

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** DIOXANE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for DIOXANE

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 DIOXANE.

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 dioxane in concentrations not in excess of 100 parts per million (ppm) (360 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 dioxane.

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

(c) EXPOSURE MEASUREMENT

- (1) INITIAL DETERMINATION - Each employer who has a place of employment in which dioxane is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of dioxane 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 dioxane. 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 dioxane;
 - (ii) Any measurements of airborne concentrations of dioxane taken;
 - (iii) Any employee complaints of symptoms which may be attributable to exposure to dioxane; 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 dioxane 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 dioxane 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 dioxane 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.
- (5) EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE - If an employee exposure measurement reveals that an employee is exposed to airborne

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concentrations of dioxane above the permissible exposure, the employer shall:

- (i) Inform the employee of the exposure as required by paragraph (K)(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 dioxane 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 dioxane 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 dioxane 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 dioxane is present in concentrations greater than 5000 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 dioxane 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:

- a. During the time period necessary to install engineering controls; or

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- 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), and (f).

TABLE 2 RESPIRATORY PROTECTION FOR DIOXANE

| CONDITION | PERMISSIBLE RESPIRATORY PROTECTION |
|---|---|
| Vapor Concentration | |
| Equal to or less than 2000 ppm | Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece. |
| Greater than 2000 ppm or escape and entry from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure demand or other positive pressure or continuous flow mode and an auxiliary self-contained breathing apparatus 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 providing protection against organic vapors. |

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Any escape self-contained breathing
apparatus.

(f) Fire and Safety

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

- (1) Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of dioxane shall be Class I Group C.
- (2) Portable fire extinguishers - For the purposes of compliance with section 1910.157, dioxane 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 dioxane shall be Class I Group C.
- (4) Flammable liquids - For the purposes of compliance with section 1910.106, liquid dioxane 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 dioxane is handled, used or stored in a manner so as to create a potential fire or explosion hazard.
- (6) Storage - Dioxane shall be stored so as not to come in contact with strong oxidizers, moisture and heat. Stored lots of dioxane shall be checked for the presence of explosive peroxides. Dioxane containing peroxides may not be distilled to dryness.

(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 dioxane. Face shields shall comply with section 1910.133(a)(6).
- (ii) Employers shall ensure that non-impervious clothing contaminated with liquid dioxane be removed promptly and not reworn until the dioxane is removed from the clothing.
- (iii) Employers shall ensure that clothing which becomes wet with liquid dioxane be removed immediately and not reworn until the dioxane is removed from the clothing.
- (iv) Employers shall ensure that clothing wet with liquid dioxane is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of dioxane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dioxane, the employer shall inform the person performing the operation of the hazardous properties of dioxane.

(2) Eye Contact

- (i) Employers shall provide, and require employees to use, splash-proof safety goggles (cup-cover type dust and splash

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safety goggles), which comply with section 1910.133 (a)(6), where eye contact to liquid dioxane may occur.

- (h) Spills
 - (1) Spills of dioxane shall be cleaned up immediately after eliminating potential sources of ignition and utilizing available ventilation.
 - (2) Liquid dioxane 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 dioxane promptly wash or shower to remove any dioxane from the skin.
 - (2) Employers shall ensure that employees do not eat or smoke in areas where liquid dioxane is handled, processed or stored.
 - (3) Employers shall ensure that employees who handle liquid dioxane wash their hands thoroughly with soap or mild detergent and water before eating, smoking or using toilet facilities.
 - (iv) Employers shall ensure that clothing wet with liquid dioxane is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of dioxane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dioxane, the employer shall inform the person performing the operation of the hazardous properties of dioxane.
- (j) Training and Information - Each employer who has employees exposed to dioxane in excess of the action level, or employees who may have skin or eye contact with liquid dioxane, or employees who work where accidental release, spill, fire, or explosion of dioxane may occur, shall annually:
 - (1) Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for dioxane, which is contained in Appendix A; and
 - (2) Medical -
 - (I) Advise employees as to the signs and symptoms of exposure to dioxane.
 - (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to dioxane which are listed in Appendix A.
 - (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 dioxane.
 - (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 Examination - The employer shall make available to each employee who is to be exposed to liquid dioxane or airborne concentrations of dioxane at or above the action level or is at risk

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- to skin exposure, a medical examination which shall include as a minimum the following:
- (i) A medical history and physical examination with emphasis on the liver and kidneys.
 - (ii) A profile of liver function.
 - (iii) Urinalysis to include specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.
- (3) The employer shall obtain from the physician, as a record of the examination, the following information:
- (i) The physician's written opinion stating whether or not the employee has any detected medical conditions which would place him at increased risk from exposure to dioxane.
 - (ii) A record of the results of liver function tests.
 - (iii) A record of the results of urinalysis.
- (4) Periodic Examinations - The employer shall make available to each employee, exposed to dioxane in excess of the action level at 12 months from the date of the employee's first exposure, and at every 12 months of exposure above the action level thereafter, a medical examination which must include the following:
- (i) A medical history and physical examination (see (k)(2)(i) of this section).
 - (ii) Tests of liver function (see (k)(2)(ii) of this section).
 - (iii) Urinalysis (see (k)(2)(III) of this section).
- (5) The employer shall obtain from the physician, as a record of the periodic examination, the following information:
- (i) The physician's written opinion stating whether or not the employee has any detected medical conditions which would place him at increased risk to further exposure to dioxane.
 - (ii) A record of the results of liver function tests.
 - (iii) A record of the results of urinalysis.
- (6) Exclusion or Removal from Exposure - No employee shall be exposed to dioxane if such exposure could place the employee at increased risk of material impairment of his health.
- (7) Emergency Procedures - The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to dioxane.
- (8) 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 dioxane;
 - (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.
- (9) Physician's Written Opinion
- (i) The physician's written opinion shall be a signed statement by the examining physician specifically stating:

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- (A) Whether the employee has any detected medical conditions which could be directly or indirectly aggravated by exposure to dioxane 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 on the employee's exposure to dioxane.
 - (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 dioxane.
- (10) Alternative Medical Examinations - If the examining physician chooses to use alternative medical examinations to those specified in sections (2) and (4), the employer may accept such alternative medical surveillance examinations as meeting the requirements of this part provided that the employer:
- (i) Obtains a statement from the examining physician setting forth the alternative medical examinations and the rationale for substitution and evidence that they will be equally effective.
 - (ii) Informs each exposed employee of the fact that alternative medical examinations to those required in section (2) or (4) above are to be made available.
- (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 dioxane.
 - (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 dioxane which is being monitored;
 - (d) Sampling and analytical methods used and evidence of their accuracy;
 - (e) Number, duration, and results of samples taken;

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- (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;
 - (c) Result of measurement.
 - (iii) This record shall be maintained for at least one year.
- (4) Annual training.
 - (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 employee 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) Results of tests required in Section (k)(3) and (k)(5) of this section;
 - (b) Physician's written opinion;
 - (c) Any employee medical complaints relative to exposure to dioxane;
 - (d) A signed statement of any refusal to be examined;
 - (e) A copy of information provided to the physician pursuant to paragraph (k)(8) (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 employee 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 dioxane which is conducted pursuant to this section.

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- (2) Exercise of opportunity to observe monitoring.
 - (i) When observation of the monitoring of employee exposure to dioxane 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 dioxane 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 dioxane above the permissible exposure. The employee shall also be notified of the level of his exposure and 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 IDENTIFICATION

SUBSTANCE: Dioxane (Diethylene Dioxide)

PERMISSIBLE EXPOSURE: 100 parts of dioxane per million parts of air (ppm) or 360 milligrams of dioxane per cubic meter of air (mg/cu m)

APPEARANCE AND ODOR: Colorless liquid with a mild ether-like odor

II. HEALTH HAZARD DATA

A. Ways in Which the Chemical Affects Your Body: Dioxane can affect your body if you inhale it or if it comes in contact with your eyes or skin, or if you swallow it. It may enter your body through the skin.

B. Effects of Overexposure:

1. Overexposure to dioxane may cause irritation of the eyes, nose and throat. It may also cause drowsiness, dizziness, loss of appetite, headache, nausea and vomiting, stomach pain and liver and kidney damage. Prolonged skin exposure to the liquid may cause drying and cracking.

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

III. EMERGENCY FIRST AID PROCEDURES

A. Eye Exposure: If dioxane gets into your eyes, wash the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing get medical attention. Contact lenses should not be worn when working with this chemical.

B. Skin Exposure: If dioxane gets on your skin, promptly wash the contaminated skin with water. If dioxane soaks through your clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing get medical attention. Do not wear the clothing again until the dioxane is removed. Replace or repair impervious clothing that has developed leaks.

C. Breathing: If you or any other person breathes in large amounts of dioxane 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 dioxane 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 the 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 dioxane. You can only be required to wear them for routine use if your employer is in the process of installing controls or if 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 dioxane 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 repeated or prolonged skin contact with liquid dioxane.
- C. EYE PROTECTION: You must wear splash-proof safety goggles (cup-cover type dust and splash safety goggles) where eye contact with liquid dioxane may occur.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Dioxane is a flammable liquid and its vapor easily forms explosive mixtures with air.
- B. Dioxane must be stored in tightly closed containers in a cool, well ventilated area away from heat, sparks, flames, moisture, and strong oxidizers.
- C. Sources of ignition such as smoking and open flames are prohibited wherever dioxane is handled, used or stored in a manner that could create a potential fire or explosion hazard.
- D. You must use non-sparking tools when opening or closing metal containers of dioxane, and containers must be bonded and grounded when pouring or transferring liquid dioxane.
- E. If your skin becomes contaminated with liquid dioxane, you must promptly wash or shower to remove the dioxane from your skin.
- F. Clothing wet with dioxane can be easily ignited. You must immediately remove any clothing that becomes wet with liquid dioxane and this clothing must not be reworn until the dioxane is removed from the clothing.

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- G. You must not eat or smoke in areas where liquid dioxane is handled, processed or stored.
- H. If you handle liquid dioxane, you must wash your hands thoroughly with soap or mild detergent and water before eating, smoking or using toilet facilities.
- I. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them.
- J. Ask your supervisor where dioxane is used in your work area and for any additional plant safety and health rules.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
DIOXANE

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Diethylene dioxide; diethylene ether; dioxan; p-dioxane; 1,4-dioxane
2. Formula: $OCH_2CH_2OCH_2CH_2$
3. Molecular weight: 88

B. Physical Data

1. Boiling point (760 mm Hg): 101 C (214 F)
2. Specific gravity (water=1): 1.03
3. Vapor density (air=1 at boiling point of dioxane): 3.0
4. Melting point: 11.8 C (53 F)
5. Vapor pressure at 20 C (68 F): 29 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): Miscible in all proportions
7. Evaporation rate (butyl acetate=1): 2.7
8. Appearance and odor: Colorless liquid with a mild ether-like odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: 12 C (54 F) (closed cup)
2. Autoignition temperature: 180 C (356 F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 22.0
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: Dioxane is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where dioxane is handled, used or stored. Dioxane 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 dioxane is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, dioxane is classified as a Class IB flammable liquid. At 5000 ppm, one-fourth of the lower flammable limit, dioxane 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 dioxane shall be Class I Group C.

B. Reactivity

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1. Conditions contributing to instability: Heat, long exposure to moisture.
2. Incompatibilities: Contact with strong oxidizing agents may cause fire and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dioxane.
4. Special precautions: Dioxane is hygroscopic and will produce peroxides in the presence of moisture. Dioxane containing peroxides should not be distilled to dryness because of the potential explosion of non-volatile peroxides.

III. SPILL, LEAK AND DISPOSAL PROCEDURES

- A. If dioxane 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 duct work, then burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber. Dioxane 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:

Dioxane 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 eight-hour exposure may be determined from a single eight-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 eight-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 dioxane 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 dioxane to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.

V. MISCELLANEOUS PRECAUTIONS

- A. Store dioxane in tightly closed containers in a cool, well-ventilated area.
- B. High exposures to dioxane can occur when transferring the liquid from one container to another.
- C. Non-sparking tools must be used to open and close metal dioxane containers. These containers must be effectively grounded and bonded prior to pouring.
- D. Dioxane in storage must be checked for peroxide content in accordance with manufacturers' recommendations.
- E. Employers must advise employees of all plant areas and operations where exposure to dioxane could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to dioxane is likely to occur are: its use as a solvent for resin-based varnishes, lacquers, paints, fats, oils, waxes, greases, resins; its use as a solvent in the pulping of wood; its use as a wetting agent and degreaser; in the formulation and use of paint and varnish removers; its use in the preparation of cosmetics, deodorants and detergents; and its use in purifying drugs.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation; skin absorption.

II. TOXICOLOGY

Dioxane vapor is a mucous membrane irritant, and on prolonged exposure is toxic to the liver and kidneys. Repeated exposure of several animal species to 1,000 ppm produced damage to kidneys and liver and the repeated inhalation of 800 ppm over 30 days resulted in fatal kidney injury in some rabbits. Human volunteers exposed for 15 minutes to 300 ppm reported mild transient irritation of the eyes, nose and throat. There is significant absorption of the liquid through the skin, adding to the inhalation hazard. Prolonged or repeated skin contact may also result in drying and cracking due to defatting action. Fatal intoxication due to liver necrosis and severe kidney damage has been reported in workers after two months of heavy exposure to dioxane vapor; the onset of poisoning was marked by drowsiness and headache, nausea, vomiting and irritation of the eyes and respiratory passages. In another fatal case there was significant damage to the brain as well as to liver and kidney. Due to its mild odor, serious or fatal exposures have been experienced without forewarning. Tumors of the nose, liver, and lungs have been reported in animals following ingestion of high concentrations of dioxane. Immersion of chick embryos in dioxane has been reported to cause possible mutagenic effects. The significance of these findings in humans is unknown.

III. SIGNS AND SYMPTOMS

Drowsiness and headache; nausea and vomiting; irritation of the eyes, nose and throat; prolonged heavy exposure may produce liver damage and renal failure; skin irritation.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Flush eyes with water and wash skin with soap and water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation if indicated.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of dioxane are caused by its irritant effect on mucous membranes, and on prolonged heavy exposure, by its serious toxic effects on liver and kidneys. Tumors and mutagenic effects

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have been reported in animals. It is important that the physician becomes familiar with plant operating conditions in which exposure to dioxane 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

The following medical procedures must be made available to each employee who is exposed to dioxane:

1. A complete history and physical examination -- The purpose is to detect preexisting conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.
2. Liver function tests -- Dioxane may cause liver damage. A profile of liver function shall be obtained by utilizing a medically acceptable array of biochemical tests.
3. Urinalysis -- Since kidney damage has also been observed from exposure, a urinalysis shall be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated on an annual basis.

References

1. American Conference of Governmental Industrial Hygienists: "Dioxane," (3d ed., 2d printing), Documentation of the Threshold Limit Values for Substances in Workroom Air, Cincinnati, 1974, p. 316-317.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1537-1541.
3. Hygienic Guide Series: "Dioxane," American Industrial Hygiene Association Journal, 21:533-534, 1960.
4. Browning, Ethel: Toxicity and Metabolism of Industrial Solvents, Elsevier Publishing Company, Amsterdam, 1965, pp. 722-727.

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- (d) Methods of Compliance - Open surface tank classification based on relative evaporation rate of 2.5 hours. A. K. Doolittle, "The Technology of Solvents and Plasticizers", John Wiley & Sons, Inc., New York, 1954, pp. 354-357.
- (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. 13.
- (f) Personal Protective Equipment, and, (h) Sanitation
- Eye: Union Carbide Toxicology Study; Patty, "Ind. Hyg. and Tox."; Grant, "Toxicology of the Eye"
- Skin: Documentation of TLV's; Union Carbide Toxicology Study; and Patty, "Ind. Hyg. and Tox."
- Ingestion: Documentation of TLV's; Union Carbide Toxicology Study; Patty, "Ind. Hyg. and Tox."; and PHS-149, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity"

COMMENTS

Eye - Classification: 2

Output statement numbers: 10

Exceptions: None

Union Carbide reports that "one average-sized drop of the chemical causes burns in the rabbit eye while a small droplet, as from a fine spray, causes minor injury." Patty notes that the liquid is painful and irritating to the eye. Grant, in summarizing the work of others, states that, "dioxane has caused no serious disturbances by external contact with the eye. In human beings, irritation of the eye is noted only at concentrations greater than 220 ppm of vapor in air, and testing by drop application on rabbit corneas causes mild transient injury, graded 4 on a scale of 1 to 10 after 24 hours."

Based on Grant's statement that any injury caused is transie a classification of 2 is concluded to be appropriate.

Skin - Classification: 2

Output statement numbers: 2, 17g and 21 combined, 17i, 20a

Exceptions: 7 deleted because of evaporation rate,

17 substituted for 16

The Documentation of TLV's's has the notation "skin" after the name of the chemical because one of its sources indicated that "there was a possibility of skin absorption." Union Carbide gives a rabbit skin penetration LD50 of 7.6 ml/kg. It is noted that "the undiluted chemical caused no reaction on the tender skin of the rabbit belly greater than a faint redness of short duration." Patty reports that it is "irritating to the skin upon prolonged or repeated contact, and can be absorbed through the skin in toxic amounts." It is noted that repeated topical applications have caused liver and kidney injury in rabbits

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and guinea pigs.

Dioxane has a vapor pressure of 29 mm Hg at 20 degrees C. It is miscible in all proportions with water and has a flash point of 54 degrees F.

A classification of 2 is concluded to be sufficient to prevent local and systemic effects from skin contact. To be noted is that though the substance can be absorbed through intact skin in toxic amounts, the skin penetration LD50 suggests that it is not rapidly absorbed.

Ingestion - Classification: 1

Output statement numbers: 19, 20a

Exceptions: None

Documentation of TLV's reports "that dogs given dioxane orally over a period of 9 days died after a total consumption of about 3 g/kg, with severe liver and kidney damage." Union Carbide gives an acute oral rat LD50 of 7.12 g/kg and notes that isopropyl alcohol is more toxic. Spector gives the above LD50 plus others for rats, guinea pigs, and rabbits which range from 2.17 - 6.0 g/kg. Patty considers it low in single-dose oral toxicity. PHS-149 gives the results of long-term feeding studies with rats given small amounts in their drinking water. Total doses of slightly more than 100 grams administered over 1 to 1.5 years produced carcinogenic activity.

The possible carcinogenicity of this substance leads to the conclusion that a classification of 1 is warranted.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Dioxane (diethylene dioxide)

D. O. L. STANDARD: 100 ppm

WARNING PROPERTIES:

Odor Threshold: Summer reports an odor threshold of 170 ppm; Staub reports 2.7 and 170 ppm.

Eye Irritation Level: Grant states that "in human beings, irritation of the eye is noted only concentrations greater than 220 ppm of vapor in air." Patty states that at 300 ppm, dioxane "caused irritation of the eyes, nose, and throat; and at 500 ppm, it was objectionable. Even at higher concentrations, the initial irritation to eyes and respiratory passages is transitory . . ."

Evaluation of Warning Properties: Patty states that the initial irritation produced by exposure to dioxane is transitory and that the "warning properties of dioxane are completely inadequate to prevent exposure to toxic amounts." The AIHA Hygienic Guides also note that "the vapor has poor warning properties and can be inhaled in amount which may cause serious intoxication or death with injury of the liver and kidneys." For the purposes of this standard, gas sorbent respiratory equipment is not permitted.

-IDLH: 2000 ppm

Basis for IDLH Value: Based upon the acute inhalation toxicity information given by the AIHA Hygienic Guides in which a lethal concentration of 1000 - 3000 for three hours is reported for guinea pigs, and upon the lethal concentration of 2085 ppm for mice (8 hrs.) reported by Spector, an IDLH of 2000 ppm is assumed. Since the Documentation of TLV's states that guinea pigs "could

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tolerate 2000 ppm for several hours without serious symptoms," exposure humans to 2000 ppm for a half-hour probably would not impede escape or cause any irreversible health effects.

Other Toxicological Information: Patty states that "Yant et al. exposed guinea pigs for 3 hours to concentrations of from 1000 to 30,000 ppm. Gross exposed rats, mice, guinea pigs, and rabbits for 8 hours to concentrations ranging from 4000 to 11,000 ppm. At the higher concentrations, marked irritation of the mucous membranes was apparent. Deaths occurring during exposure or shortly afterwards were usually due to respiratory failure because of lung edema, but the animals also exhibited congestion of the brain. Delayed deaths were usually due to pneumonia. Liver and kidney injuries were almost always apparent upon microscopic examination in animals dying days after exposure and in those apparently recovering if they were killed several days after exposure."

The AIHA Hygienic Guides state that "animal studies suggest that single exposure to less than 1000 ppm for a period not over one-half hour would be relatively safe. One-and-one-half hour exposures to 1,000 ppm repeated twice daily for five to sixty-seven weeks produced severe liver kidney injury, but no deaths in several animal species. (The) atmospheric concentrations immediately hazardous to life (is) not known for humans. A single three-hour exposure to 30,000 ppm (near saturation) is fatal to animals."

According to the Chemical Company Guides of Union Carbide Corporation "breathing a concentration of vapors at 4000 parts per million in air for four hours was not fatal to six animals (rats). Repeated breathing of that concentration, seven hours a day for thirty days, was not fatal to twenty rats so exposed. A concentration of 8,000 parts per million killed eighteen rats exposed for the same period of time."

Browning gives lethal concentrations by inhalation "for guinea pig 1000 - 3000 ppm for 3h or more; mice, 8000 ppm; cats, 10,900 ppm (death sometimes delayed for several days); for mice, rats, guinea pigs and rabbits 4000 - 11000 ppm."

According to the Documentation of the TLV's, "Yant and associates found that guinea pigs could tolerate 2000 ppm for several hours without serious symptoms . . . Fairley et al. found that animals survived exposures of 2000 ppm for three hours a day up to a total of 100 hours, but that even 1000 ppm caused injury to kidneys and liver . . . The TLV of 100 ppm is believed to be low enough to prevent systemic poisoning."

Spector gives the following information concerning animal exposure to dioxane:

| Animal | Dose | Concentration ppm | Exposure time | Time of death |
|------------|------|----------------------|------------------|------------------|
| Mouse | LC | 2085 | 8 hr | 21 1/2 |
| - Mouse | LC | 10,000 | Cont | 3 hr |
| Mouse | LC | 5000 | Cont | 3-51 hr |
| Rat | LC | 10,000 | Cont | 3-10 1/2 |
| Rat | LC | 5000 | Cont | 9-15 hr |
| Guinea Pig | LC | 10,000 | Cont | 3-7 1/2 |
| Guinea Pig | LC | 5000 | Cont | 43.5 hr |

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| | | | | |
|--------|----|--------|---------|---------|
| Rabbit | LC | 5000 | Cont | 16.5 hr |
| Cat | LC | 18,000 | 258 min | 4-5 da |

LFL: 20,000 ppm

VAPOR PRESSURE AT 20 C: 29 mm Hg

SATURATED CONCENTRATION AT 20 C: Approximately 38,200 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT
DIOXANE

| Use/Exposure | Principal Route of Entry | Currently Used Control Methods |
|---|--------------------------|--|
| 1. Inhalation of vapor during spray application of natural and synthetic resin-based varnishes, lacquers, and paints | A | Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices) |
| 2. Inhalation of vapor during application of natural and synthetic resin-based varnishes, lacquers, and paints by dipping, roller coating, tumbling, knifing or brushing | A | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices) |
| 3. Inhalation of vapor and skin contact with liquid during cleaning and maintenance of dioxane processing equipment such as reactors and storage vessels | A, B, D | Personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 4. Inhalation of vapor and skin contact with liquid during use as a solvent for fats and oils, waxes, greases, natural resins such as cellulose (surface coatings and adhesives), and synthetic resins such as polycarbonate, polyvinyl chloride, polyvinyl acetate, acetate butyrate, and epoxies (surface coating, adhesives and structural components) | A, B, D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 5. Inhalation of vapor and skin contact with liquid during use as a wetting agent in textile processing, dye baths, and stain and printing compositions | A, B, D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 6. Inhalation of vapor and skin | A, B, D | Local exhaust ventilation; |

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| | | |
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| contact with liquid during use of varnish, lacquer, and paint removers | | general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 7. Inhalation of vapor during air or oven drying of natural and synthetic resin-based varnishes, lacquers, and paints | A | Local exhaust ventilation; general dilution ventilation |
| 8. Inhalation of vapor and skin contact with liquid when used as a degreaser | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 9. Inhalation of vapor and when used as a dehydrating agent in the preparation of histological slides | A | Local exhaust ventilation |
| 10. Inhalation of vapor and skin contact with liquid when used during the manufacture of detergents and other cleaning preparations | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective devices, gloves, aprons, eye goggles) |
| 11. Inhalation of vapor and skin contact with liquid when used in the manufacture of polishing compounds | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 12. Inhalation of vapor and skin contact with liquid when used as a solvent in the pulping of wood | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective devices, gloves, aprons, eye goggles) |
| 13. Inhalation of vapor and skin contact with liquid when used in the manufacture of polishing compounds | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 14. Inhalation of vapor and skin contact with liquid | A,B,D | Local exhaust ventilation; general dilution ventila- |

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| | | |
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| when used as a stabilizer for chlorinated solvents | | tion; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 15. Inhalation of vapor and skin contact with liquid when used in the pre- paration of cosmetics and deodorants | A,B,D | Local exhaust ventilation; general dilution ventila- tion; personal protective equipment (respiratory protecti- ve devices, gloves, aprons, eye goggles) |
| 16. Inhalation of vapor and skin contact with liquid when used to purify drugs such as aspirin by recrystallization | A,B,D | Local exhaust ventilation; general dilution ventila- tion; personal protective equipment (respiratory protective devices, gloves, aprons, eye goggles) |
| 17. Inhalation of vapor and skin contact with liquid during use as a working fluid for scintillation counter samples | A,B,D | General dilution ventila- tion; personal protective equipment (gloves, eye goggles) |

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