

Occupational Health Guideline for Silver Metal and Soluble Silver Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

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

SUBSTANCE IDENTIFICATION

Silver, metallic

- Formula: Ag
- Synonyms: None
- Appearance and odor: Characteristic white metallic solid with no odor.

Silver nitrate

- Formula: AgNO₃
- Synonyms: Argerol; lunar caustic
- Appearance and odor: Colorless and odorless solid which may become gray on storage.

Silver fluoride

- Formula: AgF
- Synonyms: None
- Appearance and odor: Yellow-white, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for silver metal and soluble silver compounds is 0.01 milligram of silver metal and soluble silver compounds per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for silver metal and soluble silver compounds from 0.01 mg/m³ to 0.1 mg/m³.

HEALTH HAZARD INFORMATION

• Routes of exposure

Silver or soluble silver compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Silver or soluble silver compounds can cause discoloration or blue-gray darkening of the eyes, nose, throat, and skin. Silver nitrate is strongly corrosive and can cause burns and permanent damage to the eyes and can burn the skin.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to silver metal or soluble silver compounds.

• Recommended medical surveillance

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

1. Initial Medical Examination:

—Examination of the nasal septum, eyes, and skin for evidence of pigmentation: The purpose is to establish a baseline for future observations of silver deposition in tissues.

2. Periodic Medical Examination: The aforementioned

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

The dust of silver and its soluble compounds cause argyria, the local or generalized impregnation of the mucous membranes, skin, and eyes with silver. Localized argyria occurs in the skin, eyes, nasal septum and throat, where gray-blue patches of pigmentation are formed without evidence of tissue reaction. Generalized argyria is recognized by the widespread pigmentation of the skin and may be seen first in the conjunctiva, with some localization in the inner canthus. Argyrosis of the respiratory tract has been described in two workers involved in the manufacture of silver nitrate; their only symptom was mild, chronic bronchitis; bronchoscopy revealed tracheobronchial pigmentation; biopsy of the nasal mucous membrane showed silver deposition in the subepithelial area. A total body burden from 1 to 5 g of silver will lead to generalized argyria. Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. Silver nitrate (lunar caustic) may cause irritation, ulcers, and discoloration of skin; if ingested, it may cause abdominal pain and gastroenteritis.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Silver, metallic**

1. Molecular weight: 107.9
2. Boiling point (760 mm Hg): 2200 C (3992 F)
3. Specific gravity (water = 1): 10.4
4. Vapor density (air = 1 at boiling point of metallic silver): Not applicable
5. Melting point: 966 C (1771 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver nitrate**

1. Molecular weight: 169.9
2. Boiling point (760 mm Hg): 444 C (831 F) (decomposes)
3. Specific gravity (water = 1): 4.4
4. Vapor density (air = 1 at boiling point of silver nitrate): Not applicable
5. Melting point: 209 C (408 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 245
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver fluoride**

1. Molecular weight: 126.9
2. Boiling point (760 mm Hg): 1159 C (2119 F) (approximately)
3. Specific gravity (water = 1): 5.8
4. Vapor density (air = 1 at boiling point of silver fluoride): Not applicable

5. Melting point: 435 C (815 F)

6. Vapor pressure at 20 C (68 F): Negligible

7. Solubility in water, g/100 g water at 20 C (68 F):

64

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

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of metallic silver and soluble silver compounds with acetylene may cause formation of silver acetylide that is sensitive to shock. Contact with ammonia may cause formation of compounds that are explosive when dry. Contact with strong hydrogen peroxide solutions will cause violent decomposition to oxygen gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when some soluble silver compounds decompose.

4. Special precautions: Soluble silver compounds will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Most soluble silver compounds are not combustible. However, silver nitrate is a strong oxidizing material capable of increasing the flammability of combustible, organic, or other readily oxidizable materials. The following soluble silver compounds are explosives and should be stored and handled in accordance with 29 CFR 1910.109: silver acetylide, silver azide, silver fulminate, silver oxalate mixtures, silver styphnate, silver tartarate mixtures, and silver tetrazene.

• **Warning properties**

According to Stecher "many silver salts are irritating . . . to mucous membranes." Grant notes that many simple silver salts and silver ammonium compounds are injurious to the eye. According to Grant, "a great many reports have been published describing argyrosis of the eye, either from local contact with silver compounds or as a part of a generalized argyrosis from systemic absorption of silver or its compounds." Since there are inadequate data to assess the effects on the eye at or near the permissible exposure limit, for the purposes of this guideline, silver metal and soluble silver compounds are considered to have poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for silver metal and soluble silver

compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with powdered metallic silver or solids or liquids containing soluble silver compounds, where skin contact may occur.

- If employees' clothing may have become contaminated with solids or liquids containing soluble silver compounds, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with metallic silver or soluble silver compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substances from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the substances, the person performing the operation should be informed of substances' hazardous properties.

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

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of powdered metallic silver or solids or liquids containing soluble silver compounds contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to silver nitrate or solutions containing 5 percent or more silver nitrate by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with metallic silver or soluble silver compounds should be promptly

washed or showered to remove any metallic silver or soluble silver compounds.

- Eating and smoking should not be permitted in areas where metallic silver or solids or liquids containing soluble silver compounds are handled, processed, or stored.

- Employees who handle powdered metallic silver or solids or liquids containing soluble silver compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during mining and purification from ore; during refining from secondary sources	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of silver nitrate for use in photography, mirrors, plating, inks, dyes, and porcelain; and as germicides, antiseptics, caustics, and analytical reagents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

Operation

Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints

Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get into the eyes, wash 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 this chemical.

• Skin Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get on the skin, flush the contaminated skin with water. If powdered metallic silver or solids or liquids containing soluble silver compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention. Other silver compounds should be removed by promptly flushing the skin with water.

• Breathing

If a person breathes in large amounts of silver metal or soluble silver compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

If silver nitrate or other corrosive soluble silver compounds have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the silver nitrate or other corrosive silver compounds. Do not attempt to make the exposed person vomit. Get medical attention immediately. When non-corrosive soluble silver compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If powdered silver metal or soluble silver compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
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. Liquid containing silver metal or soluble silver compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Silver metal and soluble silver compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Silver," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Buckley, W. R., et al.: "Localized Argyria. II. Clinical Nature of the Silver Containing Particles," *Archives of Dermatology*, 92:697-705, 1965.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hunter, D.: *Diseases of Occupations* (4th ed.), Little, Brown, Boston, 1969.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.
- *Survey of Compounds Which Have Been Tested for Carcinogenic Activity*, U.S. Public Health Service Publication No. 149, Original, Supplements 1 and 2, 1961-1967, 1968-1969, and 1970-1971.

RESPIRATORY PROTECTION FOR SILVER METAL AND SOLUBLE SILVER COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 0.01 mg/m ³
Particulate Concentration	
0.5 mg/m ³ 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.
10 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 mg/m ³ 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 20 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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