

# Occupational Health Guideline for Soluble Molybdenum Compounds (as 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 soluble molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

### SUBSTANCE IDENTIFICATION— Molybdenum trioxide

- Formula:  $\text{MoO}_3$
- Synonyms: Molybdenum anhydride; molybdic oxide
- Appearance and odor: Yellow to white, odorless solid.

### SUBSTANCE IDENTIFICATION— Ammonium molybdate

- Formula:  $(\text{NH}_4)_2\text{MoO}_4$
- Synonyms: 85% molybdic acid
- Appearance and odor: Yellow to white, odorless solid.

### SUBSTANCE IDENTIFICATION— Ammonium paramolybdate

- Formula:  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

### SUBSTANCE IDENTIFICATION— Calcium molybdate

- Formula:  $\text{CaMoO}_4$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

### SUBSTANCE IDENTIFICATION— Sodium molybdate, dihydrate

- Formula:  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$
- Synonyms: Sodium molybdate
- Appearance: White crystalline powder.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble molybdenum compounds is 5 milligrams of soluble molybdenum compounds (as molybdenum) per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift.

## HEALTH HAZARD INFORMATION

- **Routes of exposure**  
Soluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They might also affect the body if they are swallowed.
- **Effects of overexposure**
  1. **Short-term Exposure:** Soluble molybdenum compounds have caused loss of appetite, incoordination, and irritation of eyes, nose, and throat, difficulty in breathing, anemia, and colic in animals.
  2. **Long-term Exposure:** Animal data suggest that repeated exposure to soluble molybdenum compounds might be associated with gout.
  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 soluble molybdenum compounds.

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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.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble molybdenum compounds at potentially hazardous levels:

**1. Initial Medical Screening:** Routine medical histories and physical examinations are not considered necessary. However, the employer should screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble molybdenum compounds exposure. Only those giving a positive history of these conditions should be referred for further medical examinations.

—Kidney disease: Although soluble molybdenum compounds are not known as kidney toxins in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

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

—Blood disease: Soluble molybdenum compounds cause anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Gout: Soluble molybdenum compounds may cause gout. Persons with pre-existing conditions may be more susceptible to the effects of these agents.

**2. Periodic Medical Examination:** Routine periodic examinations are not considered necessary. However, anyone developing the above listed conditions should be referred for further medical examination.

• **Summary of toxicology**

Soluble molybdenum compounds have a low toxicity but may cause anemia and deformities of the forelegs when fed to rabbits in high doses. In rats, the approximate oral LD50 for daily repeated doses of ammonium molybdate was 333 mg molybdenum/g/day; sodium molybdate was fatal to rabbits within a few weeks at a dietary level of 0.1%. In rats and guinea pigs, oral doses of 1.2 g/kg ammonium molybdate caused anorexia, colic, trembling, incoordination, and dyspnea; anemia and deformity of the forelegs occurred in rabbits. Exposure of mice for 1 hour to a high concentration of the dust of ammonium molybdate caused a transitory irritation of mucous membranes. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of other 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. There have been no reports of systemic effects from industrial exposure. A study from the

Ankavan Province of Russia, where dietary molybdenum intake ranges from 10 to 15 mg per day due to high natural levels, has shown elevated blood xanthine oxidase activity and increased uric acid concentrations in blood of residents compared with controls living in an area with lower molybdenum exposure. A high percentage (31%) of the population examined from the Ankavan Province were diagnosed as having a gout-like disease.

## CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Molybdic trioxide**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 795 C (1463 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F):

0.5

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Ammonium molybdate**

1. Molecular weight: 196
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.3
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F):

Soluble, decomposes

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Ammonium paramolybdate**

1. Molecular weight: 1238
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F):

43

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Calcium molybdate**

1. Molecular weight: 200
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.35
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 695 C (1283 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F):

0.01

8. Evaporation rate (butyl acetate = 1): Not applicable

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- **Physical data—Sodium molybdate, dihydrate**
  1. Molecular weight: 241.95
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 3.28
  4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
  5. Melting point: Loses its water at 100 C (212 F)
  6. Vapor pressure at 20 C (68 F): Data not available
  7. Solubility in water, g/100 g water at 0 C (32 F): 56.2
  8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Ammonium molybdate and ammonium paramolybdate decompose above 360 C (680 F). Other are stable.

2. Incompatibilities: Contact with alkali metals such as sodium and potassium or with molten magnesium may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia and carbon monoxide) may be released when some soluble molybdenum compounds decompose.

4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

According to Patty, "exposure to molybdenum oxide is irritating to eyes . . ." but he gives no quantitative information concerning the concentrations necessary. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.

## 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 soluble molybdenum compounds on a filter, followed by leaching-off of analyte with hot water and atomic absorption spectrophotometric analysis. An analytical method for soluble 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.

## 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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds.

- Non-impervious clothing which becomes contaminated with soluble molybdenum compounds should be removed promptly and not reworn until the soluble molybdenum compounds are removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble molybdenum compounds or liquids containing soluble molybdenum compounds may contact the eyes.

## SANITATION

- Skin that becomes contaminated with soluble molybdenum compounds should be promptly washed or showered with soap or mild detergent and water to remove any soluble molybdenum compounds.

- Eating and smoking should not be permitted in areas where soluble molybdenum compounds are handled, processed, or stored.

- Employees who handle soluble molybdenum compounds or liquids containing soluble molybdenum compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble molybdenum compounds

may occur and control methods which may be effective in each case:

<b>Operation</b>	<b>Controls</b>
Liberation during rolling of hot billets in processing molybdenum steel; for use as electrodes; during welding operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical reagent for laboratory analyses; in petroleum refining and chemical processing; as an intermediate in the manufacture of corrosion inhibitors; use as coloring agents for enamels and ceramic glazes; agricultural chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in electroplating process; use in formulation of corrosion inhibitors for aqueous systems; pigments for paints, lacquers, and coloring animal fibers and hair	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in enamel processes for adherence of vitreous coatings to ceramics and metal; use in leather and skin tanning	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chlorination catalysts; in fire-retardant resins; as a brazing flux and as an intermediate for organo-metallic compounds; use in photography; ion exchange processes and formulation of plastics and adhesives; as a catalyst in desulfurization of gasoline; use as a reagent for determination of phosphorus and lead	General dilution ventilation; local exhaust 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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds get 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 these chemicals.

### • Skin Exposure

If soluble molybdenum compounds or liquids containing soluble molybdenum compounds get on the skin, flush the contaminated skin with water. If soluble molybdenum compounds or liquids containing soluble molybdenum compounds penetrate through the clothing, remove the clothing and flush the skin with water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of soluble 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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds have 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 AND DISPOSAL PROCEDURES

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

• If soluble molybdenum compounds or liquids containing soluble 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 and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquids containing soluble molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble molybdenum compounds may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

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## RESPIRATORY PROTECTION FOR SOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

<b>Condition</b>	<b>Minimum Respiratory Protection* Required Above 5 mg/m<sup>3</sup></b>
<b>Particulate Concentration</b>	
25 mg/m <sup>3</sup> or less	Any dust or mist respirator**.
50 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use or quarter mask respirators**. Any high efficiency particulate filter respirator**.
250 mg/m <sup>3</sup> 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.
5000 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
10,000 mg/m <sup>3</sup> or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mg/m <sup>3</sup> 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.  Any escape self-contained breathing apparatus.

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

\*\*In those cases where eye irritation occurs, full facepiece respirators are recommended. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.