

Occupational Health Guideline for Methyl Methacrylate

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: $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$
- Synonyms: Methacrylic acid, methyl ester
- Appearance and odor: Colorless liquid with an acrid, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl methacrylate is 100 parts of methyl methacrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 410 milligrams of methyl methacrylate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- Routes of exposure
Methyl methacrylate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.
- Effects of overexposure
 1. *Short-term Exposure:* Overexposure to methyl methacrylate may cause irritation of the nose, throat, skin, and eyes. It may also cause drowsiness and, at very high levels, perhaps unconsciousness.
 2. *Long-term Exposure:* Prolonged exposure may cause a skin rash.
 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 methacrylate.

- Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to methyl methacrylate 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 methacrylate exposure.

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

—Skin disease: Methyl methacrylate can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although methyl methacrylate 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 possible impairment of renal function.

—Liver disease: Although methyl methacrylate 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.

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

- Summary of toxicology

The main toxic effect of methyl methacrylate is irritation of the respiratory tract by exposure to the vapor of the monomer. Rabbits exposed to 13,500 ppm for 3 hours died. Dust generated from the solid polymer is also irritating. Application to the eyes of rabbits caused irritation requiring several days for recovery. Dental technicians molding the polymer by hand developed dermatitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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: 100
2. Boiling point (760 mm Hg): 100 C (212 F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of methyl methacrylate): 3.6
5. Melting point: -48 C (-54 F)
6. Vapor pressure at 20 C (68 F): 35 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 3.1

• Reactivity

1. Conditions contributing to instability: Heat/and or lack of appropriate inhibitor concentration can cause methyl methacrylate to polymerize violently and burst container.

2. Incompatibilities: Contact with nitrates, oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and strong acids may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl methacrylate.

4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

• Flammability

1. Flash point: 10 C (50 F) (closed cup)
2. Autoignition temperature: 421 C (790 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.2
4. Extinguishant: Dry chemical, foam, carbon dioxide

• Warning properties

1. Odor Threshold: May reports an odor threshold for methyl methacrylate of 0.21 ppm.

2. Eye Irritation Level: According to Grant, "on application to rabbit eyes it (methyl methacrylate) has caused irritation requiring several days for recovery. The TLV is recommended "to protect against discomfort from irritation."

3. Other Information: According to the *Documentation of TLVs*, some "investigators noted irritation at 170 to 250 ppm, but workers tolerated without complaint levels approximating 200 ppm . . . It was the opinion of men in the field that 100 ppm could be tolerated continuously for 8 hours without discomfort."

4. Evaluation of Warning Properties: Since its odor threshold is below the permissible exposure limit, and since irritation occurs within 3 times the permissible exposure limit, methyl methacrylate is treated as a material with good 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

Sampling and analyses may be performed by collection of methyl methacrylate vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl methacrylate may be used. An analytical method for methyl methacrylate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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 methacrylate.

• Clothing wet with liquid methyl methacrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

methyl methacrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl methacrylate, the person performing the operation should be informed of methyl methacrylate's hazardous properties.

- Any clothing which becomes wet with liquid methyl methacrylate should be removed immediately and not reworn until the methyl methacrylate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl methacrylate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl methacrylate should be promptly washed or showered with soap or mild detergent and water to remove any methyl methacrylate.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use during casting of acrylic sheets	Local exhaust ventilation; personal protective equipment
Use during molding of acrylic sheets or polymethacrylate powders	Local exhaust ventilation; general dilution ventilation
Use during spray application of unsaturated polyester resins (surface coatings or structural components); use during brush or roller applications of unsaturated polyester resins (surface coatings or structural components)	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of methyl methacrylate resins for surface coatings; during polymerization to produce molding and extruding powders	Process enclosure; general dilution ventilation

Operation

Liberation during production of synthetic fibers; during manufacture of unsaturated polyester resins

Liberation during dye molding of articles from polyester resins; during production of emulsion polymers for use in adhesives, sealants, fabrics, sizes, leather finishes, paper coatings, polishes, etc.; during machining of articles from resins (acrylic plastics)

Controls

Process enclosure; local exhaust ventilation; general dilution ventilation

General dilution ventilation

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 methyl methacrylate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If methyl methacrylate gets on the skin, promptly flush the contaminated skin with water. If methyl methacrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• Breathing

If a person breathes in large amounts of methyl methacrylate, 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 methacrylate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• 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 methacrylate 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 collected and atomized in a suitable combustion chamber. Methyl methacrylate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Methyl methacrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.

2. By atomizing in a suitable combustion chamber.

REFERENCES

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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Material Safety Data Sheet - Methyl Methacrylate*, New York, 1971.

RESPIRATORY PROTECTION FOR METHYL METHACRYLATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4000 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.

