

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** COPPER DUSTS AND MISTS ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for COPPER DUSTS AND MISTS

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 COPPER DUSTS AND MISTS.

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 copper dusts and mists not in excess of 1 milligram 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 copper dusts and mists.

(b) Exposure determination and measurement. (1) Each employer who has a place of employment in which copper dusts and mists is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of copper dusts and mists 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 copper dusts and mists.

(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 copper dusts and mists;

(ii) Any measurements of copper dusts and mists taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to copper dusts and mists; 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 copper dusts and mists 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 copper dusts and mists 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 copper dusts and mists 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 copper dusts and mists 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 copper dusts and mists 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.

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

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(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
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Above permissible exposure	$\pm 25\%$
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At or below permissible exposure and above the action level	$\pm 35\%$
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At or below the action level	$\pm 50\%$
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(d) Compliance. (1) No employee shall be exposed to copper dusts and mists above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of copper dusts and mists 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. 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 copper dusts and mists.

(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

(ii) In work situations in which engineering and work practice controls are technically not feasible; or

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(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of copper dusts and mists to at or below the permissible exposure; or

(iv) 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 COPPER DUSTS AND MISTS

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Particulate Concentration	
50 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.
2000 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.
Greater than 2000 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 copper dusts and mists.

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(2) Powdered copper and copper salts shall be stored so as not to come in contact with acetylene and magnesium.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use impervious clothing, gloves, face shields (eight-inch minimum) and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts. Face shields shall comply with § 1910.133(a)(2), (a)(4), (a)(5), and (a)(6).

(2) Employers shall ensure that employees whose clothing may have become contaminated with powdered copper, copper salts or liquids containing copper salts change into uncontaminated clothing before leaving the work premises.

(3) Employers shall ensure that clothing contaminated with copper salts is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of the copper salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the copper salts, the employer shall inform the person performing the operation of the hazardous properties of copper salts.

(4) Employers shall ensure that non-impervious clothing which becomes contaminated with copper salts be removed promptly and not reworn until the copper salts are removed from the clothing.

(5) Employers shall provide and ensure that employees use safety goggles (cup-cover type dust and splash safety goggles) which comply with § 1910.133 (a)(2)-(a)(6) where powdered copper or dusts, mists, or liquids containing copper salts may contact the eyes.

(g) Spills and disposal. In the event that copper dusts and mists are spilled or released, the employer shall immediately provide available ventilation and then clean up the spill.

(h) Sanitation. (1) Employers shall ensure that employees whose skin becomes contaminated with copper salts promptly wash or shower with soap or mild detergent and water to remove any copper salts from the skin.

(2) Employers shall ensure that employees do not eat or smoke in areas where powdered copper, copper salts or liquids containing copper salts, are handled, processed or stored.

(3) Employers shall ensure that employees who handle powdered copper, copper salts, or liquids containing copper salts wash their hands thoroughly with soap or mild detergent and water before eating, smoking or using toilet facilities.

(i) Training and information. (1) Each employer who has a workplace in which copper dusts and mists 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.

(2) Each employer who has employees exposed to copper dusts and mists above the action level or employees who may have skin or eye contact with copper dusts and mists, or employees who work where a spill or release of powdered copper, copper salts, or liquids containing copper salts may occur, shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for copper dusts and mists (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to copper dusts and mists.

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(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to copper dusts and mists 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 copper dusts and mists.

(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 airborne concentrations of copper dusts and mists 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
- (iv) Skin disease
- (v) Blood disorders
- (vi) Wilson's 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 copper dusts and mists which are listed in Appendix A which the employee suspects are caused by exposure to copper dusts and mists.

(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 copper dusts and mists;

(ii) A description of the affected employee's duties as they relate to his exposure to copper dusts and mists;

(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 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 copper

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dusts and mists or would directly or indirectly aggravate any detected medical condition;

(B) Any recommended limitations upon the employee's exposure to copper dusts and mists 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 copper dusts and mists.

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

(7) No employee shall be exposed to liquid copper dusts and mists or airborne concentrations of copper dusts and mists 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 copper dusts and mists.

(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 copper dusts and mists.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to copper dusts and mists 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.

(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:

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- (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 copper dusts and mists;

(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 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 copper dusts and mists which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to copper dusts and mists 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.

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- (ii) Visually observe all steps related to the measurement of the airborne concentration of copper dusts and mists 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 COPPER DUSTS AND MISTS

- I. SUBSTANCE IDENTIFICATION
 - A. Substance: Copper dusts and mists
 - B. Permissible Exposure: 1 milligram of copper dusts and mists per cubic meter of air (mg/M3) averaged over an eight-hour work shift.
 - C. Appearance and Odor: Odorless solids
- II. HEALTH HAZARD DATA
 - A. Ways in which the chemical affects your body: Copper dusts and mists can affect your body if you inhale them or if they come in contact with your eyes or skin. They may also affect your body if you swallow them.
 - B. Effects of Overexposure:
 - 1. Short-term Exposure: Powdered copper or dusts and mists of copper salts may cause a feeling of illness similar to the common cold with sensations of chills and stuffiness of the head. Small copper particles may enter the eye and cause irritation, discoloration and damage.
 - 2. Long-term Exposure: Repeated or prolonged exposure to copper dusts or mists may cause skin irritation or discoloration of the skin or hair.
 - 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 copper dusts and mists.
- III. EMERGENCY FIRST AID PROCEDURES
 - A. Eye Exposure: If copper dusts or mists get into your eyes, wash your eyes immediately with copious 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.

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- B. Skin Exposure: If copper salts or liquids containing copper salts get on your skin, promptly wash the contaminated skin using soap or mild detergent and water. If copper salts or liquids containing copper salts penetrate your clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.
- C. Breathing: If you or any other person breathes in large amounts of copper dusts or mists 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 powdered copper, copper salts, or liquids containing copper salts 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.
- 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 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 copper dusts and mists. 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: You must wear impervious clothing, gloves, face shield or other appropriate protective clothing to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts. Replace or repair impervious clothing that has developed leaks.
- C. Eye Protection: You must wear dust-resistant safety goggles where powdered copper or dusts containing copper salts may contact your eyes. You must wear splash-proof safety goggles where mists or liquids containing copper salts may contact your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

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- A. Copper dust clouds can be ignited at temperatures above 700 C
- (1292 F).
- B. Powdered copper and copper salts must be stored away from extreme heat, acetylene, and magnesium.
- C. If your work clothing may have become contaminated with powdered copper, copper salts or liquids containing copper salts, you must change into uncontaminated clothing before leaving the work premises.
- D. You must promptly remove any non-impervious clothing that becomes contaminated with copper salts and this clothing must not be reworn until the copper salts are removed from the clothing.
- E. If your skin becomes contaminated with copper salts, you must promptly wash or shower with soap or mild detergent and water to remove the copper salts from your skin.
- F. You must not eat or smoke in areas where powdered copper, copper salts, or liquids containing copper salts are handled, processed or stored.
- G. If you handle powdered copper, copper salts or liquids containing copper salts, you must wash your hands thoroughly with soap or mild detergent and water before eating, smoking or using toilet facilities.
- H. Ask your supervisor where copper dusts and mists may be released in your work area and for any additional plant 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 copper dusts and mists. In addition, your employer must instruct you in the safe use of powdered copper and copper salts, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to copper dusts and mists. 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

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SUBSTANCE TECHNICAL GUIDELINES
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I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Common compounds: Copper sulfate dust or mist; cuprous chloride dust
2. Formula: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; CuCl
3. Molecular weight: CuSO_4 - 249.7; CuCl - 99

B. Physical Data

1. Boiling point (760 mm Hg): Not applicable
2. Specific gravity (water = 1): Greater than 1
3. Vapor density (air = 1 at boiling point of copper dusts and mists): Not applicable
4. Melting points: Higher than 100 C (212 F). For example, copper sulfate = 150 C (302 F); cuprous chloride = 430 C (806 F)
5. Vapor pressure at 20 C (68 F): Not applicable
6. Solubility in water, % by weight at 20 C (68 F): Ranges from very low (e.g. cuprous chloride = 0.006) to high (e.g. copper sulfate = 35)
7. Evaporation rate (butyl acetate = 1): Not applicable
8. Appearance and odor: Odorless solids

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Ignition Temperature: copper dusts; -700 C (1292 F).

B. Reactivity

1. Conditions contributing to instability: Extreme heat.
2. Incompatibilities: Copper dusts and mists may react with acetylene gas to form copper acetylides, which are solids that are sensitive to shock. Some copper mists may react with magnesium metal to form flammable hydrogen gas.
3. Hazardous decomposition products: None.
4. Special precautions: None.

III. SPILL AND DISPOSAL PROCEDURES

A. If copper dusts and mists are spilled or released, the following steps should be taken:

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

B. Persons not wearing protective equipment should be restricted from areas of release until cleanup has been completed.

C. Waste disposal methods: Copper dusts and mists and copper 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 average 8-hour exposure may be

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determined from a single eight-hour sample or two (2) 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 copper dusts and mists 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 copper dusts and mists to plus or minus 25%.

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. Employers should advise employees of all areas and operations where exposure to copper dusts and mists could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to copper dusts and mists is likely to occur are: during the mining, extraction and refining of copper ores, and the use of copper compounds and their solutions as fungicides, insecticides, germicides, catalysts, pigments, wood preservatives; in the manufacture of electroplating solutions and in the manufacture and fabrication of copper rods, wire, sheet, tubing and piping, and copper alloys.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

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Inhalation of dusts and mists of copper and copper salts results in irritation of the upper respiratory tract, with occasional ulceration and perforation of the nasal septum. Inhalation of copper and its compounds by animals caused injury to the lungs and liver with hemochromatosis. Access of sheep to salt licks containing 5 to 9 per cent copper sulfate caused the sudden onset of hemolytic anemia, icterus, and hemoglobinuria followed by death in a day or two; at necropsy, the liver, kidneys, and spleen showed severe degenerative changes. Workers exposed to copper dust in concentrations of 0.075 to 0.120 mg/m³ complained of mild nasal discomfort. Exposure to the dust of copper acetate produced sneezing, coughing, digestive disorders and fever. Metal workers exposed to complex copper salts in dust form complained of metallic taste with irritation of nasal and oral mucosa; atrophic changes in the mucous membranes were noted in subjects exposed for long periods of time. On ingestion, copper salts act as irritants and cause nausea, vomiting, abdominal pain, hemorrhagic gastritis, and diarrhea. Copper salts splashed in the eye cause conjunctivitis, corneal ulceration and turbidity, and may produce palpebral edema. Copper particles embedded in the eye result in pronounced foreign body reaction with characteristic discoloration of ocular tissue. Allergic contact dermatitis due to copper exposure, although rare, has been reported. Greenish discoloration of the skin and hair of some copper workers has been observed. It should be noted that copper is an essential element for health; but conversely, the fact that a material may be essential at one level does not preclude its ability to produce harmful effects at a higher level.

III. SIGNS AND SYMPTOMS

Irritation of nasal mucous membranes and pharynx; nasal ulceration and perforation; eye irritation; metallic taste; dermatitis from prolonged contact; by analogy to effects caused in animals it may cause lung, liver, kidney damage and anemia.

IV. SPECIAL TESTS

Elevated urinary copper levels may be indicative of increased exposure.

V. TREATMENT

Remove from exposure. Flush eyes and skin with water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation if indicated.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of copper are caused by its irritant properties on the upper respiratory tract. It is important that the physician become familiar with plant operating conditions in which exposure to copper occurs. Those with skin disease may not tolerate

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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 copper exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Chronic respiratory disease -- Copper dusts and mists cause respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper dusts and mists might cause exacerbation of symptoms due to its irritant properties.
2. Liver disease -- Copper dusts and mists cause liver damage in animals. Persons with preexisting liver disease may be more susceptible to the effects of this agent.
3. Kidney disease -- Copper dusts and mists cause kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.
4. Skin disease -- Skin sensitization in human subjects has occurred. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.
5. Hematopoietic disorders -- Anemia has occurred in animals given copper salts orally. Persons with preexisting blood disorders may be more susceptible to the effects of this agent.
6. Wilson's disease -- Persons with preexisting Wilson's disease may be more susceptible to the effects of this agent.

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

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2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1033-1037.
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5. Gleason, R.P.: "Exposure to Copper Dust," American Industrial Hygiene Association Journal, 29:461-462, 1968.
6. Saltzer, E.I. and J.W. Wilson: "Allergic Contact Dermatitis Due to Copper," Archives of Dermatology, 98:375-376, 1968.
7. Grant, W. Morton: Toxicology of the Eye (2d ed.), Charles C. Thomas, Illinois, 1974, pp. 311-319.
8. Askergrén, A. and M. Mellgren: "Changes in the Nasal Mucosa after Exposure to Copper Salt Dust, a Preliminary Report," Scandinavian Journal of Work, Environment and Health, 1:45-49, 1975.

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REFERENCES AND SOURCES
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- (f) Personal Protective Equipment, and, (h) Sanitation
Eye: Grant, "Toxicology of the Eye;" Patty, "Industrial Hygiene and Toxicology;" Sax, "Dangerous Properties of Industrial Materials"
Skin: Patty, "Industrial Hygiene and Toxicology;" Sax, "Dangerous Properties of Industrial Materials"
Ingestion: Patty, "Industrial Hygiene and Toxicology;" Deichmann and Gerarde, "Toxicology of Drugs and Chemicals;" "Encyclopedia of Occupational Health and Safety," International Labour Office

COMMENTS

Eye - Classification: 2 and 6

Output statement numbers: 10, 12

Exceptions: 10 and 12 combined

Grant contains an extensive discussion of the toxic effects of copper in the eye. The characteristic reaction to metal bodies includes a purulent inflammatory reaction and discoloration in the conjunctiva, cornea, sclera, anterior chamber, and posterior chamber. "As a rule copper rapidly causes (serious) widespread inflammatory and degenerative changes in the vitreous and retina." When copper enters the lens by diffusion in some soluble form from a source outside of the lens, the discoloration is shimmering and multicolored and not accompanied by opacification; but when the lens have been directly entered or injured by a copper-containing foreign body, there may be formation of a dense cataract and accompanying yellow-green discoloration of the lens." Glaucoma from retained intraocular copper foreign bodies is noted as being a "rarely reported but particularly intriguing complication."

Sax notes that "copper chloride and sulfate have been reported as causing irritation . . . of the conjunctivae," and reports "cuprous oxide is irritating to the eye . . ."

Patty states "contact of the eye (with Cu salts) will result in conjunctivitis, edema of the eyelids, and ulceration and turbidity of the cornea."

Copper and its compounds can obviously cause significant effects upon the eye. To prevent excessive exposures, it is concluded sufficient to require eye protection where "powdered dusts, mists, or liquids containing copper salts" may contact the eyes.

Skin - Classification: 2 and 6

Output statement numbers: 2, 5b, 7a, 17g, 17i, 20a

Exceptions: None.

Patty notes "contact with the skin with Cu salts may result in an itching eczema of papulovesicular nature, which may be due to sensitization." Sax reports that copper chloride and sulfate can cause skin irritation "which may be on an allergic basis." He also notes that "discoloration of the

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skin is often seen in persons handling copper, but this does not indicate any actual injury from copper."

Classifications of 2 and 6 are considered appropriate only for copper salts and liquids containing them. The pure metal has no significant effect.

Ingestion - Classification: 2 and 6

Output statement numbers: 19, 20a

Exceptions: See below

Patty reports that "copper poisoning in animals leads to injury of the liver, kidneys, and spleen," and that sulfate fed ad libitum in the diet of rats at a level of 4000 ppm caused starvation and death." Deichmann and Gerarde report that "acute copper poisoning (doses of 5 - 50 mg) can be expected following ingestion" of foods "that have remained in contact with a copper container for any length of time." ILO notes that "at least 99.9995% of the world's population is essentially immune to poisoning by copper. But approximately 1 in 200,000 individuals has inherited a pair of abnormal genes, as a result of which copper toxicity - Wilson's disease - will ultimately develop. This will occur with the ingestion of only a normal diet containing 2 - 5 mg of copper per day and will probably occur more rapidly and more severely if the individual . . . ingests more of the metal . . ."

Classifications of 2 and 6 for liquids containing copper salts and solid copper or copper salts respectively are concluded to be appropriate. Of note is that statement 20a is required for copper salts to prevent sensitization while 20b is required for copper in powdered form to prevent excessive ingestion. For the purposes of this standard, statement 20a is simply used for both the salts and powdered form of the copper.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

"Lange's Handbook of Chemistry," McGraw - Hill, New York, 1973, 11th edition (Lange)

Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd edition, Vol. 6, p. 265 (K-O)

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1973 (NFPA)

Sources of data items used:

- | | | | |
|-----|----|----|--|
| I. | A. | 1. | Synonyms: ACGIH |
| | | 2. | Formula: Lange |
| | | 3. | Molecular weight: Lange |
| | B. | 1. | Boiling point: Not applicable |
| | | 2. | Specific gravity: Lange |
| | | 3. | Vapor density: Not applicable |
| | | 4. | Melting point: Lange |
| | | 5. | Vapor pressure: Not applicable |
| | | 6. | Solubility in water: Lange |
| | | 7. | Evaporation rate: Not applicable |
| | | 8. | Appearance and odor: Lange |
| II. | A. | 1. | Ignition Temperature: Bureau of Mines, |

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- RI 6516, "Explosibility of Metal Powders".
- B. 1. Conditions contributing to instability: Not applicable
2. Incompatibilities: NFPA-491M
3. Hazardous decomposition products:
4. Special precautions: None
- III. A. Steps if released or spilled: ADL
C. Waste disposal method: Not applicable
- V. Miscellaneous precautions:

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

- American Conference of Governmental Industrial Hygienists, "Documentation of Threshold Limit Values," 1971 (TLV)
- Briggs, B. A., "Safer Pesticides for Home and Garden," 1972 (NIOSH Technical Information Service - NIOSH 20959)
- Browning, E., "Toxicity of Industrial Metals," Butterworths, 1969 (Browning)
- Considine, D. M., "Chemical and Process Technology Encyclopedia," McGraw Hill, 1974 (Considine)
- "Copper Dusts and Mists," Allied Chem. Co., Plating Technical Bulletin PTB - 1, 1973, "Copper for P - C Boards" (Allied Plating)
- "Copper Dusts and Mists," Allied Chem. Co., Material Safety Data Sheet (Allied MSDS)
- "Copper Dusts and Mists," Diamond Shamrock Chem. Co., Material Safety Data Sheet, October 4, 1972 (Shamrock MSDS)
- "Copper Dusts and Mists," Harshaw Chem. Co., Material Data Sheet, Jan. 5, 1973 (Harshaw)
- "Copper Dusts and Mists," Hazard Process Index, Hazard Entry No. 47, NIOSH HSM-99-73-62 (HPI)
- "Copper Dusts and Mists," Cincinnati Milacron Chems., Inc., Technical Bulletin 0401 - 7K1, 0402 - 7K1, "Naphthenates - Copper" (Milacron)
- "Copper Dusts and Mists," Commonwealth of Pennsylvania, Department of Health, Division of Occupational Health, Hygienic Information Guide No. 73, "Copper" (Penna #73)
- "Copper Dusts and Mists," Tennessee Corp., "Copper Sulfate," 1965 (Tennessee)
- Deichmann, W. B. and Gerarde, H., "Toxicity of Drugs and Chemicals," Academic Press, 1969 (Deichmann)
- "Electroplating," Occupational Health Branch, Division of Public Health, Wellington: Occupational Health Bulletin No. 3, 1969 (NIOSH Technical Information Service - NIOSH 2525)
- Fairhall, L. T., "Industrial Toxicology," 2nd edition, Williams and Wilkins, Co., 1957 (Fairhall)
- Gleason, M. N. et al., "Chemical Toxicology of Commercial Products," Williams and Wilkins Co., 1969 (Gleason)
- Gleason, R. P., "Exposure to Copper Dust," AIHA Journal 29(5), p. 461 - 2, 1968 (Gleason - AIHA Journal)
- Grant, W. M., "Toxicology of the Eye," 2nd edition, C. C. Thomas, 1974 (Grant)
- Hamilton, A. and Hardy, H. L., "Industrial Toxicology," Publishing Sciences Group, Inc., 3rd edition, 1974 (H/H)
- International Labour Organization, "Encyclopedia of Occupational Health and Safety," Geneva, 1972 (ILO)
- Jager, L. E., "Hazards in the Plating Industry," Occupational Health Review 18, p. 3 - 10, 1966 (NIOSH Technical Information Service - NIOSH 11461)

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- Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience, 2nd edition, 1972 (K-O)
- Mosher, R. H., "Industrial and Specialty Papers," Vol. I, Chemical Publishing Co., 1968 (Mosher)
- "New Catalytic Route to Acrylamide," Chem Eng. 80(27), p. 68 - 9, 1973 (Acrylamide)
- Patty, F. A., "Industrial Hygiene and Toxicology," Vol. II, Interscience, 1965 (Patty)
- Stanford Research Institute, "Chemical Economics Handbook," Menlo Park, California (SRI)
- Sorenson, J. R., Kober, T. E. and Petering, H. G., "The Concentration of Cd, Cu, Fe, Ni, Pb and Zn in Bituminous Coals from Mines with Differing Incidences of Coal Worker's Pneumoconiosis," AIHA Journal 35(2), p 93 - 8, 1974 (Sorenson)
- Thienes, C. H. and Haley, T. J., "Clinical Toxicology," 5th edition, Lea and Febiger, 1972 (Thienes)

References for Specific Use/Exposure

1. H/H, HPI, Considine, SRI, K-O, Browning, Patty, Sorenson
2. Patty, Browning, HPI, SRI, Considine, K-O, Fairhall, Gleason - AIHA Jou
3. HPI, Patty, Browning, SRI, K-O, Considine
4. Patty, Fairhall, Tennessee Corp., NIOSH 30959, Penna #73, K-O, Gleason, HPI, Considine
5. Considine, K-O, Penna #73, Browning, Patty, HPI, Milacron, Fairhall, Mosher
6. K-O, HPI, Considine, NIOSH 2525, 11461, Harshaw, Allied Plating
7. HPI, K-O, Considine, Milacron, Patty, Fairhall
8. HPI, K-O, Considine, Acrylamide
9. K-O, Considine, HPI
10. K-O, HPI, ILO
11. Considine

References for Specific Control Methods

Penna #73, Shamrock MSDS, Harshaw, Allied MSDS, ILO, Deichmann, TLV, HPI, H/H, Browning, Thienes, Grant and Gleason - AIHA Journal were the references used in all the Specific Control Methods.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Copper dusts and Mists

D. O. L. STANDARD: 1 mg/M3

WARNING PROPERTIES:

Eye Irritation: According to Grant, copper acetoarsenite, copper chloride, copper sulfate, copper carbonate and oxide, and copper metal all produce local irritant effects when in contact with the eye. The Documentation of TLV's also notes that copper salts on the eye may cause "conjunctivitis or even ulceration and turbidity (sic) of the cornea." Concentrations producing these effects are not given. Only full facepiece respirators shall be worn in copper dust and mist atmospheres.

-IDLH: There is no evidence that an acute exposure to a high concentration of copper dusts and mists could impede escape. For the purposes of this standard, therefore, respirators have been selected on the basis of the protection factor afforded by each device.

Other Toxicological Information: The Documentation of TLV's states that "inhalation of dusts and mists of copper salts in considerably higher

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(more than 0.1 mg/M3), but generally unmeasured, concentrations can result in congestion of nasal mucous membranes, sometimes of the pharynx and, on occasion, ulceration with perforation of the nasal septum. If copper salts in sufficient concentration reach the gastro-intestinal tract they act as irritants producing salivation, nausea, vomiting, gastric pain, hemorrhagic gastritis and diarrhea. Chronic exposures may result in an anemia but chronic poisoning as from lead does not occur. On the skin, copper salts also act as irritants producing itching eczema; and on the eye, conjunctivitis or even ulceration and turbidity (sic) of the cornea."

Patty reports that "few instances of illness from exposure to copper and its compounds have been reported. . . . Men exposed to dusts of copper acetate have complained of sneezing, coughing, digestive disorders, and fever."

Browning reports that "acute poisoning from inhalation of copper containing dust has also been reported by Flury and Zangger to cause symptoms of heavy metal poisoning, and Kroner observed moderately severe disturbances - pain in the chest, dyspnoea and a metallic taste in the mouth - in an industrial laboratory where a solution containing 0.6 - 1 per cent of copper and 0.1 - 0.2 per cent of ammonia was being sprayed under pressure; in the case with the greatest exposure the symptoms included nausea and vomiting Similar symptoms of acute gastro-intestinal disturbance, as well as some respiratory irritation and dyspnoea, were observed by Lewin (1910) in his extensive investigation of workers exposed to the dust of metallic copper and its oxides, but he attributed the digestive disturbance to the conversion of the swallowed metallic copper to its irritating salts, and the respiratory symptoms to the non-specific reaction to the inhaled dust as a foreign body in the lungs."

Browning notes that "there is little evidence that copper presents a serious industrial hazard, either from acute or chronic poisoning."

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USE/EXPOSURE AND CONTROL DOCUMENT
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	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of dust and mist and skin contact with solid during mining, extraction, and refining of copper ores. Extracting of copper from ores involves crushing, roasting, and smelting.	A, B	Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice
2.	Inhalation of dust during manufacture and fabrication of copper rod, wire, sheet, piping and tubing used in electrical, plumbing, and building industries and in the manufacture of domestic utensils	A	Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice
3.	Inhalation of dust during manufacture and fabrication of copper alloys - brasses (5-40% zinc), bronzes (5-20% lead), and alloys containing silicon, aluminum, chromium, beryllium, nickel, manganese, phosphorus, and iron which can be cast, forged, molded, rolled, extruded, drawn, and machined (used for general engineering purposes, domestic utensils, canning, coinage, munitions, automotive manufacture, hardware, jewelry and furniture)	A	Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice
4.	Inhalation of dust and mist and skin contact with solid or solution during use of copper salts (sulfate, oxides, hydroxide, acetate, copper-zinc chromate mixture (Crag fungicide), copper-lime mixtures) as insecticide, fungicides,	A, B	Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice

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germicides for treatment
of soils, feed and grains,
textiles, water supplies,
sewers and drains

- | | | | |
|----|---|-----|--|
| 5. | Inhalation of dust and skin contact with solid during use of copper salts in paint pigments (acetoarsenite - Paris green, arsenite, acetate, cyanide), in marine and other paints as antifouling agents (oxides, hydroxide, acetate, acetoarsenite, naphthenate), and in glass and ceramic glazes as coloring agents (nitrate, hydroxide, oxides) | A,B | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice |
| 6. | Inhalation of dust and mist and skin contact with mist, solution or solid during use of copper salts (sulfate, pyrophosphate, oxide, fluoborate, carbonate, nitrate, cyanide) in electroplating baths for manufacture of products such as record masters, printing rolls, wire, printed circuits | A,B | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice |
| 7. | Inhalation of mist and skin contact with mist, solution, or solid during use of copper salts (naphthenate, acetoarsenite) for preservation of wood, cotton, sisal, and jute cordage | A,B | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice |
| 8. | Inhalation of dust and mist and skin contact with solid during use of copper salts (nitrate, acetate, oxide) as catalysts (for automobile emission control, organic chemical reactions) | A,B | Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice |
| 9. | Inhalation of dust and mist and skin contact | A,B | Local exhaust ventilation; general dilution ventila- |

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with solid during use of copper salts (nitrate, acetate) for textile treatment (as dyeing assists, for mildew proofing)

tion; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice

10. Inhalation of dust and mist and skin contact with solid during manufacture and distribution of copper salts and during maintenance of equipment and storage containers

A,B

Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice

11. Inhalation of dust and mist and skin contact with solid or solution during use of copper salts (chloride, iodide, sulfate) for organic synthesis

A,B

Local exhaust ventilation; general dilution ventilation; personal protective equipment (respiratory protective devices, gloves, goggles, face shield, apron); good personal hygiene practice

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