

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** ETHYL FORMATE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ETHYL FORMATE

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 ETHYL FORMATE.

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 ethyl formate in concentrations not in excess of 100 parts per million (ppm) (300 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 ethyl formate.

(b) EMPLOYEE INFORMATION - Each employer who has a workplace in which ethyl formate 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 ETHYL FORMATE - Inform affected employees of the quantity, location, and manner of use or storage of ethyl formate.

(c) EXPOSURE MEASUREMENT

- (1) INITIAL DETERMINATION - Each employer who has a place of employment in which ethyl formate is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of ethyl formate 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 ethyl formate. 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 ethyl formate;
 - (ii) Any measurements of airborne concentrations of ethyl formate taken;
 - (iii) Any employee complaints of symptoms which may be attributable to exposure to ethyl formate; 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 ethyl formate 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 ethyl formate 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 ethyl formate 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 ethyl formate 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 ethyl formate 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 ethyl formate 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 ethyl formate 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) In the design of open surface tank ventilation for the purposes of compliance with section 1910.94(d), operations involving ethyl formate shall be classified as B-1 at 70 F.
- (iii) Where a fan is located in duct work and where ethyl formate is present in concentrations greater than 7000 ppm, one fourth of the lower flammable limit, the fan rotating element shall consist of, or be lined with nonsparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.

(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 the permissible exposure. Where technically feasible engineering and work practice controls are not sufficient to reduce 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),(f) and (g).

TABLE 2. RESPIRATORY PROTECTION FOR ETHYL FORMATE

Condition	Permissible Respiratory Protection
Concentration of Vapor	
Equal to or less than 1000 ppm	organic vapor cartridge(s).
Equal to or less than 5000 ppm	organic vapor canister. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or Entry and Escape from Unknown Concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand (positive pressure) mode A combination respirator which includes a Type C supplied air respirator with a full facepiece operated in pressure-demand mode. auxiliary self-contained air supply operated in pressure-demand mode.

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Fire Fighting Self-contained breathing apparatus with a full facepiece
operated in pressure-demand or continuous flow mode.

Escape Any gas mask providing protection against organic vapors
Any escape self-contained breathing apparatus.

(f) Fire and Safety - Employers shall familiarize themselves with the information contained in the Substance Technical Guidelines for ethyl formate which is contained in Appendix B in order to ensure the safe handling and use of ethyl formate.

(1) Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of ethyl formate shall be Class I Group D.

(2) Portable fire extinguishers - For the purposes of compliance with section 1910.157, ethyl formate 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 ethyl formate shall be Class I Group D.

(4) Flammable liquids - For the purposes of compliance with section 1910.106, liquid ethyl formate is classified as a Class IB 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 ethyl formate is handled, used or stored in a manner so as to create a potential fire or explosion hazard.

(6) Storage - Ethyl formate shall be stored so as not to come in contact with nitrates, strong oxidizers, strong acids or strong alkalies.

(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 repeated or prolonged skin contact to liquid ethyl formate. Face shields shall comply with section 1910.133(a)(6).

(ii) Employers shall ensure that clothing which becomes wet with liquid ethyl formate be removed immediately and not reworn until the ethyl formate is removed from the clothing.

(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 eye contact to liquid ethyl formate may occur.

(h) Spills

(1) Spills of ethyl formate shall be cleaned up immediately after eliminating potential sources of ignition and utilizing available ventilation.

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- (2) Ethyl formate liquid 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 wet with liquid ethyl formate promptly wash or shower as necessary to remove any ethyl formate from the skin.
- (j) Training and Information - Each employer who has employees exposed to ethyl formate in excess of the action level, or employees who may have skin or eye contact with liquid ethyl formate, or employees who work where accidental release, spill, fire, or explosion of ethyl formate may occur, shall annually:
 - (1) Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for ethyl formate, which is contained in Appendix A; and
 - (2) Medical -
 - (I) Advise employees as to the signs and symptoms of exposure to ethyl formate.
 - (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to ethyl formate 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 ethyl formate.
 - (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.
 - (2) Preplacement Questionnaire - The employer shall obtain from each employee who will be exposed to liquid ethyl formate, or airborne concentrations of ethyl formate at or above the action level, a written statement as to whether such employee has a history of any of the following:
 - (I) Chronic lung disease
 - (II) Skin disease
 - (III) Liver disease
 - (IV) Kidney 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).

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- (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 ethyl formate.
- (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 ethyl formate 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 ethyl formate.
- (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 for ethyl formate
 - (II) A description of the employee's duties as they relate to his exposure to ethyl formate;
 - (III) A description of any personal protective equipment 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 ethyl formate or which could significantly interfere with the ability of the employee to follow recommended or required procedures for protecting himself from unusual or emergency exposure.
 - (B) Any recommended limitations upon the employee's exposure to ethyl formate.

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- (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 ethyl formate.
- (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.

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- (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 for at least one year.
 - (2) Exposure measurements.
 - (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to ethyl formate.
 - (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 ethyl formate 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 for 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;
 - (c) Result of measurement.
 - (iii) This record shall be maintained for 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 for at least one year.
 - (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 ethyl formate;
 - (d) A signed statement of any refusal to be examined;

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- (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 ethyl formate which is conducted pursuant to this section.
 - (2) Exercise of opportunity to observe monitoring.
 - (i) When observation of the monitoring of employee exposure to ethyl formate 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 ethyl formate that are being performed at the place of exposure.
 - (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 ethyl formate 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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Formate

APPENDIX A

SUBSTANCE SAFETY DATA SHEET

I. SUBSTANCE IDENTIFICATION

SUBSTANCE: Ethyl formate

PERMISSIBLE EXPOSURE: 100 parts of ethyl formate vapor per million parts of air (ppm) or 300 milligrams of ethyl formate vapor per cubic meter of air (mg/cu m)

APPEARANCE AND ODOR: Colorless liquid with a fruity odor.

II. HEALTH HAZARD DATA

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

B. Effects of Overexposure:

1. Short-Term Overexposure: Overexposure to ethyl formate may cause irritation of the eyes, nose, throat and skin. At high concentrations it may cause drowsiness and unconsciousness.
2. Long-Term Overexposure: Long-term overexposure to ethyl formate may cause irritation of the skin.
3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms associated with ethyl formate exposure.

III. EMERGENCY FIRST AID PROCEDURES

A. Eye Exposure: If ethyl formate gets into your eyes, wash the eyes immediately with large amounts of water, 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 clothing becomes wet with ethyl formate, immediately remove and clean the clothing before wearing again. If ethyl formate gets on your skin, flush the contaminated skin with water immediately. If there is skin irritation, get medical attention.

C. Breathing: If you or any other person breathes in large amounts of ethyl formate, remove the exposed person to fresh air at once. If

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breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- D. Swallowing: When ethyl formate has been swallowed get medical attention immediately. If medical attention is not immediately available, get the affected person to vomit by having him touch the back of his throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.

- 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 ethyl formate. 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.) If you can smell ethyl formate 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, faceshield and other appropriate protective clothing to prevent repeated or prolonged skin contact with liquid ethyl formate.
- C. EYE PROTECTION: You must wear splash-proof safety goggles (cup-cover type dust and splash safety goggles) where eye contact with liquid ethyl formate may occur. your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

Ethyl formate is a flammable liquid and its vapors easily form explosive mixtures with air. It must be stored in tightly closed containers in a cool, well-ventilated area away from heat, sparks and flames. Store ethyl formate away from nitrates, strong oxidizers, strong alkalies, and strong acids. Sources of ignition such as smoking and open flames are prohibited wherever ethyl formate 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 ethyl formate, and containers must be bonded and grounded when pouring or transferring liquid ethyl formate. If your skin becomes wet with liquid ethyl formate, you must promptly wash or shower as necessary to remove any ethyl formate from the skin. You must immediately remove any clothing that becomes wet with liquid ethyl formate and this clothing must not be reworn until the ethyl formate is removed from the clothing. Fire extinguishers, and eye flushing facilities, where provided, must be readily available and you should know where they are and how to operate

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them. Ask your supervisor where ethyl formate is used in your work area and for any additional plant safety rules.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
ETHYL FORMATE

- I. PHYSICAL AND CHEMICAL DATA
 - A. Substance Identification
 - 1. Synonyms: Ethyl methanoate; formic acid ethyl ester
 - 2. Formula: HCOOC2H5
 - 3. Molecular weight: 74
 - B. Physical Data
 - 1. Boiling point (760 mm Hg): 54.5 C (130 F)
 - 2. Specific gravity (water=1): 0.92
 - 3. Vapor density (air=1 at boiling point of ethyl formate): 2.6
 - 4. Melting point: -79 C (-110 F)
 - 5. Vapor pressure at 20 C (68 F): 194 mm Hg
 - 6. Solubility in water, % by weight at 20 C (68 F): 13.6
 - 7. Evaporation rate (butyl acetate=1): Data not available
 - 8. Appearance and odor: Colorless liquid with a fruity odor
- II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA
 - A. Fire
 - 1. Flash point: -20 C (-4 F) (closed cup)
 - 2. Autoignition temperature: 455 C (851 F)
 - 3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 16
 - 4. Extinguishing media: Alcohol foam, dry chemical, carbon dioxide
 - 5. Special fire-fighting procedures: Do not use solid stream of water since stream will scatter and spread fire. Use water spray to cool containers exposed to a fire.
 - 6. Unusual fire and explosion hazards: Ethyl formate is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where ethyl formate is used, handled or stored. Ethyl formate vapors are heavier than air and may travel along the ground and be ignited by sparks or open flames at locations remote from the site at which ethyl formate is handled.
 - 7. For purposes of conforming to the requirements of 29 CFR 1910.106, ethyl formate is classified as a Class IB flammable liquid. At 7000 ppm, one-fourth of the lower flammable limit, ethyl formate 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 ethyl formate shall be Class I, Group D.

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B. Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalis, and strong acids may cause fire and explosion.
3. Hazardous decomposition products: Toxic gases and vapors (such as Carbon monoxide) may be released in a fire involving ethyl formate.
4. Special precautions: None

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

A. If ethyl formate 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) and burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber. Ethyl formate 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:

Ethyl formate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary land fill.
2. By 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 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 ethyl formate 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 ethyl formate to plus or minus

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25%. Methods meeting these accuracy requirements are available in the "NIOSH Monitoring Methods Manual".

V. MISCELLANEOUS PRECAUTIONS

- A. Store ethyl formate in tightly closed containers in a cool, well-ventilated area.
- B. High exposures to ethyl formate can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal ethyl formate 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 ethyl formate could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to ethyl formate is likely to occur are: operations involved in its manufacture and the application of lacquers containing ethyl formate, its use as a solvent in the manufacture of artificial silk and leather and in the shoe industry, and in the application of fumigant and larvacide for tobacco, cereal and dried fruit.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation; insignificant skin absorption.

II. TOXICOLOGY

Ethyl formate is irritating to the eyes and nose at concentrations of 330 ppm. Narcosis occurs in animals, but only at exposure levels near the lethal concentration of 10,000 ppm. Dogs exposed to this very high concentration died of pulmonary edema. Rats survived at 4000 ppm. Application to the skin caused only slight irritation, but dropped into the eye, caused moderate injury to the cornea. No chronic systemic effects have been reported in humans.

III. SIGNS AND SYMPTOMS

Irritation of the eyes and upper respiratory tract. High sustained levels may cause narcosis.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

None specific. Remove from exposure, give artificial resuscitation if indicated, and wash eyes and contaminated skin. Recovery is usually rapid and complete.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of ethyl formate are caused by its irritant properties. The physician should become familiar with plant operating conditions in which exposure to this substance 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 ethyl formate exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

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1. Chronic respiratory disease -- In persons with impaired pulmonary function, especially those with obstructive airway diseases, the inhalation of this substance might cause exacerbation of symptoms due to its irritant properties.
2. Skin disease -- This substance is a defatting agent and can cause dermatitis on prolonged exposure. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.
3. Liver disease -- Although ethyl formate 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.
4. Kidney disease -- Although ethyl formate is not known as a kidney toxin in humans, the importance of the organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

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. Patty, Frank A: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishers, New York, 1963, pp. 1855-1856.
2. American Conference of Governmental Industrial Hygienists: "Ethyl Formate," (3d ed., 2d printing), Documentation of the Threshold Limit Values for Substances in Workroom Air, Cincinnati, 1974, p. 107.
3. Grant, W. Morton: Toxicology of the Eye (2d ed.), Charles C. Thomas, Illinois, 1974, pp. 554-556.

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REFERENCES AND SOURCES

ETHYL FORMATE

1910.93

(f) Personal Protective Equipment, and (h) Sanitation

Eye: "Ethyl Formate," Union Carbide Corp. Toxicology Study; Patty, "Industrial Hygiene and Toxicology;" Browning, "Toxicity and Metabolism of Industrial Solvents;" Smyth et al., "Range-Finding Toxicity Data - List V," Arch. Indus. Hyg. Occup. Med., 10:61, July 1954

Skin: "Ethyl Formate," Union Carbide Corp. Toxicology Study; Patty, "Industrial Hygiene and Toxicology;" Browning, "Toxicity and Metabolism of Industrial Solvents;" Smyth et al., "Range-Finding Toxicity Data - List V," Arch. Indus. Hyg. Occup. Med., 10:61, July, 1954

Ingestion: "Ethyl Formate," Union Carbide Corp. Toxicology Study; Sax, "Dangerous Properties of Industrial Materials;" Smyth et al., "Range-Finding Toxicity Data - List V," Arch. Indus. Hyg. Occup. Med., 10:61, July, 1954

COMMENTS

Eye - Classification: 2

Output statement numbers: 10

Exceptions: None

Union Carbide reports that "one small drop as from a mist caused a minor eye injury." Patty reports that "direct contact . . . with eye produced moderate irritation." Browning notes that it causes "moderate injury." Browning references a 1954 paper by Smyth et al. which gives an injury grade of 4 on a scale of 1 to 10 after 24 h for the ethyl ester of formic acid. This grade indicates that 0.1 ml of the undiluted chemical causes less than severe injury while 0.1 ml produces severe injury, as defined by Smyth and Carpenter, after 24 h.

There is no indication in the literature that any injury caused would be irreversible. The substance is therefore assigned a classification of 2.

Skin - Classification: 2

Output statement numbers: 2, 21, 16i

Exceptions: 7b and 20a deleted because of vapor pressure

Smyth et al., as cited in Patty and Browning, give a single skin penetration LD50 to rabbits of greater than 20 ml/kg. For local effects, Union Carbide reports "the undiluted chemical caused no reaction on the tender skin of the rabbit belly greater than a faint redness of short duration." Patty, interpreting the rabbit skin irritation grade of 1 given to the substance by Smyth et al., reports "injury to the skin from contact was mild." Browning agrees by noting "application to the skin caused only slight irritation." Patty also notes in general, however, that such esters are fat solvents and may cause cracking and drying of the skin.

Ethyl formate has a vapor pressure of 194 mm Hg at 20 degrees. It is 13.6% soluble in water and has a flash point of -4 degrees.

The high vapor pressure of the substance and its rather innocuous acute effects indicate that a classification of 2 is appropriate if only statements 2, 21, and 16i are utilized. Statement 7b is not specified because the substance would in all likelihood evaporate from wet clothing before the clothing could be washed to remove it.

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Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

Union Carbide lists a single oral dose LD50 to rats of 3.36 Smyth et al. determined the LD50 to be 4.3 g/kg. Sax reports that the substance is a general purpose food additive.

The high vapor pressure of the substance and its moderate toxicity indicates that ingestion would not be a hazard in the industrial environment.

SUBSTANCE TECHNICAL GUIDELINES
ETHYL FORMATE

- I. PHYSICAL AND CHEMICAL DATA
 - A. Substance Identification
 - 1. Synonyms: Ethyl methanoate; formic acid ethyl ester
 - 2. Formula: HCOOC2H5
 - 3. Molecular weight: 74
 - B. Physical Data
 - 1. Boiling point (760 mm Hg): 54.5 C (130 F)
 - 2. Specific gravity (water=1): 0.92
 - 3. Vapor density (air=1 at boiling point of ethyl formate): 2.6
 - 4. Melting point: -79 C (-110 F)
 - 5. Vapor pressure at 20 C (68 F): 194 mm Hg
 - 6. Solubility in water, % by weight at 20 C (68 F): 13.6
 - 7. Evaporation rate (butyl acetate=1): Data not available
 - 8. Appearance and odor: Colorless liquid with a fruity odor
- II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA
 - A. Fire
 - 1. Flash point: -20 C (-4 F) (closed cup)
 - 2. Autoignition temperature: 455 C (851 F)
 - 3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 16
 - 4. Extinguishing media: Alcohol foam, dry chemical, carbon dioxide
 - 5. Special fire-fighting procedures: Do not use solid stream of water since stream will scatter and spread fire. Use water spray to cool containers exposed to a fire.
 - 6. Unusual fire and explosion hazards: Ethyl formate is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where ethyl formate is used, handled or stored in a manner that could create a potential fire or explosion hazard. Ethyl formate vapors are heavier than air and may travel along the ground and be ignited by sparks or open flames at locations remote from the site at which ethyl formate is handled.
 - 7. For purposes of conforming to the requirements of 29 CFR 1910.106, ethyl formate is classified as a Class IB flammable liquid. For example, 7000 ppm, approximately one-fourth of the lower flammable limit, is one situation in which ethyl formate 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 ethyl formate shall be Class I, Group D.

B. Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fire and explosion.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl formate.
4. Special precautions: None

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

- A. If ethyl formate 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 hood ductwork, then burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber. Ethyl formate 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: Ethyl formate may be disposed of by 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 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 ethyl formate 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

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Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of ethyl formate to plus or minus 25%. Methods meeting these accuracy requirements are available in the "NIOSH Monitoring Methods Manual".

V. MISCELLANEOUS PRECAUTIONS

- A. Store ethyl formate in tightly closed containers in a cool, well-ventilated area.
- B. High exposures to ethyl formate can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal ethyl formate 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 ethyl formate could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to ethyl formate is likely to occur are: operations involved in its manufacture and the application of lacquers containing ethyl formate, its use as a solvent in the manufacture of artificial silk and leather and in the shoe industry, and in the application of fumigant and larvacide for tobacco, cereal and dried fruit.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Ethyl formate

D.O.L. STANDARD: 100 ppm

WARNING PROPERTIES:

Odor Threshold: There is no information available concerning the odor threshold of ethyl formate.

Eye Irritation Level: According to the Documentation of TLV's, "in man, a concentration of 330 ppm produced a slight irritation of the eyes and a rapidly increasing nasal irritation . . . A threshold limit of 100 ppm is recommended to prevent eye and nasal irritation."

Evaluation of Warning Properties: Since eye and nasal irritation occur at a concentration which is approximately only three times the permissible exposure limit, ethyl formate is treated as a material with good warning properties. Gas sorbent respiratory equipment is permitted.

IDLH: 8000 ppm

Basis for IDLH Value: This IDLH is based upon the report by Union Carbide Corporation and by Patty that 5 out of 6 rats died following a 4-hour exposure to 8000 ppm ethyl formate. No rats died from a 4-hour exposure to 4000 ppm ethyl formate.

Other Toxicological Information: The ILO states that "in animal experiments, inhalation of vapours caused tremors, progressive depression of the central nervous system and death through circulatory and respiratory insufficiency, the narcotic dose being the same as the lethal dose. No cases have so far been reported of industrial ethyl formate poisoning, although workers with the ester have experienced irritation of the conjunctivae and mucous membranes, which may persist for several hours after contact has ceased."

The Chemical Company Guides of Union Carbide Corporation

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report that a 4-hour exposure to 4000 ppm killed no rats, but a 4-hour exposure to 8000 ppm killed 5 out of 6 rats.

Patty gives the following table concerning the "physiological response to inhalation of ethyl formate:

Compound	Species	Concentration		Results
		p.p.m.	Duration of Exposure	
Ethyl formate	Rat	Conc. vapor	5 min.	No deaths
	Rat	8,000	4 hr.	5 deaths of 6 e
	Rat	4,000	4 hr.	No deaths
	Mouse	10,000	20 min.	Eye irritation,
	Mouse	5,000	20 min.	Eye irritation,
	cat	10,000	80 min.	Eye irritation,
	Cat	5,000	20 min.	Eye irritation,
	Dog	10,000	4 hr.	Pulmonary edema
	Man	330		Eye and nose ir

LFL: 28,000 ppm

VAPOR PRESSURE AT 20 C: 194 mm Hg

SATURATED CONCENTRATION AT 20 C: 255,300 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT

ETHYL FORMATE

Principal Route
of Entry

Currently Used
Control Methods

Use/Exposure

- | | | | |
|----|---|-----|--|
| 1. | Inhalation of vapor and skin contact with liquid during the spray, brush or dip application of lacquers containing ethyl formate | A,B | Local exhaust ventilation; general dilution ventilation; personal protective equipment (goggles, respiratory protection, gloves) |
| 2. | Inhalation of vapor and skin contact with liquid during the use as a solvent for cellulose acetate in artificial silk manufacture | A,B | General dilution ventilation; personal protective equipment (chemical goggles and barrier creams) |
| 3. | Inhalation of vapor and skin contact with liquid during the use in the shoe industry to dissolve celluloid heel coverings | A,B | General dilution ventilation; personal protective equipment (goggles) |
| 4. | Inhalation of vapor and skin contact with liquid during use as a solvent in the manufacture of artificial leather | A,B | General dilution ventilation; personal protective equipment (gloves) |
| 5. | Inhalation of vapor and skin contact with liquid during the manufacture of safety glass | A,B | General dilution ventilation |
| 6. | Inhalation of vapor and skin contact with liquid during the use as a fumigant and larvacide for tobacco, cereals and dried fruits | A,B | Personal protective equipment (gloves, respiratory protection) |
| 7. | Inhalation of vapor during the use as an intermediate in organic synthesis | A | General dilution ventilation |
| 8. | Inhalation of vapor during the formulation of synthetic flavors | A | General dilution ventilation |
| 9. | Inhalation of vapor and | A | Process enclosure; general |

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skin contact with liquid
during the synthesis
of ethyl formate

dilution ventilation

- A -- Inhalation
- B -- Skin contact resulting in
localized irritation
- C -- Ingestion
- D -- Skin contact resulting in
absorption and subsequent
systemic poisoning