Occupational Health Guideline for Molybdenum and Insoluble Molybdenum

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.

APPLICABILITY

The general guidelines contained in this document apply to all molybdenum and insoluble molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic molybdenum

- Formula: Mo
- Synonyms: None
- Appearance: Silvery white metal or gray-black powder.

Molybdenum disulfide

- Formula: MoS_2
- Synonyms: Molybdenite
- Appearance and odor: Shiny gray, odorless plates.

Lead molybdate

- Formula: $PbMoO_4$
- Synonyms: Sulfenite
- Appearance and odor: Colorless to pale yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for molybdenum and insoluble molybdenum compounds is 15 milligrams of molybdenum and insoluble molybdenum compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for molybdenum and insoluble molybdenum compounds a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Molybdenum and insoluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Molybdenum trioxide has caused irritation of the eyes, nose, and throat, weight loss, and digestive disturbances in animals.

2. Long-term Exposure: Not 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 molybdenum and insoluble molybdenum compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to molybdenum and insoluble molybdenum compounds 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 molybdenum and insoluble molybdenum compounds exposure.

—Kidney disease: Fume from arcing molybdenum metal causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

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Public Health Service Centers for Disease Control
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—Chronic respiratory disease: Fume from arcing molybdenum metal causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of insoluble molybdenum compounds might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Fume from arcing molybdenum metal causes liver damage in animals. 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**

Molybdenum and its insoluble compounds, which include molybdenum disulfide, calcium molybdate, and many of the oxides and halides, have a low toxicity; however, molybdenum trioxide irritates the eyes and mucous membranes. Guinea pigs repeatedly exposed to molybdenum trioxide dust at a concentration of 200 mg molybdenum/m^3 for 1 hour daily developed nasal irritation, diarrhea, weight loss, and incoordination. In guinea pigs exposed to fume from arcing molybdenum metal, there were some deaths at 190 mg/m^3 but minimal effects at 53 mg/m^3; autopsy revealed bronchial and alveolar irritation with moderate fatty changes in the liver and kidneys. Animals receiving daily oral doses of up to 500 mg molybdenum per day in the form of molybdenum trioxide or calcium molybdate showed anorexia, listlessness, and weight loss. The metabolism of molybdenum is closely associated with that of copper; molybdenum toxicity to animals can be alleviated by the administration of copper. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of these enzymes. High intake of molybdenum in rats resulted in a substantial reduction in activity of sulfide oxidase in the liver. The reduced activity of this enzyme leads to accumulation of sulfide in the tissues and subsequent formation of highly undissociated copper sulfide, thus removing copper from metabolic activity. This is a probable explanation for the induction of copper deficiency by molybdate. High dietary intake of molybdenum has been reported to be associated with a gout-like disease and high blood uric acid.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Metallic molybdenum**

1. Molecular weight: 95.94
2. Boiling point (760 mm Hg): 5,560 C (10,040 F)
3. Specific gravity (water = 1): 10.22
4. Vapor density (air = 1 at boiling point of metallic molybdenum): Not applicable
5. Melting point: 2,610 C (4,730 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Molybdenum disulfide**

1. Molecular weight: 160.1
2. Boiling point (760 mm Hg): Oxidizes above 315 C (599 F)
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of molybdenum disulfide): Not applicable
5. Melting point: 1370 C (2498 F) (oxidizes above 315 C (599 F))
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Lead Molybdate**

1. Molecular weight: 367.1
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 6.8
4. Vapor density (air = 1 at boiling point of lead molybdate): Not applicable
5. Melting point: 1066 C (1950 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.000012
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of finely divided molybdenite with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as molybdenum oxide fume, sulfur dioxide gas, and carbon monoxide) may be released when insoluble molybdenum compounds decompose.
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: Molybdenum: 360 C (680 F) (layer); 720 C (1328 F) (cloud); Molybdenite: 290 C (554 F) (layer); 570 C (1058 F) (cloud)
3. Minimum explosive concentration: Data not available
4. Extinguishant: Molybdenum and molybdenum disulfide: Dry sand, dry dolomite, dry graphite

• **Warning properties**

None of the insoluble compounds of molybdenum are known to be significant eye irritants.

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 molybdenum and insoluble molybdenum compounds on a filter, followed by chemical treatment, and atomic absorption spectrophotometric analysis. An analytical method for molybdenum and insoluble molybdenum compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

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.

SANITATION

• Eating and smoking should not be permitted in areas where solids containing molybdenum and insoluble molybdenum compounds are handled, processed, or stored.

• Employees who handle solids or liquids containing insoluble molybdenum compounds should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation from mining and processing of ore; from grinding and other abrasive treatment of metal or alloys for use in electrical contacts, spark plugs, x-ray tubes, grids for radio tubes, missle and aircraft parts, and iron/steel alloys	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as lubricants in greases, oil dispersions, resin-bonded films, and dry powders; as catalysts in petroleum refining and chemical processing	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in pigment mixture for labelling glass bottles, for printing inks, for paints, and for plastics; as reagents in analytical chemistry laboratories	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in powder as chemical intermediates; use in molybdic acid; use as alloying agents in production of iron/steel	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as catalysts in organic synthesis in medicinals, in decorative and protective coatings for metal, and as feed additives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during temperature application as protective coatings for electrical resistors and engine parts, and as catalysts	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical intermediates and plating agents for mirrors; use in metal brazing and in manufacture of cutting tools	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

Liberation during use as solid lubricants	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation as catalysts in manufacture of propylene oxide	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical laboratory	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.

• **Breathing**

If a person breathes in large amounts of molybdenum and insoluble molybdenum compounds, 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 molybdenum and insoluble molybdenum compounds have been swallowed, 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 AND DISPOSAL PROCEDURES

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

• If molybdenum and insoluble molybdenum compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill. Liquid containing insoluble molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Molybdenum and insoluble molybdenum compounds may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR MOLYBDENUM AND INSOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Dust or Mist Concentration	
75 mg/m³ or less	Any dust and mist respirator, except single-use.
150 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
150 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
7,500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7,500 mg/m³ 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.

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