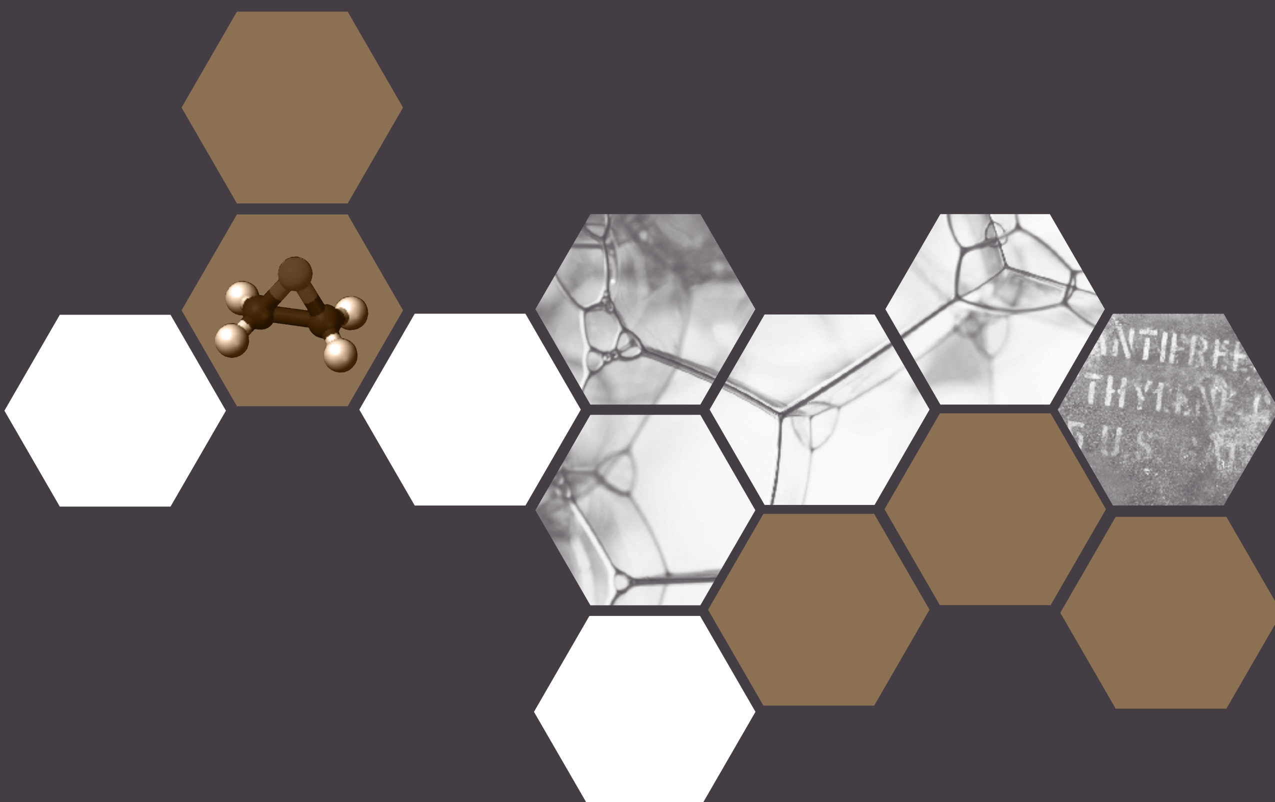
ethyleneoxide

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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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.

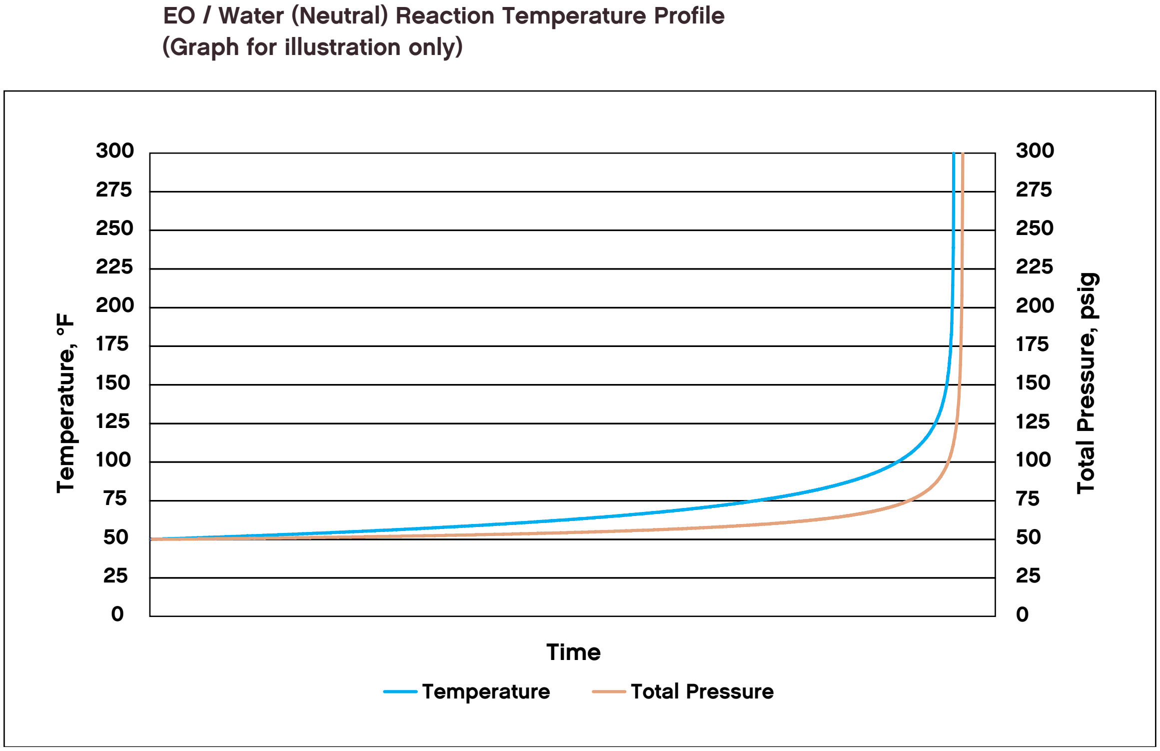
  CAUTION: DO NOT RETURN THE RAILCAR IF CONTAMINATION IS SUSPECTED WITHOUT FIRST DISCUSSING WITH THE SUPPLIER AS THERE MAY BE A RUNAWAY REACTION INSIDE THE RAILCAR.

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



- 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.

