Occupational Health Guideline for Methyl Formate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $HCOOCH_3$
- Synonyms: Methyl methanoate; formic acid, methyl ester
- Appearance and odor: Colorless liquid with a pleasant odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl formate is 100 parts of methyl formate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 250 milligrams of methyl formate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl formate can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to methyl formate may cause irritation of the eyes, nose, throat, and lungs. It may also cause drowsiness and, at high levels, unconsciousness and death.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl formate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl formate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methyl formate exposure.

—Eye disease: Methyl formate is an eye irritant. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl formate might cause exacerbation of symptoms due to its irritant properties.

—Neurological disorders: By analogy to effects observed in animals and by effects observed in humans, persons with pre-existing neurological disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methyl formate vapor at high concentrations is an irritant of the eyes and respiratory tract; it also causes narcosis in animals. Exposure of guinea pigs to 10,000 ppm for 3 hours was fatal; effects were eye and nose irritation, incoordination, narcosis, and pulmonary edema. Workers exposed to the vapor of a solvent containing 30% methyl formate, in addition to ethyl formate, methyl acetate, and ethyl acetate, complained of irritation of mucous membranes, oppression in the chest, dyspnea, symptoms of central nervous system depression, and temporary visual disturbances; air concentrations were not determined. No short-term effects were noted from experimental human exposures to 1500 ppm for 1 minute.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.1
2. Boiling point (760 mm Hg): 31.7 C (89 F)
3. Specific gravity (water = 1): 0.98
4. Vapor density (air = 1 at boiling point of methyl formate): 2.1
5. Melting point: −100 C (−148 F)
6. Vapor pressure at 20 C (68 F): 476 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 30
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as formic acid and carbon monoxide) may be released in a fire involving methyl formate.
4. Special precautions: Methyl formate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18.9 C (−2 F) (closed cup)
2. Autoignition temperature: 465 C (869 F)
3. Flammable limits in air, % by volume: Lower: 5.0; Upper: 23
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold of 2000 ppm for methyl formate. Browning, however, states that "men exposed for 1 minute to 1500 ppm of the vapour in air noticed the odour of methyl formate . . . ." Browning states that olfactory fatigue occurs, and thus odor may not be an effective warning of exposure to dangerous concentrations.
2. Eye Irritation Level: Grant states that the vapor of methyl formate "has been found to cause no eye irritation in experimental animals at a concentration of 1500 ppm in air, but does cause some irritation at 3500 ppm."
3. Other Information: According to Grant, methyl formate in high concentrations causes nasal irritation also, but quantitative information is not given.
4. Evaluation of Warning Properties: Since the thresholds of odor and of irritation are well above the permissible exposure limit, methyl formate is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for methyl formate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl formate.
- Clothing wet with liquid methyl formate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl formate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl formate, the person performing the operation should be informed of methyl formate's hazardous properties.
- Any clothing which becomes wet with liquid methyl formate should be removed immediately and not reworn until the methyl formate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl formate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl formate should be promptly washed or showered to remove any methyl formate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl formate may occur and control methods which may be effective in each case:

Operation	Controls
Use as insecticide and larvicide for fumigating dried fruits, nuts, tobacco, cereals, and infected clothing	Personal protective equipment
Use as a general industrial solvent for greases, fatty acids, cellulose acetate, collodion, and celluloid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for production of sulfa drugs, perfumes, dyes, military poison gases, and embalming fluid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of methyl formate	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid methyl formate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid methyl formate gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid methyl formate soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl formate, move 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.

• **Swallowing**

When methyl formate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the 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. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If methyl formate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Methyl formate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of methyl formate vapors are permitted.

• Waste disposal method:

Methyl formate may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL FORMATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3500 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.**
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand 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. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.