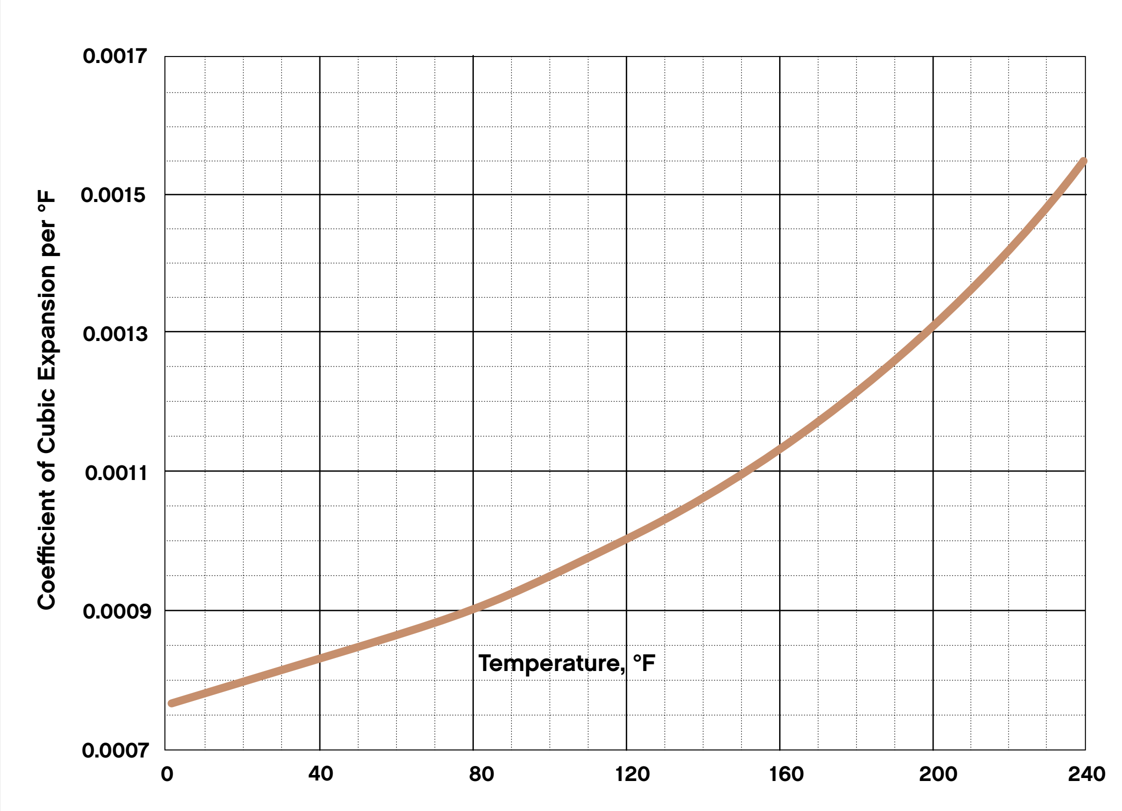


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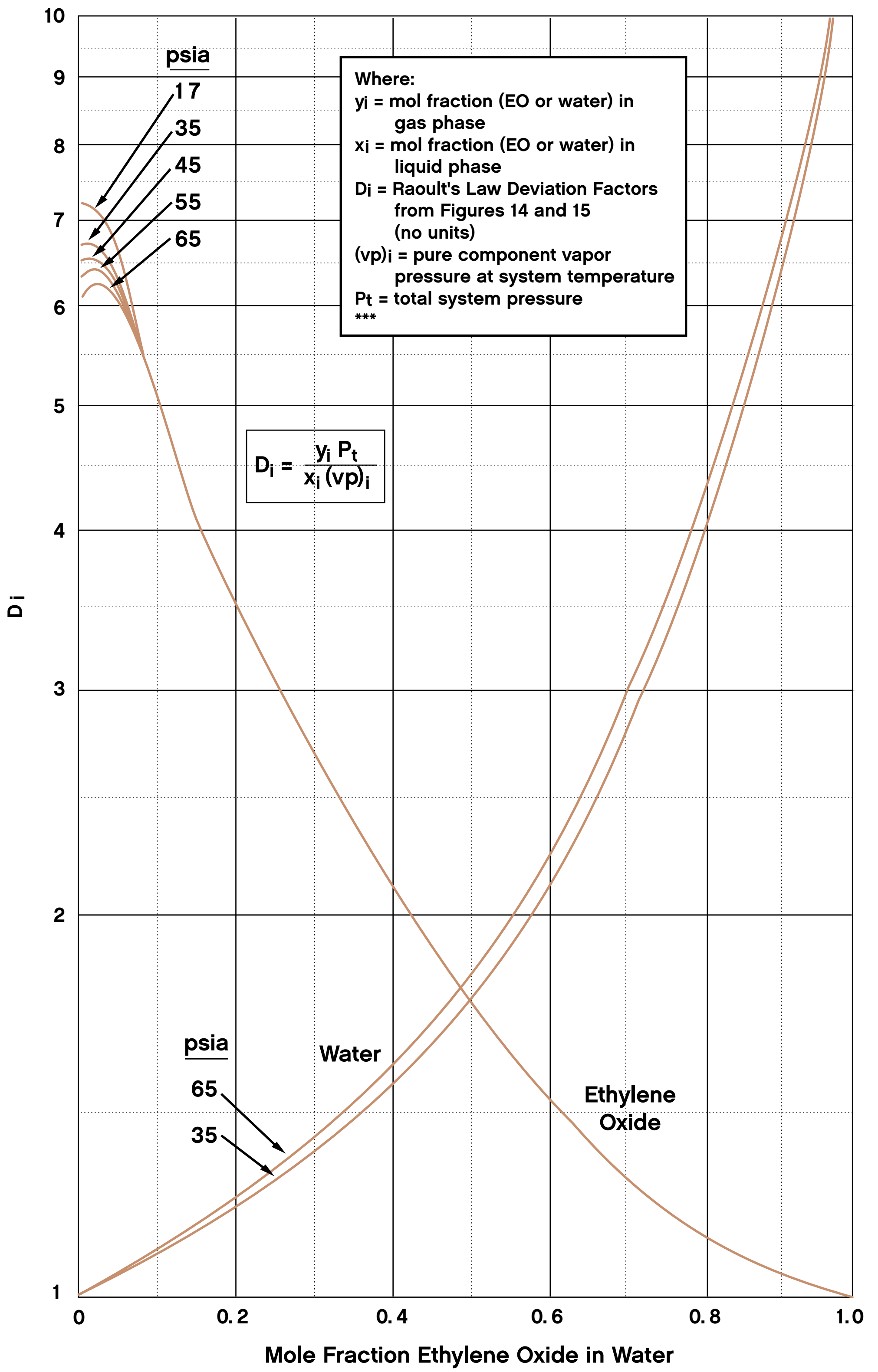
Figure 14 Raoult's Law Deviation Factors for Ethylene Oxide/Water Mixtures

Terminal Regions are Expanded in the Next Figure

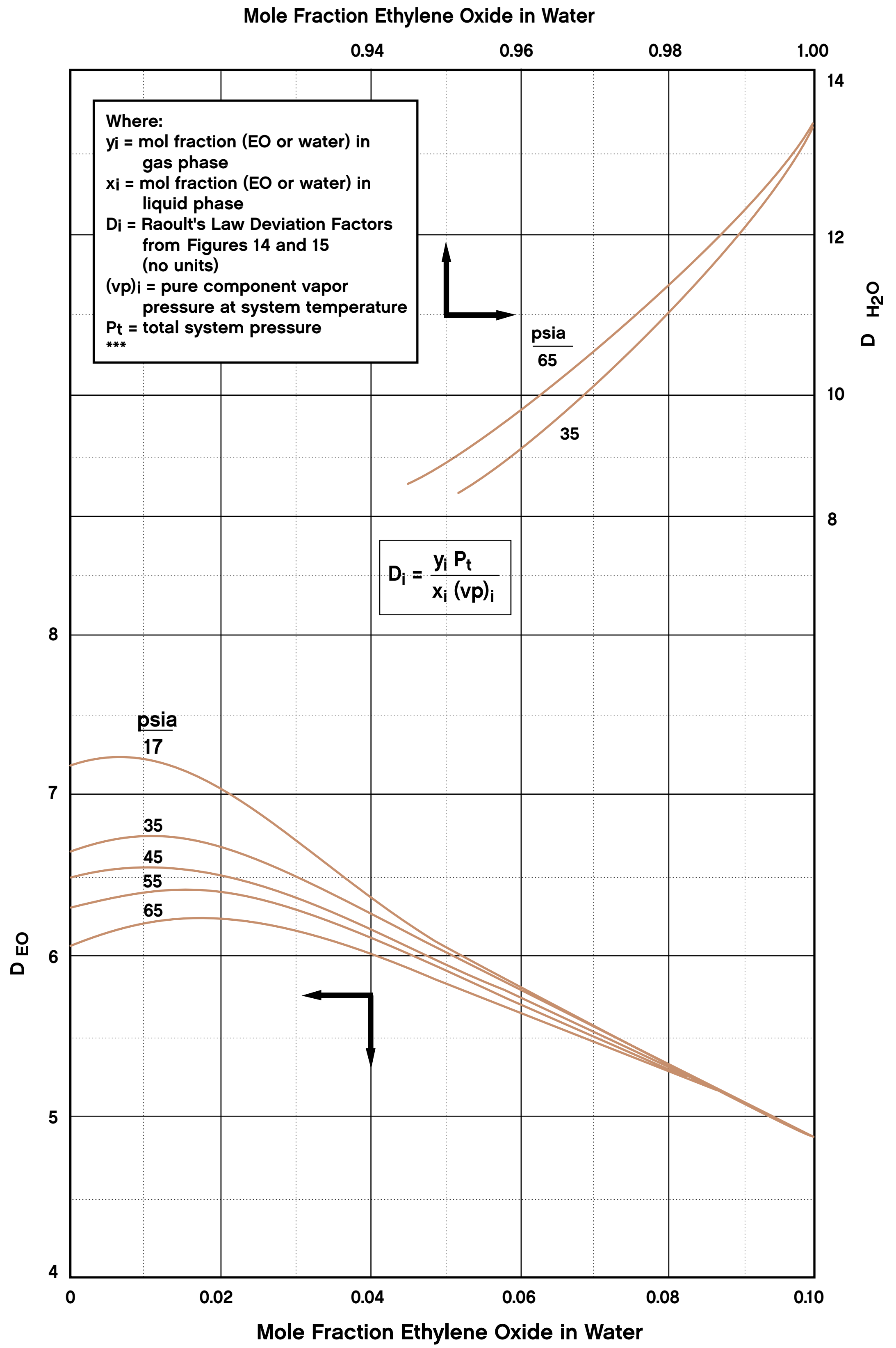


Where:
y_i = mol fraction (EO or water) in gas phase
x_i = mol fraction (EO or water) in liquid phase
D_i = Raoult's Law Deviation Factors from Figures 14 and 15 (no units)
$(vp)_i$ = pure component vapor pressure at system temperature
P_t = total system pressure
***

$$D_i = \frac{y_i P_t}{x_i (vp)_i}$$

*** Any pressure units can be used, so long as the unites for vapor pressure and total pressure are the same.

Figure 15 Raoult's Law Deviation Factors for Ethylene Oxide/Water Mixtures



Where:

y_i = mol fraction (EO or water) in gas phase

x_i = mol fraction (EO or water) in liquid phase

D_i = Raoult's Law Deviation Factors from Figures 14 and 15 (no units)

$(vp)_i$ = pure component vapor pressure at system temperature

P_t = total system pressure

***

$$D_i = \frac{y_i P_t}{x_i (vp)_i}$$

*** Any pressure units can be used, so long as the unites for vapor pressure and total pressure are the same.

Figure 16 Flammability Data on EO-Air Mixtures at Subatmospheric Pressures

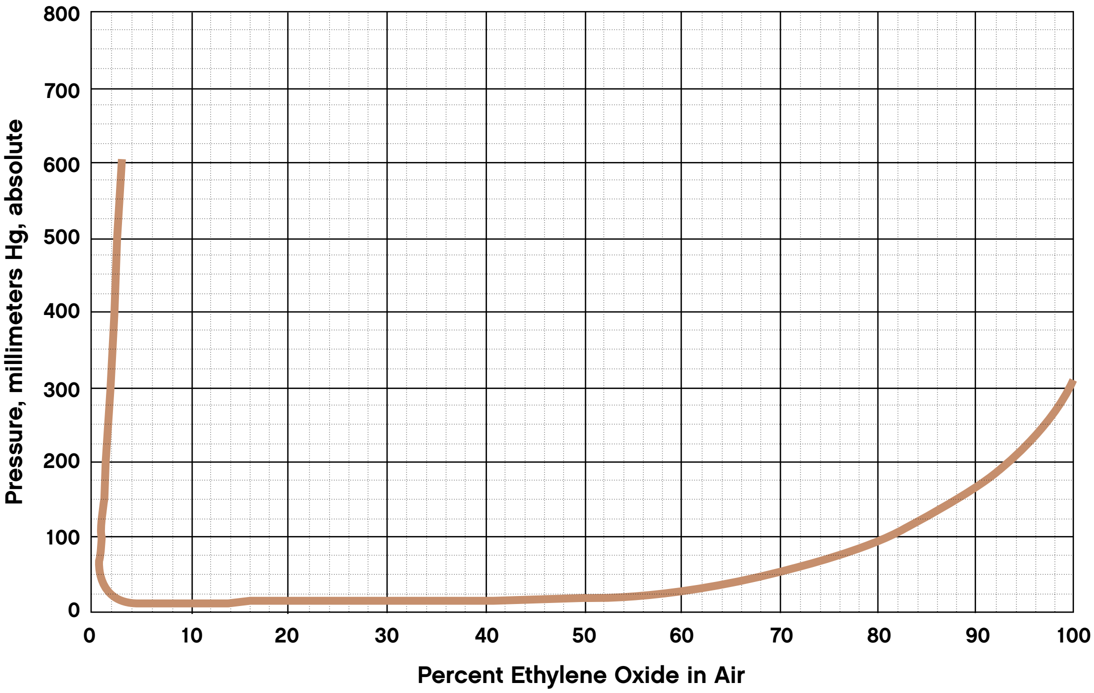


Figure 17 Vapor/Liquid Equilibria of Ethylene Oxide/Water Systems

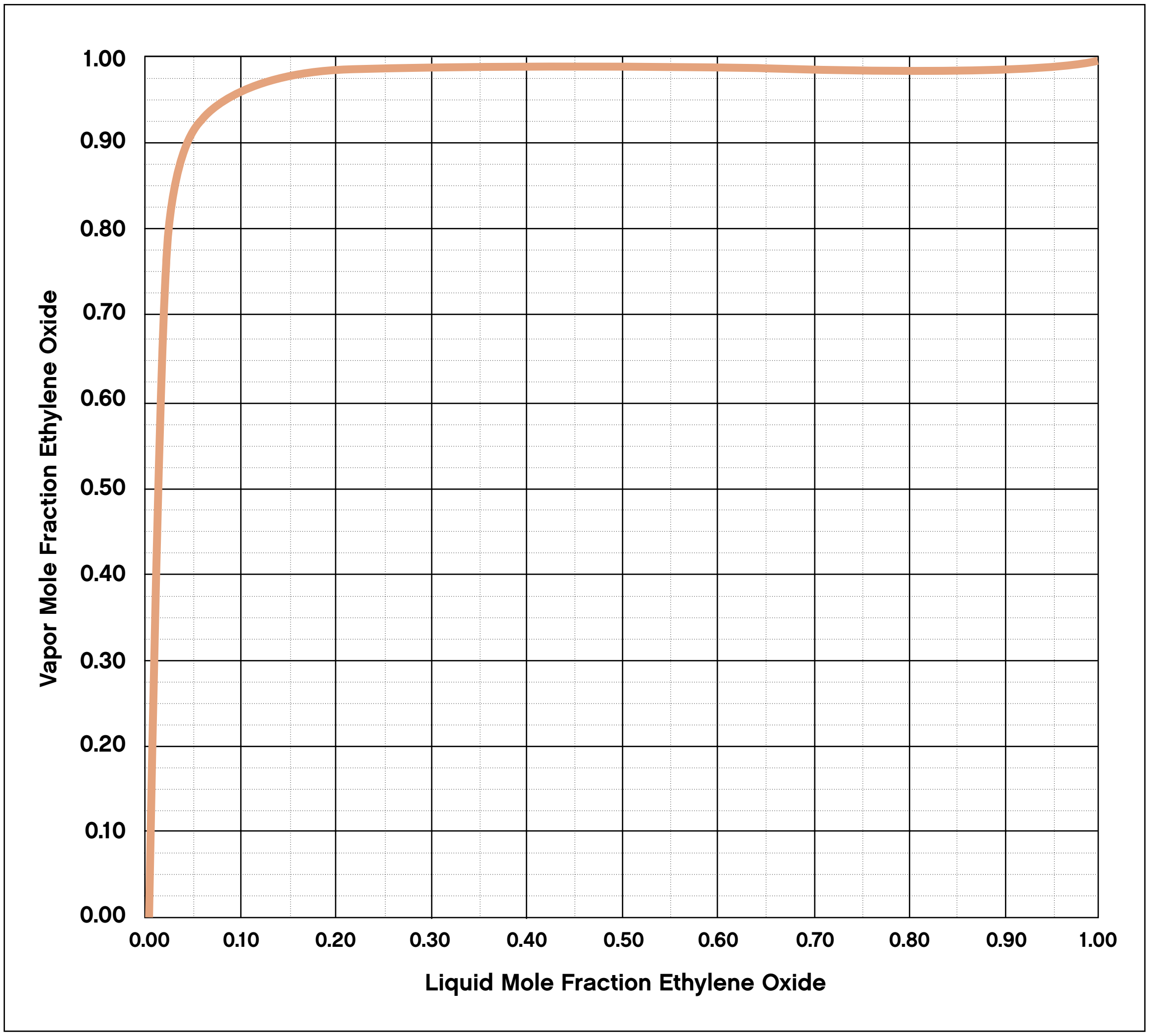


Figure 18 Density vs. Composition of Ethylene Oxide/Water Systems

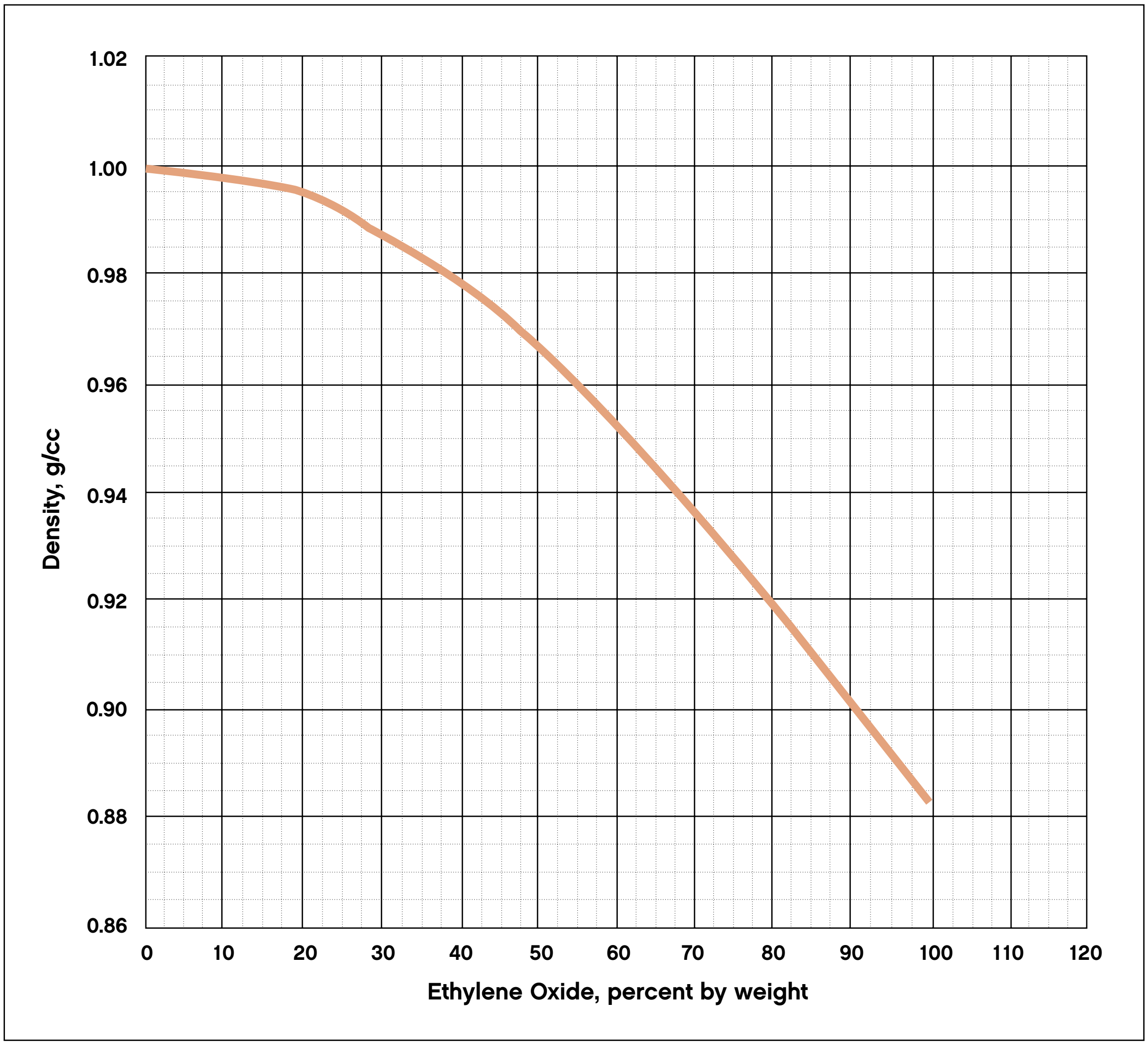


Figure 19 Boiling points of aqueous EO concentrations

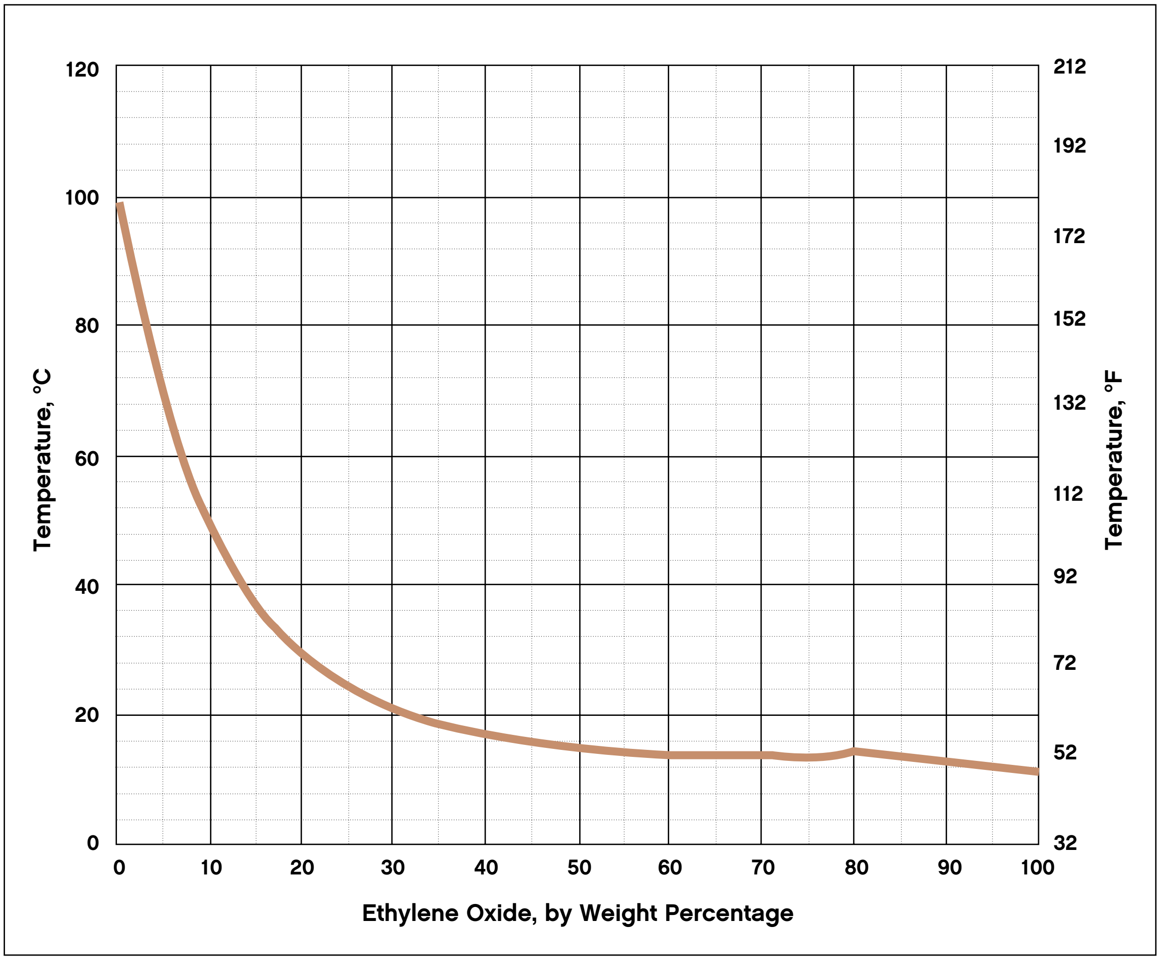


Figure 20 Decomposition Data

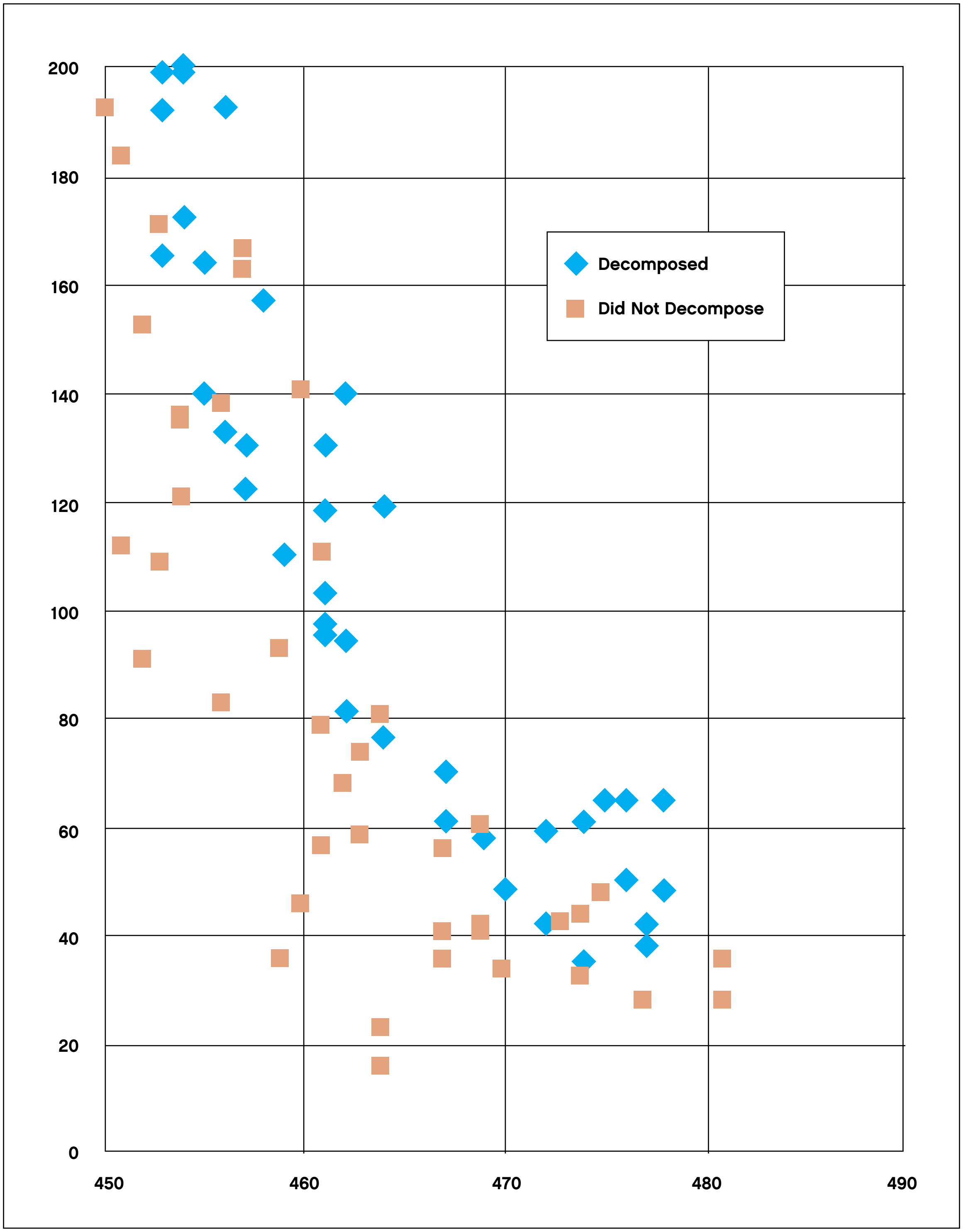


Figure 21 Vapor Compressibility vs. Pressure as a Function of Temperature

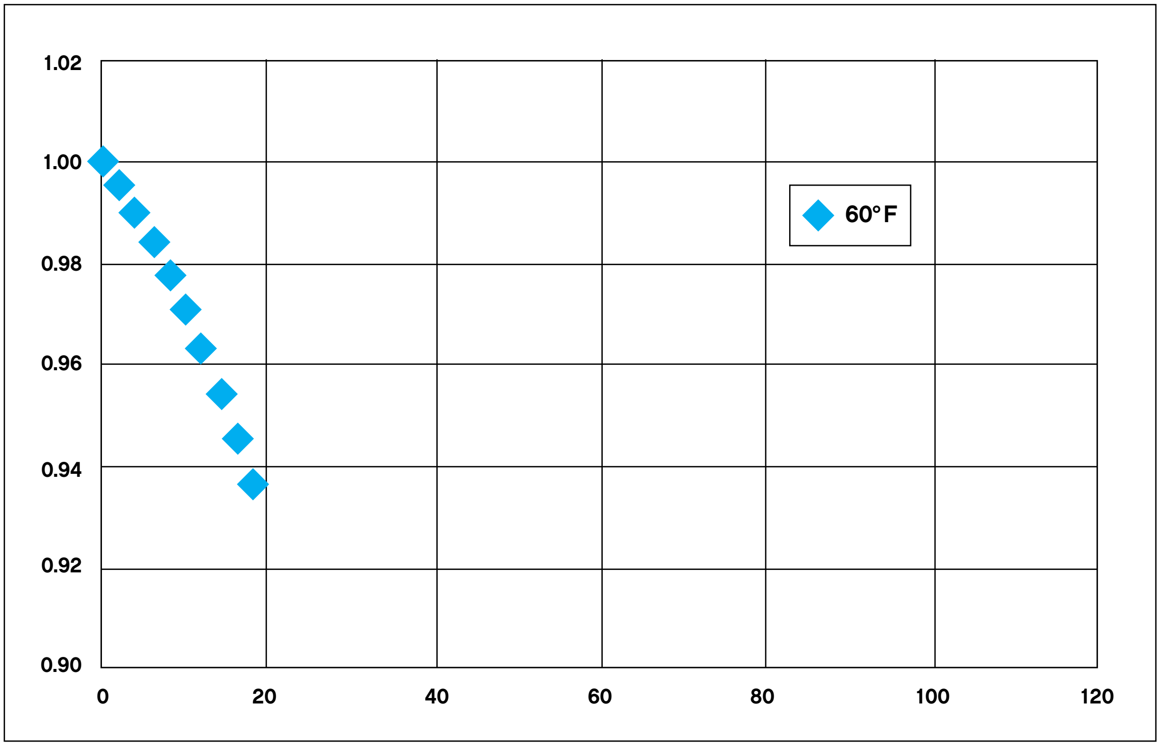


Table A1 Physical Property Equations

EQUATION COEFFICIENTS (ALL PROPERTIES IN SI UNITS)					
PROPERTY	UNITS	A	B	C	D
Solid Density	KgMOL/M^3	2.75E+01			
Liquid Density	KgMOL/M^3	1.8360E+00	2.6024E-01	4.6915E+02	2.6960E-01
Coeff of Expansion	per°K		2.6024E-01	4.6915E+02	2.6960E-01
Vapor Density	KgMOL/M^3	3.3904E+00	-5.0556E-02	2.9019E-04	-7.6743E-07
Vapor Pressure	Pa	9.1944E+01	-5.2934E+03	-1.1682E+01	1.4902E-02
Heat of Vaporization	J/KgMOL	3.6652E+07	3.7878E-01		
Solid Heat Capacity	J/KgMOL*°K	-2.1143E+04	1.4903E+03	-1.1881E+01	3.8745E-02
Liquid Heat Capacity	J/KgMOL*°K	1.4471E+05	-7.5887E+02	2.8261E+00	-3.0640E-03
Ideal Gas Heat Capacity	J/KgMOL*°K	3.3460E+04	1.2116E+05	1.6084E+03	8.2410E+04
Second Virial Coefficient	M^3 KgMOL	6.0016E-02	-5.2057E+01	-1.8056E+07	6.9368E+19
Liquid Viscosity	Kg/M*S	-8.5210E+00	6.3502E+02	-3.3140E-01	
Vapor Viscosity	Kg/M*S	2.9540E-06	4.7120E-01	7.874E0+02	-2.3580E+04
Liquid Thermal Conductivity	W/M*°K	2.6957E-01	-3.9840E-04		
Vapor Thermal Conductivity	W/M*°K	-3.7880E+04	1.1150E+00	-5.6410E+03	
Surface Tension	N/M	7.4730E-02	1.1410E+00		

*Note: The symbol * denotes multiplication. The symbol ^ denotes exponentiation.*
T is temperature, deg Kelvin. Tr is reduced temperature, T/T critical

Table A2 Conversion Factors

To Convert From	To	Multiply By	Notes
KgMOL/M^3	Lb/Gal	0.3676	1
Pascals	Lb$_f$/sq in	.445E-04	
J/KgMOL	BTU/Lb	9.785E-06	1
J/KgMOL*°K	BTU/Lb*°F	5.422E-06	1
KgM*S	Centipoise	1E+03	
W/M*°K	BTU/Ft*Hr*°F	0.578	
N/M	Lb$_f$/ft	6.852E-02	

Notes: 1. Only valid for Ethylene Oxide

E	USABLE RANGE		EQUATIONS
	MIN°K	MAX°K	
		161	Y = A + (B*T) +(C*T^2) + (D*T^3) + (E*T^4)
	161	469	Y = A/(B^(1+(1-T/C)^D))
	161	469	Y= (-D/C)*LN(B)*((1-T/C)^ (D-1))
7.9840E-10	233	383	Y= A + (B*T) + (C*T^2) + (D*T^3) + (E*T^4)
1.0000E+00	161	469	Y = exp (A + (B/T) +(C*lnT) + (D*T^E))
	161	469	Y = A*((1-Tr)^(B + (C*Tr) + (D*Tr^2) + (E*Tr^3)))
	25	161	Y= A + (B*T) + (C*T^2) + (D*T^3) + (E*T^4)
	161	284	Y= A + (B*T) + (C*T^2) + (D*T^3) + (E*T^4)
7.3730E+02	50	1500	Y = A + B*((C/T)/SINH (C/T)) ^2 + D*((E/T)/COSH(E/T))^2
-1.7212E+00	235	1500	Y = A +(B/T) + (C/T^3) +(D/T^8) +(E/T^9)
	161	284	Y = exp (A + (B/T) +(C*lnT) + (D*T^E))
	161	1000	Y = (A*T^B) / (1 + (C/T) + (D/T^2))
	161	284	Y= A + (B*T) + (C*T^2) + (D*T^3) + (E*T^4)
	273	1000	Y = (A*T^B) / (1 + (C/T) + (D/T^2))
	161	469	Y = A*((1-Tr)^(B + (C*Tr) + (D*Tr^2) + (E*Tr^3)))

Table A3 Henry's Law Constants (Atm/mole fraction)

T (°C)	Nitrogen	Argon	Methane	Ethane
32	2800	1671	613	84.3
77	2180	1420	614	109
122	1820	1270	595	129

Henry's Law Constants can be used with the following equation to determine solubility of these gases:

$$X_i = \frac{Y_i P_t}{H_i}$$

Table A4 Henry's Law Constants (MPa/mole fraction)

T (°C)	Nitrogen	Argon	Methane	Ethane
0	284	169	62.1	8.5
25	221	144	62.2	11.0
50	184	129	60.3	13.1

Where:

Xi = mol fraction of gas (N2, Ar, Methane, or Ethane) in liquid EO

Yi = mol fraction of gas in vapor space above liquid EO

Pt = total pressure, Atm

Hi = Henry's Law Constants for gas, Atm

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Appendix B Laboratory Compatibility Testing of Elastomers with Ethylene Oxide

An EO producer tested several elastomers (O-Rings) to determine their compatibility with EO. The materials selected included those that are commonly used in the industry along with some that lab data has indicated are incompatible with EO. The test methods used by the producer and the results of the testing are summarized below. The results of the testing – a combination of physical property and mechanical property data - can be used to provide a screening mechanism to aid in the selection of materials or for materials to be investigated further. The data is not necessarily predictive of whether a particular material will be successful or fail in EO service.

Experimental Procedure

The ten O-rings studied are listed in Table B1. The materials were exposed to EO according to the NACE International Standard Test Method TM0196-96 – Chemical Resistance of Polymeric Materials by Periodic Evaluation. The method was followed as closely as possible with some minor modifications made due to the hazards in handling and storing EO. The detailed procedure is further described below.

Four samples of each of the materials tested were prepared in quadruplicates (16 samples total for each material). One sample served as a blank and was not exposed to EO. The other three samples for each material were submerged in liquid EO. The EO was contained in either Teflon-PFA autoclaves or reinforced glass autoclaves (the autoclaves were not expected to have any significant impact on the variables of interest). The first sample of each material was removed after 30 days, the second removed after 60 days, and the third removed after 90 days. The autoclaves were maintained at a constant temperature of 27°C using a temperature-controlled oil bath. The autoclaves were pressured to 480 kPa with nitrogen to ensure the vapor remained in the non-decomposable region.

Upon removal from the EO, the O-ring samples were allowed to degas for 30 minutes, then these samples were sealed in glass vials. This allowed residual EO on the surface to evaporate, thus minimizing the exposure risks of those handling the samples. However, it was not sufficient time for the majority of the EO that had diffused into the polymer matrix of the materials to desorb. Physical and mechanical tests were conducted on the same day the samples were removed from the EO; therefore, the measurements should provide an accurate representation of the effects of EO submersion.

Physical properties were obtained by making accurate measurements of the weight and density of the samples. Density measurements were made using the water displacement method according to ASTM D792 - Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement. Dividing the weight by the density provided the volume of each sample.

Table B1 O-Rings Selected for Compatibility Testing

O-Ring	Description
Chemraz®[1] 505	Perfluoroelastomer
Kalrez®[2] 1050 LF	Perfluoroelastomer
Kalrez®[2] 2035	Perfluoroelastomer
Kalrez®[2] 6375	Perfluoroelastomer
Parker E515-80 EPR	Ethylene-propylene copolymer
Parker E962-90 EPDM	Ethylene-propylene-butadiene terpolymer
Parker E740-75 EPR	Ethylene-propylene copolymer
Viton®[2]F (V1163-75 FKM75A)	Partial perfluoroelastomer
Nitrile (N304-75 LT Nitrile 75)	Acrylonitrile-butadiene copolymer
Butyl Rubber (Bu-70)	Isobutylene polymer

1. Registered U.S. Trademark of Green Tweed and Company
2. Registered U.S. Trademark of DuPont Dow Elastomers LLC

Figure B1 Weight Change of O-rings Exposed to EO at 27°C

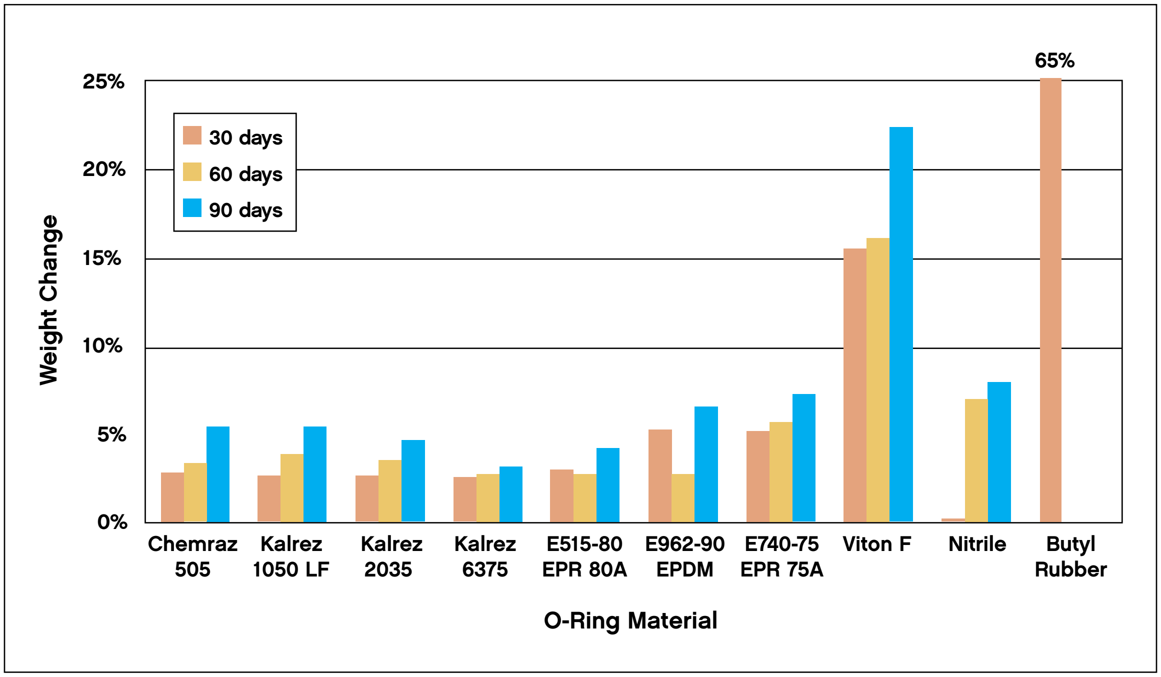
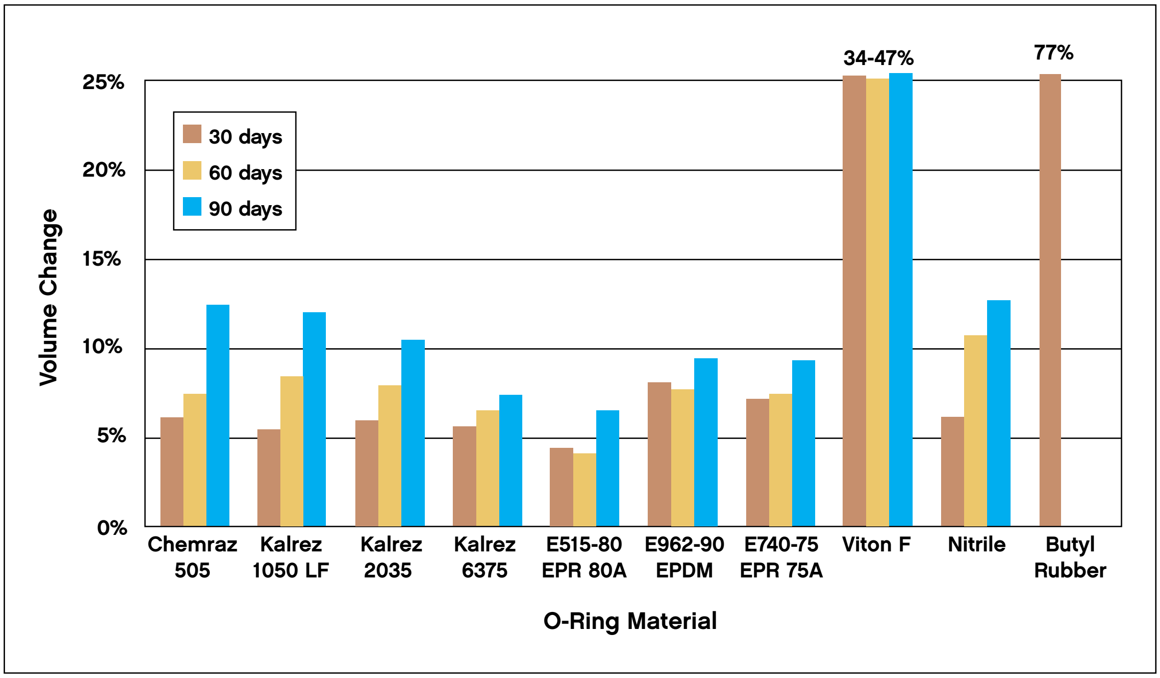


Figure B2 Volume Change of O-rings Exposed to EO at 27°C



Mechanical properties were obtained using an Instron mechanical testing apparatus. Properties of the O-rings were obtained as outlined in ASTM D638 - Standard Test Method for Tensile Properties of Plastics. The O-rings were not cut for analysis according to ASTM D412 - Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers: Tension. Therefore, the modulus of the o-ring samples could not be obtained. For these experiments, the O-rings were tested with no additional modifications (all O-rings were size 214).

Tensile properties are basic material properties that can be used to characterize changes in the mechanical property of a material. Comparison of a material's tensile properties before and after exposure to EO is expected to provide an indication of the ability of that material to maintain its mechanical properties. Therefore, this measurement provides a relatively quick and simple means to characterize samples before and after EO exposure.

Results and Discussion

The results of the physical measurements of the o-rings are shown in Tables B2 and B3. These compare the percent weight gain and percent volume gain for each of the O-rings after periods of 30, 60, and 90 days. For the samples that are off scale in Tables B2 and B3 (butyl rubber for weight change and viton F and butyl rubber for volume change), the actual values are listed above the bars in the chart. Also, only the results of the 30-day sample are shown for butyl rubber. After 30 days, the sample was swollen and degraded to the point that it was not necessary to perform the measurements for the 60 day and 90 day samples.

It is important to note that the EO absorption of the O-rings is a time-dependent behavior and varies with the material. For example, the nitrile O-ring exhibits decidedly less weight gain and volume swell after 30 days than the Parker E962-90 EPDM O-ring. However, after 90 days of exposure, the opposite is true, with Parker E962-90 EPDM O-ring exhibiting fewer changes in physical properties than the nitrile O-ring. Therefore, the expected duration that an O-ring will be in service is of paramount importance when selecting a suitable O-ring for a given application.

The mechanical properties of the O-rings are shown in Tables B4 and B5. Ultimate strength, or tensile strength (Table B4), is the measured stress of the material at its breaking point while ultimate strain (Table B5) is the maximum deformation of the material just prior to the breaking point. Most of the O-rings showed significant decreases in tensile strength upon exposure to EO compared to the unexposed, control samples. By comparison, ultimate strain measurements revealed much smaller percentage changes between the exposed and unexposed samples.

Figure B3 Tensile Strength of O-rings Exposed to EO at 27°C
(control samples were not exposed to EO)

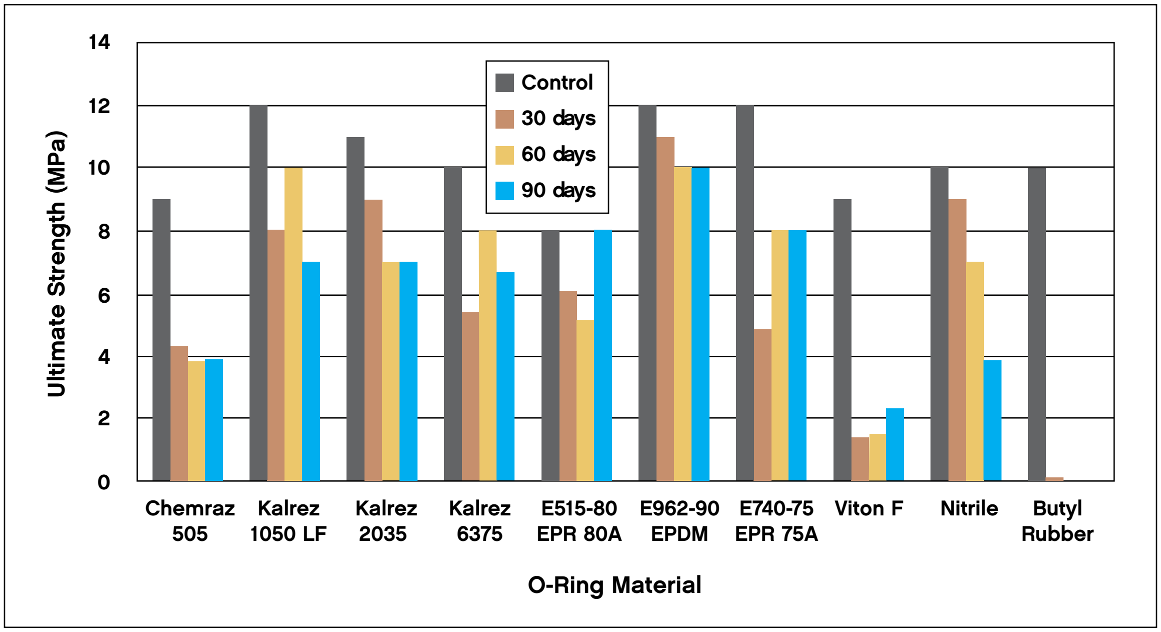
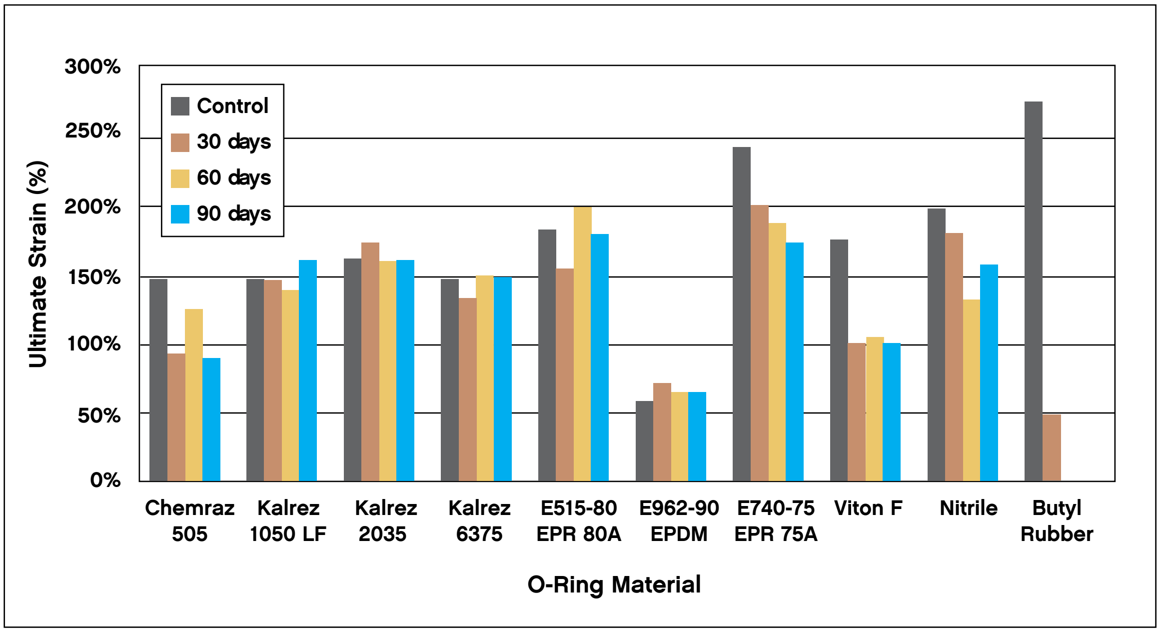


Figure B4 Maximum Deformation of O-rings Exposed to EO at 27°C
(control samples were not exposed to EO)



Appendix C Railcar Repressurization

This Appendix C contains additional discussion on considerations for pressurizing EO Railcars supplementing the primary discussion in Chapter 9.

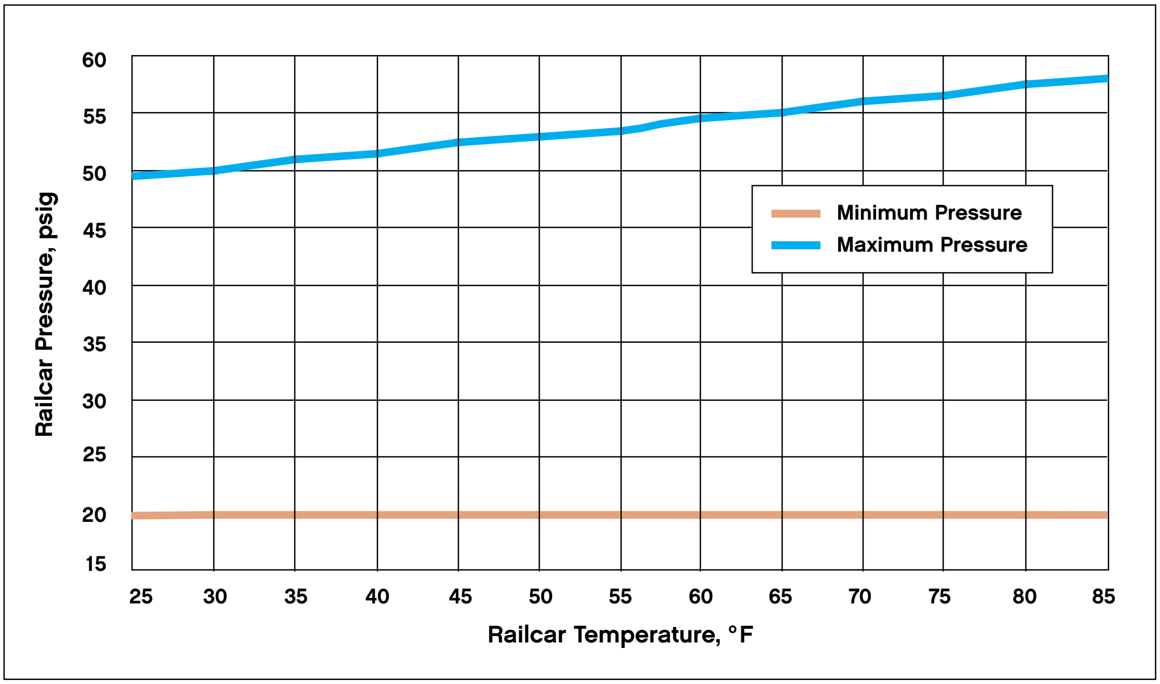
Follow federal regulatory requirements and criteria EO supplier guidelines for pressurizing railcars. Chapter 9 of this Manual and this supplemental discussion offer additional considerations for pressurization.

The guidelines discussed here are intended to maintain an inert atmosphere within the railcar up to a temperature of 105°F (DOT requirement), while maintaining the railcar pressure below the setpoint of the pressure safety valve.

Note that the use of Figure 6.16 is inappropriate for pressurizing railcars in EO service as the temperature in the railcar changes in transit. That particular Figure applies to EO storage facilities where either storage temperature and/or pressure can be continuously monitored and controlled to maintain the vapor space in the inert, non-decomposable region.

- Railcars utilized for the transportation of bulk quantities of EO must be pressurized with an inert gas to maintain the vapor contents in a safe, non-combustible, non-decomposable state up to a temperature of 105° F (41°C). This is a requirement specified by the US Department of Transportation as found in 49 CFR, Chapter 1, Part 173.323(f). To provide an inert vapor space in an EO railcar, either (a) pure nitrogen or (b) storage tank vapors composed primarily of nitrogen (from an unloading practice typically referred to as vapor balancing) are most often used.
- The requirement for maintaining an inert, non-combustible, non-decomposable vapor space applies to both “full” and “unloaded” EO railcars. An unloaded railcar contains residual amounts of EO liquid that cannot be completely discharged into a receiving storage tank or vessel. Consequently, a potentially hazardous condition could be created if the railcar vapor space is not properly inerted.
- Railcars used for the transportation of bulk quantities of EO are designed to leave minimal volumes of residual liquid (e.g., < 50 gallons) after the cargo is discharged. This assumes many factors, such as (a) the railcar internals are in good repair; (b) the rail siding is level, thereby not allowing an accumulation of liquid (“ponding”) at either end of the railcar; and (c) the cargo is unloaded to the maximum extent possible (e.g., not terminating the discharge of EO from the railcar before the unloading pump loses suction, or before nitrogen begins to blow through the liquid unloading line). The railcar pressurization information provided in Chapter 9 and this Appendix C is intended only for those situations where no more than 50 gallons of liquid EO remain in the railcar following unloading.
- The gas selected to provide an inert atmosphere within the vapor space of the railcar must not be reactive with EO, or contain any contaminants that might be reactive with EO. The availability and inertness of nitrogen mean that it is frequently used for pressurizing railcars to provide a non-combustible, non-decomposable vapor space. Nitrogen can be used as (a) pure gas, or (b) the major component of displaced vapors from an EO storage tank. Contact your EO supplier if a gas other than nitrogen is to be used to inert an EO railcar.
- While sufficient pressure must be applied to render the vapor space inert up to 105°F , applying an excessive level of pressure could result in the railcar safety valve relieving at temperatures below 105°F, releasing EO vapors into the environment and depleting the inventory of nitrogen in the railcar. The temperature and pressure of a railcar are not constant and are influenced by many factors such as sun exposure and ambient air temperature. As a railcar increases in temperature, additional EO from any remaining liquid heel will evaporate, increasing both the concentration of EO in the vapor space and the pressure within the railcar. The ranges of pressures outlined in Chapter 9 have been established to provide for:
  - — an inert, non-combustible, non-decomposable vapor space up to 105°F, and
  - — remaining at or below the 75 psig safety valve set pressure at 105°F.

Figure C1 Unloaded Railcar Repressuring — Nitrogen — Less than 50 Gallon EO Heel



Nitrogen Padding

Pure nitrogen is frequently used both to (a) pressure out liquid EO from railcars into storage vessels, and (b) pressurize the unloaded railcar for the return trip to the EO supplier.

The composition of the railcar vapor space, and accompanying temperature and pressure, determine whether the vapor space is inert and non-decomposable. The composition of the vapor space is influenced by the volume of the EO heel remaining in the railcar, and the nitrogen pressure applied to the railcar after unloading. Generally speaking, the larger the quantity of liquid EO heel, the greater the quantity of EO that can evaporate within the railcar. If an insufficient volume of nitrogen is injected into the railcar (using pressure as an indirect measure of nitrogen volume), the vapor space may not remain inert as additional EO evaporates from the remaining liquid heel. Conversely, injecting too much nitrogen upon initial pressurization could lead to a later discharge from the pressure safety valve.

Although pure nitrogen may be injected into the railcar during or immediately after unloading, some EO will evaporate into the vapor space during the time interval required to discharge the contents of the railcar. As a consequence, immediately after the railcar is unloaded, repressured, and secured for return to the supplier, the vapor space will also contain some finite quantity of EO in addition to the nitrogen that was injected into the railcar. How much EO evaporates into the vapor space during the unloading process is dependent on both the length of time required to unload the railcar, and the temperature of the railcar.

- The minimum pressure levels illustrated in the section of Chapter 9 titled “Inerting the Unloaded Railcar for Return” accommodate the evaporation of EO into the nitrogen during the unloading and repressuring process. The Table provided assumes that at the completion of the unloading process, the partial pressure of the EO in the vapor space is no less than 21% of the vapor pressure of EO at the temperature of the railcar.
- The minimum repressure levels discussed within these guidelines are intended to account for:
  - (a) possible errors in the measured railcar temperatures and pressures, and
  - (b) uncertainties in the predicted physical and chemical characteristics of EO used to develop these guidelines

- The Tables set out in Chapter 9 (9.1, 9,2) are intended to guide the user to calculate minimum and maximum pressure levels for an unloaded railcar with an initial heel of less than 50 gallons of EO. Figure C1 is a graphical representation.

Vapor Balancing

This discussion assumes the EO tank from which the balancing vapors originate is padded with nitrogen. Contact your EO supplier if vapor balancing is utilized, and nitrogen is not used as the inerting gas for the EO storage vessel.

Unloading EO from railcars into storage facilities using vapor balancing is frequently practiced. EO that is unloaded and directed into a tank or receiving vessel displaces vapor from that storage vessel. This same vapor is then redirected back to the railcar.

Unlike the nitrogen vapors that result from pressuring unloaded EO railcars with pure nitrogen, the vapors displaced and originating from EO storage tanks are mixtures of nitrogen and EO. Higher EO storage tank temperatures will result in a higher percentage of EO and a lower quantity of nitrogen in the tank vapors. As a consequence, determining the appropriate level of pressurization for empty railcars when utilizing vapor balancing is a more complex process.

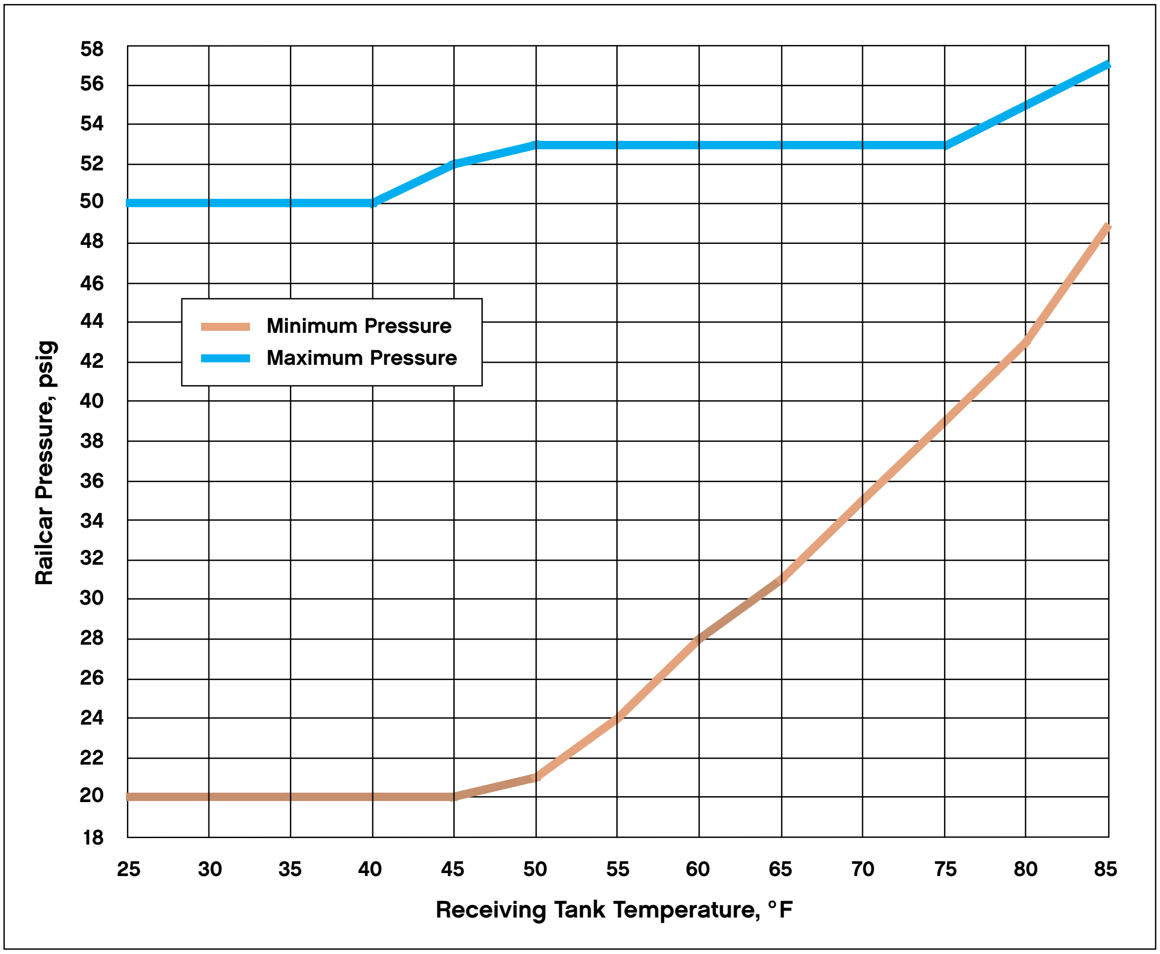
Depending on the temperature of the railcar, and the composition of the vapors displaced from the receiving storage tank into the railcar, some additional EO could evaporate into the vapor space during the unloading process. How much, if any, additional EO evaporates into the railcar vapor space is directly influenced by (a) the composition of the blanketing vapor displaced from storage tankage, (b) the temperature of the railcar, and (c) duration of time required to unload the railcar.

The minimum pressure levels illustrated in Chapter 9 are intended to accommodate the potential for additional EO to enter the vapor space of the railcar during the unloading and repressuring process. The illustrations assume that immediately after the railcar is unloaded, repressured, and secured for return to the supplier, the vapor space of the railcar has an EO content corresponding to either (a) the composition of the vapors balancing vapors displaced from the EO storage vessel, or (b) a composition corresponding to an EO partial pressure of no less than 21% of the vapor pressure of EO at the temperature of the railcar, whichever of the two represents the greater concentration of EO.

- The minimum repressure levels within the guidelines is intended to account for:
  - (a) Possible errors in the measured railcar/storage tank temperatures and pressures, and
  - (b) Uncertainties in the predicted physical and chemical characteristics of EO utilized in the development of these guidelines.

The illustrations in Chapter 9 set out examples of minimum and maximum repressure levels for an unloaded railcar when using vapor balancing. These illustrations are applicable only for circumstances where an initial EO heel exists of no greater than 50 gallons. The following Figure C2 is a graphical representation.

Figure C2 Unloaded Railcar Repressuring — Vapor Balancing — Less than 50 Gallon Heel



Appendix D References

2.0 Properties of Ethylene Oxide

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Appendix E Glossary of Selected Terms, Abbreviations and Organizations

A

AAEE	American Academy for Environmental Engineers. **www.aaee.net**
AAR	Association of American Railroads. **www.aar.org**
ABIH®	American Board of Industrial Hygiene®. **www.abih.org**
ACC	American Chemistry Council (Formerly the Chemical Manufacturers Association). **www.americanchemistry.com**
ACH	Air Changes per Hour (unit for quantifying air flow).
ACHMM	Academy of Certified Hazardous Materials Managers. **www.achmm.org**
ACGIH®	American Conference of Governmental Industrial Hygienists. **www.acgih.org**
ACS	American Chemical Society. **www.chemistry.org**
ADI	Acceptable Daily Intake
AEGL	Acute Exposure Guidleline Levels. **www.epa.gov/oppt/aegl**
AIChE®	American Institute of Chemical Engineers. **www.aiche.org**
AIHA	American Industrial Hygiene Association (issues EPRGs). **www.aiha.org**
ALARA	As Low As Reasonably Achievable
ALARP	As Low As Reasonably Practicable
ANSI	American National Standards Institute. **www.ansi.org**
APHA	American Public Health Association. **www.apha.org**
API	American Petroleum Institute. **www.api.org**
APIH	Association of Professional Industrial Hygienists. **www.apih.us**
AQS	Air Quality Standard

ASHI	American Safety and Health Institute. **www.ashinstitute.org**
ASME	American Society of Mechanical Engineers. **www.asme.org**
ASSE	The American Society of Safety Engineers. **www.asse.org**
ASTM	American Society for Testing & Materials International (a Standards Development Organization that issues, among other things, standards for test methods). **www.astm.org**
ATSDR	Agency for Toxic Substances and Disease Registry, part of the U.S. Department of Health and Human Services, is a publich health agency. **www.atsdr.cdc.gov**
B	
BACT	Best Available Control Technology
BADCT	Best Available Demonstrated Control Technology
BAT	Best Available Technology
BCSP	Board of Certified Safety Professionals. **www.bcsp.org**
BCT	Best Conventional Technology
BDAT	Best Demonstrated Available Technology
BEIs®	Biological Exposure Indices (ACGIH). **www.acgih.org/TLV**
BEJ	Best Engineering Judgment
BI	Business Interruption
BLEVE	Boiling Liquid Expanding Vapor Explosion
BMP	Best Management Practices
BOD	Biochemical Oxygen Demand. A measure of the oxygen required to oxidize any organic matter present in a water during a set period of time (usually 5 days).
Bonding	The connection of two or more conductive objects by means of a conductor (most commonly a wire or metal plate)
B.P.	Boiling Point
BPCS	Basic Process Control System
BTU	British Thermal Unit
C	
C	Consequence factor, related to magnitude of severity
C#	The number of carbon atoms present in a molecular composition.

CAA	U.S. Clean Air Act. **www.epa.gov/oar/caa/contents.html**
CAS®	Chemical Abstracts Service. A division of the American Chemical Society, CAS products an index of scientific literature in the chemical field (Chemical Abstracts) and maintains the CAS Registry℠, a database of chemical substances. **www.cas.org/**
CASRN	CAS RegistrySM Numbers are unique, numerical identifiers for chemical substances (chemical compounds, polymers, mixtures, alloys, and biological sequences). CAS numbers are assiged by the Chemical Abstracts Service of the American Chemical Society. The CAS RegistrySM Number for ethylene oxide is 75-21-8. **www.cas.org/EO/regsys.html#q2**
CANUTEC	Canadian Transport Emergency Centre. **www.tc.gc.ca/canutec/**
CCF	Common Cause Failure
CCOHS	Canadian Centre for Occupational Health and Safety. **www.ccohs.ca**
CCPS	Center for Chemical Process Safety, a part of AIChE that addresses process safety issues across the chemical, petroleum, and pharmaceutical industries. **www.aiche.org/CCPS/About/index.aspx**
CDC	Centers for Disease Control & Prevention, part of the U.S. Department of Health and Human Services. **www.cdc.gov**
CEI	Chemical Exposure Index
CEPA	Canadian Environmental Protection Act. **www.ec.gc.ca/CEPARegistry/the_act**
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act. **www.epa.gov/superfund/action/law/cercla.htm**
CFR	U.S. Code of Federal Regulations. **www.access.gpo.gov/nara/cfr/cfr-table-search.html**
CGA	Compressed Gas Association. **www.cganet.com**
CHEMNET®	Chemical Industry Mutual Aid Network. **www.chemtrec.org/Chemtrec/ProductsAndServices/CHEMNET**
CHEMTREC®	Chemical Transportation Emergency Center (part of the American Chemistry Council). **www.chemtrec.org**
CMA	Chemical Manufacturers Association (now the American Chemistry Council)
CNS	Central Nervous System
COD	Chemical Oxygen Demand. The amount of oxygen needed to oxidize any organic matter in water using harsh chemical conditions.
Confined Space	An area that by design has limited openings for entry and exit. A confined space has unfavorable natural ventilation and is not intended for continuous worker occupancy.

CPC	Chemical Protective Clothing
CPQRA	Chemical Process Quantitative Risk Assessment
CRBOH	Canadian Registration Board of Occupational Hygienists. **www.crboh.ca**
CSB	U.S. Chemical Safety and Hazard Investigation Board. **www.chemsafety.gov**
CSSB	Canadian Society of Safety Engineering. **www.csse.org**
CW	Cooling Water

D

D	Number of times a component or system is challenged (hr-1 or year-1)
DCS	Distributed Control System
DHS	U.S. Department of Homeland Security. **www.dhs.gov/dhspublic**
DIERS	The Design Institute for Emergency Relief Systems, a part of AIChE, develops methods for emergency relief system design focusing on handling runaway reactions. **www.aiche.org/TechnicalSocieties/DIERS/index.aspx**
DIPPR®	The Design Institute for Physical Properties, a part of AIChE, develops thermophysical and environmental property data. **www.aiche.org/TechnicalSocieties/DIPPR/index.aspx**
DO	Dissolved Oxygen. The amount of molecular oxygen dissolved in water.
DOE	U.S. Department of Energy. **www.doe.gov**
DOT	U.S. Department of Transportation. **www.dot.gov**
DSL	Domestic Substances List (Canada). **www.ec.gc.ca/CEPARegistry/subs_list/Domestic.cfm**

E

EBV	Emergency Block Valve
EC	European Community
EG	Ethylene Glycol
EO	Ethylene Oxide
EO/EGs Panel	Ethylene Oxide/Ethylene Glycols Panel of the American Chemistry Council.
EOSTG	Ethylene Oxide Safety Task Group of the American Chemistry Council
EPA	U.S. Environmental Protection Agency. **www.epa.gov**
EPCRA	Emergency Planning and Community Right-to-Know Act. **http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/epcraOverview.htm**

ERPG	Emergency Response Planning Guidelines (issued by the AIHA). **www.aiha.org/1documents/Committees/ERP-erpglevels.pdf**
ERG	Emergency Response Guidebook. This book was developed jointly by the U.S., Canada, and Mexico to assist first responders to hazmat transportation incidents. **www.chemtrec.org/Chemtrec/Resources/ERG.htm**
ESD	Electrostatic Discharge
ES&H	Environment, Safety & Health
EtO	Ethylene Oxide
EU	European Union. **www.eurunion.org**
EuReData	European Reliability Data (a series of conferences)
EVC	Equilibrium Vapor Concentration

F

F	Failure rate (hr-1 or year-1)
ƒ	Frequency (hr-1 or year-1)
FCE	Final Control Element
F&EI	Fire and Explosion Index
Flashpoint	The minimum temperature at which a liquid gives off vapor in sufficient concentrations to form an ignitable mixture with air near the surface of a liquid.
FMEA	Failure Mode and Effects Analysis
F/N	Fatality Frequency versus Cumulative Number
FR	U.S. Federal Register. **www.gpoaccess.gov/fr/index.html**
FTA	Fault Tree Analysis

G

GC	Gas Chromatography
GDP	Gross Domestic Product. In the U.S., this is calculated by the Bureau of Economic Analysis by the U.S. Department of Commerce. **www.bea.gov**
GHS	Globally Harmonized System
GLP	Good Laboratory Practices. GLPs are set out by applicable regulation.
Grounding	The connection of one or more conductive objects to the ground: a specific form of bonding. Grounding is also referred to as “earthing.”

H

HAP	Hazardous Air Pollutant. **www.epa.gov/ttn/atw/pollsour.html**
HAZCOM	Hazard Communication (Standard)

HAZMAT	Hazardous Materials
HAZOP	Hazard and Operability Analysis
HAZWOPER	Hazardous Waste Operations and Emergency Response Standard. Hazwoper is a set of OSHA requirements. **www.osha.gov/html/faq-hazwoper.html**
HCS	Hazard Communication Standard, an OSHA requirement. **www.osha.gov/SLTC/hazardcommunications/standards.html**
HE	Hazard Evaluation
HHC	Highly Hazardous Chemical
HMIRS	Hazardous Materials Information Resource System, a U.S. DOD automated system functioning as the repository for MSDS for U.S. agencies and the military. **www.dlis.dla.mil/hmirs/default.asp**
HMIS®	The Hazardous Materials Identification System was developed by the National Paint & Coatings Association to help employers comply with OSHA's Hazard Communication Standard. **www.paint.org/hmis/index.cfm**
HON	Hazardous Organic NESHAP. **www.epa.gov/ttn/atw/hon/honpg.html**
HRA	Human Reliability Analysis
HSDB	Hazardous Substances Data Bank, a database of toxicology data managed by the National Library of Medicine. **http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB**

I

IARC	International Agency for Research on Cancer, a part of the World Health Organization. **www.iarc.fr**
ICSC	International Chemical Safety Cards, issued through the International Programme on Chemical Safety. **www.cdc.gov/niosh/ipcs/ipcscard.html**
IDLH	Immediately Dangerous to Life or Health as defined by NIOSH. **www.cdc.gov/niosh/idlh/intridl4.html**
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronic Engineers. **www.ieee.org**
IMDG	International Maritime Dangerous Goods (IMDG) Code, an international code addressing the transport of dangerous goods by sea. **www.imo.org/Safety/mainframe.asp?topic_id=158**
IMO	International Maritime Organization. **www.imo.org**
IOMC	Inter-Organization Programme for the Sound Management of Chemicals, a group that focuses on international coordination on chemical safety matters. **www.who.int/iomc/en**

IPCS	International Programme on Chemical Safety. Develops International Chemical Safety Cards. **www.who.int/ipcs/publications/icsc/en/**
IPCT	Industrial Process Cooling Towers.
IPL	Independent Protection Layer
IRIS	Integrated Risk Information System, EPA's database for human health effects from environmental exposures. **www.epa.gov/iris**
ISA	The Instrumentation, Systems and Automation Society (formerly, Instrument Society of America)
ISHM	Institute for Safety and Health Management. **www.ishm.org**
ISO	International Organization for Standardization. **www.iso.org/iso/en**
J	
JHA	Job Hazard Analysis
JSA	Job Safety Analysis
K	
L	
LAH	Level Alarm – High
LDAR	Leak Detection and Repair
LEL	Lower Explosive Limit
LFL	Lower Flammability Limit
LI	Level Indicator
LIC	Level Indicator – Control
LLDPE	Linear Low Density Polyethylene
LNG	Liquefied Natural Gas
LOPA	Layer of Protection Analysis
LOTO	Lock-Out Tag-Out
LPGs	Liquefied Petroleum Gases
LT	Level Transmitter
M	
MACT	Maximum Achievable Control Technology
MAWP	Maximum Allowable Working Pressure

MedlinePlus®	A service of the U.S. National Library of Medicine and NIH, MedlinePlus contains health information and articles from medical journals. **http://medlineplus.gov**
MeSH	Medical Subject Headings (browser service of the National Library of Medicine).
M&O	Management & Operating
MOC	Management of Change
MSDS	Material Safety Data Sheet, a requirement of the OSHA Hazard Communication Standard. **www.osha.gov/SLTC/hazardcommunications/index.html**

N

N2	Nitrogen
NCEA	National Center for Environmental Assessment of the U.S. Environmental Protection Agency. **http://cfpub.epa.gov/ncea.**
NDE	Nondestructive Evaluation
NDT	Nondestructive Testing
NEC®	National Electrical Code®, a publication of the National Fire Protection Association. **www.nfpa.org**
newton	Unit of force in the meter-kilogram-second system equal to the force required to impart an acceleration of one meter per second to a mass of one kilogram.
NFPA	National Fire Protection Association. **www.nfpa.org**
NGLs	Natural Gas Liquids
NIH	National Institutes of Health, part of the U.S. Department of Health and Human Services. **www.nih.gov**
NIOSH	National Institute for Occupational Safety and Health, part of the Centers for Disease Control & Prevention of the U.S. Department of Health and Human Services. **www.cdc.gov/niosh/homepage.html**
NLM	The U.S. National Library of Medicine of the National Institutes of Health. **www.nlm.nih.gov**
NMAM	NIOSH Manual of Analytical Methods. **www.cdc.gov/niosh/nmam**
NOEL	No Observed Effect Level
NOAEL	No Observed Adverse Effect Level
NPRI	National Pollutant Release Inventory
NSMS	National Safety Management Society. **www.nsms.us**

NSPE	National Society of Professional Engineers. **www.nspe.org**
NTP	National Toxicology Program
O	
OECD	Organisation for Economic Cooperation and Development. **www.who.int/iomc/participants/po/en/index2.html**
OEL	Occupational Exposure Limit
OES	Occupational Exposure Standard
OPPT	U.S. EPA's Office of Pollution Prevention and Toxics. **www.epa.gov/opptintr**
OREDA	The Offshore Reliability Date Project
ORD	Office of Research and Development, U.S. Environmental Protection Agency. **www.epa.gov/ord**
OSBL	Outside Battery Limits
OSHA	U.S. Occupational Safety and Health Administration. **www.osha.gov**
P	
P	Probability
Pfatality	Probability of Fatality
Pignition	Probablility of Ignition
Pperson present	Probability of Person Present
PEL	Permissible Exposure Limit, set by OSHA. **www.osha.gov/SLTC/pel**
P&ID	Piping and Instrumentation Diagram
PFA	Perfluoroalkoxy Polymer Resin is a polymer resin with properties similar to PTFE.
PFD	Probability of Failure on Demand
PIH	Poison Inhalation Hazard
PHA	Process Hazard Analysis
PHMSA	The Pipeline and Hazardous Materials Safety Administration, part of the U.S. DOT, is responsible for safe and secure movement of hazardous materials to industry and consumers by all transportation modes, including the nation's pipelines. **www.phmsa.dot.gov**
PI	Pressure Indicator
PL	Protection Layer
PM	Preventative Maintenance
PPE	Personal Protective Equipment

ppm	Parts Per Million
ppmv	Parts Per Million by Volume
ppmw	Parts Per Million by Weight
PrHA	Process Hazard Analysis
PSI	Process Safety Information
psia	Absolute pressure in Pounds per Square Inch
psig	Pounds per Square Inch Gauge
PSM	Process Safety Management
PSR	Pre-Startup Safety Review
PSV	Pressure Safety Valve (Relief Valve)
PTFE	Polytetrafluoroethylene, a thermoplastic fluropolymer, is a polymer of fluorinated ethylene. PTFE has the lowest coefficient of friction of any known solid material. Very non-reactive, this material is often used in containers and piping for reactive chemicals.
PubMed	PubMed, run by the National Library of Medicine, includes citations from MEDLINE and other life science journals for biomedical articles. **www.ncbi.nlm.nih.gov/entrez/query.fcgi?DB=pubmed**
Q	
QA	Quality Assurance
R	
R	Risk
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit, set by NIOSH. **www.cdc.gov/niosh**
RMP	Risk Management Plan
RQs	Reportable Quantities
RREL	Risk Reduction Engineering Laboratory
RV	Relief Valve
S	
SAR	Safety Analysis Report
SASS	Safety Assurance System Summary
SCBA	Self-Contained Breathing Apparatus
SCC	Standards Council of Canada. **www.ssc.ca**
SCE	Safety Critical Equipment

SCHC	Society for Chemical Hazard Communication. This organization promotes effective international hazard communication for chemicals. **www.schc.org/schcnewsite/home.php**
SHI	Substance Hazard Index
SIF	Safety Instrumented Function
SIL	Safety Integrity Level
SIS	Safety Instrumented System
SOCMA	Synthetic Organic Chemicals Manufacturing Association
SOP	Safe Operating Practice / Standard Operating Procedure
SOT	Society of Toxicology. **www.toxicology.org**
STEL	Short Term Exposure Limit (ACGIH)

T

T	Test Interval for the Component or System (hours or years)
TDI	Tolerable Daily Intake
TIH	Toxic Inhalation Hazard
TLV®	Threshold Limit Value (ACGIH). **www.acgih.org/TLV**
TLV-TWA	Threshold Limit Value, Time Weighted Average (ACGIH)
TOC	Total Organic Carbon
ToxFAQs™	ToxFAQs™ are summaries about hazardous substances developed by ATSDR's Division of Toxicology. **www.atsdr.cdc.gov/toxfaq.html**
TOXNET®	The Toxicology Data Network is a group of databases covering toxicology, hazardous chemicals, environmental health, and related topics. It is managed by the Toxicology and Environmental Health Information Program in the Division of Specialized Information Services of the National Library of Medicine. **http://toxnet.nlm.nih.gov**
TPQ	Threshold Planning Quantity
TQ	Threshold Quantity
TRI	Toxics Release Inventory. **www.epa.gov/tri**
TRS	Terminology Reference System. The US EPA's glossary of commonly used terms. **www.epa.gov/trs**
TSCA	Toxic Substances Control Act. **www.access.gpo.gov/uscode/title15/chapter53_.html**
TSD	Treatment, Storage, and Disposal
TWA	Time-Weighted Average

U	
UEL	Upper Explosive Limit
UF	Uncertainty Factor
UES	Uniform Emission Standard
UL	Underwriters Laboratory
Ullage	Amount by which a packaging falls short of being liquid full
UN	United Nations. **www.un.org**
USCG	United States Coast Guard. **www.uscg.mil**
V	
Vapor Pressure	The pressure exerted by a volatile liquid while under defined equilibrium conditions. Vapor pressure is usually measured in millimeters of mercury (mm Hg).
VCE	Vapor Cloud Explosion
VLE	Vapor Liquid Equilibrium
VOC	Volatile Organic Chemical
W	
WAO	Wet Air Oxidation
WEBWISER	Internet information system for first responders in hazmat incidents. **http://webwiser.nlm.nih.gov**
WEEL	Workplace Environmental Exposure Levels (AIHA). **www.aiha.org/Content/InsideAIHA/Committees/WEELcomm.htm**
WHMIS	Workplace Hazardous Materials Information System (Canada). **www.hc-sc.gc.ca/ewh-semt/occup-travail/whmis-simdut/index_e.html**
WHO	World Health Organization, the United Nations' specialized agency addressing public health. **www.who.int/en/**
WISER	Wireless Information System for emergency responders. A service of the U.S. National Library of Medicine, the system assists first responders in hazmat incidents. **http://wiser.nlm.nih.gov**
XYZ	
XV	Remote Activated/Controlled Valve