

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** SELENIUM COMPOUNDS ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for SELENIUM 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 SELENIUM 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 selenium and inorganic compounds (as selenium) not in excess of 0.2 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 selenium compounds averaged over an eight-hour work shift.

(3) This section does not apply to hydrogen selenide or selenium hexafluoride.

(b) Initial determination and exposure measurement. (1) Each employer who has a place of employment in which selenium compounds is released into the workplace air shall determine if there is any possibility that any employee may be exposed to airborne concentrations of selenium compounds above the permissible level. The initial determination shall be made each time there is a change in production, process, or control measures which may result in an increase in airborne concentrations of selenium compounds.

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

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

(ii) Any measurements of selenium compounds taken;

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

(iv) Date of initial determination, work being performed at the time, location within work site, and employees considered.

(3) If the employer determines that any employee may be exposed to selenium compounds above the permissible exposure, 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 selenium compounds above the action level, the employer shall:

(i) Identify all employees who may be exposed above the permissible level; and

(ii) Measure the exposure of the employees so identified.

(5) If an employee exposure measurement reveals that an employee is exposed to selenium compounds above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every three months.

(6) If an employee exposure measurement reveals that an employee is exposed to selenium 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 selenium compounds above the permissible exposure. The employee shall also be notified of the results of the exposure measurements and of the corrective action being taken to reduce the exposure to 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 selenium 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 (Percent of True Value)
Above permissible exposure	± 25
At or below permissible exposure and above the action level	± 35

At or below the action level	± 50
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(d) Compliance. (1) No employee shall be exposed to selenium and inorganic compounds above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of selenium and inorganic 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 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. When local exhaust is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity or static pressure 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 selenium and inorganic compounds.

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

(i) During the time period necessary to install or implement engineering or work practice controls; or

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- (ii) In work situations in which engineering and work practice controls are not feasible; or
 - (iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of selenium and inorganic 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. When an employee informs his employer that he is experiencing eye irritation from selenium or inorganic selenium compounds while wearing a respirator allowed in Table 2, the employer shall provide and ensure that the employee use an equivalent respirator with a full facepiece, helmet or hood.

TABLE 2 RESPIRATORY PROTECTION FOR SELENIUM AND INORGANIC COMPOUNDS (AS SELEN

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Particulate Concentration	
10 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.
100 mg/M3 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.
	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
Greater than 100 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

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operated in pressure-demand or other positive pressure mode.

Escape

Any escape self-contained breathing apparatus with full facepiece.

A high efficiency particulate filter respirator with a full facepiece.

(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 selenium and inorganic compounds.

(2) Sources of ignition such as smoking or open flames are prohibited where selenium and inorganic compounds present a fire or explosion hazard.

(3) Selenium and inorganic compounds shall be stored so as not to come in contact with acids and strong oxidizers.

(4) In the design of open surface tank ventilation for the purposes of § 1910.94(d), operations involving selenium and inorganic compounds shall be classified as B-2 at 21 degrees C (70 degrees F).

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride. Face shields shall comply with § 1910.133 (a)(2), (a)(4), (a)(5), and (a)(6).

(2) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds. Face shields shall comply with § 1910.133(a)(2), (a)(4), (a)(5), and (a)(6).

(3) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur. Face shields shall comply with § 1910.133(a)(2), (a)(4), (a)(5), and (a)(6).

(4) Employers shall ensure that employees whose clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds change into uncontaminated clothing before leaving the work premises.

(5) Employers shall ensure that clothing which has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of the contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the employer shall inform the person performing the operation of the hazardous properties of the contaminant.

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(6) Where there is any possibility of exposure of an employee's body to selenium, selenium oxychloride, selenium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.

(7) Employers shall ensure that non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, or selenium dioxide be removed promptly and not reworn until the contaminant is removed from the clothing.

(8) Employers shall ensure that non-impervious clothing which becomes contaminated with selenium oxychloride be removed immediately and not reworn until the selenium oxychloride is removed from the clothing.

(9) Employers shall provide and ensure that employees use safety goggles which comply with § 1910.133 (a)(2)-(a)(6) where there is any possibility of selenium dioxide, selenium oxychloride or liquids containing these compounds contacting the eyes.

(10) Employers shall provide and ensure that employees use safety goggles which comply with § 1910.133(a)(2)-(a)(6) where sodium selenite, sodium selenate or liquids containing these compounds may contact the eyes.

(11) Where there is any possibility that an employee's eyes may be exposed to selenium oxychloride, selenium dioxide or liquids containing these compounds, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

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

(h) Sanitation. (1) Employers shall ensure that all employees subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds at the end of each work day.

(2) Employers shall ensure that employees whose skin becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these substances promptly wash or shower to remove any contaminant from the skin.

(3) Employers shall ensure that employees whose skin becomes contaminated with selenium oxychloride immediately wash or shower to remove any selenium oxychloride from the skin.

(4) Employers shall ensure that employees do not eat or smoke in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds are handled, processed or stored.

(5) Employers shall ensure that employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds wash their hands thoroughly before eating, smoking or using toilet facilities.

(i) Training and information. (1) Each employer who has a workplace in which selenium and inorganic compounds is 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 selenium and inorganic compounds above the action level without regard to the use of respirators, or employees who may have any possibility of skin contact with liquid selenium oxychloride or liquids containing selenium oxychloride or who may have skin contact with solid selenium dioxide or liquids containing selenium dioxide or who may have repeated or prolonged skin contact with solid selenium, sodium selenite, sodium selenate or liquids containing these compounds or who may have any possibility of eye contact with solid selenium dioxide, liquid selenium oxychloride, or liquids containing these compounds or who may have eye contact with solid sodium selenite, sodium selenate or liquids containing these compounds, or employees who work where selenium and inorganic compounds present a fire or explosion hazard shall annually:

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

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

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

(iv) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to selenium and inorganic 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) Preplacement medical examination. The employer shall make available to each employee who is exposed, or will be exposed, to airborne concentrations of selenium and inorganic compounds above the action level, without regard to the use of respirators, or employees who may have any possibility of skin contact with liquid selenium oxychloride or liquids containing selenium oxychloride or who may have skin contact with solid selenium dioxide or liquids containing selenium dioxide, or who may have repeated or prolonged skin contact with solid selenium, sodium selenite, sodium selenate or liquids containing these compounds or who may have any possibility of eye contact with solid selenium dioxide, liquid selenium oxychloride or liquids containing these compounds, or who may have eye contact with solid sodium selenite, sodium selenate, or liquids containing these compounds, a preplacement medical examination which must include the following:

(i) A medical history and physical examination with emphasis on the respiratory system, eyes, gastrointestinal tract, blood, liver, kidneys and skin;

(ii) Urinalysis to include specific gravity, albumin, glucose and a microscopic on centrifuged sediment;

(iii) A profile of liver function.

(3) Periodic medical examination. The employer shall make available to each employee exposed to airborne concentrations of selenium and inorganic compounds above the action level, without regard to the use of respirators, or employees who may have any possibility of skin contact with liquid

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selenium oxychloride or liquids containing selenium oxychloride or who may have skin contact with solid selenium dioxide or liquids containing selenium dioxide, or who may have repeated or prolonged skin contact with solid selenium, sodium selenite, sodium selenate or liquids containing these compounds or who may have any possibility of eye contact with solid selenium dioxide, liquid selenium oxychloride or liquids containing these compounds, or who may have eye contact with solid sodium selenite, sodium selenate, or liquids containing these compounds, twenty-four months from the date of the employee's first exposure, and every twenty-four months thereafter, a periodic medical examination which must include the following:

(i) A medical history and physical examination with emphasis on the respiratory system, eyes, gastrointestinal tract, blood, liver, kidneys and skin;

(ii) Urinalysis to include specific gravity, albumin, glucose and a microscopic on centrifuged sediment;

(iii) A profile of liver function.

(4) Alternative medical procedures. If the examining physician chooses to use alternative medical procedures to those specified in paragraphs (j)(2) and (j)(3) of this section, the employer may accept such alternative medical procedures as meeting the requirements of this section provided that the employer:

(i) Obtains a statement from the examining physician setting forth the alternative medical procedures, the rationale for substitution, and evidence that they will be equally effective;

(ii) Informs each exposed worker of the fact that alternative medical procedures to those required in paragraphs (j)(2) and (j)(3) of this section are to be made available.

(5) Interim medical examination. The employer shall provide an interim medical examination for the employee if the employee informs the employer of any of the signs or symptoms of exposure to selenium and inorganic compounds which are listed in Appendix A which the employee suspects are caused by exposure to selenium and inorganic compounds.

(6) Informing the physician. The employer shall provide to the physician performing any medical examination required by this section the following information:

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

(ii) A description of the affected employee's duties as they relate to his exposure to selenium and inorganic 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 level; and

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

(7) Where a medical examination is required by paragraphs (j)(2), (j)(3), or (j)(5) of this section, following such examination the employer shall obtain from the examining physician a written opinion which conforms with paragraph (j)(8) of this section.

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(8) Physician's written opinion. (i) The physician's written opinion by the examining physician shall specifically state:

(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 selenium and inorganic compounds;

(B) Any recommended limitations upon the employee's exposure to selenium and inorganic 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 the employee's employment.

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

(9) Results of tests. Where a preplacement or periodic medical examination is required by paragraphs (j)(2) or (j)(3) of this section, following such examination the employer shall obtain from the examining physician for inclusion in the employee's medical record:

(i) A recording of the results of the liver function tests and urinalysis;

(ii) Where alternative medical procedures have been performed in accordance with paragraph (j)(4) of this section, a recording of such alternative procedures.

(10) No employee shall be exposed to selenium and inorganic compounds in such a way as would put the employee at increased risk of material impairment of his health from such exposure. The employer shall base this decision on any information available including the physician's written opinion.

(11) No medical procedure which would be performed pursuant to paragraphs (j)(2) or (j)(3) of this section need be performed if records of a previous such procedure performed within the past six months are acceptable to the examining physician.

(12) 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.

(13) The employer shall provide emergency medical treatment for any employee injured through exposure to selenium and inorganic compounds.

(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 selenium and inorganic compounds.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to selenium and inorganic compounds which are being monitored;

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- (C) Sampling and analytical method used and evidence of their accuracy;
- (D) Number, duration, and results of samples taken; and
- (E) Name, social security number and exposure of the employee monitored.
- (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) The name and social security number of the employee;
 - (B) Results of tests required by paragraph (j)(2) and (j)(3) of this section and results of any tests conducted pursuant to paragraphs (j)(4) of this section;
 - (C) Any employee medical complaints relative to exposure to selenium and inorganic compounds;
 - (D) A copy of information provided to the physician pursuant to paragraph (j)(6)(ii), (iii), (iv), (v), and (vi) of this section.
 - (E) Physician's written opinion; and
 - (F) A signed statement of any refusal to be examined.
- (iii) This record shall be maintained for the duration of and for five years 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) Each employee or former employee shall have access to the exposure determination and exposure measurement records required to be maintained by this section which indicate his own exposure to selenium and inorganic compounds.
- (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.

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(1) Employee observation of measurement. (1) The employer shall give each employee or his representative an opportunity to observe any measurement of his exposure to selenium and inorganic compounds which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to selenium and inorganic compounds requires entry into an area where the use of personal protective devices, including respirators, is required, the 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 selenium and inorganic compounds that are being performed at the place of exposure; and

(iii) Record the results obtained.

NOTE: The information contained in the following appendix for selenium and inorganic compounds is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligations. To the extent the information supplements this regulation for selenium and inorganic compounds, it is advisory in nature.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET
FOR SELENIUM AND INORGANIC COMPOUNDS (AS SELENIUM)

I. SUBSTANCE IDENTIFICATION

- A. Substance: Selenium and inorganic compounds
- B. Permissible exposure: 0.2 milligram of selenium and inorganic compounds (as selenium) per cubic meter of air (mg/M3) averaged over an eight-hour work shift.
- C. Appearance and odor: a) Selenium: Black, grey, or red odorless solid; b) Sodium selenate: White odorless solid; c) Sodium selenite: White odorless solid; d) Selenium dioxide: White odorless solid; e) Selenium oxychloride: Colorless, odorless liquid

II. HEALTH HAZARD DATA

- A. Ways in which the chemical affects your body: Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect your body if you inhale them or if they come in contact with your eyes or skin or if you swallow them. Selenium oxychloride and selenium dioxide may enter your body through your skin.

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B. Effects of Overexposure:

1. Short-term Exposure: Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye", an allergy of the eyelids in which they may become puffy.
2. Long-term Exposure: Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.
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 selenium, sodium selenite, sodium selenate, or selenium dioxide.

III. EMERGENCY FIRST AID PROCEDURES

- A. Eye Exposure: If selenium and its inorganic compounds get into your eyes, wash your eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.
- B. Skin Exposure: If selenium and its inorganic compounds get on your skin, immediately wash the contaminated skin using If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through your clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.
- C. Breathing: If you or any other person breathes in large amounts of selenium, sodium selenite, sodium selenate, or selenium dioxide 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.
- D. Swallowing: When selenium, sodium selenite, sodium selenate, selenium oxychloride or selenium dioxide has 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.
- E. 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

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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 selenium and inorganic 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 can smell selenium oxychloride while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.
- B. Protective Clothing: You must wear appropriate protective clothing and equipment to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds, and to prevent skin contact with selenium dioxide or liquids containing selenium dioxide when skin contact may occur. Replace or repair impervious clothing that has developed leaks.
- C. Eye Protection: You must wear safety goggles which comply with 1910.133 (A)(2)-(A)(6) where there is any possibility of selenium dioxide or selenium oxychloride or liquids containing these compounds contacting your eyes. You must wear dust-resistant safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact your eyes. You must wear splash-proof safety goggles where there is any possibility of liquids containing selenium dioxide contacting your eyes or where liquids containing sodium selenite may contact your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING, AND STORAGE

- A. Selenium is a combustible solid. Selenium, sodium selenite, sodium selenate, or selenium dioxide must be stored in tightly closed containers in a well ventilated area.
- B. Selenium must be stored so as not to come in contact with acids and strong oxidizers.
- C. All sources of ignition must be controlled where selenium is used, handled, or stored in a manner that could create a potential fire or explosion hazard.
- D. If your work clothing has had any possibility of being contaminated with sodium selenite, sodium selenate, selenium dioxide, selenium oxychloride, or liquids containing these compounds, you must change into uncontaminated clothing before leaving the work premises.

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- E. You must promptly remove any non-impervious clothing that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide and this clothing must not be reworn until the contaminant has been removed from the clothing.
- F. If your skin becomes contaminated with selenium sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, you must promptly wash or shower to remove any contaminant from your skin.
- G. If your are subject to skin contact with sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, at the end of each workday you must wash any areas of the body which may have contacted a contaminant.
- H. You must not eat or smoke in areas where sodium selenate, sodium selenite, selenium dioxide, or liquids containing these compounds are handled, processed or stored.
- I. If you handle sodium selenate, sodium selenite, selenium dioxide, or liquids containing these compounds, you must wash your hands thoroughly before eating, smoking, or using toilet facilities.
- J. Fire extinguishers and eye-wash fountains, where provided, must be readily available and you should know where they are and how to operate them.
- K. Ask your supervisor where selenium and inorganic 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 Selenium and inorganic compounds. In addition, your employer must instruct you in the safe use of selenium and inorganic compounds, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to selenium, sodium selenite, sodium selenate, or selenium dioxide. 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 the actions which are being taken to reduce your exposure.
- C. Your employer is required to keep records of your exposure and medical examinations. Your employer is required to keep exposure data for at least one year and to keep medical data during your employment, and for a period of five years following your termination of employment. Your employer is required to make the exposure data available to you upon your request. Your employer is also required to release your medical records to your physician upon your written request.
- D. Your employer must give you a copy of the physicians written opinion for any physical examination required by this standard.

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NOTE: The information contained in the following appendix for selenium and inorganic compounds is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligations. To the extent the information supplements this regulation for selenium and inorganic compounds, it is advisory in nature.

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
FOR SELENIUM AND INORGANIC COMPOUNDS (AS SELENIUM)

(This standard for selenium and inorganic compounds should not be interpreted to apply only to the substances listed below for which specific information has been provided)

a. selenium

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Selenium, metallic; selenium, elemental
2. Formula: Se
3. Molecular weight: 78.96

B. Physical Data

1. Boiling point (760 mm Hg): 685 C (1265 F)
2. Specific gravity (water = 1): 4.45 - 4.8
3. Vapor density (air = 1 at boiling point of selenium): Not applicable
4. Melting point: 150 C (302 F)
5. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
6. Solubility in water, grams of selenium per 100 grams of water at 20 C (68 F): Insoluble
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Black, gray, or red odorless solid

b. sodium selenite

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: None
2. Formula: Na₂SeO₃
3. Molecular weight: 173

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): 3.1
3. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
4. Melting point: 710 C (1310 F) decomposes
5. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
6. Solubility in water, grams of sodium selenite per 100 grams of water at 20 C (68 F): 85

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7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless and odorless solid

c. sodium selenate

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: None
2. Formula: Na_2SeO_4
3. Molecular weight: 188.9

B. Physical Data

1. Boiling point (760 mm Hg): Decomposes
2. Specific gravity (water = 1): 3.1
3. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable
4. Melting point: Decomposes
5. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
6. Solubility in water, grams of sodium selenate per 200 grams of water at 20 C (68 F): 83
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless and odorless solid

d. selenium dioxide

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: None
2. Formula: SeO_2
3. Molecular weight: 110.9

B. Physical Data

1. Boiling point (760 mm Hg): 315 C (599 F) sublimes
2. Specific gravity (water = 1): 3.95
3. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable
4. Melting point: 340 C (644 F)
5. Vapor pressure at 20 C (68 F): 0.001 mm Hg
6. Solubility in water, grams of selenium dioxide per 100 grams of water at 20 C (68 F): 257
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Colorless and odorless solid

e. selenium oxychloride

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: None
2. Formula: SeOCl_2
3. Molecular weight: 165.9

B. Physical Data

1. Boiling point (760 mm Hg): 176 C (349 F)
2. Specific gravity (water = 1): 2.42
3. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7
4. Melting point:
5. Vapor pressure at 20 C (68 F): 0.35 mm approx.
6. Solubility in water, grams of selenium oxychloride per 100 grams of water at 20 C (68 F): Decomposes
7. Evaporation rate (butyl acetate = 1): Not applicable

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8. Appearance and odor: Colorless to yellow liquid

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: Not applicable
2. Autoignition temperature: Selenium - data not available; Sodium selenite, sodium selenate, selenium oxychloride, and applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishing media: For selenium, water.
5. Special fire-fighting procedures: Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Selenium is a combustible solid. All ignition sources must be controlled where selenium is used, handled or stored in a manner that could create a potential fire or explosion hazard.

B. Reactivity

1. Conditions contributing to instability: None hazardous.
2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, or selenium oxychloride.
4. Special precautions: None.

III. SPILL AND DISPOSAL PROCEDURES

A. If selenium or its inorganic 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 selenium or its inorganic 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 or leaks until cleanup has been completed.

C. Waste disposal methods: Selenium or its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

IV. MONITORING AND MEASUREMENT PROCEDURES

A. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the eight-hour exposure may be determined from a single eight-hour sample or 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

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inhaled by the employee). Sampling and analyses may be performed by collection of the particulates and vapors using a high efficiency membrane filter with subsequent chemical analysis of the filter. Detector tubes certified by NIOSH under 42 CFR part 84 or other direct-reading devices calibrated to measure selenium and inorganic compounds may be used. The method of measurement must determine the concentration of total selenium and inorganic compounds to plus or minus 35% of the true value.

B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements under this section should be essentially the same as described above. 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 total selenium and inorganic compounds to plus or minus 25% of the true value.

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 M" (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

A. Store selenium or inorganic compounds in tightly closed containers in a cool, well ventilated area.

B. Employers should advise employees of all areas and operations where their exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide could occur.

VI. COMMON OPERATIONS

Common operations in which high exposures to selenium, sodium selenite, sodium selenate, or selenium dioxide may occur are: a) Selenium: During its use in the manufacture of selenium rectifiers, photoconductors, semiconductors, blasting caps, and ruby glass; as a decolorizing agent for glass; as a dehydrogenating agent in organic chemical synthesis; b) Sodium selenite: During its use in photography to produce brown-colored prints; during one process for the recovery of selenium from electrolytic copper refining slimes; c) Sodium selenate: During its use in chromium plating baths; as an insect repellant in soils; during one process for the recovery of selenium from electrolytic copper refining slimes; d) Selenium dioxide: During its use as an oxidizing agent in organic chemical synthesis; as a decolorizing agent for glass; for pre-treatment of metals before chromates; as an intermediate in the manufacture of selenium metal for the electronics industry.

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NOTE: The information contained in the following appendix for selenium and inorganic compounds is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligations. To the extent the information supplements this regulation for selenium and inorganic compounds, it is advisory in nature.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation; skin absorption.

II. TOXICOLOGY

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes are irritants of the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/M3 for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised based upon observations in animals, but is not established in man. Eleven of 53 rats developed adenoma or low grade carcinoma in cirrhotic livers, and 4 others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7 or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In control rats, 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1 per cent. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/M3 while urinary levels ranged from below 0.10 to 0.43 mg/liter of urine; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were

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normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

III. SIGNS AND SYMPTOMS

Irritation of eyes, nose and throat; visual disturbances; headache; chills, fever; dyspnea, bronchitis; metallic taste, garlic breath, gastrointestinal complaints; dermatitis; skin and eye burns; by analogy to effects caused in animals, anemia, as well as liver and kidney damage may occur.

IV. SPECIAL TESTS

Determination of selenium in the urine may be a useful indicator of exposure.

V. TREATMENT

Remove from exposure. Immediately flush eyes with water and wash skin with soap and water. Give artificial resuscitation if indicated. Consideration should be given to hospitalization and observation for the possible delayed onset of pulmonary edema. Recovery is usually complete. If swallowed and the person is conscious, immediately administer water orally and induce vomiting.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Selenium and certain selenium compounds are irritants of the eyes, upper respiratory tract and skin. They have caused liver damage and anemia in animals. Teratogenic effects have also been observed in animals. Long term feeding of ammonium potassium selenite to animals caused liver cancer. Certain selenium compounds may be absorbed through the skin. Teratogenic effects have also been observed in animals. It is important that the physician become familiar with plant operating conditions in which exposure to selenium occurs. 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

The following medical procedures must be made available to each employee who is exposed to selenium:

1. A complete history and physical examination -- The purpose is to detect pre-existing conditions that might

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place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver, or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

2. Urinalysis -- Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis shall be obtained to include at a minimum specific gravity, albumin, glucose and a minimum a microscopic on centrifuged sediment.
3. Liver function tests -- Selenium causes liver damage and tumors in animals. A profile of liver function shall be obtained by using a medically acceptable array of biochemical tests.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated on an annual basis.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Selenium Compounds (as Se)," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 224-225.
2. Hygienic Guide Series: "Selenium and Compounds," American Industrial Hygiene Association Journal, 20:254-255, 1959.
3. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 886-890.
4. Browning, Ethel: Toxicity of Industrial Metals (2d ed.), Butterworths, London, 1969, pp. 286-295.
5. Cerwenka, E.A., Jr., and W.C. Cooper: "Toxicology of Selenium and Tellurium and Their Compounds," Archives of Environmental Health, 3:189-200, 1961.

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6. Grant, W. Morton: Toxicology of the Eye (2d ed.), Charles C. Thomas, Illinois, 1974, pp. 903-905, 1191, 1194.
7. Halverson, A.W., et al: "Development of Hemolytic Anemia in Rats Fed Selenite," Toxicology and Applied Pharmacology, 17:151-159, 1970.
8. Nelson, A.A., et al: "Liver Tumors Following Cirrhosis Caused by Selenium in Rats," Cancer Research, 3:230-236, 1943.
9. Robertson, D.S.F.: "Selenium - A Possible Teratogen?," Lancet, 1:518-519, 1970.
10. International Labour Office: Encyclopaedia of Occupational Health and Safety, Vol. II, L-Z, McGraw Hill Book Company, New York, 1974, pp. 1294-1296.

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(AS SELENIUM)
1910.1000

- (f) Personal Protective Equipment, and, (h) Sanitation
- Eye: Hunter, "The Diseases of Occupations;" "Encyclopedia of Occupational Health and Safety," ILO; "Selenium and Its Industrial Toxicology," Indus. Med., 39(1), Jan. 1970, p. 50-54; Grant, "Toxicology of the Eye"; Penn. Dept. of Env. Resources Hygienic Information Guide
- Skin: Deichmann and Gerarde, "Toxicology of Drugs and Chemicals;" Sax, "Dangerous Properties of Industrial Material;" Hunter, "Diseases of Occupations;" Browning, "Toxicity of Industrial Metals;" Patty, "Industrial Hygiene and Toxicology;" "Encyclopedia of Occupational Health and Safety," International Labour Office; Hamilton and Hardy, "Industrial Toxicology;" Glover, "Selenium and Its Industrial Toxicology," Indus. Med., 39(1), Jan. 1970, p. 50-54; Gleason, "Clinical Toxicology of Commercial Products;" Stecher, "The Merck Index;" Penn. Dept. of Env. Resources Hygienic Information Guide
- Ingestion: Browning, "Toxicity of Industrial Metals;" Gleason, "Clinical Toxicology of Commercial Products;" Patty, "Industrial Hyg. and Toxicology;" Hunter, "Diseases of Occupations;" Documentation of Threshold Limit Values;" Penn. Dept. of Env. Resources Hygienic Information Guide; Deichmann and Gerarde, "Toxicology of Drugs and Chemicals"
- GENERAL Although the ACGIH "Documentation of Threshold Limit Values for Substances in Workroom Air" refers to "Selenium Compounds (as Se)" in general, the following discussions, while outlining the bulk of information available in the literature for selenium and its compounds results in specific requirements for selenium, selenium selenite, selenium oxychloride, sodium selenate and selenium dioxide in the personal protection and sanitation sections of the standard.

COMMENTS

- Eye - Classification: See below Output statement numbers: As appropriate for noted classifications Exceptions: None
- Reporting on the work of Middleton, Hunter describes a chemist sprayed with a solution of selenium dioxide and sustaining burns of both eyes, the entire face and back of the neck. He notes that "in spite of repeated irrigation of the eyes . . . and local anesthetics (the chemist) suffered severe persistent, intolerable pain in both eyes, with lachrymation and photophobia lasting 24 hours." Hunter continues, "there were first degree burns of the eyelids, intense chemosis of the bulbar conjunctivus with clouding of the lower half of each cornea." A complete recovery occurred within 10 days. The ILO notes, "splashes of selenium dioxide entering the eye may cause conjunctivitis if not treated immediately . . . and persons who work in atmospheres containing selenium dioxide dust may develop a condition

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known as 'rose eye,' a pink allergy of the eyelids which often become puffy." They also add that there "is usually a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctivitis." According to Glover, after continued or repeated exposure some workers' eyelids appear to become allergic to selenium dioxide (dust) and their eyes puff up whenever they enter rooms where others can work without any ill effect.

Grant also describes the case of the chemist. He reports that "injury appeared slight and the corneas did not stain with fluorescein immediately after the exposure. In the course of six hours, although vision remained clear, photophobia and pain developed, and the lower portions of both corneas became stainable with fluorescein. Within sixteen hours vision was blurred and the lower three-fourths of both corneas appeared dull, and the bulbar conjunctiva whitened. From the third to fifth days the corneas cleared from above downward, and by the sixteenth day the corneas were essentially normal." He cites another source which indicates that "contamination of the eye with selenium dioxide is not serious if the eyes are irrigated promptly with water."

For selenium sulfide, Grant states that "employed in a shampoo for treating dandruff when tested on rabbit eyes was found to cause superficial keratitis, but ointments containing 0.5% of selenium sulfide caused no damage to rabbit eyes, and only occasional irritation or transient keratitis in human eyes." In general he notes "a number of other compounds, e. g., selenium oxychloride, which is a severe vesicant, are potentially injurious in contact with the eye, but their effects appear not to have been described in the literature. The effects of several inorganic selenium compounds including sodium selenide, sodium selenite, sodium selenate, and selenium oxide have been examined in the frog retina by direct injection of microquantities, demonstrating reversible changes in the ERG."

The Penn. Dept. of Environmental Resources generally reports, "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." The ILO adds that "the elemental forms of selenium are probably completely harmless to man"

Selenium dioxide has been shown to cause rather severe and persistent effects when in direct contact with the eye. Although these effects have not been reported to be permanent, they are concluded to provide significant justification for classifications of 1 and 5. Because of its high potential for causing injury to the eye, selenium oxychloride is also assigned a classification of 1 and 5. Specific information concerning the effects of direct eye contact with sodium selenite or sodium selenate could not be located in the literature. Nevertheless, based upon the chemical structure of these compounds and the effects of

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selenium compounds in general, classifications of 2 and 6 are presently concluded necessary to provide minimal protective measures.

Since no source could be found which indicated that elemental forms of selenium are harmful to the eye, selenium itself is assigned a classification of zero.

As usual, statements 9, 11, and 13 are used for classifications 1 and 5, and statements 10 and 12 are used for classifications of 2 and 6.

Skin - Classification: See below

Output statement numbers: See below

Exceptions: See below

The ILO reports that "selenium oxychloride readily destroys skin on contact, causing third degree burns." Browning states "selenium oxychloride is extremely toxic to animals . . . 0.01 c. cm applied to the skin of rabbits caused acute vesicant and death in less than 24 hours." Patty, citing the work of Dudley, found the MLD for selenium oxychloride when applied to rabbit skin was 7 mg/kg; this being equivalent to approximately 0.2 ml applied to a man of average size. He also adds that "the application of less than 0.005 ml to the arm of a man caused a painful burn with swelling and its healing required a month."

Browning notes "contact with fumes of heated selenium dioxide caused a condition resembling seborrhoea with a watery discharge and in two cases a high degree of sensitization developed." She also reports a toxic necrosis of the skin from an accidental contact with selenium dioxide inside a rubber glove. According to the ILO, "dermatitis due to exposure to airborne selenium oxide dust usually starts at the point of contact of the dust with the wrist or neck and may extend to contiguous areas of the arms and upper portions of the trunk . . . (consisting of) discrete red itchy papules which may become confluent on the wrist where selenium dioxide is liable to penetrate between the glove and sleeve of overalls." They add, "painful paronychia may be produced but one more frequently sees cases of excruciating painful throbbing nailbeds, due to the selenium dioxide penetrating under the free edge of the nail." Hamilton and Hardy comment that Amor and Pringle emphasize that the absorption of selenium through the denuded surface (of the skin) may result in late toxic effects. Glover reports that sometimes an individual becomes allergic to the minute crystals of the dioxide in the air with the resultant outbreak of a true urticarial type of body rash and must be removed not only from his present job but from any selenium work.

According to Browning, "actual contact in one case with a splash of selenic acid caused a purpuric-like lesion with inflammatory spots round the hair follicles; of another, small shallow ulcers resembling septic burns." Selenium trioxide reacts with water to form selenic acid.

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Gleason reports for selenium sulfide that "unlike many selenium salts, it is not decomposed by water of dilute acid to selenic or selenious acids. Only traces are absorbed through the skin . . . Local irritation and sensitization are rare."

Gleason considers sodium selenate to be "a general protoplasmic poison . . . (which is) highly toxic by all routes."

Stecher reports that selenium oxychloride is also a strong irritant and vesicant.

Patty and Deichmann and Gerarde agree that selenium salts are poorly absorbed through the skin.

The Penn. Dept. of Environmental Resources reports that contact with "selenium itself can cause dermatitis." Stecher agrees with this statement.

The ILO states that "the elemental forms of selenium are probably completely harmless to man . . ."

Sax rates selenium compounds in general as acute and chronic local irritants of moderate toxic hazard. The chronic systemic effects by skin absorption are similarly rated.

Selenium is a black, gray, or red odorless solid at normal ambient temperatures. Sodium selenite, sodium selenate, and selenium dioxide are all colorless and odorless solids. At 20 degrees C, the vapor pressure of all four substances is less than 0.001 mm Hg. The respective solubilities of the substances listed directly above are 0%, 85%, 83%, and 257%.

It is obvious from the literature that selenium oxychloride is an extremely toxic substance through skin contact and clearly warrants a classification of 1 and 5.

It is clear from the above that selenium dioxide in virtually every form can cause significant effects when in contact with the skin. To prevent these effects, classifications of 2 and 6 are concluded to be adequate, if statement 2 is used to prevent contact to the compound where it "may occur."

Specific data for sodium selenite and sodium selenate are sparse. Nevertheless, the various general comments in the literature suggest that repeated or prolonged contact should be avoided at the very least. Consequently, classifications of 2 and 6 are assigned for these compounds, as they also are for selenium itself.

Statements 1, 6, 8a, 14g, 14i, and 20a are necessary for selenium oxychloride while statements 2, 6, 17g, 17i, and 20a are specified for sodium selenite, sodium selenate, and selenium dioxide. As noted previously, statement 2 is especially modified for use with selenium dioxide. For selenium, only statements 2, 17g, and 17i are specified.

Ingestion - Classification: 1 and 5

Output statement numbers: 5a, 6, 15, 19, 20a

Exceptions: 6 and 15 added

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According to Browning, in humans the systemic effects of selenium poisoning are indicated by a rather vague syndrome of gastric disturbances, while in animals acute disturbances occur in a form called "blind staggers," and more chronic effects are termed "alkali disease." In the former there is some impairment of vision, a tendency to wander, paralysis, abdominal pain and a difficulty in judging near objects, and death is usually due to respiratory failure. The prominent symptoms of "alkali disease" are emacipation, lack of vitality, loss of hair, with lesions of the internal organs as the heart, liver, kidneys, erosion of the leg bones and anemia. Pathological changes include acute congestion of the liver with areas of local necrosis, congestion of the kidneys, endocarditis, myocarditis and atony of the smooth muscle of the gastrointestinal tract. Quoting the work of Moxon and Rhian, she adds that animal diets in which selenium is added in amounts sufficient to cause subacute toxicity (15 - 25 ppm) result in marked depression of appetite and growth, anemia, congestion of the liver and hind-leg paralysis; the chronic effects of prolonged feedings in amounts of 5 - 15 ppm produces liver injury in the form of atrophy, necrosis, cirrhosis, haemorrhage and anemia. Gleason classifies sodium selenate as toxicity class six meaning "super toxic," with a taste (less than 7 drops) being fatal for the average 150 lb man and adds, that it is "slightly less toxic than sodium selenite." He lists a rabbit oral LD₅₀ for both sodium selenate and sodium selenite of 4 mg/kg. Patty found that as selenium poisoning progresses, there develop respiratory difficulties and dyspnea, followed by opisthotonus, tetanic spasms, clonic spasms, a drop in blood pressure and respiratory failure, resulting from action on the central nervous system. Hunter reports that with chronic poisoning, death results from anemia and emacipation. Kirk-Othmer states that selenium is a cumulative poison to man and animals. The Documentation of TLV's reports that rats "fed selenium in a grain diet at concentrations of 3, 5, 7, 10, 20, and 40 ppm . . . showed toxic effects at all levels. A concentration of 10 ppm killed most of the animals within eight weeks. Lower concentration produced chronic symptoms, which included a decreased growth rate, a restriction of food consumption and slight to severe pathologic lesions. The LD₅₀'s of soluble selenium compounds (selenite and selenate) for various animals and by different routes of administration range from 1.5 to 5 mg/kg" Gleason reports for the water insoluble compound sodium sulfide that "ingestion is hazardous." Deichmann and Gerarde state that selenious acid, selenium dioxide, the selenites, and the selenates are highly toxic.

Browning also reports that metallic selenium is poorly absorbed from the gastrointestinal tract and that elemental selenium has been stated to be harmless because of its relative insolubility. The ILO agrees and notes "the

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elemental forms of selenium are probably completely harmless to man" The Penn. Dept. of Environmental Resources generally states "experience has shown that selenium itself . . . presents hazards of both acute and chronic exposure," but is unclear as to which routes of exposure are being referred to.

It is clear from the above that soluble compounds of selenium, including selenium dioxide, selenium oxychloride, sodium selenite, and sodium selenate, are extremely toxic by ingestion. Consequently, these compounds are assigned classifications of 1 and 5. And their hazard is considered sufficient to warrant the use of statements 6 and 15 in the standard as exceptions. Elemental forms of selenium are generally stated to be of considerably less, if not negligible, hazard by ingestion. Selenium itself is therefore assigned a classification of zero.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

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Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd. edit., Vol. 17,
p. 809 (K-O)

Gmelin's Handbuch der Anorganischen Chemie, Vols. 10 and 12, with supplements
(Gmelin)

Phelps Dodge Refining Co., Material Safety Data Sheet (Phelps)

Lange's Handbook of Chemistry, 11th ed. (Lange)

National Fire Protection Association, "Fire Protection Guide on Hazardous
Materials," 5th ed., 1975 (NFPA)

Sources of data items used:

- I. A.1. Synonyms: K-O
2. Formula: Ried, Lange
3. Molecular weight: Ried, Lange
- B.1. Boiling point: Ried, K-O
2. Specific gravity: Ried, Gmelin
3. Vapor density: Not applicable
4. Melting point: Gmelin, Ried, K-O
5. Vapor pressure: Gmelin
6. Solubility in water: Gmelin, Lange
7. Evaporation rate: Not applicable
8. Appearance and odor: Lange, Gmelin
- II. A.1. Flash point: Not applicable
2. Autoignition temperature: Not applicable; for selenium: Data not available
3. Flammable limits: Not applicable
4. Extinguishing media: ADL for selenium
5. Special fire fighting procedures: Ried, ADL
6. Unusual fire and explosion hazards: K-O
- B.1. Conditions contributing to instability: ADL
2. Incompatibilities: Phelps, NFPA-491M
3. Hazardous decomposition products: ADL
4. Special precautions: None
- III. A. Steps if released or spilled: K-O, ADL
- C. Waste disposal method: Phelps

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- V. Miscellaneous precautions: Ried, Phelps
VI. Common Operations: K-O, Ried

USE/EXPOSURE AND CONTROL DOCUMENT

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"Xerox Unit's Mission: Safety, Health, Clean Environment for Employees, Customers and Community," National Safety News, 103, p. 73 - 83, 1971 (NIOSH Technical Information Service - NIOSH 14674)
- References for Specific Use/Exposure
1. Considine, Bu Mines, Waitkins, Penna #59, K-O
 2. Considine, Waitkins, Jacobs, K-O, H/H, Guide, Mining Rev., Penna #59, Am. Hoechst, Bu Mines

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3. H/H, Jacobs, ILO, Drinker, Guide, Mining Rev., Browning, Considine, Am. Hoechst, Bu Mines
4. K-O, Mosher, Mining Rev., Considine, NIOSH 14674, NSC, Bu Mines, Klayman
5. Browning, Considine, K-O, H/H, Jacobs, Bu Mines, Klayman
6. K-O, Penna #59, Waitkins, H/H, Mining Rev., Considine, Jacobs, Browning Am. Hoechst, Bu Mines
7. Waitkins, K-O, Am. Hoechst, Bu Mines
8. K-O, Penna #59, Jacobs, Waitkins, Browning, Considine, Am. Hoechst, Bu Mines, Klayman
9. NSC, Bu Mines, Klayman
10. Waitkins, K-O, Browning, Bu Mines
11. Stolman, H/H, Penna #59, Waitkins, Browning, Bu Mines
12. Penna #59, Jacobs
13. K-O, Bu Mines
14. Browning, Bu Mines
15. Waitkins, Penna #59, Am. Hoechst, Bu Mines
16. H/H, Penna # 59
17. Waitkins, H/H, Jacobs, Clinton
18. Browning, Am. Hoechst, Bu Mines
19. Nutrition

References for Specific Control Methods

Penna #59, K-O, Guide, Waitkins, Cerwenka, ILO, NSC, Phelps Dodge, and Am. Hoechst were the references used in all of the Specific Control Methods.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Selenium and inorganic compounds

D. O. L. STANDARD: 0.2 mg/M3 (as Selenium)

WARNING PROPERTIES:

Eye Irritation Level: The Documentation of TLV's notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The Hygienic Information Guide for selenium of the Pennsylvania Department of Environmental Resources, Occupational Health, states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation is not available. For the purposes of this standard, only full facepiece respirators are permitted.

IDLH: 100 mg/M3

Basis for IDLH Value: This IDLH is based upon the report in the Documentation of TLV's that the LD50's of soluble selenium compounds (selenate) for various animals and by different routes of administration 1.5 to 5.0 mg/kg according to Hall, et al. Respirators have been assigned protection factors afforded by each device up to a concentration of 100 permissible exposure limit.

Other Toxicological Information: Deichmann and Gerarde state that

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"selenium salts are poorly absorbed through the skin. If ingested or inhaled, selenious acid (one of the ingredients in gun-bluing compound), selenium dioxide, the selenites, and the selenates (sic) are highly toxic. They induce a marked intoxication resulting in injury to the kidney, liver, and heart muscle. Signs and symptoms of intoxication include nausea, coughing, sternal pain, pallor, gastroenteric disorders, conjunctivitis, and irritability Wilson reported on the treatment and follow-up of 37 men who suffered accidental exposure to selenium oxide. Inhalation of the vapors induced bronchial spasms and symptoms of asphyxiation. Secondary symptoms included chills, fever, headache, and bronchitis. Pneumonitis and bilateral pulmonary consolidation appeared in 5 men within 12 hours."

According to the ILO, "the sudden inhalation of large quantities of selenium fume (or) selenium oxide . . . may produce pulmonary oedema due to local irritant effects on the alveoli; this oedema may not set in for 1 - 4h after exposure." The ILO also points out that "selenium oxide is the main selenium problem in industry since it is formed when selenium is boiled in the presence of air."

The Documentation of TLV's notes that "inhalation for eight hours of selenium dust at a concentration of 33 mg/M3 resulted in the death of two of 20 rats. The chief pathological finding was mild interstitial pneumonitis. Guinea pigs and rabbits survived four four-hour exposures at the same concentration but showed pneumonitis and, in the case of guinea pigs, mild congestion of lungs, liver and spleen."

Sax notes that "elemental selenium has low systemic toxicity, but dust or fumes can cause serious irritation of the respiratory tract."

According to the Documentation of TLV's, "the limit of 0.2 mg/M3 for elementary selenium and its common inorganic compounds is believed low enough to prevent systemic toxicity and to minimize irritation of eyes and respiratory passages."

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USE/EXPOSURE AND CONTROL DOCUMENT
SELENIUM AND INORGANIC COMPOUNDS

	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of dust or fume and skin contact with solid during mining, recovery, and purification of selenium (principal source - by-product of electrolytic copper refining) and during manufacture of selenium compounds	A,B,D	Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing)
2.	Inhalation of vapor and skin contact with solid or solution during use of selenium and salts (sodium or barium selenate, sodium selenite, selenium oxides) in glassware industries (used for decolorization of glass for special purposes - e.g. fiberglass, scientific glassware; used to produce pink and ruby glass for tableware, vehicular tail lights, traffic and other signal lenses, light filters, infrared equipment; used in tinted or "black" glass for modern buildings)	A,B,D	Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing)
3.	Inhalation of vapor and skin contact with solid during use of selenium and compounds (selenium dioxide) in manufacture of electrical components (rectifiers - used in electroplating, welding, d.c. motors, battery chargers, etc; transformers; semiconductors; photoelectric cells - used in photometers, colorimeters, pyrometers, exposure meters; used in TV cameras, magnetic computer cores, solar	A,B,D	Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing)

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batteries, relays)

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| 4. | Inhalation of dust and skin contact with solid or liquid during use of selenium and compounds in manufacture of photography and photocopying devices (xerox equipment; photographic printing; and reproduction chemicals; photographic dyes, photosensitizers, and tones) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 5. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium and compounds for manufacture of dyes, pigments, and colored glazes (cadmium sulfoselenide pigments - yellow, orange, red, maroon; zinc - chromium selenate - olive drab) used in ceramics, paints, plastics, and inks (for metal etching and for printing on glass) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 6. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium and compounds (selenic acid, sodium selenate) for hardening and toughening of metals and in electroplating baths (improves machine ability, casting, and forging properties of some steels; provides corrosion resistance to stainless steel, copper, magnesium, and chromium; used as brighteners in electroplating) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 7. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, |

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compounds (selenium dioxide, dialkyl selenides, phosphine selenite, barium, calcium, and zinc salts of selenic acids $RSeOOH$) in manufacture of lubricating oils and extreme pressure lubricants (used as anti-oxidants and detergency improvers), linseed and tung oils (improve non-drying properties). Dry, powdered lubricants containing diselenides of tungsten, tantalum, and molybdenum are manufactured for use at elevated temperatures and in ultrahigh vacuum

respiratory protective devices, protective clothing)

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| 8. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium compounds in the rubber industry for manufacture and use as vulcanization accelerators and antioxidants (selenium increases abrasion resistance of vulcanized rubber - used for electric cables, electric shovels, dredges, welding equipment) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 9. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium compounds (selenium sulfide) for manufacture and use as pharmaceuticals (preparation of niacin, cortisone, fungicides for dandruff and dermatitis control, studies of biologic processes) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 10. | Inhalation of dust or vapor and skin contact with solid or liquid during use of selenium compounds (selenium dioxide, hydrogen selenide) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective |

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as catalysts (hardening
fats for soaps, waxes,
edible fats, and plastics
conversion of heavy oils
to motor fuels)

devices, protective cloth-
ing)

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| 11. | Inhalation of dust or vapor and skin contact with liquid or solid during use of selenium compounds (sodium selenate, selocide - selenium in potassium ammonium sulfide) for manufacture and use as insecticides, parasit-icides, bactericides, and herbicides used for control of aphids, mites, and red spiders on citrus fruit, grapes, apples, corn, and ornamentals | A,B,D | Local exhaust ventilation; general dilution ventila-tion; personal protective equipment (gloves, goggles, respiratory protective devices, protective cloth-ing) |
| 12. | Inhalation of dust or vapor and skin contact with liquid or solid during use of selenium compounds for manufacture of flameproofing agents (for textiles, electric cables) | A,B,D | Local exhaust ventilation; general dilution ventila-tion; personal protective equipment (gloves, goggles, respiratory protective devices, protective cloth-ing) |
| 13. | Inhalation of dust or vapor and skin contact with liquid or solid during use of selenium compounds in delayed action blasting caps | A,B,D | Local exhaust ventilation; general dilution ventila-tion; personal protective equipment (gloves, goggles, respiratory protective devices, protective cloth-ing) |
| 14. | Inhalation of dust or vapor and skin contact with liquid or solid during use of selenium compounds (oxychloride) as solvents (paint and varnish removers; rubber, resin, and glue solvent) | A,B,D | Local exhaust ventilation; general dilution ventila-tion; personal protective equipment (gloves, goggles, respiratory protective devices, protective cloth-ing) |
| 15. | Inhalation of dust or vapor and skin contact with liquid or solid during use of selenium com-pounds (selenium dioxide) for organic chemical synthesis | A,B,D | Local exhaust ventilation; general dilution ventila-tion; personal protective equipment (gloves, goggles, respiratory protective devices, protective cloth- |

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(oxidation, hydrogenation,
dehydrogenation)

ing)

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|-----|--|-------|---|
| 16. | Inhalation of hydrogen selenide gas which may be evolved (from nascent hydrogen and soluble selenium compounds) during processing of selenium or selenium compounds | A | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 17. | Inhalation of dust or vapor and skin contact with solid or liquid selenium compounds during refining of copper, gold, silver, or nickel ores or during recycling of scrap metal (selenium occurs as an impurity) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 18. | Inhalation of dust or vapor and skin contact with solid or liquid during miscellaneous uses of selenium compounds (manufacture of insect repellants, activator for phosphorescent and luminescent compounds, hardening of phenol molding compounds, manufacture of special ceramic materials, plasticizers, mercury vapor detectors) | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |
| 19. | Inhalation of dust and skin contact with solid during use of selenium compounds (sodium selenate or selenite) for preparation of feed additives for poultry and swine | A,B,D | Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, respiratory protective devices, protective clothing) |

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

----- JES2 JOB STATISTICS -----

2,000 CARDS READ

0 SYSOUT PRINT RECORDS

0 SYSOUT PUNCH RECORDS

0.00 MINUTES EXECUTION TIME

