

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** METHYLAL ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

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 METHYLAL.

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.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

(a) DEFINITIONS

- (1) PERMISSIBLE EXPOSURE - "Permissible Exposure" means inhalation of methylal in concentrations not in excess of 1,000 parts per million (ppm) (3,100 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 methylal.

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

(c) EXPOSURE MEASUREMENT

- (1) INITIAL DETERMINATION - Each employer who has a place of employment in which methylal is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of methylal 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 methylal. 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 methylal;
 - (ii) Any measurements of airborne concentrations of methylal taken;
 - (iii) Any employee complaints of symptoms which may be attributable to exposure to methylal; 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 methylal 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 methylal 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 methylal 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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

concentrations of methylal 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 methylal 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 methylal 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 methylal 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 methylal is present in concentrations greater than 4000 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 methylal 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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

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

TABLE 2. RESPIRATORY PROTECTION FOR METHYLAL

Condition	Permissible Respiratory Protection
Vapor Concentration	
Equal to or less than 8,000 ppm	
Equal to or less than 15,000	
Greater than 15,000 ppm or Entry & Escape from Unknown Concentrations	demand or other positive pressure or continuous flow mode or an auxiliary self-contained air supply operated in pressure demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.
(f) Fire and Safety	

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

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

- (1) Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of methylal shall be Class I Group C.
- (2) Portable fire extinguishers - For the purposes of compliance with section 1910.157, methylal 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 methylal shall be Class I Group C.
- (4) Flammable liquids - For the purposes of compliance with section 1910.106, liquid methylal 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 methylal is handled, used or stored in a manner so as to create a potential fire or explosion hazard.
- (6) Storage - Methylal shall be stored so as not to come in contact with strong oxidizers or acids.

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

(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 methylal may occur.

(h) Spills

- (1) Spills of methylal shall be cleaned up immediately after eliminating potential sources of ignition and utilizing available ventilation.
- (2) Liquid methylal may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

(i) Sanitation

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

- (1) Employers shall ensure that employees whose skin becomes wet with liquid methylal, promptly wash or shower to remove any methylal from the skin.
- (j) Training and Information - Each employer who has employees exposed to methylal in excess of the action level, or employees who may have skin or eye contact with liquid methylal, or employees who work where accidental release, spill, fire, or explosion of methylal may occur, shall annually:
 - (1) Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for methylal, which is contained in Appendix A; and
 - (2) Medical -
 - (I) Advise employees as to the signs and symptoms of exposure to methylal.
 - (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to methylal 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 methylal.
 - (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 methylal, or airborne concentrations of methylal at or above the action level, a written statement as to whether such employee has a history of any of the following:
 - (I) Skin disease
 - (II) Liver disease
 - (III) Kidney disease
 - (IV) Chronic lung disease
 - (3) Preplacement Medical Examination - The employer shall provide a medical examination for an employee if the employee provides a history of any of the conditions named in paragraph (k)(2).
 - (4) Results of Preplacement Examination - The employer shall obtain a physician's written opinion based on the medical examination pursuant to paragraph (k)(3).
 - (5) Periodic Medical Examinations - The employer shall provide a medical examination for an employee if the employee advises the employer of the development of:
 - (I) Any of the medical conditions listed in (k)(2).
 - (II) Signs and symptoms listed in Appendix A which the employee suspects may be caused by exposure to

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

methylal.

- (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 methylal 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 methylal.
- (9) Informing the Physician - The employer shall provide to the examining physician the following information:
 - (I) A copy of this section with its Appendices A, B, and C;
 - (II) A description of the employee's duties as they relate to his exposure to methylal;
 - (III) A description of any personal protective equipment, including respirators, required to be used;
 - (IV) The results of any employee's exposure measurement, if available;
 - (V) The employee's anticipated exposure level; and
 - (VI) Upon request of the physician, information from previous medical examination of the employee.
- (10) Physician's Written Opinion
 - (I) The physician's written opinion shall be a signed statement by the examining physician specifically stating:
 - (A) Whether the employee has any detected medical conditions which could be directly or indirectly aggravated by exposure to methylal 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 methylal.
 - (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 methylal.
- (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.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

- (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 methylal.
 - (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 methylal which are being monitored;
 - (d) Sampling and analytical methods used and evidence of their accuracy;
 - (e) Number, duration, and results of samples taken;
 - (f) Name, Social Security number, and exposure of the employee monitored.
 - (iii) This record shall be maintained until replaced by a more recent record but in no event for less than one year.
- (3) Mechanical ventilation.
- (i) When mechanical ventilation is used as an engineering control, the employer shall maintain a record of measurements demonstrating the effectiveness of such ventilation as required by paragraph (e)(1)(i) of this section.
 - (ii) This record shall include:
 - (a) Date of measurement;
 - (b) Type of measurement taken;
 - (c) Result of measurement.
 - (iii) This record shall be maintained for at least one year.
- (4) Training and information.
- (i) The employer shall keep an accurate record of all employee training and advice required by paragraph (j) of this section.
 - (ii) The record shall include:
 - (a) Date of training;
 - (b) Name and Social Security number of employees trained;
 - (c) Substance of training provided.
 - (iii) This record shall be maintained until replaced by a more recent record.
- (5) Medical records.
- (i) The employer shall keep an accurate medical record for each employee.
 - (ii) The record shall include:
 - (a) Physician's written opinion;
 - (b) Preplacement questionnaire;
 - (c) Any employee medical complaints relative to exposure to met.
 - (d) A signed statement of any refusal to be examined;

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

- (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 methylal which is conducted pursuant to this section.
 - (2) Exercise of opportunity to observe monitoring.
 - (i) When observation of the monitoring of employee exposure to methylal 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 methylal 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 methylal 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.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

APPENDIX A

SUBSTANCE SAFETY DATA SHEET

SUBSTANCE TECHNICAL GUIDELINES

I. SUBSTANCE IDENTIFICATION

SUBSTANCE: Methylal (Dimethoxymethane)

PERMISSIBLE EXPOSURE: 1000 parts of Methylal per million parts
of air (ppm) or 3100 milligrams of methylal per cubic meter
of air (mg/cu m)

APPEARANCE AND ODOR: Colorless liquid with a mild pungent odor.

II. HEALTH HAZARD DATA

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

B. Effects of Overexposure:

1. Short-Term Overexposure: Overexposure to methylal may cause irritation of the eyes, nose and throat, light headedness, incoordination, and unconsciousness.
2. Long-Term Overexposure: Prolonged overexposure to methylal 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 methylal exposure.

III. EMERGENCY FIRST AID PROCEDURES

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

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

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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

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

- D. Swallowing: When methylal 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 methylal. You can only be required to wear them for routine use if your employer is in the process of installing controls or other control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA)/National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where their use is required. If you can smell methylal 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 methylal.
- C. EYE PROTECTION: You must wear splash-proof safety goggles (cup - cover type dust and splash safety goggles) where eye contact to liquid methylal may occur.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

Methylal 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, flames, acids and strong oxidizers. Sources of ignition such as smoking and open flames are prohibited wherever methylal 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 methylal, and containers must be bonded and grounded when pouring or transferring liquid methylal. If your skin becomes wet with liquid methylal, you must promptly wash or shower to remove the methylal from your skin. You must immediately remove any clothing that becomes wet with liquid methylal and this clothing must not be reworn until the methylal is removed from the

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

clothing. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them. Ask your supervisor where methylal is used in your work area and for any additional plant safety and health rules.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
METHYLAL

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Dimethoxymethane; methyl formal; formal;
dimethylacetal formaldehyde
2. Formula: $\text{CH}_3\text{OCH}_2\text{OCH}_3$
3. Molecular weight: 76

B. Physical Data

1. Boiling point (760 mm Hg): 44 C (111 F)
2. Specific gravity (water=1): 0.86
3. Vapor density (air=1 at boiling point of methylal): 2.6
4. Melting point: -105 C (-157 F)
5. Vapor pressure at 20 C (68 F): 330 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): 33
7. Evaporation rate (butyl acetate = 1): 23.1
8. Appearance and odor: Colorless liquid with a pungent odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: -18 C (0 F) (open cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6;
Upper: 17.6
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: Methylal is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where methylal is handled, used or stored. Methylal 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 methylal is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, methylal is classified as a Class IB flammable liquid. At 4000 ppm, one-fourth of the lower flammable limit, methylal 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 methylal shall be Class I Group C.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

B. Reactivity

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fire and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber and coatings

III. SPILL, LEAK AND DISPOSAL PROCEDURES

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

1. Remove all ignition sources
2. Ventilate area of spill or leak
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear the hood ductwork, then burn the paper. Large quantities may be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal 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:

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

IV. MONITORING AND MEASUREMENT PROCEDURES

a. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, gas and vapor adsorption tubes with subsequent chemical analyses or dosimeters. The method of measurement must determine the concentration of methylal 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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of methylal to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.

V. MISCELLANEOUS PRECAUTIONS

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

VI. COMMON OPERATIONS

Common operations in which exposure to methylal is likely to occur are: its use as a solvent for adhesives, protective coatings, resins, gums, waxes and for extraction of alkaloids, barbituates, organic acids and hydroxy-acids; during the formulation of special fuel additives for gasoline, rocket, jet and diesel engines; and its use as a chemical intermediate.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney and heart. At 4,000 ppm rats were unaffected by daily 6 hour exposures. Skin irritation may be expected to occur due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

III. SIGNS AND SYMPTOMS

Mild irritation of the eyes and upper respiratory tract at high concentrations; anesthetic effects at high concentrations; irritation of the skin from prolonged exposure.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

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

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of methylal are caused by its irritant properties. It is important that the physician becomes familiar with plant operating conditions in which exposure to methylal 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

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

medical conditions (listed below) which might place the employee at increased risk from methylal exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Skin disease -- Methylal 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.
2. Liver disease -- Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.
3. Kidney disease -- Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.
4. Chronic respiratory disease -- In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

C. PERIODIC EXAMINATIONS

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

References

1. American Conference of Governmental Industrial Hygienists: "Methylal (Dimethoxymethane)," (3d ed., 2d printing), Documentation of the Threshold Limit Values for Substances in Workroom Air, Cincinnati, 1974, pp. 154-155.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1984-1986.
3. Weaver, F.L., et al.: "Toxicity of Methylal," British Journal of Industrial Medicine, 8:279-283, 1951.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

REFERENCES AND SOURCES

METHYLAL

1910.93

- (d) Methods of Compliance - Open surface tank classification based on relative evaporation rate of approximately 0.35 hour.
- (e) Fire and Safety
- (1) Electrical - Classification based on "Fire Hazard Classification of Chemical Vapors Relative to Explosion-proof Electrical Equipment," H. Carhart et al., National Academy of Sciences, 1973, report to U. S. Coast Guard, report no. CG-D-92-74, p. 17.
- (f) Personal Protective Equipment, and (h) Sanitation
- Eye: Patty, "Ind. Hyg. and Tox.;" Grant, "Toxicology of the Eye"
- Skin: Sax, "Dangerous Properties of Ind. Materials;" Celanese Corp. Product Bulletin; and Patty, "Ind. Hyg. and Tox."
- Ingestion: Sax, "Dangerous Properties of Ind. Materials"

COMMENTS

Eye - Classification: 2

Output statement numbers: 10

Exceptions: None

Patty lists methylal vapor in a table as being moderately irritant to the eyes of guinea pigs. The following information from Grant indicates that methylal vapor can cause moderate eye irritation: "Because methylal is made from the notoriously toxic substances methyl alcohol and formaldehyde, it has been investigated with special attention to possible injurious effect on the eyes. Exposure of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially was found cause damage to the lungs, liver, heart, and kidneys, and caused occasional superficial irritation of the eyes. Furthermore, tests for free formaldehyde and formic acid in the vitreous humor and were negative." Based on the above available information, it is assumed that eye contact with the liquid causes no more than moderate irritation and that a classification of 2 is appropriate.

Skin - Classification: 2

Output statement numbers: 2, 7b, 16i, 21

Exceptions: None

Sax lists it as having no acute or chronic local effects. Celanese Product Bulletin simply states that "as with most organic solvents prolonged or repeated skin contact should be avoided." Patty states the same.

Methylal has a vapor pressure of 330 mm Hg at 20 degrees C. It is also 33% soluble in water and has a flash point of 0 degrees C.

A classification of 2 is concluded to be appropriate.

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

Sax reports ingestion to be of moderate toxic hazard. According to Patty, "no toxic effects from its industrial use have been recorded."

Given its high vapor pressure and no indication that the substance is highly toxic, it is concluded that ingestion would not present a hazard in the industrial environment.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

SUBSTANCE TECHNICAL GUIDELINES
METHYLAL

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Dimethoxymethane; methyl formal; formal;
dimethylacetal formaldehyde
2. Formula: $\text{CH}_3\text{OCH}_2\text{OCH}_3$
3. Molecular weight: 76

B. Physical Data

1. Boiling point (760 mm Hg): 44 C (111 F)
2. Specific gravity (water=1): 0.86
3. Vapor density (air=1 at boiling point of methylal): 2.6
4. Melting point: -105 C (-157 F)
5. Vapor pressure at 20 C (68 F): 330 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): 33
7. Evaporation rate (butyl acetate = 1): 23.1
8. Appearance and odor: Colorless liquid with a pungent odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: -18 C (0 F) (open cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6;
Upper: 17.6
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: Methylal is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where methylal is handled, used or stored in a manner that could create a potential fire or explosion hazard. Methylal 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 methylal is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, methylal is classified as a Class IB flammable liquid. For example, 4000 ppm, approximately one-fourth of the lower flammable limit, is one situation in which methylal 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 methylal shall be Class I Group C.

B. Reactivity

1. Conditions contributing to instability: Heat, presence of acids.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

2. Incompatibilities: Contact with strong oxidizing agents may cause fire and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber and coatings.

III. SPILL, LEAK AND DISPOSAL PROCEDURES

- A. If methylal is spilled or leaked, the following steps should be taken:
 1. Remove all ignition sources
 2. Ventilate area of spill or leak
 3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear the hood ductwork, then burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber. Methylal 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: Methylal 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 8-hour sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, gas and vapor adsorption tubes with subsequent chemical analyses or dosimeters. The method of measurement must determine the concentration of methylal 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 methylal to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.

V. MISCELLANEOUS PRECAUTIONS

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

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

VI. COMMON OPERATIONS

Common operations in which exposure to methylal is likely to occur are: its use as a solvent for adhesives, protective coatings, resins, gums, waxes and for extraction of alkaloids, barbituates, organic acids and hydroxy-acids; during the formulation of special fuel additives for gasoline, rocket, jet and diesel engines; and its use as a chemical intermediate.

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

USE/EXPOSURE AND CONTROL DOCUMENT
METHYLAL

Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1. Inhalation of vapor and skin or eye contact with liquid or vapor during use as a solvent for adhesives, resins, gums waxes and protective coatings	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
2. Inhalation of vapor and skin or eye contact with liquid or vapor during use as a solvent for the extraction of alkaloids, barbiturates, organic acids and hydroxy-acids	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
3. Inhalation of vapor and skin or eye contact with liquid or vapor during use in the manufacture of artificial resins	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
4. Inhalation of vapor and skin or eye contact with liquid or vapor during use as a gasoline and diesel fuel additive	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
5. Inhalation of vapor and skin or eye contact with liquid or vapor during use as a special fuel for rocket and jet engines	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
6. Inhalation of vapor and skin or eye contact with liquid or vapor during use as a reaction solvent (with acetylene or in Grignard and Reppe reaction)	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
7. Inhalation of vapor and skin or eye contact with liquid or vapor during use as source of formaldehyde and methanol	A,B	General dilution ventilation; process enclosure, where possible; personal protective equipment (gloves, goggles)
8. Inhalation of vapor and	A,B	General dilution ventila-

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for METHYLAL

skin or eye contact with
liquid or vapor during use
as methylating agent or
chemical intermediate

tion; process enclosure,
where possible; personal
protective equipment
(gloves, goggles)

9. Inhalation of vapor and
skin or eye contact with
liquid or vapor during
the manufacture of
perfume

A,B

General dilution ventila-
tion; process enclosure,
where possible; personal
protective equipment
(gloves, goggles)

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