HETA 2000-0041-2796
OmniSource Corporation
Precious Metal Recycling Facility
Ft. Wayne, Indiana

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PREFACE

The Hazard Evaluations and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health (OSHA) Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

HETAB also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Kristin K. Gwin and Jeffrey B. Nemhauser of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Kevin C. Roegner. Analytical support was provided by Data Chem Laboratories, Inc. Desktop publishing was performed by Robin Smith. Review and preparation for printing were performed by Penny Arthur.

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Highlights of the NIOSH Health Hazard Evaluation

Exposures to Metals and Chemicals in the PMR Facility

In January 2000, NIOSH investigators conducted a health hazard evaluation at OmniSource Corporation's precious metal recycling facility. We looked into management and employee concerns about exposure to silver and components of the photographic fixer solution.

What NIOSH Did

We took air samples for metals, glutaraldehyde, hydroquinone, and hydrogen cyanide.

We checked the ventilation by releasing a "smoke" to see air flows.

We looked at work tasks, work practices, general housekeeping, and potential safety hazards.

We talked with and examined all PMR facility employees.

What NIOSH Found

Employees of the PMR facility were over-exposed to silver.

No glutaraldehyde, hydroquinone, or hydrogen cyanide were found in the air.

The exhaust hoods over both furnaces were not working. Fumes were seen escaping the hoods.

The powered winch used to lift crucibles out of the furnaces is a safety concern.

Employees were not wearing the correct gloves to protect them against skin exposure to the fixer solution.

Employees were not wearing safety glasses while working in the furnace room.

Employees were not wearing fire retardant boots or protective coverings when pouring molten metal from the crucibles.

General housekeeping was poor in the PMR facility.

What OmniSource Corporation Managers Can Do

Lower exposures to airborne silver by improving the design of exhaust hoods over both furnaces (see full report for more details).

Repeat air sampling after changes to the exhaust hoods are made to determine if silver exposures decrease.

Check the condition of the powered winch used to lift crucibles out of furnace and start periodic maintenance checks.

Provide fire retardant boots or protective coverings to be worn while pouring molten metal.

Provide neoprene rubber gloves to be worn when in contact with fixer solution.

Start a housekeeping maintenance schedule.

Instead of using hair and urine tests to monitor silver exposure, use regular skin and eye exams performed by a physician.

What the PMR Facility Employees Can Do

Do not eat, drink, or smoke in facility.

Properly clean and store respirators daily after use.

Wear safety glasses in the furnace room.

Wash hands after working and before eating and drinking to lower their exposure to silver dust.

Keep the doors to the furnace room and work station/office area closed as much as possible.

CDC
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What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513/841-4252 and ask for HETA Report # 2000-0041-2796

National Institute for Occupational Safety and Health
NIOSH

Health Hazard Evaluation Report 2000-0041-2796
OmniSource Corporation
Precious Metal Recycling Facility
Ft. Wayne, Indiana
May 2000

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SUMMARY

On November 1, 1999, the National Institute for Occupational Safety and Health (NIOSH) received a management request from OmniSource Corporation to conduct a health hazard evaluation (HHE) to evaluate occupational exposure to silver at their company's precious metal recycling (PMR) facility in Ft. Wayne, Indiana. The request was prompted by concerns about one employee who had been diagnosed as having argyria, a blue-grey discoloration of the skin, mucous membranes, and/or eyes resulting from prolonged silver exposure. Management also expressed concern about worker exposure to the fixer solution from which the silver is recovered.

A site visit, conducted on January 10-11, 2000, consisted of an environmental and medical component. The environmental evaluation included a full-shift personal breathing-zone (PBZ) air sample to assess worker exposure to silver and 26 other metals and minerals and full-shift area air sampling to assess exposure to 26 different metals and minerals, glutaraldehyde, hydroquinone, and hydrogen cyanide. Qualitative ventilation measurements were also performed to determine airflow patterns. The medical evaluation consisted of a record review, employee interviews to assess a medical and occupational history, and focused physical examinations of each of the three PMR facility employees.

The one full-shift PBZ sample taken on an operator revealed a time-weighted average (TWA) silver exposure of 0.14 milligrams per cubic meter (mg/m^3), 14 times greater than the Occupational Safety and Health Administration (OSHA) and NIOSH exposure limit of 0.01 mg/m^3. Full-shift area air sampling revealed silver concentrations ranging from 0.009 to 0.19 mg/m^3. All area samples, with the exception of one, had concentrations that exceeded the OSHA and NIOSH exposure limits. The PMR facility furnace operator wore a half-mask powered air-purifying respirator (PAPR) in the furnace room and main PMR facility; however, respirators were not worn when employees were in the work station and office area, where silver concentrations ranged from 0.012 to 0.02 mg/m^3. These levels exceed OSHA and NIOSH exposure limits. Full-shift area air sampling for glutaraldehyde, hydroquinone, and hydrogen cyanide revealed no detectable amounts of those substances. None of the 26 other metals or minerals analyzed for in the air samples exceeded any applicable exposure limit.

The qualitative ventilation assessment indicated that the furnace room was under strong negative pressure, that should prevent silver dust and fume from escaping the room. However, silver was detected in area

samples taken throughout the rest of the facility, suggesting that silver is migrating from the furnace room to other areas. Neither exhaust hood (one was in place over each of the two working furnaces) was operating during our visit. Fumes off-gassing from the furnaces could periodically be seen escaping the hoods. During the loading and unloading of the crucibles, the furnace room doors are left open and airborne silver may escape the room. Pressure tests indicated the work station and office area to be under neutral pressure. It is also possible that the furnace operators are unknowingly transferring silver from their clothes, gloves, and shoes to other areas of the facility.

Of the three workers interviewed, none revealed health effects thought to be related to exposures at OmniSource other than the one worker with a diagnosis of argyria. However, based on the history provided by the worker with the skin lesion, it is unlikely that the lesion represents localized argyria.

NIOSH investigators concluded that employees in the PMR facility are overexposed to silver when powered air-purifying respirators (PAPRs) are not worn. Although the furnace room is under negative pressure, it appears that airborne silver may be escaping the furnace room and migrating to other areas of the PMR facility, including the work station and office area where respirators are not usually worn. Recommendations are offered in this report for improved exhaust ventilation, personal protective equipment, general safety, and housekeeping in the workplace to decrease worker exposures. Medical recommendations to assess the body burden of silver are also included.

Keywords: SIC 3341 (Secondary Smelting and Refining of Nonferrous Metals), precious metal recycling, silver, gluteraldehyde, hydroquinone, hydrogen cyanide, argyria

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INTRODUCTION

On November 1, 1999, the National Institute for Occupational Safety and Health (NIOSH) received a management request from OmniSource Corporation to conduct a health hazard evaluation (HHE) to evaluate occupational exposures to silver at OmniSource's Precious Metals Recycling (PMR) facility in Ft. Wayne, Indiana. The request was prompted by management concerns about one worker who had been presumptively diagnosed with localized argyria on his arm by a physician. In response to the request, NIOSH investigators completed a survey in January 2000.

On January 10, 2000, NIOSH investigators held an opening conference with members of OmniSource Corporation's division management and safety management teams and PMR facility workers. Following the conference, NIOSH investigators performed an inspection of the PMR facility that included observing work practices, gathering information about the facility's process, and interviewing management and workers. Environmental sampling and a medical evaluation took place on January 11, 2000. Three PMR employees underwent a medical evaluation consisting of a medical and occupational history and a directed physical examination.

BACKGROUND

OmniSource Corporation reclaims metals such as iron, copper, aluminum, steel, lead, and silver, from a variety of sources in 29 locations throughout the United States. The PMR facility is located at one of the plant sites in Ft. Wayne. Silver reclamation, the largest portion of the PMR business, occurs in a small building at this site. The building consists of a large entrance area that is used mainly for storage, a small furnace room containing two furnaces, and an area on the west end of the building divided into a work station, an office, and a restroom. Two to three employees work in the facility each shift. The number of shifts per week and their duration are determined by the amount of recoverable material received. Before production increased in February of 1999, the company ran the furnaces for four- or five-hour shifts every two weeks. At the time of this survey, the furnaces were being run continuously from 4 a.m. to 10 p.m. five days a week. The first shift begins at 4 a.m.and ends at 12:30 p.m.; the second shift starts at 12:30 p.m. and concludes at 10 p.m. One furnace operator reclaims silver in the PMR facility each shift, and a supervisor periodically stops in throughout the shift to monitor operations.

Although OmniSource acquires silver from several different waste streams, the primary source is silver salts in spent photographic fixer solution. Couriers collect silver recovery cartridges (also known as metallic replacement cartridges) and metallic silver that deposits on electrodes suspended in fixer solution tanks. Recovery sites can include hospital radiology departments, x-ray clinics, and commercial photography labs.

Before processing of metallic replacement cartridges takes place, OmniSource PMR employees pour off any remaining fixer solution into 55-gallon drums (uncovered) against the far northeast wall of the PMR facility. OmniSource has contracted an outside company (Safety Kleen) to remove and process the contents of these drums when they are full. The material safety data sheet (MSDS) for the photographic fixer solution indicates that the principal component is water (85 – 90% by weight). Sodium/potassium sulfite mixture, glutaraldehyde bis-bisulfite, hydroquinone, and potassium carbonate comprise 1 – 5% percent of the total weight of the solution. Hydroquinone is listed on the MSDS as the principal hazardous component due to its properties as an irritant and possible skin sensitizer. Although it is not listed on the MSDS, thiocyanate can also be a component of the fixer solution. It is added to accelerate the silver recovery process. The following are descriptions of the two different methods currently used to extract silver from fixer solution residue at the PMR facility.

Metallic Replacement

The metallic replacement method utilizes steel wool and fiberglass recovery cartridges to recover the dissolved silver ions in the fixer solution. The silver ions react with the cartridge and bind to the filter, displacing the steel wool, which then goes into solution. At a routinely scheduled time the filter is replaced, and the spent cartridge is brought to the PMR facility.

After the remaining fixer solution is poured off, the metallic replacement cartridges are individually placed into silicon carbide or clay graphite crucibles. Soda ash and borax, used as refluxing agents, are added to the crucible before it is placed into the furnace. The furnaces, powered by natural gas, run between 2200 – 2300°F. After two hours of heating, the crucibles are lifted from the furnaces and lowered to a mold, using a powered winch. Molten liquid containing the silver is then poured into the molds and allowed to cool for approximately two hours. At this point, the sludge cake is removed from the mold and the recovered silver is broken away from the remaining material with a hammer.

Electrolytic Recovery

The electrolytic recovery process uses an electrolytic machine to recover the silver flake, or chip, which is approximately 90 – 98% pure silver. An electric current is passed between a stainless steel cathode and a carbon anode that are suspended in the fixer solution. Silver deposits on the stainless steel cathode in a nearly pure silver plate. The cathodes are periodically removed, placed in a plastic bag, then struck with a hammer to strip the silver off of the cathode. This method recovers approximately 75 – 80% of the silver from the fixer solution, whereas the metallic replacement method collects approximately 90 – 95% of silver in the solution.

After two hours of heating, crucibles containing silver flake or chip are also lifted from the furnace using a powered winch. The crucible is then lowered onto a stand and the molten silver is poured off into a drum of cold water. As the molten silver splatters onto the surface of the water, it cools rapidly to form silver shot. After the shot is poured, the used water is pumped into a silver sludge recovery drum. Any remaining silver residue is collected on a filter and the water is drained into an unused toilet.

METHODS

Industrial Hygiene

On January 11, 2000, a total of six area air samples were collected for silver and 26 other metals and minerals (see table I) during the first shift. A metal scan analysis was done to determine if any metals other than silver were present in the furnace room. A full-shift personal breathing-zone (PBZ) measurement was collected on the furnace operator working in the PMR facility. Full-shift area air samples were collected on the east and south walls of the furnace room. The sample on the south wall of the furnace room was collected above a heater where the silver ingots are placed on a pan to dry after they are removed from the barrel of water. Three more area air samples were collected in the following areas: just outside the furnace room on a rack used to store the crucibles, on the east wall of the work station area, and on a desk in the office. Air samples for the metals were collected on 0.8-micrometer (µm) cellulose ester membrane (CEM) filters, using battery-powered air sampling pumps calibrated at a flowrate of 1.7 liters per minute (Lpm). Air samples were analyzed according to NIOSH method 7300, using an inductively coupled plasma (ICP) emission spectrometer.[1]

During that same shift, four full-shift area air samples for glutaraldehyde and hydrogen cyanide were collected in the following areas: the east wall of the furnace room, the south wall of the furnace room above the heater used to dry the silver ingots, outside the furnace room on the crucible rack, and on the east wall of the work station area. Air samples for glutaraldehyde were collected on silica gel sorbent tubes treated with 2,4-dinitrophenylhydrazine hydrogen chloride, using battery-powered air sampling pumps calibrated at a flowrate of 0.05 Lpm. Samples were analyzed by high-performance liquid chromatograph (HPLC), in accordance with NIOSH method 2532.[1] Air samples for hydrogen cyanide were collected on soda lime sorbent tubes using battery-powered air sampling pumps calibrated at a flowrate of 0.1 Lpm. Samples were analyzed by visible absorption spectrophotometry, in accordance with NIOSH method 6010.[1]

A total of six area air samples were collected for hydroquinone during the first shift on the east wall and southwest corner of the furnace room. Air samples were collected on 0.8-µm CEM filters using battery-powered air sampling pumps calibrated at a flowrate of 1.3 Lpm. The filters were replaced every 2 ½ to 3 hours and placed in 10 milliliters (mL) of 1% acetic acid. Samples were analyzed according to NIOSH method 5004, using HPLC.[1]

Samples for glutaraldehyde, hydroquinone, and hydrogen cyanide were collected because glutaraldehyde and hydroquinone are components of the fixer solution. Thiocyanate, a possible component of the fixer solution, decomposes during the recovery process and hydrogen cyanide is formed.

To determine whether metals generated in the furnace room were being distributed throughout the PMR facility, qualitative airflow measurements were made using ventilation smoke tubes. These measurements determined whether work areas were under positive, negative, or neutral pressures. Airflow measurements were made at the entrance of the PMR facility, the entrance of the furnace room, and the entrance of the work station and office area. The airflow patterns in the work station and office were also qualitatively evaluated using smoke tubes.

A general inspection was made to identify potential safety hazards in the PMR facility. Pertinent documents reviewed included the MSDS for the photographic fixer solution and the results of previous industrial hygiene PBZ and area air sampling conducted by OmniSource Corporation.

Medical

Prior to the NIOSH site visit, the NIOSH medical officer spoke by telephone with the physician in Ft. Wayne who made the diagnosis of localized argyria in one of the furnace operators. This physician forwarded all pertinent medical records of the PMR employees to the NIOSH medical officer who reviewed them before his visit to the PMR facility.

On January 11, 2000, an individual medical evaluation was conducted on all three PMR employees, one of whom had been diagnosed with localized argyria. The evaluation consisted of a medical and occupational history and a directed physical examination focusing on the skin and eyes.

EVALUATION CRITERIA

As a guide to the evaluation of workplace exposure hazards, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. Several factors may account for the presence of adverse health effects in a worker whose exposure to a given agent does not exceed the recommended criteria.

A small percentage of exposed workers may experience adverse health effects from a chemical or physical agent because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker. These combined effects are often not considered in the evaluation criteria. In such instances, exposure to a given chemical or physical agent may result in an adverse health effect even if occupational exposures are controlled at or below the level set by the criterion. Furthermore, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increases the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available. In other words, an exposure level considered safe at one point in time may not be regarded as such at some future time as knowledge about and experience with the agent increase.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),[2] (2) the American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLVs®),[3] and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).[4] Employers are encouraged to follow the NIOSH RELs, ACGIH TLVs, OSHA PELs, or whichever are the more protective criteria.

Employers should understand that not all hazardous chemicals have specific exposure limits such as REL's, TLV's, or PEL's. Nonetheless, OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970, Public Law 95–596, sec. 5.(a)(1)]. An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Silver

Introduction

The accumulation of a body burden of silver may, over time, result in a condition known as argyria. This condition, the primary health effect seen after prolonged silver exposure, has been described as an "unsightly blue-grey discoloration of the skin, mucous membranes, and eyes." Argyria may develop as a result of exposure to both soluble and insoluble forms of silver. Occupational exposure to mixtures of other metals (e.g., arsenic, antimony, cadmium, selenium) or chemicals, has not been reported to be related to the development of argyria in a silver-exposed worker.[3]

Occupational argyria is thought to occur due to the absorption of silver through the lungs, the digestive tract, or through wounds in the skin.[5,6,7] Localized argyria may result from local trauma and deposition of fine particles of metallic silver into the skin.[3]

Absorption

The primary site of absorption of silver is the lungs. Ten to 20% of an ingested dose of silver is absorbed through the intestinal tract. Only about 1% or less of a total dose of silver is absorbed through intact skin.

Kinetics

The intake of silver from dietary sources is negligible and estimated to range from 60-80 µg/day; the majority of occupational silver exposure is secondary to inhalation.[8]

Excretion

The main route of silver excretion from the body, regardless of the route of exposure, is via the feces. Eighty-five to 90% of absorbed silver is collected in the liver, secreted with the bile and eliminated in the feces.[9]

Toxicology

Metallic silver and insoluble silver compounds have not been shown to represent significant dangers to human health. One author described metallic silver as "harmless."[7] Pifer, et. al., studied 27 silver reclaimers with long-term exposure to primarily insoluble silver compounds and found "no unusual health patterns."[10] A case report of massive exposure to the heated vapor of metallic silver describes resultant lung damage and pulmonary edema in the worker. Based on the description available, however, it is unclear whether the health effects are due to prolonged inhalation of vapors or secondary to inhalation at extremely high temperatures.[3]

Aside from the possibility of causing argyria and argyrosis (see below) insoluble silver does not appear to pose either acute or chronic health effects. There is currently no evidence to suggest that metallic silver is a carcinogen.[11] It should be noted, however, that soluble silver salts (in contrast with metallic silver and insoluble silver salts) have been known to compromise human health. In addition to their ability to cause both argyria and argyrosis, soluble silver salts have, in high doses, been implicated as cytotoxic agents. Silver sulfadiazine, silver nitrate and silver chloride exposures, both therapeutically and occupationally, have caused health effects that include burns, methemoglobinemia and gastrointestinal hemorrhage.[12]

Absorption and retention of silver have been implicated as a cause for several possible disease states, including renal injury, chronic bronchitis and blood dyscrasias such as thrombocytopenia and leukopenia. Current evidence would suggest that these conditions, when seen, are most likely due to exposure to soluble forms of silver and not metallic silver[8,11,13] (see Appendix A for a more thorough treatment and discussion of the toxiocology of silver).

Argyria

The most prominent physiologic effect related to exposure to silver is argyria. This grey or bluish-black discoloration of the skin results from the deposition of silver in the skin and is a permanent and irreversible cosmetic disorder. The deposition of silver in the skin does not cause any recognized disease or other chronic health effects.[6,10,11,14,15]

Most authors are unable to determine the minimal environmental concentrations that will result in the development of generalized argyria.[3] Reports exist of argyria developing in workers exposed to air concentrations of silver of 1 mg/m^3. Even lower levels (0.1 mg/m^3) gave rise to staining of mucous membranes of the upper respiratory tract and also the eyes.[3] Based on the current TLV-TWA, a minimum of 24 years of uninterrupted workplace exposure has been estimated for workers to retain sufficient silver to develop signs of argyria.[8]

As compared to generalized argyria, localized argyria is an even more rare condition.[3] Localized argyria is accidental tattooing from deposition of fine particles of metallic silver in the skin.[11,16] Inhalation or ingestion of silver does not result in localized argyria.

Argyrosis

Silver deposition in the tissues of the eye is known as argyrosis. This phenomenon is reportedly the first objective sign of generalized argyria.[5,15] The presence of argyrosis may be used clinically as an identifier of chronic silver exposure. A routine eye exam, including slit lamp examination of the anterior portion of the eye is the most sensitive noninvasive measure of a body burden of silver. It is superior to a dermatological exam for identifying chronic silver exposure.[5,15]

Silver Deposition Elsewhere In the Body

Chest x-ray findings in unprotected workers with chronic exposure to silver metal and polishing dust reveals increased densities in their lungs. Although regarded as a form of pneumoconiosis, silver dust inhalation does not carry any hazard of fibrosis.[3,11]

Occupational Exposure Limits

The current TLV-TWA for silver metal dust and fume (0.1 mg/m^3) is recommended to prevent argyria. The calculation of this value relies on a 25% (not 50%) retention of silver dust or fume with inhalation and a 10 m^3/day respiratory volume. The current TLV-TWA therefore results in a total body burden of no more than 1.5 grams of silver in 25 years of daily work exposure.[3] The ACGIH TLV for soluble silver is 0.01 mg/m^3 (as silver). The NIOSH REL and OSHA PEL for silver metal dust and soluble compounds is 0.01 mg/m^3 (as silver) as an 8-hour TWA.

Glutaraldehyde

Glutaraldehyde has a pungent odor with an odor recognition threshold of 0.04 parts per million (ppm) by volume in air and an irritation response level of 0.3 ppm.[17] In individuals without previous sensitization, glutaraldehyde acts as a mild mucous membrane, respiratory, and skin irritant.[18] Repeated or prolonged contact resulting in sensitization of the skin results in allergic contact dermatitis. Glutaraldehyde can be absorbed through the skin.[19] Chronic inhalation exposure may cause asthma in some individuals.[19] Symptoms from exposure may include cough, labored breathing, headache, nausea, and vomiting.

ACGIH recommends a TLV of 0.05 ppm as a ceiling limit. The NIOSH REL is 0.2 ppm as a ceiling limit. There is no OSHA PEL for glutaraldehyde.

Hydroquinone

The major expression of hydroquinone toxicity in industrial settings involves the eye and the skin without evidence of systemic illness or effects. Acute exposure to hydroquinone dust or to a high concentration of vapor causes conjunctival irritation, photophobia, and corneal ulceration.[3,18,20] Chronic exposure to hydroquinone produces: (1) a brown discoloration of the conjunctiva and cornea; (2) small corneal opacifications; and (3) structural changes in the cornea resulting in loss of visual acuity.[18] Dermatitis represents the other important form of chronic, occupational hydroquinone toxicity.[18,20]

The ACGIH TLV and OSHA PEL for hydroquinone is 2 mg/m^3 for an 8-hour TWA. NIOSH recommends a REL of 2 mg/m^3 as a 15-minute ceiling limit.

Hydrogen Cyanide

Cyanide causes rapid death due to metabolic asphyxiation. Signs and symptoms of acute intoxication are indicative of varying degrees of cellular hypoxia. Less severe intoxications may manifest as flushing, excitement or drowsiness, perspiration, opisthotonus, trismus, tremors, stupor, paralysis, weakness, headache, confusion, vertigo, fatigue, dyspnea, anxiety, and occasionally nausea and vomiting. Initially, respiratory rate and depth are increased and then become slow and gasping at later stages. As the severity of the poisoning worsens, prostration, seizures, and coma occur.[18] If large amounts of cyanide are absorbed, collapse is instantaneous and the victim dies within minutes.[20]

ACGIH and NIOSH recommend 4.7 ppm as a 15-minute STEL for hydrogen cyanide. The OSHA PEL is 10 ppm as an 8-hour TWA.

RESULTS

Industrial Hygiene

Air Samples

Table 1 contains the air sampling results for silver. A full-shift PBZ air sample collected on one furnace operator revealed a TWA concentration of 0.14 mg/m^3. This concentration exceeds both the OSHA PEL and NIOSH REL of 0.01 mg/m^3 and the ACGIH TLV of 0.1 mg/m^3, as an 8-hour TWA. Area air samples collected throughout the PMR facility revealed full-shift TWA concentrations ranging from 0.009-0.19 mg/m^3. All of these samples, with one exception, exceeded OSHA and NIOSH exposure limits. Two of five area air samples had silver concentrations greater than the ACGIH TLV. The highest concentrations for the remaining 26 metals and minerals analyzed were less than 20% of the most stringent exposure criteria.

None of the ten area air samples collected throughout the PMR facility yielded detectable amounts of glutaraldehyde or hydroquinone. The minimum detectable concentration (MDC) for glutaraldehyde and hydroquinone at the PMR were 0.008 mg/m^3 and 0.0004 mg/m^3, respectively. Similarly, hydrogen cyanide was not detected in any of the four air samples that we collected. The MDC was 0.002 mg/m^3.

Ventilation Evaluation

Qualitative airflow measurements showed the main entrance of the PMR facility to be under negative pressure. Measurements showed the entrance of the furnace room to be under strong negative pressure with the exhaust fan operating. The work station and office area were under neutral pressure in relation to the rest of the facility.

Other Findings

- The exhaust hoods over the furnaces were not operable, and fumes could be seen escaping the hoods into the furnace room.

- The winch used to hoist the crucibles out of the furnace appeared to be in poor condition.

- During our site visit, the powered air-purifying respirator (PAPR) was worn in the main PMR facility and furnace area, but not in the work station and office area. During pouring of molten liquid from the crucibles, a fireproof hooded jacket, faceshield, gloves, and leather work boots were worn.

- Safety glasses were not available for use while working in the furnace room or when using a hammer to separate sludge from the mold or silver from the sludge cake. The hammering process results in flying pieces of slag that can easily hit the eye. Fire retardant boots or protective covers were not available to be worn when pouring molten liquid out of the crucibles.

- Gloves capable of providing adequate protection against dermal exposure to glutaraldehyde and hydroquinone were not available to the furnace operator. Both of these components of the fixer solution are skin sensitizers and may cause dermatitis. The process of emptying fixer solution from drums was observed in another building separate from the PMR facility.

- At the time of the NIOSH visit, the silver sludge recovery canister system had been in use for four months, but the filter load had never been checked.

- Storage drums containing fixer solution, pending collection and disposal by the contractor, were stored in 55-gallon uncovered drums, potentially allowing vapors to escape into the facility.

- The general housekeeping of the PMR facility was poor. The floors and walls in the furnace room and main PMR facility were covered with black dust. Traces of black dust were also seen on the counter top in the work station area and on the desk in the office. The floor, walls, and ceiling tiles around the perimeter of the work station room were also dirty.

Medical

No worker had knowledge of any occupational exposures to silver prior to his employment at OmniSource. One worker had previously worked in a plant producing hard anodized, nickel-plated precision parts. He denied working in the dipping process at that facility. The worker with the most seniority and longest exposure to metallic silver (5 years) was diagnosed as having localized argyria.

None of the interviewed workers reported health problems consistent with those related to occupational exposure to silver, glutaraldehyde, or hydroquinone. Specifically, no worker reported abdominal pain, bowel or bladder problems, or respiratory difficulties. The workers each described fairly healthy appetites. No worker identified generalized pigmentary changes to his skin or any changes to the appearance of his eyes. No worker reported changes in visual acuity. Medical record review reveals that all PMR workers had recently undergone slit lamp evaluation of their eyes; no abnormalities were identified in any worker.

The worker previously diagnosed as having localized argyria had, on his right forearm, a small (1 mm x 1 mm) blue-black lesion. This lesion was neither palpable nor tender. The lesion initially appeared on this worker's arm in September 1999. According to his history, the lesion has not changed appreciably in size or in appearance since that time. Review of the worker's medical records confirms this history and indicates no change to the appearance of the lesion in the four months since he first noted it. He reported no similar lesions elsewhere. This worker had no evidence of pigment deposition to his corneas, conjunctivae, nail beds, or other sun-exposed areas of skin. Examination of the other two workers revealed no evidence of localized or generalized argyria or argyrosis.

DISCUSSION

Industrial Hygiene

Air Sampling

Air sampling in the PMR facility indicated that silver exposures exceed the NIOSH, OSHA, and ACGIH exposure limits. Half-mask powered air-purifying respirators (PAPRs), such as those being used on-site, have an assigned protection factor (APF) of 50 (APF is the expected workplace level of respiratory protection that would be provided by a properly functioning respirator to a correctly fitted and trained user).[21] Maximum use concentration (MUC) indicates the maximum airborne concentration of a toxin at which a specific respirator will provide sufficient protection to the user. MUC values are calculated by using the APF of a given respirator and the PEL of the toxin in question. The half-mask PAPR used by the furnace workers at the OmniSource PMR is rated to provide protection from exposure to airborne silver at concentrations not exceeding 0.5 mg/m^3. Assuming proper fit and training, these respirators should give adequate protection at the levels of airborne silver to which the PMR workers are being exposed.

Airborne silver exposures throughout the PMR facility indicate that silver dust is escaping the furnace room and being distributed to other areas of the facility. The lowest concentration of silver (0.009 mg/m^3) was found just outside the furnace room at the crucible rack. The work station and office area, separated from the rest of the facility by a door, had higher concentrations of airborne silver (0.012 mg/m^3 and 0.02 mg/m^3, respectively). Although these TWA exposures are lower than the exposures found in the furnace room (0.145 mg/m^3 and 0.19 mg/m^3), they would still exceed the OSHA PEL and NIOSH REL if they were personal exposures.

OmniSource management and workers also expressed concern about possible glutaraldehyde, hydroquinone, and hydrogen cyanide exposures from the photographic fixer solution. Air sampling results indicate that these compounds were not an inhalation hazard in the PMR facility at the time of our survey. Dermal contact with glutaraldehyde and hydroquinone may, however, cause dermititis and skin sensitization; personal protective equipment (PPE) providing adequate skin protection should therefore be available to workers in the PMR facility.

Ventilation Concerns

With the exhaust fan in the furnace room operating, qualitative ventilation measurements showed the furnace room to be under negative pressure (air flowed into the furnace room and out through the exhaust fan). Negative pressure should limit silver dust and fume from migrating to other areas of the facility. Despite the finding that the furnace room is under negative pressure, air sample results reveal that silver is escaping the furnace room. When the furnace room doors are left open, ventilation controls (keeping the room under negative pressure) become less effective. This allows some airborne silver to escape and migrate to other areas of the facility. Although the doors generally remained closed during the heating of the crucibles, during our visit, the furnace operators kept the doors open whenever pouring molten silver from the crucibles into molds. Qualitative airflow measurements at the entrance of the work station and office area showed these areas to be under neutral pressure. To prevent airborne silver from migrating to this area, the door should remain shut as much as possible, and the work station and office areas should be under positive pressure relative to the rest of the facility.

It is also possible that silver dust is inadvertently being transferred throughout the facility by the furnace operators. Silver dust may collect on an operator's clothes, shoes, and gloves when working in the furnace room, and then be tracked to other areas when he leaves.

During the site visit both furnaces were observed emitting fumes that escaped the exhaust hoods located overhead. Conduction and convection currents cause significant quantities of heat to be transferred to the air above and around the furnaces creating a thermal draft. These thermal drafts create an upward air current that can achieve air velocities approaching 400 feet/minute, causing the rising air column to mix turbulently with the surrounding air and disrupting laminar flow. Exhaust hoods for hot processes, therefore, require different considerations in design than do exhaust hoods for cold processes, since the thermal draft must be taken into consideration when determining the exhaust rate.

Thermal drafts result in an air column diameter that increases in both diameter and volumetric flow rate as it moves away from the source. The diameter of the column and the velocity of the rising hot air column can be approximated by mathematical calculations so that the diameter of the hood can be designed to capture the rising hot air column and assure complete capture of the contaminant.[22] The effectiveness of receiving hoods can also be improved by enclosing the source so that only one side is left open. This reduces the air requirements for the same control velocity.

Medical

Based on the history provided by the worker with the skin lesion, it is unlikely (although not impossible) that the lesion represents localized argyria. Localized argyria usually results from the local deposition of silver into the dermis from direct trauma and typically presents as a localized blue-grey "blush" to the skin and not as a discrete lesion. This worker denied a history of local trauma to that specific location on his forearm. He also denied any recollection of having an open wound at that site wherein silver dust may have become trapped.

The only definitive means of ascertaining the nature of this worker's lesion is a punch biopsy of the skin. This would permit a dermatopathologist to evaluate the lesion under the microscope and make a diagnosis as to its cause. Short of microscopic analysis, a diagnosis in this case probably cannot be made.

Blood silver values are not associated with the presence of argyria, argyrosis, or total duration of exposure to silver. Urinary excretion does not represent an important route of elimination of silver. Hair, subject to environmental contamination from the airborne silver in the workplace, should no longer be used as a reference for the workers in the PMR. Fecal samples, which may adequately reflect total body burden, are somewhat impractical to collect in the occupational setting. Of all the possibilities for biomonitoring, however, fecal silver levels may have the greatest utility.

CONCLUSIONS

NIOSH investigators concluded that workers at the OmniSource PMR facility are overexposed to silver when the PAPRs are not worn. Locations with the potential for overexposure to airborne silver include the office and work station area, where it was observed that respirators were not usually worn. Full-shift PBZ and area air sampling identified exposure to silver metal dust and fume throughout the PMR facility in excess of the OSHA PEL, ACGIH TLV (five of the six samples collected), and the NIOSH REL.

Exhaust hoods over the furnaces were not operating during the site visit. We also observed additional safety deficiencies at the time of our evaluation. Safety glasses and fire retardant boots/protective covers were not worn when working in the furnace room. Gloves offering adequate dermal protection while handling photographic fixer solution were not available for use. The improper storage of the fixer solution in the PMR facility poses a potential hazard of spills and subsequent exposure to glutaraldehyde and hydroquinone. The winch used to hoist the crucible out of the furnaces did not appear to be properly maintained, and failure of the winch when lifting a hot crucible could result in severe burn and/or crush injury to the furnace operator.

RECOMMENDATIONS

Industrial Hygiene

- To minimize migration of silver dust and fume throughout the PMR facility, the exhaust hoods over the furnaces should be in good operating condition and should capture all released contaminants. Two different modifications can improve the performance of the existing exhaust hoods. Increasing the diameter of the hood so that it is larger than the diameter of the air column rising from the furnace would help ensure complete capture of contaminants. A second measure would be to install a vertical baffle around the sides of the hood to prevent room air currents from disturbing the rising air column. One possible design would be to enclose the area extending from the furnace to the hood so that only one vertical side was left open. This would allow the winch to swing over and above the furnace and gain access to hoist out the crucibles. If only one side were left open and the hood kept at the same height from the furnace surface, then the air requirement for the same control velocity would be reduced by two-thirds.[23] Another possibility would be to construct one side of the baffle as a temporary enclosure. When workers need to use the winch to remove crucibles, the enclosure could be opened to provide access to the furnace. Once modifications are made to the exhaust hoods, air sampling should be repeated to indicate the capture efficiency of the hoods and whether or not respirator use is still needed.

- Air sampling results indicate that employees should be wearing the PAPR at all times inside the PMR until the distribution of silver into the work station and office areas is eliminated through engineering controls.

- The PAPRs should be properly cleaned and stored each day after use, according to the OSHA Respirator Protection Standard, 29 CFR 1910.134.[24] At the end of each day the cartridges should be removed, and the inside of the respirator surface should be washed with soap and cold water or a respirator wipe. The cartridges should then be placed in a clean, dust free area, or a sealable bag for storage. The facepiece should be stored in a separate storage bag, in a clean, well ventilated, dust-free area.

- A program should be implemented to perform periodic maintenance checks on the powered winch used to lift the crucibles out of the furnace.

- Although no smoking was observed inside the PMR facility, cigarette butts were seen on the floor of the work station area and also in the main facility. Smoking, eating, and drinking should be prohibited in the entire facility to minimize the possibility of silver ingestion.

- Safety glasses with side shields should always be worn in the furnace room. They should also be worn by the furnace operators whenever they use the hammer to separate the silver from the rest of the sludge cake. Fire retardant boots or protective shoe coverings should be worn by the furnace operators whenever they pour molten liquid from the crucibles.

- Employees should be required to wear neoprene rubber gloves whenever they empty fixer solution from storage drums (these gloves are resistant to breakthrough for four hours under conditions of continuous contact).[25] Leather gloves are inadequate protection against penetration from glutaraldehyde and hydroquinone.

- Fire-retardant gloves worn by the furnace operator during handling and pouring of hot crucibles should be in good condition and replaced at the first sign of visible defects. Gloves with missing layers of material do not provide sufficient protection against burns.

- Changing certain work practices can reduce the amount of silver dust currently being spread throughout the facility. Gloves used when working in the furnace room should not be shaken outside the furnace room to remove trapped dust. This practice generates not only an inhalation hazard, but also an ingestion hazard after the dust settles on surfaces. Dust is also generated when furnace operators use a metal rod to scrape waste residue from the crucibles. Additional dust is generated when workers dispose of the waste residue into the trash can. Dumping the waste into a more enclosed bin, or wetting the crucible before scraping, would decrease the amount of dust generated.

- Storage drums containing fixer solution, pending collection and disposal by the contractor, should be covered with lids to prevent the escape of vapors into the facility.

- A maintenance program should be implemented to monitor the silver sludge recovery canister system. The canister filter should be checked periodically to ensure that it has not become saturated with silver residue. A saturated filter is less efficient and can result in the improper discard of impurity-containing water.

- General housekeeping should be improved in the PMR facility. The floors should be mopped and the walls, counter tops, and ceiling tiles should be wiped down with a wet cloth to prevent silver dust from becoming reentrained in the air. A maintenance schedule should be implemented to periodically clean the PMR facility in an effort to reduce the chance for inadvertent ingestion and inhalation of silver.

Medical

- Since biological specimens, other than feces, are not useful for monitoring occupational silver exposure, hair monitoring should be discontinued.

- Continue periodic dermatologic and ophthalmologic examinations by a physician and eliminate biological sampling. The examination of the skin should focus primarily on sun-exposed regions of the body. The ophthalmologic examination should include a slit-lamp evaluation of the anterior portion of the eye in order to identify silver deposition in the cornea at the earliest possible opportunity. If silver deposition were to be found, the employee needs to be informed of the findings and a decision about continued exposure to silver could be made in consultation with a physician experienced in occupational health. Reduction of exposure by the variety of means discussed in this report, however, will provide the greatest benefit to the employees in minimizing the likelihood of developing elevated body burdens of silver and argyria.

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Table I
FULL-SHIFT AIR SAMPLING RESULTS FOR SILVER
HETA 00-0041-2796
OMNISOURCE CORPORATION
PMR FACILITY
January 11, 2000

Sample Location	Sample Type	Sampling Time (minutes)	Sample Flow Rate (liters per minute)	Sample Volume (liters)	Silver Concentration, milligrams per cubic meter (mg/m^3)
Furnace operator	PBZ	503	1.7	854	0.14
East wall of furnace room	Area	485	1.7	828	0.145
South wall of furnace room	Area	490	1.7	839	0.19
Outside furnace room	Area	487	1.7	836	0.009
Work station area	Area	430	1.7	731	0.02
Office	Area	435	1.7	738	0.012
Minimum Detectable Concentration (MDC)				854	0.00009
Minimum Quantifiable Concentration (MQC)				854	0.0003
Exposure Criteria (expressed in milligrams per cubic meter, mg/m^3)					
NIOSH Recommended Exposure Limit (REL)					0.01 TWA (for metal dust and soluble compounds)
OSHA Permissible Exposure Limit (PEL)					0.01 TWA (for metal dust and soluble compounds)
ACGIH Threshold Limit Value (TLV)					0.1 TWA (for metal)

Abbreviations:
PBZ = Personal Breathing-Zone
TWA = Time Weighted-Average (8-hours)
Comments:
The following 26 elements were either not detected or were present at concentrations less than 20% of the most stringent occupational exposure criteria.

Aluminum	Cobalt	Lithium	Phosphorus	Thallium	Zirconium
Arsenic	Chromium	Magnesium	Platinum	Titanium	
Beryllium	Copper	Manganese	Selenium	Vanadium	
Calcium	Iron	Molybdenum	Sodium	Yttrium	
Cadmium	Lead	Nickel	Tellurium	Zinc	

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APPENDIX A

INTRODUCTION

The accumulation of a body burden of silver may, over time, result in a condition known as argyria. This condition, the primary pathological consequence of prolonged silver exposure, has been described as an "unsightly blue-grey discoloration of the skin, mucous membranes and eyes." Although argyria develops as a result of exposure to both soluble and insoluble forms of silver, workers in silver reclamation facilities primarily encounter the insoluble forms of this metal. And, although silver reclaimers may be exposed to a mixture of other metals (e.g., arsenic, antimony, cadmium, selenium) and other chemicals, these other exposures do not facilitate the development of argyria in a silver-exposed worker.[26]

Sources differ as to the date that the first description of occupational argyria appeared in the medical literature. One report, published in France in 1872, described a case of argyria in an elderly woman who had worked polishing silver for 50 years.[27,28] Accounts of non-occupational exposure to silver and resultant argyria date back even further. A Roman pharmacopoeia from 69 BC describes the use of silver nitrate for the treatment of nervous disorders. In the middle of the 17th century, large doses of silver were being used to treat epilepsy despite the knowledge that such exposure could lead to developing the characteristic skin discoloration.[29,30]

Occupational exposure to silver occurs in a variety of industries. Silver miners, silversmiths, and workers in the photographic industry are all known to have substantial exposure to elemental silver.[31] In addition to these three occupations, mirror platers and others involved in the application of silver to glass or metal surfaces have been reported to develop generalized argyria.[3] Generalized occupational argyria occurs in these workers due to the absorption of silver through the lungs, the digestive tract, or through wounds in the skin.[4,32,33] Localized argyria may result from local trauma and deposition of fine particles of metallic silver into the skin.[1]

ABSORPTION

The primary site of absorption of silver is the lungs. Over half of an inhaled dose of metallic silver is absorbed through the wall of the alveolus and passes into the blood stream. Some portion of inhaled silver dusts are ultimately cleared from the lungs by coughing. These are then swallowed into the stomach where, it is believed, acid may convert the silver into a form that is more easily absorbed by the duodenum and small intestine.[7,34] One case report in the medical literature described a gentleman who developed argyria as a consequence of chewing photographic film as an alternative to smoking cigarettes.[6] Ten to 20% of an ingested dose of silver is absorbed through the intestinal tract. Only about 1% or less of a total dose of silver is absorbed through intact skin, however.

KINETICS

The current TLV-TWA for silver metal dust and fume (0.1 mg/m^3) is recommended to prevent argyria. The calculation of this value relies on a 25% (not 50%) retention of silver dust or fume with inhalation and a 10 m^3/day respiratory volume. The current TLV-TWA therefore results in a total body burden of no more than 1.5 grams of silver in 25 years of daily work exposure.[1]

Some experimental data from both humans and animals indicate that the percentage of absorbed silver retained by the body may be on the order of 1-5%. This represents absorption from all potential sources: via inhalation, ingestion, and transdermally. Since the intake of silver from dietary sources is negligible and estimated to range from 60-80 µg/day, the majority of occupational silver exposure is secondary to inhalation.[35]

Absorbed silver avidly binds to high molecular-weight proteins and metallothionein in cells. This binding renders ingestion of insoluble silver compounds essentially non-toxic. This characteristic, combined with the ready excretion of absorbed silver further minimizes total body burden of metallic silver.[3,6,8]

EXCRETION

The main route of silver excretion from the body, regardless of exposure, is via the feces. Mice, rats, monkeys, and dogs fed measured amounts of silver passed greater than 90% of the administered doses through their gastrointestinal tracts within 2-4 days.[7] Likewise, fecal elimination serves as the primary means of excretion in humans with inhalational exposure to silver.[8] In a case of accidental inhalation of radioactive silver, the metal began accumulating in the liver between 2 and 6 days after exposure.[1] Eighty-five to 90% of absorbed silver is collected in the liver, secreted into the bile and eliminated in the feces.[9]

In humans, elimination of silver from the body occurs in two distinct phases. The first phase, which represents clearance of unabsorbed silver particles from the gastrointestinal tract has a half-life of approximately 24 hours. The second phase extends over the next one to two months (half-life of 50 days) and represents the time required to clear silver from the bloodstream via the liver with ultimate secretion into the gastrointestinal tract for final elimination. At 8 to 30 weeks after exposure, tracing of radioactive silver acetate revealed that slightly less than 20% of the dose remained in the body.[7]

As compared to fecal excretion, urinary excretion represents a minor pathway for eliminating silver from the body.[7] Whereas almost 90% of absorbed silver passes through the gastrointestinal tract, only about 10% passes from the body through the kidneys.[9] Under ordinary circumstances urinary silver levels are negligible. Even when exposures are high, monitoring urine for silver is of limited value. In a study involving workers inhaling silver dust, mean silver concentrations in the urine measured 1.5 µg/g. These levels were compared with mean silver concentrations in the feces of 15 µg/g. The measurement of silver in the feces, therefore, provides the more accurate measurement of total body burden of the metal.[1,10]

TOXICOLOGY

Metallic silver and insoluble silver compounds have not been shown to represent a significant dangers to human health. One author described metallic silver as "harmless."[8] Pifer, et al., studied 27 silver reclaimers with long-term exposure to primarily insoluble silver compounds and found "no unusual health patterns."[2] A case report of massive exposure to the heated vapor of metallic silver describes resultant lung damage and pulmonary edema in the worker. Based on the description available, however, it is unclear whether the health effects are due to the toxicity of silver or the inhalation of extremely high temperature vapors.[1]

Aside from the possibility of causing argyria and argyrosis (see below), insoluble silver does not appear to pose either acute or chronic health effects. There is currently no evidence to suggest that metallic silver is a carcinogen.[36] Although NTP has not conducted genetic toxicology or other short-term toxicology and carcinogenesis bioassays on metallic silver or its compounds, there exists neither historical nor clinical evidence to support initiating such research.[1]

Soluble silver salts (in contrast to metallic silver and insoluble silver salts) have been known to compromise human health. In addition to their ability to cause both argyria and argyrosis, soluble silver salts have, in high doses, been implicated as cytotoxic agents. Silver sulfadiazine, silver nitrate, and silver chloride exposures, both therapeutically and occupationally, have caused health effects that include burns, methemoglobinemia, and gastrointestinal hemorrhage.[5] Renal injury, chronic bronchitis, and blood dyscrasias such as thrombocytopenia and leukopenia are also most likely due to exposure to soluble forms of silver and not metallic silver.[10,11,37]

ARGYRIA

The most prominent physiologic effect related to exposure to metallic silver is argyria. This grey or bluish-black discoloration of the skin results from the deposition of silver in the skin and is a permanent and irreversible cosmetic disorder. The deposition of silver in the skin does not cause any recognized disease or other chronic health effects.[2,3,6,7,11]

Although silver may bind throughout the body, it seems to bind preferentially to the skin and its connective tissues. Electron microscopy reveals that silver deposits in highest concentrations at the dermoepidermal junction, the basal lamina of eccrine and sebaceous sweat glands, and the collagen and elastic fibers of the dermis. Silver has also been identified in the connective tissues surrounding the walls of arteries and nerves.[2,5,6,8] Once bound in the tissues of the skin and its structures, silver stimulates melanocytes to increase the degree of skin pigmentation. This process, coupled with the sunlight induced reduction of the silver salts within the tissues results in the characteristic blue-grey appearance of argyria.[5,7]

Most authors are unable to determine the minimal environmental concentrations that will result in the development of generalized argyria.[1] Moreover, the minimal tissue concentrations of silver resulting in argyria is also unknown.[8] What is known is that the form of silver, its inherent solubility, and its route of entry into the body are determinant factors as to whether an exposed individual will manifest signs of argyria.[7]
Literature from the 1930s suggests that "a total dose of between 1 and 8 grams of silver would be required to induce the condition following long-term inhalation exposure."[7,8] Reports exist of argyria developing in workers exposed to air concentrations of silver of 1 mg/m^3. Even lower levels (0.1 mg/m^3) gave rise to staining of mucous membranes of the upper respiratory tract and also the

eyes.[1] Based on the current TLV-TWA, a minimum of 24 years of uninterrupted workplace exposure has been estimated for workers to retain sufficient silver to develop signs of argyria.[10]

As compared to generalized argyria, localized argyria is an even more rare condition.[1] Localized argyria is accidental tattooing from deposition of fine particles of metallic silver in the skin.[11,38] The characteristic blue-grey discoloration results from precipitation of silver sulfide in the dermis of the skin. Unlike generalized argyria, the patches of discoloration do not involve binding to the structural components of the skin and stimulation of the melanocytes does not appear to be part of the process.[1] Inhalation or ingestion of silver does not result in localized argyria.

ARGYROSIS

Silver deposition in the tissues of the eye is known as argyrosis. This phenomenon is reportedly the first objective sign of generalized argyria.[3,4] Silver complexes deposit most predominantly in the inner lining of the cornea, Descemet's membrane. Silver may also be found in the conjunctiva. As with argyria, the longer the exposure to silver, the greater the likelihood of developing argyrosis.[3,4]

Although reports of decreased night vision and general alterations in visual acuity due to argyrosis have appeared in the literature, current thought does not support this.[2,3,4,12] This condition appears to be a cosmetic problem and, like the deposition of silver in the skin, does not lead to long-term disability or illness.

The presence of argyrosis may be used clinically as an identifier of chronic silver exposure. A routine eye exam, including slit lamp examination of the anterior portion of the eye is the most sensitive noninvasive measure of a body burden of silver. It is superior to a dermatological exam for identifying chronic silver exposure.[3,4]

SILVER DEPOSITION ELSEWHERE IN THE BODY

Deposition of insoluble silver occurs throughout the body and is not limited exclusively to the skin and eyes. The highest concentrations of silver may be found in the kidney, liver, and spleen; this has been confirmed in autopsy studies of individuals with argyria.[3,6,7,8] Lymph nodes, bone marrow, brain, and lung are also potential sites for silver deposition to occur. Chest x-ray findings in unprotected workers with chronic exposure to silver metal and polishing dust reveals increased densities in their lungs. Although regarded as a form of pneumoconiosis, silver dust inhalation does not carry any hazard of fibrosis.[1,11]

BIOMONITORING

In 1985, DiVincenzo, et al., evaluated several techniques for biological monitoring of workers exposed to metallic silver, silver fume, and silver particulates.[10] The authors estimated that the workers participating in the study had been exposed to an 8 hour TWA of silver of between 1 and 100 μg/m^3 of silver. In their study, participants provided blood, urine, hair, and fecal samples for analysis of total silver content. The mean concentration of silver in the blood, urine, and feces of silver workers measured 0.011 μg/ml, <0.005 μg/g, and 15 μg/g, respectively. The authors selected workers in non-silver exposed areas of the same plant to serve as control subjects. The mean concentration of silver in the blood, urine, and feces of controls measured <0.005 μg/ml, <0.005 μg/g, and 1.5 μg/g, respectively.

Blood

There exists some controversy among authors as to the suitability of using blood samples to monitor occupational exposure to silver. In the study cited above, 7 of 37 workers exposed to silver (19%) had blood concentrations of silver below the limit of detection.[10] Nearly 90% of a dose of silver is excreted in the feces within days of exposure.[7] Due to the rapid clearance of silver from the body, it is unclear if the concentration of silver in the blood actually represents an accurate index of exposure.

Some authors contend that blood silver levels do reflect recent exposure.[11] Given the length of time required to clear absorbed silver from the blood (approximately 1 - 2 months), it is believed that levels of silver in the blood are reasonable measures of exposure.[7] Since silver workers are exposed to the metal on a chronic basis, absorption and excretion are ongoing processes. Moreover, blood levels of silver are easily measured by readily available analytical techniques (atomic absorption spectroscopy), making this method of monitoring convenient and attractive.[9] Despite the ease with which blood samples for silver are obtained and measured, however, blood silver values are not associated with the presence of argyria, argyrosis, or total duration of exposure to silver.[3]

Urine

Urinary excretion is an unimportant route of elimination for silver.[9] Only in workers with very large exposures to silver will levels of urinary silver be detectable. In the study by DiVincenzo, et. al., 2 silver workers out of 37 (5%) had detectable levels of silver in their urine.[10]

Hair

The work by DiVincenzo, et al., identified hair analysis as an inappropriate method for determining occupational exposure to silver. Airborne silver is an environmental contaminant that binds to hair and is not effectively removed from the hair shaft by detergents. X-ray analysis of hair collected from study subjects (and subsequently washed with detergent) confirmed the presence of silver on the outer layers of the hair and the absence of silver in the inner portion of the shaft. Their research calls into question the value of using hair silver levels for biological monitoring.[10]

Feces

Although fecal excretion of silver is the primary route of elimination, collection of samples may be impractical in the occupational setting.[9] The work by DiVincenzo, et al., confirmed that workers occupationally exposed to silver passed higher concentrations of silver in their feces as compared to their non-silver exposed co-workers. Dietary silver (60 - 80 µg/day) was postulated as the source of silver for control subjects. The authors suggested that since silver is predominantly eliminated in the feces, fecal measurements of silver may both be used to estimate exposure and as an index of the total body burden of the metal.[10]

OCCUPATIONAL EXPOSURE LIMITS

The current TLV-TWA for silver metal dust and fume (0.1 mg/m^3) is recommended to prevent argyria. The calculation of this value relies on a 25% (not 50%) retention of silver dust or fume with inhalation and a 10 m^3/day respiratory volume. The current TLV-TWA therefore results in a total body burden of no more than 1.5 grams of silver in 25 years of daily work exposure.[1] The ACGIH TLV for soluble silver is 0.01 mg/m^3 (as silver). The NIOSH REL and OSHA PEL for silver metal dust and soluble compounds is 0.01 mg/m^3 (as silver) as an 8-hour TWA.

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