OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT CARBONYL

INTRODUCTION

This guideline summarizes pertinent information about cobalt carbonyl (measured as Co) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

Formula

Structure

Synonyms

Cobalt octacarbonyl, cobalt tetracarbonyl, cobalt tetracarbonyl dimer, di-µ-carbonylhexacarbonyl-dicobalt, dicobalt carbonyl, dicobalt octacarbonyl, octacarbonyldicobalt

Identifiers

1. CAS No.: 10210-68-1

2. RTECS No.: GG0300000

- 3. DOT UN: 9188 31 (Hazardous substance, liquid, or solid, n.o.s.)
- 4. DOT label: None

· Appearance and odor

Cobalt carbonyl is an orange to dark brown crystalline solid, although the pure substance is white.

CHEMICAL AND PHYSICAL PROPERTIES

- · Physical data
 - 1. Molecular weight: 341.94
 - Boiling point (at 760 mm Hg): Decomposes at temperatures above 52°C (125.6°F)
 - 3. Specific gravity (water = 1): 1.87 at 20°C (68°F)
 - 4. Vapor density: Data not available
 - 5. Melting point: 51°C (123.8°F)
 - 6. Vapor pressure at 15°C (59°F): 0.07 mm Hg
 - 7. Solubility: Insoluble in water; soluble in alcohol, ether, naphtha, and carbon disulfide
 - 8. Evaporation rate: Data not available

· Reactivity

 Conditions contributing to instability: Exposure of cobalt carbonyl to air or heat causes decomposition to occur. Cobalt carbonyl is slowly attacked by sulfuric

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acid or hydrochloric acid and is more rapidly attacked by bromine and nitric acid.

- 2. Incompatibilities: None reported
- Hazardous decomposition products: Toxic gases (such as carbon monoxide) and the pyrophoric dodecacarbonyltetracobalt may be released in a fire involving cobalt carbonyl.
- 4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to cobalt carbonyl.

- 1. Flash point: Data not available
- 2. Autoignition temperature: Data not available
- Flammable limits in air (% by volume): Data not available
- Extinguishant: For small fires involving cobalt carbonyl, use dry chemical, carbon dioxide, water spray, or standard foam. For large fires, use water spray, fog, or standard foam.

Fires involving cobalt carbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Containers of cobalt carbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Do not scatter this material with high-pressure water streams. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt carbonyl. Structural firefighters' protective clothing may provide limited protection against fires involving this substance.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt carbonyl (measured as Co) [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m³ as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt carbonyl (measured as Co) a threshold limit value (TLV) of 0.1 mg/m³ as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

Rationale for limits

The NIOSH limit is based on the risk of respiratory irritation. The ACGIH limit is based on the risk of pulmonary and other acute effects associated with exposure to cobalt carbonyl.

HEALTH HAZARD INFORMATION

Routes of exposure

Exposure to cobalt carbonyl can occur through inhalation, ingestion, and contact with the skin.

Summary of toxicology

1. Effects on Animals: Cobalt carbonyl damages the respiratory and central nervous systems, liver, and kidneys, and may also irritate and sensitize the skin of animals on contact. Administered topically or subcutaneously to rats and mice, cobalt carbonyl was absorbed through the skin in toxic amounts and caused irritation of the skin [NLM 1990]. Applied to the skin of guinea pigs, cobalt carbonyl caused an allergic reaction [NLM 1990]. The LC_{so} (duration unspecified) in rats is 165 mg/m³ [NIOSH 1989] and the 2-hr LC_{so} in mice is 27 mg/m³ (Sax and Lewis 1989]. Rats exposed to concentrations of cobalt carbonyl ranging from 8 to 44 mg/m³ for 30 min showed inflammatory and proliferative changes in the lungs at autopsy; at the highest concentrations, there was evidence of pulmonary edema. Histopathological changes and adverse effects on the central nervous system, liver, and kidneys were seen at autopsy; decreased thyroid function was also observed in these animals [NLM 1990]. The oral LD_{so} is 754 mg/kg in

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rats [NIOSH 1989] and 378 mg/kg in mice [Sax and Lewis 1989].

2. Effects on Humans: Cobalt carbonyl causes sensory irritation on contact with the skin and mucous membranes [Parmeggiani 1983], and affects the respiratory system and the blood. Factory workers acutely overexposed to airborne cobalt carbonyl developed bronchospasm, showed X-ray evidence of focal infiltrations of the lungs, and had changes in several cellular blood components [NLM 1990]. Based on the toxicologic similarities between nickel carbonyl and cobalt carbonyl, it is likely that overexposure to cobalt carbonyl would give rise to nausea, headache, dizziness, coughing, dyspnea, and substernal pain [Clayton and Clayton 1981].

Signs and symptoms of exposure

- 1. Acute exposure: Acute exposure to cobalt carbonyl may cause cough, shortness of breath, lung densities, decreased pulmonary function, wheezing, and pain in the chest. Clinical evidence of changes in the cellular components of the blood may also be present. Ingestion could cause pericardial effusion, pain. vomiting, nerve deafness, convulsions, and thyroid enlargement.
- 2. Chronic exposure: Continued low-level exposure to cobalt carbonyl may cause cough, rapid breathing on exertion, decreased pulmonary function, wheezing, and shortness of breath.

Emergency procedures

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

- 1. Eye exposure: Irritation may result. Immediately and thoroughly flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Skin irritation or absorption of toxic amounts may result. Immediately remove all contam-

inated clothing and thoroughly wash contaminated skin with soap and water for at least 15 min.

3. Inhalation exposure: Move the victim to fresh air immediately. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

- 4. Ingestion exposure: Take the following steps if cobalt carbonyl or any material containing it is ingested:
 - —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.
 - -Have the victim drink a glass (8 oz) of fluid such as water.
 - -Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do not give syrup of ipecac because of possible onset of respiratory depression and seizures.
 - -Do not force an unconscious or convulsing person to drink fluid or to vomit.
- 5. Rescue: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt carbonyl and result in worker exposures to this substance:

- --- Use as a catalyst for organic reactions
- —Use as a catalyst in the plastics industry
- -Preparation of metals of high purity

The following methods are effective in controlling worker exposures to cobalt carbonyl, depending on the feasibility of implementation:

- —Process enclosure
- —Local exhaust ventilation
- General dilution ventilation
- -Personal protective equipment

Good sources of information about control methods are as follows:

- ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- 3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
- Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.
- Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

· Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to cobalt carbonyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory and nervous systems, liver, kidneys, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt carbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or nervous system, liver, kidneys, or blood.

Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt carbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt carbonyl on the respiratory or nervous system, liver, kidneys, or blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt carbonyl.

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· Medical examinations recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to cobalt carbonyl may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt carbonyl (measured as cobalt) is determined by using a 0.8 micron mixed cellulose ester filter. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Computerized Information System [OSHA 1990], the OSHA Analytical Methods Manual [OSHA 1985], the OSHA Chemical Information Manual [OSHA 1987], and in Method 7027 of the NIOSH Manual of Analytical Methods [NIOSH 1984].

PERSONAL HYGIENE

If cobalt carbonyl contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min, and then wash with soap and water.

Clothing contaminated with cobalt carbonyl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cobalt carbonyl, particularly its potential to cause headache, nausea, and pulmonary effects.

A worker who handles cobalt carbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt carbonyl or a solution containing this substance is handled, processed, or stored.

STORAGE

Cobalt carbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt carbonyl should be protected from physical damage and should be stored separately from hydrochloric acid, sulfuric acid, nitric acid, bromine, heat, sparks, and open flame. Because containers that formerly contained cobalt carbonyl may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cobalt carbonyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

- 1. Cover the spill area with a plastic sheet or tarp to minimize spreading.
- 2. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

• Emergency planning requirements

Employers owning or operating a facility at which there are 10,000 lb or more of cobalt carbonyl must comply with EPA's emergency planning requirements [40 CFR Part 355.30]. (If cobalt carbonyl is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of cobalt carbonyl are present at the facility.)

· Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for cobalt carbonyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

- —Notify the National Response Center immediately at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].
- —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].
- —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

· Community right-to-know requirements

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt carbonyl emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt carbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt carbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [1987a].

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PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt carbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt carbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt carbonyl.

If cobalt carbonyl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt carbonyl might contact the eyes (e.g., through dust particles or splashes of solution). Evewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt carbonyl. Contact lenses should not be worn if the potential exists for cobalt carbonyl exposure.

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