

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** MOLYBDENUM INSOLUBLE COMPOUNDS ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for MOLYBDENUM INSOLUBLE COMPOUNDS

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 MOLYBDENUM INSOLUBLE COMPOUNDS.

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.

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(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of molybdenum and insoluble compounds (as molybdenum) not in excess of 15 milligrams per cubic meter (mg/M3) averaged over an eight-hour work shift (time weighted average), as stated in § 1910.1000, Table Z-1.

(2) "Action level" means one half of the permissible exposure for molybdenum and insoluble compounds.

(b) Exposure determination and measurement. (1) Each employer who has a place of employment in which molybdenum or insoluble compounds are released into the workplace air shall determine if any employee may be exposed to airborne concentrations of molybdenum and insoluble compounds 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 molybdenum and insoluble compounds.

(2) A written record of the determination shall be made and shall contain at least the following information:

(i) Any information, observations, or calculations which may indicate employee exposure to molybdenum or insoluble compounds;

(ii) Any measurements of molybdenum or insoluble compounds taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to molybdenum or insoluble compounds; and

(iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.

(3) If the employer determines that any employee may be exposed to molybdenum and insoluble compounds at or above the action level, the exposure of the employee in each work operation who is believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum eight-hour time weighted average exposure of the employee.

(4) If the exposure measurement taken pursuant to paragraph (b) (3) of this section reveals employee exposure to molybdenum and insoluble compounds 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.

(5) If an employee exposure measurement reveals that an employee is exposed to molybdenum and insoluble compounds 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.

(6) If an employee exposure measurement reveals that an employee is exposed to molybdenum and insoluble compounds above the permissible exposure, the employer shall:

(i) Measure the exposure monthly of the employee so exposed; and

(ii) Institute control measures as required by paragraph (d) of this section; and

(iii) Individually notify, in writing, within five days, every employee who is found to be exposed to molybdenum and insoluble compounds above the permissible exposure. The employee shall also be notified of the corrective action being taken to reduce the exposure to at or below the permissible exposure.

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(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to molybdenum and insoluble compounds below the action level, the employer may terminate measurement for the employee.

(8) For purposes of this paragraph, employee exposure is that which would occur if the employee were not using a respirator.

(c) Methods of measurement. (1) 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 (See Appendix B (IV) of this section).

(2) The method of measurement shall have an accuracy, to a confidence level of 95 percent, of not less than that given in Table 1.

Table 1

Concentration	Required Accuracy
Above permissible exposure	$\pm 25\%$
At or below permissible exposure and above the action level	$\pm 35\%$
At or below the action level	$\pm 50\%$

(d) Compliance. (1) No employee shall be exposed to molybdenum and insoluble compounds above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of molybdenum and insoluble compounds shall be controlled to at or below the permissible exposure by engineering and work practice controls:

(i) Engineering and work practice controls shall be instituted to reduce exposures to at or below the permissible exposure, except to the extent that such controls are not technically feasible.

(ii) Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nonetheless be used to reduce exposure to the lowest level feasible and shall be supplemented by respirators in accordance with paragraph (d)(4) of this section.

(3) Engineering controls. (i) When mechanical ventilation is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity, static pressure, or air volume, shall be made at least every three months. Measurements of system effectiveness shall also be made within five days of any change in production, process, or control which might result in an increase in airborne concentrations of molybdenum and insoluble compounds.

(ii) Open surface tank operations shall be performed in accordance with §1910.94(d).

(4) Compliance with the permissible exposure shall not be achieved by the use of respirators except:

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- (i) During the time period necessary to install or implement engineering or work practice controls; or
 - (ii) In work situations in which engineering and work practice controls are technically not feasible; or
 - (iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of molybdenum and insoluble compounds to at or below the permissible exposure; or
 - (iv) For operations which require entry into tanks or closed vessels; or
 - (v) In emergencies.
- (5) Where respirators are needed and permitted under this paragraph to reduce employee exposure, the employer shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

TABLE 2 RESPIRATORY PROTECTION FOR MOLYBDENUM AND INSOLUBLE COMPOUNDS

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
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.

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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. -----

(6) Respirators shall be approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(7) The employer shall institute a respiratory protection program in accordance with § 1910.134(b), (d), (e), and (f).

(e) Fire and safety. (1) The employer shall familiarize himself with the information contained in the Substance Technical Guidelines (Appendix B of this section) for molybdenum and insoluble compounds.

(2) For the purpose of compliance with §1910.309, locations classified as hazardous locations due to the presence of molybdenum disulfide and molybdenum be Class II, Group E.

(3) For the purpose of compliance with § 1910.157, molybdenum disulfide and molybdenum are classified as Class D fire hazards, except that §1910.157(b)(2)(v) shall not apply.

(4) For the purpose of compliance with § 1910.178, locations classified as hazardous locations due to the presence of molybdenum disulfide and molybdenum shall be Class II, Group E.

(5) Sources of ignition such as smoking or open flames are prohibited where molybdenum and insoluble compounds present a fire or explosion hazard.

(6) Molybdenum disulfide and molybdenum shall be stored so as not to come in contact with strong oxidizers.

(f) Reserved.

(g) Spills and disposal. In the event that molybdenum and insoluble compounds are spilled the employer shall immediately provide available ventilation and then clean up the spill.

(h) Sanitation. (1) Employers shall ensure that employees do not eat or smoke in areas where solids containing molybdenum or insoluble compounds of molybdenum are handled, processed or stored.

(2) Employers shall ensure that employees who handle solids or liquids containing insoluble compounds of molybdenum wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

(i) Training and information. (1) Each employer who has a workplace in which molybdenum and insoluble compounds are present shall keep a copy of this regulation with Appendixes A, B and C at the workplace. This material shall be made readily available to affected employees.

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(2) Each employer who has employees exposed to molybdenum and insoluble compounds above the action level or employees who work where molybdenum and insoluble compounds present a fire or explosion hazard, shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for molybdenum and insoluble compounds (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to molybdenum insoluble compounds.

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to molybdenum and insoluble compounds which are listed in Appendix A of the section;

(iv) Instruct affected employees to inform the employer if they develop any of the medical conditions listed in paragraph (j)(2) of this section; and

(v) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to molybdenum and insoluble compounds.

(j) Medical surveillance. (1) The employer shall provide medical procedures as required by this paragraph. All medical procedures shall be performed by or under the supervision of a physician at no cost to the employee.

(2) The employer shall obtain from each employee who is exposed, or will be exposed, to molybdenum or insoluble compounds or airborne concentrations of molybdenum or insoluble compounds at or above the action level information as to whether such employee has a history of any of the following medical conditions:

(i) Kidney disease

(ii) Liver disease

(iii) Chronic lung disease

(3) The employer shall provide a medical examination for the employee if:

(i) The employee provides a history of any of the medical conditions listed in paragraph (j)(2) of this section; or

(ii) The employee informs the employer of the development of any of the medical conditions listed in paragraph (j)(2) of this section or any of the signs or symptoms of exposure to molybdenum or insoluble compounds which are listed in Appendix A which the employee suspects are caused by exposure to molybdenum and insoluble compounds.

(4) The employer shall provide to the examining physician the following information:

(i) A copy of this regulation with Appendixes A, B and C for molybdenum and insoluble compounds;

(ii) A description of the affected employee's duties as they relate to his exposure to molybdenum and insoluble compounds;

(iii) A description of any personal protective equipment and respirators required to be used;

(iv) The results of any measurements which may indicate the affected employee's exposure;

(v) The affected employee's anticipated exposure; and

(vi) Upon request of the physician, any available information from previous medical examinations of the affected employee.

(5) Where a medical examination is required by paragraph (j)(3) of this section, following such examination the employer shall obtain a written

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opinion from the examining physician which conforms with paragraph (j)(6) of this section.

(6)(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 condition which would place the employee at increased risk of material impairment of the employee's health from exposure to molybdenum and insoluble compounds or would directly or indirectly aggravate any detected medical condition;

(B) Any recommended limitations upon the employee's exposure to molybdenum and insoluble compounds including limitations upon the use of personal protective equipment and respirators;

(C) That the employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.

(ii) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to exposure to molybdenum and insoluble compounds.

(iii) The employer shall provide the employee with a copy of the physician's written opinion.

(7) No employee shall be exposed to molybdenum and insoluble compounds or airborne concentrations of molybdenum and insoluble compounds in such a way as would put the employee at increased risk of material impairment of his health from such exposure. This determination may be based on the physician's written opinion.

(8) The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to molybdenum and insoluble compounds.

(9) 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 risk involved by refusal to be examined.

(10) No medical procedure which would be performed pursuant to this section need be performed if records of a previous such procedure performed within the past six months are acceptable to the examining physician.

(K) Recordkeeping. (1) Exposure determination. (i) The employer shall keep an accurate record of all determinations required to be made pursuant to paragraph (b)(1) of this section.

(ii) This record shall include the written determination required in paragraph (b)(2) 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 molybdenum and insoluble compounds.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to molybdenum and insoluble compounds which are being monitored;

(C) Sampling and analytical methods used and evidence of their accuracy, including the method, results and date of calibration of sampling equipment;

(D) Number, duration, and results of samples taken; and

(E) Name, social security number and exposure of the employee monitored.

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(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 an accurate record of the measurements demonstrating the effectiveness of such ventilation required by paragraph (d)(3) of this section.

(ii) This record shall include:

- (A) Date of measurement;
- (B) Type of measurement taken;
- (C) Result of measurement.

(iii) These records shall be maintained for at least one year.

(4) Employee training and information. (i) The employer shall keep an accurate record of all employee training and information required by paragraph (i) of this section.

(ii) This record shall include:

- (A) Date of training;
- (B) Name and social security number of employee trained;
- (C) Content or scope of training provided.

(iii) This record shall be maintained until replaced by a more recent record.

(5) Medical surveillance. (i) The employer shall keep an accurate record of employee medical surveillance required by paragraph (j) of this section.

(ii) This record shall include:

- (A) Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;
- (B) Any employee medical complaints relative to exposure to molybdenum and insoluble compounds;
- (C) A copy of information provided to the physician pursuant to paragraph (j)(4)(ii), (iii), (iv), (v), and (vi) of this section.

(D) Physician's written opinion; and

(E) A signed statement of any refusal to be examined.

(iii) This record shall be maintained for the duration and for one year after termination 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 of Labor for Occupational Safety and Health and the Director of the National Institute for Occupational Safety and Health.

(ii) Employee exposure determination and 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.

(1) Employee observation of measurement. (1) The employer shall give affected employees or their representatives an opportunity to observe any measurement of employee exposure to molybdenum and insoluble compounds which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to molybdenum and insoluble compounds requires entry into an area where the use of personal protective devices, including respirators, is required, the

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observer shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

(3) Without interfering with the measurement, observers shall be entitled to:

- (i) Receive an explanation of the measurement procedure.
- (ii) Visually observe all steps related to the measurement of the airborne concentration of molybdenum and insoluble compounds that are being performed at the place of exposure; and
- (iii) Record the results obtained.

NOTE: The information contained in the following appendixes is advisory in nature and is not intended, by itself, to create any additional obligations not otherwise imposed or detract from any existing obligation.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET
FOR MOLYBDENUM AND INSOLUBLE COMPOUNDS

I. SUBSTANCE IDENTIFICATION

- A. Substance: Molybdenum and insoluble compounds
- B. Permissible Exposure: 15 milligrams of molybdenum and insoluble compounds (as molybdenum) per cubic meter of air (mg/M3) averaged over an eight-hour work shift.
- C. Appearance and Odor: Molybdenite: Silvery white metal or gray-black powder; molybdenum disulfide: shiny gray, odorless plates; lead molybdate: Colorless to pale yellow, odorless solid

II. HEALTH HAZARD DATA

- A. Ways in which the chemical affects your body: Molybdenum and insoluble compounds can affect your body if you inhale them or if they come in contact with your eyes. They may also affect your body if you swallow them.
- B. Effects of Overexposure:
 - 1. 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: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to molybdenum and insoluble compounds.

III. EMERGENCY FIRST AID PROCEDURES

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- A. Breathing: If you or any other person breathes in large amounts of molybdenum or insoluble 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.
- B. Swallowing: When molybdenum and insoluble 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.
- C. 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 insoluble molybdenum compounds. You can only be required to wear them for routine use if your employer is in the process of installing controls or 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) or 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 experience difficulty breathing while wearing a respirator, tell your employer.
- B. Protective Clothing: None required.
- C. Eye Protection: None required.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Molybdenum disulfide and molybdenum are combustible solids and their dusts can form explosive mixtures with air.
- B. Molybdenum disulfide and molybdenum must be stored in tightly closed containers in a cool, well ventilated area away from strong oxidizers.
- C. Sources of ignition such as smoking and open flames are prohibited wherever molybdenum disulfide and molybdenum are handled, used or stored in a manner that could create a potential fire or explosion hazard.
- D. You must not eat or smoke in areas where molybdenum and insoluble compounds are handled, processed or stored.
- E. If you handle solids or liquids containing molybdenum or insoluble compounds, you must wash your hands thoroughly with soap or mild detergent and water before eating or smoking.
- F. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them.

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- G. Ask your supervisor where insoluble molybdenum compounds are used in your work area and for any additional safety and health rules.

VI. ACCESS TO INFORMATION

- A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for molybdenum and insoluble compounds. In addition, your employer must instruct you in the safe use of molybdenum and insoluble compounds, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to molybdenum and insoluble compounds. You or your representative have the right to observe employee exposure measurements and to record the results obtained. If your employer determines that you are being overexposed, he is required to inform you of the exposure and of the actions which are being taken to reduce your exposure.
- C. Your employer is required to keep records of exposure determinations, exposure measurements, and medical surveillance. Your employer is required to make records of exposure determinations and your exposure measurements available to you or your representative upon your request. Your employer is required to release your medical records to your physician upon your written request.

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
FOR MOLYBDENUM AND INSOLUBLE COMPOUNDS

(The standard for molybdenum and insoluble compounds should not be interpreted listed below for which substance specific information has been provided.)

I. PHYSICAL AND CHEMICAL DATA (Metallic Molybdenum)

- A. Substance Identification
1. Synonyms: None
 2. Formula: Mo
 3. Molecular weight: 95.94
- B. Physical Data
1. Boiling Point: 5,560 C (10,040 F)
 2. Specific gravity (water = 1): 10.22
 3. Vapor density: Not applicable
 4. Melting point: 2,610 C (4,730 F)
 5. Vapor pressure: Essentially zero
 6. Solubility in water: Insoluble
 7. Evaporation rate (butyl acetate = 1): Not applicable
 8. Appearance and odor: Silvery white metal or gray-black powder.

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II. PHYSICAL AND CHEMICAL DATA (Molybdenum disulfide)

A. Substance Identification

1. Synonyms: Molybdenite
2. Formula: MoS_2
3. Molecular weight: 160.1

B. Physical Data

1. Boiling point (760 mm Hg): Oxidizes above 315 C (599 F)
2. Specific gravity (water = 1): 4.7
3. Vapor density (air = 1 at boiling point of molybdenite): Not applicable
4. Melting point: 1370 C (2498 F) (oxidizes above 315 C (599 F))
5. Vapor pressure at 20 C (68 F): Essentially zero
6. Solubility in water, % by weight at 20 C (68 F): Insoluble
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Shiny gray, odorless plates

III. PHYSICAL AND CHEMICAL DATA (Lead molybdate)

A. Substance Identification

1. Synonyms: Sulfenite
2. Formula: PbMoO_4
3. Molecular weight: 367.1

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): 6.8
3. Vapor density (air = 1 at boiling point of lead molybdate): Not applicable
4. Melting point: 1065 C (1950 F)
5. Vapor pressure at 20 C (68 F): Essentially zero
6. Solubility in water, % by weight at 20 C (68 F): 0.000012
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless to pale yellow, odorless solid

IV. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA (Molybdenum and insoluble compounds)

A. Fire

1. Flash point: Not applicable
2. Minimum ignition temperature: 360 C (680 F) (molybdenum - layer); 720 C (1328 F) (molybdenum - cloud); 290 C (554 F) (molybdenite - layer); 570 C (1058 F) (molybdenite - cloud)
3. Minimum explosive concentration: Data not available
4. Extinguishing media: (Molybdenum and molybdenum disulfide) - dry sand, dry dolomite, dry graphite
5. Special fire-fighting procedures: Do not use a solid stream of water since a stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Molybdenum and molybdenum disulfide are combustible solids. Their dusts can form explosive mixtures with air. All ignition sources must be controlled where molybdenum and molybdenum disulfide is used, handled or stored in a manner that could create a potential fire or explosion hazard.

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7. 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 molybdenum and molybdenum disulfide shall be Class II Group E.

B. 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, carbon monoxide) may be released when insoluble molybdenum compounds decompose.
4. Special precautions: None.

III. SPILL AND DISPOSAL PROCEDURES (Molybdenum and insoluble compounds)

- A. If molybdenum and insoluble 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.
- B. Persons not wearing protective equipment should be restricted from areas of spills until cleanup has been completed.
- C. Waste disposal methods: Molybdenum and insoluble compounds may be disposed of in a secured sanitary landfill.

IV. MONITORING AND MEASUREMENT PROCEDURES (molybdenum and insoluble compounds)

- 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 eight-hour sample or two 4-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). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR part 84, portable direct-reading instruments, dosimeters, or by collection of the particulates using a high efficiency membrane filter with subsequent chemical analyses. The method of measurement must determine the concentration of insoluble molybdenum compounds to plus or minus 35%.
- B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements 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. The method of measurement must determine the concentration of insoluble molybdenum compounds to plus or minus 25%.

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- C. METHODS: Methods meeting these accuracy requirements are available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161 under the title "NIOSH Analytical Methods for Set O" (Order number XXXXXXXXXX).
- D. QUALIFIED PERSONS: Since many of the duties relating to employee protection are dependent on the results of monitoring and measuring procedures, employers should assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.
- V. MISCELLANEOUS PRECAUTIONS (molybdenum and insoluble compounds)
 - A. Store insoluble molybdenum compounds in tightly closed containers in a well ventilated area.
 - B. Employers should advise employees of all areas and operations where exposure to molybdenum and insoluble compounds could occur.
- VI. COMMON OPERATIONS
Common operations in which exposure to molybdenum and insoluble compounds are likely to occur are: During their production and during the metallurgy of molybdenum and its alloys; during the mining of molybdenite ore; during the use of molybdenum disulfide as a lubricant, and as a catalyst in petroleum refining; during the mining and subsequent handling of molybdenite, wulfenite, and powellite; and during the use of lead molybdate dust in pigment mixtures and as a reagent in analytical chemistry laboratories.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Molybdenum and insoluble compounds, which include molybdenum disulfide, calcium molybdate, and many of the oxides and halides, have a low toxicity; however, molybdenum trioxide is an irritant to the eyes and mucous membranes. Guinea pigs repeatedly exposed to molybdenum trioxide dust at a concentration of 200 mg molybdenum/M3 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/M3 but minimal effects at 53 mg/M3; 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

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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 associated with high blood uric acid.

III. SIGNS AND SYMPTOMS

None have been reported in humans. By analogy to effects caused in animals, there may be irritation of the eyes and respiratory tract; anorexia, diarrhea, weight loss; listlessness; liver and kidney damage.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Promptly flush eyes with water and wash skin with soap or mild detergent and water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation if indicated.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Molybdenum and insoluble compounds have a low toxicity but molybdenum trioxide in animals has caused irritation of the eyes and respiratory tract, diarrhea, and muscular incoordination. It is important that the physician become familiar with plant operating conditions in which exposure to insoluble compounds of molybdenum occur. 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 examinations are not required. However, the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from molybdenum and insoluble compounds exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. 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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2. 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 compounds of molybdenum might cause exacerbation of symptoms due to its irritant properties.
3. 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.

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.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Molybdenum as Mo." Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 173-174.
2. Hygienic Guide Series: "Molybdenum," American Industrial Hygiene Association Journal, 21:102-103, 1960.
3. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1112-1118.
4. Browning, Ethel: Toxicity of Industrial Metals (2d ed.), Butterworths, London, 1969, pp. 243-248.
5. International Labour Office: Encyclopaedia of Occupational Health and Safety, Vol. II, L-Z, McGraw-Hill Book Company, New York, 1974, pp. 911-912.
6. Halverson, A.W., et al: "A Mechanism for the Copper-Molybdenum Interrelationship," Journal of Nutrition, 71:95-100, 1960.
7. Kovalsky, V.V., et al: "Changes in Purine Metabolism in Man and Animals in Various Molybdenum-Rich Biogeochemical Provinces," Z. Obsc. Biol., 22:179, 1961.

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REFERENCES AND SOURCES
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1910.93

(f) Personal Protective Equipment, and (h) Sanitation
Eye: Laurant and Wergeland, "Ocular Toxicity of New Industrial
Metals;" International Labour Office, "Encyclopedia of
Occupational Health and Safety"

Skin: None

Ingestion: Browning, "Toxicity of Industrial Metals"

COMMENTS

Eye - Classification: 0

Output statement numbers: 0

Exceptions: None

Laurant and Wergeland have stated that molybdenum was among
the newer metals studied by inserting fragments into "mid -
vitreous region of rabbits' eyes." After a one-year
period, and based on clinical and pathological examinations,
molybdenum was classified as inert.

The ILO simply notes that exposure to molybdenum
trioxide produces eye irritation. The Documentation of
TLV's adds the irritation is transitory.

Since there is no indication in the literature that
the insoluble compounds are significantly irritating or
injurious to the eyes, they are assigned a classification
of 0.

Skin - Classification: 0

Output statement numbers: None

Exceptions: None

No data were found in the literature which indicates that
contact with insoluble molybdenum compounds has harmful
effects. The ILO simply notes that "dermatitis from
contact with molybdenum disulfide is unknown."

Under these circumstances, it is concluded that
a classification of zero is appropriate.

Ingestion - Classification: 2 and 6

Output statement numbers: 19, 20b

Exceptions: None

Browning reports "the hexavalent water-soluble compounds of
molybdenum are readily absorbed from the intestinal tract,
also such insoluble compounds as the trioxide and calcium
molybdate if given in large doses, but apparently not the
sulphide molybdenity." She adds that 1.2 gm/kg given to
rats and guinea pigs by mouth resulted in "anorexia,
colic, trembling, uncoordinated movements and dyspnoea."
Without giving the amounts involved, she notes that the
trioxide can cause fatty changes in the liver and kidneys
and that the trioxide and calcium and ammonium molybdate
can cause anorexia, listlessness, and loss of weight.

Patty reports "the approximate LD50 of daily repeated
doses in mg of Mo/kg/day for calcium molybdate was 100;
for molybdenum trioxide, 125; and for ammonium molybdate,
333." In general he states that animals "on high dietary

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levels of Mo show deformities of joints of the extremities," that "livers and kidneys of severely poisoned animals showed fatty degeneration," that "Mo is rapidly eliminated by the kidney," and that storage above normal of Mo in bone has been observed.

The literature generally agrees that these substances are not of high toxicity. However, since contact prevention is not required, the toxicity of the compounds by ingestion is considered sufficient to warrant classifications of 2 and 6.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

- National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1975 (NFPA)
- Kirk - Othmer, "Encyclopedia of Chemical Technology," 2nd edition, Vol. 13, p. 634 (K-O)
- "Lange's Handbook of Chemistry," 11th edition (Lange)
- K. N. Palmer, "Dust Explosions and Fires," Chapman and Hall, London, 1973 (Palmer)
- Chemical Rubber Company, Handbook of Chemistry and Physics (CRC)
- Bureau of Mines "Explosibility of Metal Powders (BOM)

Sources of data items used:

- I. A. 1. Synonyms: K-O, Lange, CRC
2. Formula: Lange, CRC
3. Molecular weight: Lange, CRC
B. 1. Boiling point: K-O, CRC
2. Specific gravity: K-O, CRC
3. Vapor density: Not applicable
4. Melting point: K-O, CRC
5. Vapor pressure: K-O
6. Solubility in water: K-O, CRC
7. Evaporation rate: Not applicable
8. Appearance and odor: K-O, Lange, CRC
- II. A. 1. Flash point: Not applicable
2. Minimum ignition temperature: Not applicable, BOM
3. Minimum explosive concentration: Not applicable
4. Extinguishing media: ADL
5. Special fire fighting procedures: ADL
6. Unusual fire and explosion hazards: Palmer, ADL
B. 1. Conditions contributing to instability: ADL
2. Incompatibilities: NFPA-491M, ADL
3. Hazardous decomposition products: ADL
4. Special precautions: None
- III. A. Steps if released or spilled: ADL
C. Waste disposal method: ADL
- V. Miscellaneous precautions: ADL

USE/EXPOSURE AND CONTROL DOCUMENT

Sources used in the preparation of this document include:

- Bech, A. O., "Hard Metal Disease and Tool Room Grinding," Journal of the Society of Occupational Medicine, Volume 24, No. 1, January 1974 (Bech)
- Browning, E., "Toxicity of Industrial Metals," Butterworths, London,

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- 1961 (Browning)
- "Chemical Origins and Markets," Stanford Research Institute, Menlo Park, California, 4th edition, 1967 (Origins)
- "Documentation of Threshold Limit Values," American Conference of Governmental Industrial Hygienists, 1971 (ACGIH)
- Fairhall, L. T., "The Toxicity of Molybdenum," Public Health Bulletin No. 293, U. S. Public Health Service, 1945 (Public Health)
- "Handbook of Chemistry and Physics," CRC Press, Cleveland, Ohio, 54th edition, 1973 (CRC Handbook)
- Hawley, G. G. - editor, "The Condensed Chemical Dictionary," Van Nostrand Reinhold Company, 8th edition, 1971 (Hawley)
- Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience Publishers, Division of John Wiley and Sons, Inc., 2nd edition, 1968 (K-O)
- "Merck Index of Chemicals and Drugs," Merck and Company, Rahway, New Jersey, 8th edition, 1968 (Merck)
- Mogilevskaja, O. Ja., "Contribution to the Establishment of Maximum Acceptable Concentrations for a Number of Non-soluble Molybdenum Compounds," Gigiena Truda i Professional - Nye Zabollevaniya, Moscow, USSR, June 1965, Vol 9, No. 6 (Mogilevskaja)
- "Molybdenum," Hygienic Guide Series, American Industrial Hygiene Association, February 1960 (AIHA)
- Molybdenum Compounds," Information Bulletin, Kennecott Copper Corporation, Utah Copper Division (Kennecott)
- Patty, F. A., "Industrial Hygiene and Toxicology," Vol. II, Interscience Publishers, 1963 (Patty)

References for Specific Use/Exposure

1. CRC Handbook, Hawley, Public Health
2. CRC Handbook, AIHA, Kennecott, Hawley, Browning, Patty, Bech
3. AIHA, Patty, K-O, Kennecott, Hawley, Origins, Merck
4. Patty, K-O, Hawley, Origins
5. Origins
6. Hawley, Origins
7. CRC Handbook, Merck, Hawley
8. Hawley, Origins
9. Hawley, K-O

Hawley was the reference used for numbers 10 - 14.

References for Specific Control Methods

ACGIH, AIHA and Kennecott were the references used in all of the Specific Control Methods.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Molybdenum and Insoluble Compounds

D. O. L. STANDARD: 15 mg/M3

Eye Irritation Level: None of the insoluble compounds of molybdenum are known to be significant eye irritants.

IDLH: There is no evidence in the available toxicological information that an acute exposure to a high concentration of insoluble molybdenum compounds would impede escape or cause any irreversible health effects within one-half hour. For the purposes of this standard, therefore, allowable respiratory protection has been determined on the basis of the protection factor afforded by each device. It is recognized, however, that for some substances for which there does not appear to exist a concentration immediately

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dangerous to life and health, the determination of allowable respiratory protection based on protection factors may result in the selection of a concentration which is not likely to be encountered in the occupational environment. Therefore, for all such particulate substances it has been arbitrarily determined that only those respirators allowed for use above IDLH concentrations are permitted for use in concentrations exceeding 500 times the permissible exposure.

Other Toxicological Information: The AIHA Hygienic Guides state that the severity of the health hazards from molybdenum is "moderate to low . . . Exposure (of guinea pigs) to molybdenite ore dust (MoS_2) at a concentration of 280 mg/M3 (of molybdenum) on the other hand caused little effect. Fume from arcing molybdenum metal caused some mortality at 190 mg/M3 but little effect at 53 mg/M3." The Documentation of TLV's points out that these were chronic exposures. The Hygienic Guides state that molybdenum is "probably not immediately hazardous to life at any concentration."

Browning states that "the chief compound of molybdenum encountered in industrial exposure (especially in mining) is the sulphide; no toxic effects in human beings or in animals have been reported from inhalation of its dust. It appears that compared with many other metals of industrial importance molybdenum is of low toxicity but the results of the investigation of Fairhall et al. particularly suggest that protective measures against the more soluble compounds should be ensured."

The Documentation of TLV's states that the threshold limit, "as far as is known, . . . (should) include . . . a relatively large factor of safety against systemic effects."

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	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of molybdenite (MoS_2), wulfenite (PbMoO_4) and powellite (CaMoO_4) dusts during the mining and subsequent handling of these ores. Molybdenite is the principal molybdenum producing ore	A	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles)
2.	Inhalation of molybdenum dust during grinding and other abrasive treatments of either the pure metal or alloys containing the metal. Uses for molybdenum include electrical contacts, spark plugs, x-ray tubes, grids for radio tubes, missile and aircraft parts, and iron and steel alloys	A	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles)
3.	Inhalation of molybdenum disulfide (MoS_2) dust during use as a lubricant in greases, oil dispersions, resin-bonded films and dry powders; as a catalyst in petroleum refining; and as a catalyst in chemical processing	A	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles)
4.	Inhalation of lead molybdate (PbMoO_4) dust during use in pigment mixtures for labeling glass bottles, for printing inks, for paints and for plastics, and as a reagent in analytical chemistry laboratories	A	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles)
5.	Inhalation of molybdenum dust during the use of metal powder as a chemical	A	General dilution ventilation; process enclosure; local exhaust ventilation;

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intermediate for other
molybdenum compounds

personal protective
equipment (respiratory
protective devices and
goggles)

- | | | | |
|-----|--|---|--|
| 6. | Inhalation of calcium molybdate (CaMoO_4) dust during use in molybdic acid and as an alloying agent in the production of iron and steel | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 7. | Inhalation of molybdenum sesquioxide (Mo_2O_3) dust during use as a catalyst in organic synthesis, in medicinals, in decorative and protective coatings for metals, and as a feed additive | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 8. | Inhalation of molybdenum disilicide (MoSi_2) dust and fume during high temperature application as a protective coating for electrical resistors and engine parts, and as a catalyst | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 9. | Inhalation of molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$) dust during use as a chemical intermediate and as a molybdenum plating (i.e., mirrors) agent | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 10. | Inhalation of molybdenum boride (MoB) dust during use for metal brazing and in the manufacture of cutting tools | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 11. | Inhalation of molybdenum aluminide dust during use as a cermet | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory |

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protective devices and
goggles)

- | | | | |
|-----|---|---|--|
| 12. | Inhalation of molybdenum diselenide (MoSe_2) dust during use as a solid lubricant | A | General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment (respiratory protective devices and goggles) |
| 13. | Inhalation of molybdenum napthenate dust during use as a catalyst in the manufacture of propylene oxide | A | General dilution ventilation; personal protective equipment (respiratory devices and goggles) |
| 14. | Inhalation of molybdenum dioxide (MoO_2) and molybdenum metaphosphate ($\text{Mo}(\text{PO}_3)_6$) dusts during use in the chemical laboratory | A | General dilution ventilation |

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