

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND  
SUPPORTING DOCUMENTATION FOR

\*\*\* PROPYLENE OXIDE \*\*\*

NIOSH/OSHA Draft Technical Standard  
and Supporting Documentation for PROPYLENE OXIDE

The basic text of this document contains the draft technical standard approved by the Joint Review Committee of the NIOSH/OSHA Standards Completion Program and the supporting documentation for the substance PROPYLENE OXIDE.

The SCP draft technical standards are recommendations to the Department of Labor for its consideration in rulemaking and have no legal status until final rules have been promulgated by that agency. This draft standard is provided for your information only.

The References and Sources, Respirator Table Documentation and Use/Exposure and Control Documentation are the working documents used by the various SCP working groups during the development of the draft technical standard and serve as the technical foundation for the standard. The classification for each substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

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- (a) DEFINITIONS
  - (1) PERMISSIBLE EXPOSURE - "Permissible Exposure" means inhalation of propylene oxide in concentrations not in excess of 100 parts per million (ppm) (240 milligrams per cubic meter, mg/cu.m.) averaged over an eight hour work shift, as stated in section 1910.93, Table G-1.
  - (2) ACTION LEVEL - "Action Level" means one half (1/2) of the permissible exposure for propylene oxide.
- (b) EMPLOYEE INFORMATION - Each employer who has a workplace in which propylene oxide is present shall:
  - (1) STANDARD AVAILABILITY - Keep a copy of this section with its appendices A, B and C, at the workplace. This material shall be made readily available to affected employees; and
  - (2) PRESENCE OF PROPYLENE OXIDE - Inform affected employees of the quantity, location, and manner of use or storage of propylene oxide.
- (c) EXPOSURE MEASUREMENT
  - (1) INITIAL DETERMINATION - Each employer who has a place of employment in which propylene oxide is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of propylene oxide at or above the action level. The determination shall be made each time there is a change in production, process, or control measures which could result in an increase in airborne concentrations of propylene oxide. A written determination shall be made and it shall contain at least the following information:
    - (i) Any information, observations, or calculations which would indicate employee exposure to propylene oxide;
    - (ii) Any measurements of airborne concentrations of propylene oxide taken;
    - (iii) Any employee complaints of symptoms which may be attributable to exposure to propylene oxide; and
    - (iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.
  - (2) INITIAL EXPOSURE MEASUREMENT - If the employer determines that any employee may be exposed to airborne concentrations of propylene oxide at or above the action level, the exposure of the employee believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum exposure of the employee.
  - (3) IDENTIFICATION OF EXPOSED EMPLOYEES - If the exposure measurement taken under paragraph (c)(2) of this section reveals employee exposure to airborne concentrations of propylene oxide at or above the action level, the employer shall:
    - (i) Identify all employees who may be exposed at or above the action level; and
    - (ii) Measure the exposure of the employees so identified.
  - (4) EXPOSURE ABOVE THE ACTION LEVEL - If an employee exposure measurement reveals that an employee is exposed to airborne concentrations of propylene oxide at or above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every two months.

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- (5) EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE - If an employee exposure measurement reveals that an employee is exposed to airborne concentrations of propylene oxide above the permissible exposure, the employer shall:
- (i) Inform the employee of the exposure as required by paragraph (N)(1) of this section; and
  - (ii) Measure the exposure of the employee at least monthly; and
  - (iii) Institute control measures as required by paragraph (E) of this section.
- (6) TERMINATION OF EXPOSURE MEASUREMENT - If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to airborne concentrations of propylene oxide below the action level, the employer may terminate measurement for the employee. For purposes of this subparagraph, use of respirators shall not constitute reduction of employee exposure below the action level.
- (d) METHODS OF MEASUREMENT - An employee's exposure shall be obtained by any combination of long term or short term samples which represents the employee's actual exposure averaged over an eight hour work shift (Appendix B (iv)). The method of measurement shall have an accuracy, to a confidence level of 95%, of not less than that given in Table 1 below.

Table 1

Concentration	Required Accuracy
Above permissible exposure	Plus or Minus 25%
At or below permissible exposure and above the action level	Plus or Minus 35%
At or below the action level	Plus or Minus 50%

- (e) Methods of Compliance
- (1) Engineering controls - No employee shall be exposed to propylene oxide above the permissible limit as defined in paragraph (a)(1) of this section. Engineering and work practice controls shall be used to reduce exposure to propylene oxide to at or below the permissible exposure.
- (i) When mechanical ventilation is used to control exposure, measurements which demonstrate system efficiency (for example: air velocity, static pressure, or air volume) shall be made at least every three months. Measurements of system efficiency shall also be made within five work days of any change in production, process or control which might result in a reduction in control.
  - (ii) Where a fan is located in duct work and where propylene oxide is present in concentrations greater than 5250 ppm, one fourth of the lower flammable limit, the fan rotating element shall consist of, or be lined with, non-sparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.
  - (iii) In the design of open surface tank ventilation for the purposes of section 1910.94 (d), operations involving propylene oxide shall be classified as B-1 at 70 F.
- (2) Respirators
- (i) Compliance with the permissible exposure may not be achieved by the use of respirators except:

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- (a) During the time period necessary to install engineering controls; or
- (b) In work situations in which engineering controls are technically not feasible; or
- (c) In work situations in which feasible engineering and work practice controls are insufficient to reduce employees exposure to at or below permissible exposure, they shall be used to reduce exposure to the lowest level feasible; or
- (d) For operations not exceeding 40 hours per year; or
- (e) In emergencies.
- (ii) Respirators shall be jointly approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) and by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.
- (iii) Employers shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.
- (iv) Employers shall institute a respiratory protection program in accordance with sections 1910.134(b),(d),(e) and (f).

TABLE 2. RESPIRATORY PROTECTION FOR PROPYLENE OXIDE

Condition	Permissible Respiratory Protection
Vapor Concentration	
Equal to or less than 1000 ppm	or hood.
Equal to or less than 2000 ppm	
Greater than 2000 ppm or Entry & Escape from Unknown Concentrations	Self-contained breathing apparatus with a full facepiece demand or other positive pressure or continuous flow mode and auxiliary self-contained air supply operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against organic vapors. Any escape self-contained breathing apparatus with a full facepiece, helmet, or hood.

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(f) Fire and Safety

Employers shall familiarize themselves with the information contained in the Substance Technical Guidelines for propylene oxide which is contained in Appendix B in order to ensure the safe handling and use of propylene oxide.

- (1) Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of propylene oxide shall be Class I Group B (Group C equipment may be used if such equipment is isolated in accordance with section 501-5(a) by sealing all conduit one-half inch size or larger).
- (2) Portable fire extinguishers - For the purposes of compliance with section 1910.157, propylene oxide is classified as a Class B fire hazard.
- (3) Powered industrial trucks - For the purposes of compliance with section 1910.178, locations classified as hazardous locations due to the presence of propylene oxide shall be Class I Group B.
- (4) Flammable liquids - For the purposes of compliance with section 1910.106, liquid propylene oxide is classified as a Class IA flammable liquid. Spray finishing operations shall be performed in accordance with sections 1910.107 and 1910.94 (c). Dip tank operations shall be performed in accordance with sections 1910.108 and 1910.94 (d).
- (5) Sources of ignition - Sources of ignition such as smoking or open flames are prohibited where propylene oxide is handled, used or stored.
- (6) Storage - Propylene oxide shall be stored so as not to come in contact with anhydrous metal chlorides, strong acids, caustics, copper or copper alloys or peroxides.

(g) Personal Protective Equipment

(1) Skin Contact

- (i) Employers shall provide, and require employees to use, impervious clothing, gloves, face shields (8-inch minimum) and other appropriate protective clothing necessary to prevent any possibility of skin contact to liquid propylene oxide. Face shields shall comply with section 1910.133 (a)(6).
- (ii) Where there is any possibility of exposure of an employee's body to liquid propylene oxide, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.
- (iii) Employers shall ensure that any non-impervious clothing contaminated with liquid propylene oxide or any clothing which becomes wet with liquid propylene oxide be removed immediately and not reworn until the propylene oxide is removed from the clothing.
- (iv) Employers shall ensure that clothing wet with liquid propylene oxide is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of propylene oxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove

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the propylene oxide, the employer shall inform the person performing the operation of the hazardous properties of propylene oxide.

- (2) Eye Contact
  - (i) Employers shall provide, and require employees to use splash-proof safety goggles (cup-cover type dust and splash safety goggles), which comply with section 1910.133 (a)(6), where there is any possibility of liquid propylene oxide contacting the eye.
  - (ii) Where there is any possibility that an employee's eyes may be exposed to liquid propylene oxide, employers shall provide an eye wash fountain within the immediate work area for emergency use.
- (h) Spills
  - (1) Spills of propylene oxide shall be cleaned up immediately after eliminating potential sources of ignition and utilizing available ventilation.
  - (2) Liquid propylene oxide may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
- (i) Sanitation
  - (1) Employers shall ensure that employees whose skin becomes contaminated with liquid propylene oxide immediately wash or shower to remove any propylene oxide from the skin.
- (j) Training and Information - Each employer who has employees exposed to propylene oxide in excess of the action level, or employees who may have skin or eye contact with liquid propylene oxide, or employees who work where accidental release, spill, fire, or explosion of propylene oxide may occur, shall annually:
  - (1) Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for propylene oxide, which is contained in Appendix A; and
  - (2) Medical -
    - (I) Advise employees as to the signs and symptoms of exposure to propylene oxide.
    - (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to propylene oxide which are listed in Appendix A.
    - (III) Instruct the employees to inform the employer if they develop any of the medical conditions listed in (k)(2) of this section; and
- (3) Procedures -
  - (I) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to propylene oxide.
  - (II) The procedures required by (j)(1), (2), and (3)(I) shall be provided to employees at the expense of the employer during the employee's normal working hours.
- (k) Medical Surveillance
  - (1) The employer shall provide medical procedures as required by paragraph (k). These procedures shall be provided at no cost to the employee.

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- (2) Preplacement Questionnaire - The employer shall obtain from each employee who will be exposed to liquid propylene oxide, or airborne concentrations of propylene oxide at or above the action level, a written statement as to whether such employee has a history of any of the following:
  - (I) Skin disease
  - (II) Kidney disease
  - (III) Chronic lung disease
  - (IV) Liver disease
- (3) Preplacement Medical Examination - The employer shall provide a medical examination for an employee if the employee provides a history of any of the conditions named in paragraph (k)(2).
- (4) Results of Preplacement Examination - The employer shall obtain a physician's written opinion based on the medical examination pursuant to paragraph (k)(3).
- (5) Periodic Medical Examinations - The employer shall provide a medical examination for an employee if the employee advises the employer of the development of:
  - (I) Any of the medical conditions listed in (k)(2).
  - (II) Signs and symptoms listed in Appendix A which the employee suspects may be caused by exposure to propylene oxide.
- (6) Results of Periodic Examinations - The employer shall obtain a physician's written opinion based on the medical examination pursuant to paragraph (k)(5).
- (7) Exclusion or Removal from Exposure - No employee shall continue to be exposed to propylene oxide if such exposure could place the employee at increased risk of material impairment of his health.
- (8) Emergency Procedures - The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to propylene oxide.
- (9) Informing the Physician - The employer shall provide to the examining physician the following information:
  - (I) A copy of this section with its Appendices A, B, and C;
  - (II) A description of the employee's duties as they relate to his exposure to propylene oxide;
  - (III) A description of any personal protective equipment, including respirators, required to be used;
  - (IV) The results of any employee's exposure measurement, if available;
  - (V) The employee's anticipated exposure level; and
  - (VI) Upon request of the physician, information from previous medical examination of the employee.
- (10) Physician's Written Opinion
  - (I) The physician's written opinion shall be a signed statement by the examining physician specifically stating:
    - (A) Whether the employee has any detected medical conditions which could be directly or indirectly aggravated by exposure to propylene oxide or which could significantly interfere with the ability of the employee to follow

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recommended or required procedures for protecting himself from unusual or emergency exposure.

- (B) Any recommended limitations upon the employee's exposure to propylene oxide.
- (C) The employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.

(II) The written opinion shall not reveal medical information unrelated to exposure to propylene oxide.

(11) Refusal to be Medically Examined - If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risks involved by refusing to be examined.

(1) Recordkeeping.

(1) Initial determination.

- (i) The employer shall keep an accurate record of all initial determinations required to be made pursuant to paragraph (c)(1) of this section.
- (ii) The record shall include the written determination and any supporting documentation as required in paragraph (c)(1) of this section.
- (iii) This record shall be maintained until replaced by a more recent record.

(2) Exposure measurements.

- (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to propylene oxide.
- (ii) This record shall include:
  - (a) The date of measurement;
  - (b) A reference to the subparagraph of this regulation which required the measurement, if any;
  - (c) Operations involving exposure to propylene oxide which are being monitored;
  - (d) Sampling and analytical methods used and evidence of their accuracy;
  - (e) Number, duration, and results of samples taken;
  - (f) Name, Social Security number, and exposure of the employee monitored.
- (iii) This record shall be maintained until replaced by a more recent record but in no event for less than one year.

(3) Mechanical ventilation.

- (i) When mechanical ventilation is used as an engineering control, the employer shall maintain a record of measurements demonstrating the effectiveness of such ventilation as required by paragraph (e)(1)(i) of this section.
- (ii) This record shall include:
  - (a) Date of measurement;
  - (b) Type of measurement taken;

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- (c) Result of measurement.
- (iii) This record shall be maintained for at least one year.
- (4) Training and information.
  - (i) The employer shall keep an accurate record of all employee training and advice required by paragraph (j) of this section.
  - (ii) The record shall include:
    - (a) Date of training;
    - (b) Name and Social Security number of employees trained;
    - (c) Substance of training provided.
  - (iii) This record shall be maintained until replaced by a more recent record.
- (5) Medical records.
  - (i) The employer shall keep an accurate medical record for each employee.
  - (ii) The record shall include:
    - (a) Physician's written opinion;
    - (b) Preplacement questionnaire;
    - (c) Any employee medical complaints relative to exposure to propylene oxide;
    - (d) A signed statement of any refusal to be examined;
    - (e) A copy of information provided to the physician pursuant to paragraph (k)(9)(ii) through (vi) of this section.
  - (iii) This record shall be maintained for the duration of the employment of the affected employee.
- (6) Access to records.
  - (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary and the Director.
  - (ii) Employee exposure measurement records required to be maintained by this section shall be made available to employees and former employees and their designated representatives.
  - (iii) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.
- (m) Observation of monitoring.
  - (1) Duty.

The employer shall give affected employees or their representatives an opportunity to observe any monitoring of employee exposure to propylene oxide which is conducted pursuant to this section.
  - (2) Exercise of opportunity to observe monitoring.
    - (i) When observation of the monitoring of employee exposure to propylene oxide requires entry into an area where the use of personal protective devices is required, the observer shall use such equipment and comply with all other applicable safety procedures.
    - (ii) Without interfering with the measurement, observers shall be entitled to:
      - (a) Receive an explanation of the measurement procedures;
      - (b) Visually observe all steps related to the measurement of exposure to propylene oxide that are being performed at the place of exposure.

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(c) Record the results obtained.

(n) Employee notification.

- (1) The employer shall notify in writing, within five work days, every employee who is found to be exposed to propylene oxide above the permissible exposure. The employee shall also be notified of the level of his exposure and the corrective action being taken to reduce the exposure to at or below the permissible exposure.
- (2) Pursuant to paragraph (k) of this Section, when an employee is medically examined the employer shall provide the employee with a copy of the physician's written opinion.

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APPENDIX A

SUBSTANCE SAFETY DATA SHEET

I. SUBSTANCE: Propylene oxide

PERMISSIBLE EXPOSURE: 100 parts of propylene oxide per million parts of air (ppm) or 240 milligrams of propylene oxide per cubic meter of air (mg/cu m)

APPEARANCE AND ODOR: Colorless liquid with an ether-like odor

II. HEALTH HAZARD DATA

A. Ways in Which the Chemical Affects Your Body: Propylene oxide can affect your body if you inhale it, swallow it, or if it comes in contact with your skin or eyes.

B. Effects of Overexposure:

1. Short-Term Overexposure: Overexposure to propylene oxide may cause irritation of the eyes, nose, throat, and lungs. Contact with propylene oxide liquid may cause skin or eye irritation or burns.

2. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms associated with propylene oxide exposure.

III. EMERGENCY FIRST AID PROCEDURES

A. Eye Exposure: If propylene oxide gets into your eyes, wash the eyes immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

B. Skin Exposure: If propylene oxide gets on your skin, immediately flush the contaminated skin with water if the propylene oxide has not already evaporated. If propylene oxide soaks through your clothing, remove the clothing immediately and flush the skin with water. Do not wear the clothing again until the propylene oxide has been removed. Replace or repair impervious clothing that has developed leaks. If there is skin irritation, get medical attention.

C. Breathing: If you or any other person breathes in large amounts of propylene oxide remove the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

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- D. Swallowing: When propylene oxide has been swallowed do not cause vomiting. Get medical attention immediately.
- E. Rescue: Move affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty yourself. Understand your emergency rescue procedures and know the locations of the equipment before the need arises.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

- A. RESPIRATORS: Respirators are not the best way to control exposure to propylene oxide. You can only be required to wear them for routine use if your employer is in the process of installing controls or other control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA)/National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where their use is required. If you can smell propylene oxide while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.
- B. PROTECTIVE CLOTHING: You must wear impervious clothing, gloves, face shield or other appropriate protective clothing to prevent any possibility of skin contact with liquid propylene oxide.
- C. EYE PROTECTION: You must wear splash-proof safety goggles (cup-cover type dust and splash safety goggles) if there is any possibility of liquid propylene oxide contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

Propylene oxide is a flammable liquid and its vapors easily form explosive mixtures with air even at low temperatures over a wide range of air concentrations. It must be stored in tightly closed containers in a cool, well-ventilated area away from heat, sparks, flames, anhydrous metal chlorides, strong acids, caustics or peroxides. Sources of ignition such as smoking and open flames are prohibited wherever propylene oxide is handled, used or stored in a manner that could create a potential fire or explosion hazard. You must use non-sparking tools when opening or closing metal containers of propylene oxide, and containers must be bonded and grounded when pouring or transferring

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liquid propylene oxide. If your skin becomes contaminated with liquid propylene oxide, you must immediately wash or shower to remove any propylene oxide from the skin. You must immediately remove any clothing that becomes wet with liquid propylene oxide and this clothing must not be reworn until the propylene oxide is removed from the clothing. Fire extinguishers, eye flushing facilities and quick drenching facilities, where provided, must be readily available and you should know where they are and how to operate them. Ask your supervisor where propylene oxide is used in your work area and for any additional plant safety and health rules.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES  
PROPYLENE OXIDE

- I. PHYSICAL AND CHEMICAL DATA
- A. Substance Identification
1. Synonyms: 1,2-Epoxypropane; propene oxide; methyloxid~~ane~~
  2. Formula: CH<sub>3</sub>CHOCH<sub>2</sub>
  3. Molecular weight: 58
- B. Physical Data
1. Boiling point (760 mm Hg): 34 C (94 F)
  2. Specific gravity (H<sub>2</sub>O=1): 0.83
  3. Vapor density (air=1 at boiling point of propylene oxide): 2.0
  4. Melting point: -112 C (-170 F)
  5. Vapor pressure at 20 C (68 F): 442 mm Hg
  6. Solubility in water, % by weight at 20 C (68 F): 40.5
  7. Evaporation rate (butyl acetate=1): 33.7
  8. Appearance and odor: Colorless liquid with an ether-like odor
- II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA
- A. Fire
1. Flash point: -37 C (-35 F) (closed cup)
  2. Autoignition temperature: 748 C (1378 F)
  3. Flammable limits in air, % by volume: Lower; 2.1; Upper: 37.0
  4. Extinguishing media: Dry chemical, alcohol foam, carbon dioxide
  5. Special fire-fighting procedures: Do not use a solid stream of water since the stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
  6. Unusual fire and explosion hazards: Propylene oxide is a flammable liquid. Its vapors can easily form explosive mixtures with air even at low temperatures over a wide range of air concentrations. All ignition sources must be controlled where propylene oxide is handled, used or stored. Propylene oxide vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which propylene oxide is handled. Contact with hot metal may cause polymerization and splattering.
  7. For purposes of conforming with the requirements of 29 CFR 1910.106, propylene oxide is classified as a Class IA flammable liquid. At 5250 ppm, one-fourth of the lower flammable limit, propylene oxide is considered to be a potential fire and explosion hazard.

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8. For purposes of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electrical Code for propylene oxide shall be Class I, Group B. Group C equipment may be used if such equipment is isolated in accordance with Section 501-5(a) by sealing all conduit 1/2 inch or larger in diameter.

B. Reactivity

1. Conditions contributing to instability: Heat, contact with acids and caustics.
2. Incompatibilities: Anhydrous metal chlorides such as iron or aluminum chloride, strong acids, caustics, and peroxides may cause polymerization with liberation of heat.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propylene oxide.
4. Special precautions: Propylene oxide will attack some forms of plastics, rubber and coatings. No acetylide-forming metals such as copper or copper alloys should be in contact with propylene oxide.

III. SPILL, LEAK AND DISPOSAL PROCEDURES

A. If propylene oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear the hood ductwork, then burn the paper. Large quantities may be collected, dissolved in alcohol of greater molecular weight than butyl alcohol and atomized in a suitable combustion chamber. Propylene oxide may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.

C. Waste disposal methods:

Propylene oxide may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

IV. MONITORING AND MEASUREMENT PROCEDURES

a. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling

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and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, gas and vapor adsorption tubes with subsequent chemical analyses or dosimeters. The method of measurement must determine the concentration of propylene oxide to plus or minus 35%.

- b. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring under this section should be essentially the same as described under paragraph IV. a. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of propylene oxide to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.

V. MISCELLANEOUS PRECAUTIONS

- A. Store propylene oxide in tightly closed containers in a cool, well-ventilated area.
- B. High exposures to propylene oxide can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal propylene oxide containers. These containers must be effectively grounded and bonded prior to pouring.
- D. Employers must advise employees of all plant areas and operations where exposure to propylene oxide could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to propylene oxide is likely to occur are: during its production; its use as a gaseous sterilant, fumigant and preservative in foods, soils, etc.; and as an intermediate in the manufacture of glycols, glycol ethers, alkanolamines, lubricants, emulsifiers, resins and surfactants.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Propylene oxide is a severe irritant and a mild depressant of the central nervous system. Excessive exposure of animals to vapors caused irritation of the eyes, upper respiratory tract and lungs, as well as central nervous system effects characterized by ataxia, incoordination and general depression. The LC50 for single exposures of rats was 3,600 ppm, while 400 to 500 ppm was lethal to some rats on repeated daily exposures. The predominant effect was lung irritation and infection. All animals tolerated repeated exposures of 100 ppm without effects. Reported adverse effects on man have been confined to injury to the eyes and skin. The vapor is irritating to the eyes and the liquid causes corneal burns. When confined to the skin, as from wearing contaminated clothing or shoes, the material and water solutions as dilute as 10 per cent are likely to cause irritation, blistering, and even burns upon single short exposures. There is some evidence which indicates that solutions more dilute than 10 percent may be more irritating than the undiluted propylene oxide. No chronic systemic effects have been reported in humans.

III. SIGNS AND SYMPTOMS

High concentrations of vapor are likely to produce irritation of the eyes, and may produce irritation of the upper respiratory tract and lungs. Water solutions may cause irritation, blistering and burns of the skin.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Flush eyes immediately with copious amounts of water; wash skin with soap and water.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of propylene oxide are caused by its severe irritant properties. Persons subjected to high exposure should be observed for possible delayed pulmonary edema. It is important that the physician becomes familiar with plant operating conditions in

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which exposure to propylene oxide occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

B. PREPLACEMENT

Routine medical histories and physical examination are not required. However, the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from propylene oxide exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Skin disease -- Propylene oxide can cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.
2. Liver disease -- Although propylene oxide is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.
3. Kidney disease -- Although propylene oxide is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.
4. Chronic respiratory disease -- In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of propylene oxide might cause exacerbation of symptoms due to its irritant properties.

C. PERIODIC EXAMINATIONS

Routine periodic examinations are not required. However, if the employer becomes aware of an employee with the above listed conditions, he must refer such employee for further medical examination.

References

1. American Conference of Governmental Industrial Hygienists: "Propylene Oxide," (3d ed., 2d printing), Documentation of the Threshold-Limit Values for Substances in Workroom Air, Cincinnati, 1974, p. 219.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1642-1648.

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3. Hygienic Guide Series: "Propylene Oxide," American Industrial Hygiene Association Journal, 20:249-250, 1959.

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REFERENCES AND SOURCES

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1910.93

- (d) Methods of Compliance - Open surface tank classification based on relative evaporate rate of 0.35 hour.
- (e) Fire and Safety  
(1) Electrical - Classification based on "Fire Hazard Classification of Chemical Vapors Relative to Explosion-proof Electrical Equipment," H. Carhart et al., National Academy of Sciences, 1973, report to U. S. Coast Guard, report no. CG-D-92-74, p. 19.
- (f) Personal Protective Equipment, and (h) Sanitation  
Eye: Union Carbide Toxicology Study; AIHA Hyg. Guides; Patty, "Ind. Hyg. and Tox.;" Dow Product Bulletin, "Alkylene Oxides from Dow"  
Skin: Union Carbide Toxicology Study; Documentation in Support of TLV's; Patty, "Ind. Hyg. and Tox.;" Dow MSDS; Dow Product, "Alkylene Oxides from Dow"  
Ingestion: Union Carbide Toxicology Study

COMMENTS

Eye - Classification: 2  
Output statement numbers: 10  
Exceptions: None

Union Carbide states that "one tiny drop, as from a fine mist, is the least concentration causing injury in the rabbit eye. The use of eye protection is advisable when handling this chemical." AIHA states only that "eye protection should be worn." Patty notes that the liquid and its solutions "causes serious local injury in the eyes of rabbits, and 3 cases of corneal burns in humans have been reported." It is also remarked "adverse physiological effects can follow . . . contact of the eyes . . . with the liquid or with solutions as dilute as 1 per cent." Dow Product Bulletin agrees with Patty. Grant reports "liquid propylene oxide dropped on rabbit eyes has caused reversible injury similar to that caused by acetone, graded 5 on a scale of 1 to 10 after 24 hours."

The rabbit eye tests referred to by Patty, and most probably those referred to by Union Carbide, were conducted by Carpenter and Smyth. The injury grade of 5 is similar to the grade they give various ketones and alcohols, a grade which does not produce irreversible injury on the basis of human experience. Under these circumstances, it is concluded that a classification of 2 is most appropriate for propylene oxide.

Skin - Classification: 1  
Output statement numbers: 1, 7b, 8a, 14i, 14g and 21 combined  
Exceptions: None

Union Carbide gives a single skin penetration LD50 in rabbit of 1.50 ml/kg and notes that "severe skin burns resulted from this covered application." Skin irritation tests showed that "the undiluted chemical caused redness of short duration on the tender skin of the rabbit belly." It is added that "there is reason to believe that repeated contact may cause skin sensitivity reactions in occasional persons." The Documentation of TLV's states that "contact with the skin, even with diluted propylene oxide, may result in irritation and necrosis of the skin." Patty states that the undiluted chemical

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is without adverse effect if it is not confined and can evaporate freely. When confined to the skin, as from wearing contaminated clothing, "the material and water solutions as dilute as 10 per cent are likely to cause irritation, blistering, and even burns upon short exposures." Some evidence indicated that solutions more dilute than 10 per cent may be more irritating than the undiluted material. Patty adds that "there is no evidence . . . to indicate that propylene oxide can produce systemic intoxication by absorption through the skin." Dow MSDS states that it is not readily absorbed by the skin. Dow manufacturer's bulletin states that the material evaporates "rapidly from the skin that a frostbite type burn may result from contact with large amounts." It is also stated that the vapors are not likely to cause significant skin effects and that, by analogy with ethylene oxide, it must be assumed that the material is capable of inducing sensitization.

There are two major inconsistencies in the above information. The first concerns the fact that only Union Carbide notes that the material is readily absorbed through the skin. The second concerns the fact that only Dow makes any mention of frostbite type burns occurring.

Propylene oxide has a vapor pressure of 442 mm Hg at 20 degrees C. It is 40.5% soluble in water and has a flash point of -35 degrees C.

Though it is realized that a single unconfined contact with a small amount of propylene oxide may not be highly hazardous, the potential of the substance to cause serious burns, frostbite, etc. leads to the conclusion that a classification of 1 is warranted.

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

Union Carbide gives a single oral dose LD50 for rats of 1.14 g/kg. The vapor pressure of the material is given as 442 mm Hg at 20 C. The chemical evaporates so quickly that it is concluded that ingestion would not, in the context of this standard, present a hazard in the industrial environment.

SUBSTANCE TECHNICAL GUIDELINES  
PROPYLENE OXIDE

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: 1,2-Epoxypropane; propene oxide; methyloxidrane
2. Formula:  $\text{CH}_3\text{CHOCH}_2$
3. Molecular weight: 58

B. Physical Data

1. Boiling point (760 mm Hg): 34 C (94 F)
2. Specific gravity (water=1): 0.83
3. Vapor density (air=1 at boiling point of propylene oxide): 2.0
4. Melting point: -112 C (-170 F)
5. Vapor pressure at 20 C (68 F): 442 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): 40.5
7. Evaporation rate (butyl acetate=1): 33.7
8. Appearance and odor: Colorless liquid with an ether-like

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odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: -37 C (-35 F) (closed cup)
2. Autoignition temperature: 748 C (1378 F)
3. Flammable limits in air, % by volume: Lower: 2.1;  
Upper: 37.0
4. Extinguishing media: Dry chemical, alcohol foam, carbon dioxide
5. Special fire-fighting procedures: Do not use a solid stream of water since the stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Propylene oxide is a flammable liquid. Its vapors can easily form explosive mixtures with air even at low temperatures over a wide range of air concentrations. All ignition sources must be controlled where propylene oxide is handled, used or stored in a manner that could create a potential fire or explosion hazard. Propylene oxide vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which propylene oxide is handled. Contact with hot metal may cause polymerization and splattering.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, propylene oxide is classified as a Class IA flammable liquid. For example, 5300 ppm, one-fourth of the lower flammable limit, is one situation in which propylene oxide is considered to be a potential fire and explosion hazard.
8. For purposes of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electrical Code for propylene oxide shall be Class I, Group B. Group C equipment may be used if such equipment is isolated in accordance with Section 501-5(a) by sealing all conduit 1/2 inch or larger in diameter.

B. Reactivity

1. Conditions contributing to instability: Heat, contact with acids and caustics.
2. Incompatibilities: Anhydrous metal chlorides such as iron or aluminum chloride, strong acids, caustics, and peroxides may cause polymerization with liberation of heat.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propylene oxide.
4. Special precautions: Propylene oxide will attack some forms of plastics, rubber and coatings. No acetylide-forming metals such as copper or copper alloys should be in contact with propylene oxide.

III. SPILL, LEAK AND DISPOSAL PROCEDURES

A. If propylene oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources

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2. Ventilate area of spill or leak.
  3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear the hood ductwork, then burn the paper. Large quantities may be collected, dissolved in alcohol of greater molecular weight than butyl alcohol and atomized in a suitable combustion chamber. Propylene oxide may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
- B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.
- C. Waste disposal methods:  
Propylene oxide may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.
- IV. MONITORING AND MEASUREMENT PROCEDURES
- a. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, gas and vapor adsorption tubes with subsequent chemical analyses or dosimeters. The method of measurement must determine the concentration of propylene oxide to plus or minus 35%.
- b. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring under this section should be essentially the same as described under paragraph IV. a. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of propylene oxide to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.
- V. MISCELLANEOUS PRECAUTIONS
- A. Store propylene oxide in tightly closed containers in a cool, well-ventilated area.
- B. High exposures to propylene oxide can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal propylene oxide containers. These containers must be effectively grounded and bonded prior to pouring.
- D. Employers should advise employees of all plant areas and operations where exposure to propylene oxide could occur.

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VI. COMMON OPERATIONS

Common operations in which exposure to propylene oxide is likely to occur are: during its production; its use as a gaseous sterilant, fumigant and preservative in foods, soils, etc.; and as an intermediate in the manufacture of glycols, glycol ethers, alkanolamines, lubricants, emulsifiers, resins and surfactants.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Propylene oxide

D. O. L. STANDARD: 100 ppm

WARNING PROPERTIES:

Odor Threshold: Patty states that "the median detectable concentration of propylene oxide vapors is reported to be 200 ppm with 95 per cent confidence limits of 114 to 353 ppm. The odor is described as sweet, alcoholic, and like natural gas, ether, or benzene."

Eye Irritation Level: Grant reports that "exposure of monkeys and rabbits to 457 ppm of vapor in air for seven hours daily had no adverse effect, but in rats and guinea pigs it irritated the eyes and induced lung edema."

The AIHA Hygienic Guides, Patty, the Documentation of TLV's and several other authors all note that propylene oxide causes eye irritation. Since no quantitative information is available, however, concerning the threshold of eye irritation, only full facepiece respirators are permitted.

Evaluation of Warning Properties: Patty states that "neither odor nor irritation can be relied upon to warn of the presence of vapor concentrations not suitable for prolonged and repeated exposure. Odor and/or irritation will warn of the presence of acutely dangerous concentrations." Since it appears that Patty considers any vapor concentrations above 100 ppm (the ACGIH threshold limit for 1961) "not suitable for prolonged and repeated exposure," propylene oxide is considered to have adequate warning properties for the purposes of this standard. The median of the detectable odor concentrations (200 ppm) is only 2 times the permissible exposure limit. The chronic exposure data given in the Documentation of TLV's quoted below does not indicate that 200 ppm causes any toxic effects.

Gas sorbent respiratory equipment is permitted.

IDLH: 2000 ppm

Basis for IDLH Value: This IDLH is based upon the 4-hour dog LC<sub>50</sub> of 2005 ppm and upon the 4-hour mouse LC<sub>50</sub> of 1740 ppm reported in the NIOSH Toxic Substances List.

Other Toxicological Information: According to the Documentation of TLV's, "propylene oxide is classified toxicologically as a primary irritant, a mild protoplasmic protein and a mild depressant of central nervous system activity. Contact with the skin, even with diluted propylene oxide may result in irritation and necrosis of the skin. Excessive exposure to the vapor irritates the eyes, upper respiratory tract and lungs. Central nervous system effects consist of incoordination, ataxia and general depression. Corneal burns have been reported in man.

"Rowe and co-workers found that repeated daily exposures of several species of animals at 200 ppm caused no ill effects.

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Female guinea pigs only were found to have a slight increase in lung weight after about six months. All animals tolerated 100 ppm without adverse effects. These authors suggested a threshold limit of 250 ppm. Jacobson et al. found propylene oxide to be one-half to one-third as toxic as ethylene oxide based on the response to a single exposure. . .

. . . "On the basis of its lesser toxicity in relation to ethylene oxide, the TLV of 100 ppm is recommended."

The following is part of a table which can be found in Patty:

Summary of Acute Response of Animals to Vapors of Propylene Oxide			
Vapor conc. (ppm)	Time (hr.)	Animal	Response: no. dying/no. exposed
900	7	Rat	0/5-no detectable injury
1,330	4	Mouse	1/10 in 1 day
	4	Rat	0/10 in 14 days
		Dog	0/3 in 14 days
1,800	2	Rat	0/5-no detectable injury
	7	Rat	0/10 in 14 days
	7	Guinea pig	0/10 in 14 days
2,480	4	Dog	3/3 within hours
3,600	1	Rat	0/5-no detectable injury
	2	Rat	4/10
	4	Guinea pig	0/5
		Rat	4/10

The AIHA Hygienic Guides states that "inhalation of 4,000 ppm for four hours has been reported as being lethal in rats. Concentrations of 4000 ppm for one-half hour, 2000 ppm for two hours, and 1000 ppm for four hours failed to cause organic injury in rats. Another author reports the LC50 for rats as being 4000 ppm for four hours."

The NIOSH Toxic Substances List gives a dog LCLo of 2005 ppm for a 5-hour exposure and a mouse LC50 of 1740 ppm for a 4-hour exposure.

The Chemical Company Guides of Union Carbide Corporation report a single skin penetration LD50 in rabbits of 1.50 ml/kg for propylene oxide.

LFL: 21,000 ppm

VAPOR PRESSURE AT 20 C: 442 mm Hg

SATURATED CONCENTRATION AT 20 C: Approximately 581,600 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT  
PROPYLENE OXIDE

	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of vapor during the manufacture of polypropylene glycol and polyether polyols which are used extensively in the production of polyurethane foam	A	Local exhaust ventilation; general dilution ventilation; enclosed process; protective equipment (goggles)
2.	Inhalation of vapor during the manufacture of propylene glycol which is used as a solvent, emulsifier and mold inhibitor	A	Local exhaust ventilation; general dilution ventilation; enclosed process; protective equipment (goggles)
3.	Inhalation of vapor during the manufacture of dipropylene glycol (solvent, ink formulations) and glycol ethers (solvents, oil additives, hydraulic brake fluids)	A	Local exhaust ventilation; general dilution ventilation; enclosed process; protective equipment (goggles)
4.	Inhalation of vapor during use as a chemical intermediate in the production of lubricants, surfactants and miscellaneous chemicals (pharmaceutical industry - therapeutic agents, cosmetic and petroleum industry - emulsifiers, textile industry - resins for printing vat dyes and oil soluble dyes, rubber industry - lubricants, soap industry - detergents and wetting agents)	A	Local exhaust ventilation; general dilution ventilation; enclosed process; protective equipment (goggles)
5.	Inhalation of vapor during the production of propylene oxide	A	Local exhaust ventilation; general dilution ventilation; enclosed process; protective equipment (goggles)
6.	Inhalation of vapor and skin contact with liquid during use as a low boiling solvent for cellulose derivatives, hydrocarbons, commercial gums and various resins (neoprene to rubber adhesives, shoe cement, vinyl chloride - acetate resins, nitrocellulose adhesives)	A,B	Local exhaust ventilation; general dilution ventilation; personal protective equipment (goggles, gloves)
7.	Inhalation of vapor and skin	A,B	Local exhaust ventilation;

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- contact with liquid during use as a fumigant (mothproofing agent for wool), herbicide (kills gooseberries and barberries), germicide (soil and hospital supplies sterilization), insecticide (solvent - stabilizer for DDT aerosols), and stabilizer (prevents discoloration of vinyl resin lacquers and deterioration of hydrocarbons)
8. Inhalation of vapor and skin contact with liquid during use as a food preservative (fungicide - powerful reagent against certain yeasts, molds and bacteria, funigant - volatile food preservative) A, B
9. Inhalation of vapor and skin contact with liquid during cleaning and maintenance of storage tanks and during cleanup operation of accidental spills A, B
10. Inhalation of vapor during hydroxypropylating of wheat flour in order to modify it to mix readily with water (thickening agents, adhesives, textile coatings and sizings, paper coatings and sizings) A
- general dilution ventilation; personal protective equipment (goggles, gloves respiratory protective devices)
- Local exhaust ventilation; general dilution ventilation; personal protective equipment (goggles, gloves)
- Local exhaust ventilation; general dilution ventilation; personal protective equipment (goggles, rubber gloves and aprons, rubber shoes or boots, respirator protective devices)
- Local exhaust ventilation; general dilution ventilation; enclosed process; personal protective equipment (goggles)
- A -- Inhalation  
B -- Skin contact resulting in localized irritation  
C -- Ingestion  
D -- Skin contact resulting in absorption and subsequent systemic poisoning